

## Chapter 2

# From Nanotechnology to Nanoengineering

### 2.1 Introduction to Nanotechnology

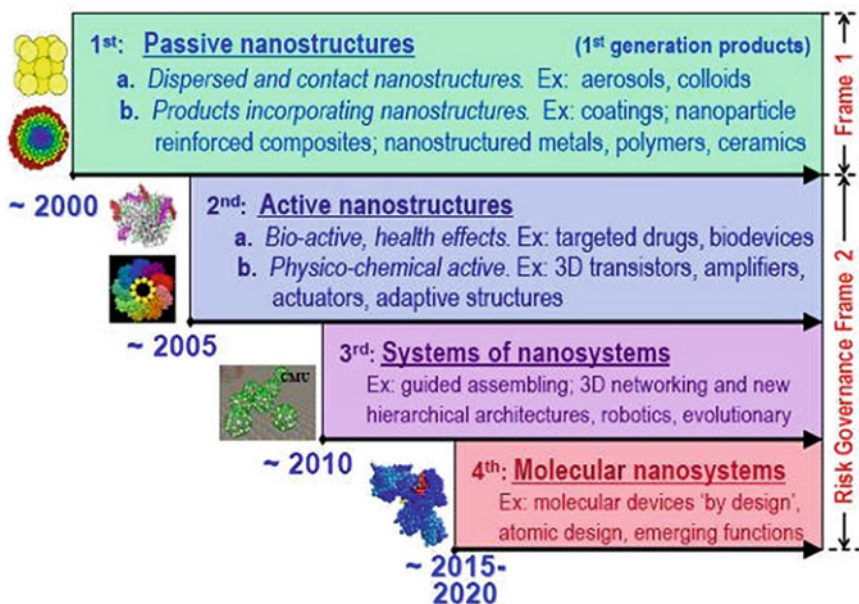
The world is presently witnessing the advancement and development of a new multidisciplinary technology, “Nanotechnology.” The concepts that seeded nanotechnology were first discussed in 1959 by renowned physicist Richard Feynman in his talk (Feynman 1961):

There’s Plenty of Room at the Bottom

In those early days, nanotechnology referred to the possibility of synthesis via direct manipulation of atoms and molecules for fabrication of macroscale products. In the 1990, K. Eric Drexler and M. Minsky used the word “nanotechnology” in their book “Engines of Creation: The Coming Era of Nanotechnology” (Drexler and Minsky 1990), in which they proposed assembling machines and devices on the scale of molecules, a few nanometers wide. Later on, as nanotechnology became an accepted concept, the meaning of the word shifted to encompass technologies related to making any type of materials, structures and devices in nanometer scale. A nanometer (nm) is one-billionth of a meter, hundred-thousandth the width of a human hair. There is a multidisciplinary convergence of science dedicated to the study of a world in such small scale. The US National Nanotechnology Initiative (Roco 2011) has described four generations of nanotechnology development (Fig. 2.1). The first era is a design of passive nanostructures and materials to perform just one task like nanostructured metals, aerosol. The second phase introduced active nanostructures for multitasking, for example, actuators, drug delivery devices and sensors. The third generation featured nanosystems with thousands of interacting components. In this era, integrated nanosystems, hierarchical systems within systems, have been developed.

Accordingly, a comprehensive definition for Nanotechnology is:

Nanotechnology is art and science of manipulating atoms and molecules to create systems, materials and devices at nanoscale as well as their application in various fields.



**Fig. 2.1** Generations of nanotechnology development (Roco 2011)

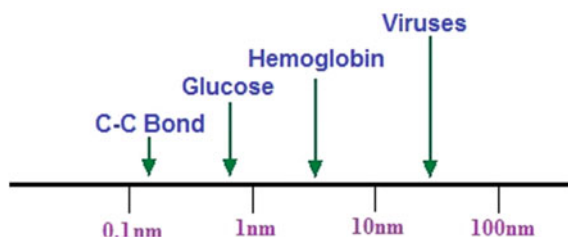
Nanotechnology can be referred to as a general-purpose technology, as it has significant impacts on almost all industries and all areas of society. Nanotechnology is expected to offer better built, longer-lasting, cleaner, safer and smarter products for the home, for communications, for medicine, for transportation, for agriculture and for industry in general. Chemistry and materials science and in some cases biology are integrated to create new properties of materials in nanoscale. However, engineering principles must be exploited to gain market opportunities.

### 2.1.1 Application of Nanotechnology in Different Fields

The expectations from nanotechnology as a key technology of the current century for innovative products and new market potentials are high. Some of these potential applications of nanotechnology-based products are presented in this section.

#### 2.1.1.1 Nanotechnology in Biotechnology

The size of nanometer is of central importance in the nature and biological systems. Cells are the main element of the living organisms that can be much smaller than the submicron size domain. A wide range of biomolecules, like proteins and



**Fig. 2.2** Various nanosized biological systems

viruses, is in the nanoscale range (Fig. 2.2). Accordingly, nanotechnology has become a part of the world of biotechnology for understanding the biological systems and their phenomena (Papazoglou and Parthasarathy 2007). Unexpected growth in the field of nanotechnology and biotechnology has brought novel technologies that make it possible to:

- Design new nanostructures by mimicking the structure and function of living systems
- Control and alter the biosystems including cellular and subcellular organelles, protein molecules, receptors and cytokines

Proteins, with a typical size of 5 nm, are comparable to the smallest nanoparticles that have been made by researchers. This circumstance has led to the improvement in the health care and medical research through the development of nanobased products, as a result of research efforts. These products have extensively found bioapplications in the fields of cosmetics, drug delivery, imaging and medical diagnosis, tissue engineering, etc. For example, biomolecules can be attached to nanoparticles by electrostatic forces including hydrogen bonding, hydrophobic forces and van der Waals forces. New approaches of using nanostructures for biomolecule immobilization assist potential applications in biosensors (glucose sensor, DNA sensors), targeted drug delivery and other biocatalytic processes (Kim and Grate 2003; Kim et al. 2006a, b). The optical properties of nanoparticles could be also implemented in imaging and characterization of biomolecules, for example, as a marker in TEM, as well as surface enhancement of fluorescent emission and Raman scattering (Wang 2000a, b).

The revolutionary advancements in bionanotechnology and biomedical research place a strong foundation for a customized, personalized and quantitative medicine in the future. The vital role of nanobiotechnology in medicine is improvement in diagnostic technologies. Diagnosis is a key stage in health care; the earlier the diagnosis of a disease the more effective the therapy is, both from outcomes and from a total cost perspective. The integration of nanotechnology with medicine has given birth to a new field of science called “nanomedicine.” The ultimate goal of nanomedicine is to develop well-engineered products (tools and materials) that could efficiently be used for the prevention, diagnosis and treatment of different diseases. These products include drug delivery platforms, imaging systems,

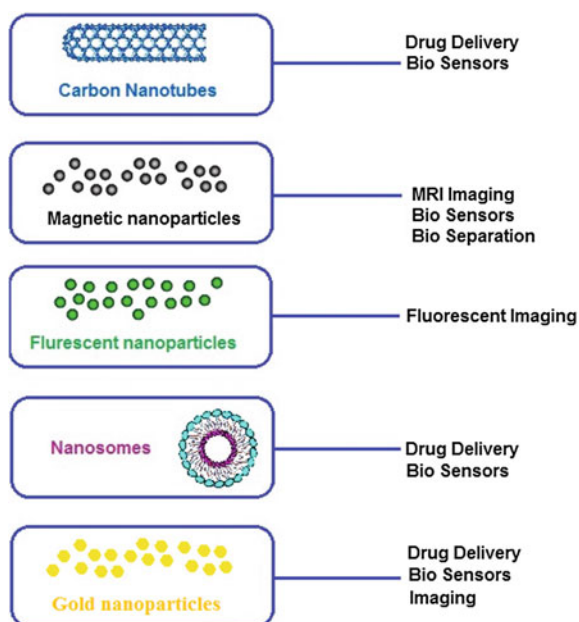
biochips and probes, needles for painless drug infusion or intracellular injections, etc. (Papazoglou and Parthasarathy 2007).

Nanostructures are an important component of biosensing platforms (Bianco and Prato 2003; Davis et al. 2003). The extraordinary properties of nanostructures (specially electrical and optical properties) in the presence of biomolecules make them possible to be used in biosensors fabrication (Vo-Dinh 2004; Hong et al. 2010; Duncan 2011). Biosensors, which act in the aqueous phase, are analytical devices incorporating biomolecule (e.g., DNA, enzymes, antibodies, microorganisms, etc.) associated with or integrated within a physico-chemical transducer (Vo-Dinh 2004). Biosensors are now employed in a wide range of applications:

- Detecting of diseases, particularly in cancer diagnostics (Fortina et al. 2007; Perfézou et al. 2012)  
These sensors capable of monitoring *in vivo* processes within living cells, leading to achieve new information on the inner workings of the entire cell and understanding the cellular function, thus revolutionizing cell biology and to differentiate normal and abnormal cells (Vo-Dinh 2004).
- Organo-phosphorus pesticides and nerve gases (Gan et al. 2010; Liang et al. 2012)
- Pathogens and toxins, or total cholesterol and glucose, etc., in blood (Lahiff et al. 2010; Kuila et al. 2011)
- Low concentration of toxic gases (Endo et al. 2008; Asefa et al. 2009).

Nanostructures have been also considered in the controlled release of active compounds in the application of pharmaceuticals (Kumar 2000) and food additives (Chaudhry et al. 2008). Drug delivery using nanostructures has demonstrated high and versatile loading capacity for therapeutic agents, some selective cargo unloading and better cell penetration than many other delivery materials (Farokhzad and Langer 2009; Verma and Stellacci 2010). To achieve the efficient performance, a suitable scheme to conjugate the drug and the nanostructure is required to make nanostructures into viable delivery vehicles (Endo et al. 2008). Another critical step is to conjugate the nanostructures in such a way that the functionality of the biomolecules is maintained. The present-day nanomedicine initiatives include a range of successful and evolving technologies encompassing targeted drug delivery aimed at minimizing side effects, creation of implantable materials as scaffolds for tissue engineering, development of implantable devices, surface modification and designing optimal topology for biomaterial implants, surgical aids, nanorobotics, as well as high-throughput drug screening and medical diagnostic imaging (Pankhurst et al. 2003; Papazoglou and Parthasarathy 2007). Medical applications of the most used nanostructures are presented in Fig. 2.3. As presented in the previous paragraph and indicated in the Fig. 2.3, medical applications of nanostructures commonly include imaging, sensing and delivery. However, magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ ) due to their unique behavior have a specific application for biomolecule separation selection. This application is especially well suited to the

**Fig. 2.3** Medical applications



separation of rare tumor cells from blood and low numbers of target cells (Pankhurst et al. 2003; McCarthy and Weissleder 2008).

Nanostructures have also attracted great attention in tissue engineering for design of medical prostheses or implants (Scholz et al. 2011). Designing medical implants or scaffolds similar to natural tissue or organs with respect to their performance is a challenging task facing materials scientists and engineers. Novel innovative technology for the fabrication of nanostructural biomaterials increases the possibility to use nanostructure in designing and producing implants or prostheses with all ideal characteristic features in order to function in a natural way in the body environment (Dastjerdi and Montazer 2010). Nanocomposites of different types of ceramics are mostly used as orthopedic implants and in dental applications to repair and replace diseased and damaged parts of the musculoskeletal system (Chevalier and Gremillard 2009). Metallic-based materials that present sufficient fatigue strength to endure the rigors of daily activity, such as walking and chewing are normally used as pins and plates and femoral stems, orthopedic implants, etc. (Minagar et al. 2012). Coating materials in which nanostructures are used can modify the surface properties of materials used in medical activities (for example, surgery) by their improvements in performance, reliability and biocompatibility (Ben-Nissan and Choi 2006).

Nanostructures are also considered for the food packaging sector, and nanocomposites have shown impressive characteristic for this purpose (Sanchez-Garcia et al. 2010; Lagaron and Lopez-Rubio 2011; Duncan 2011). According to these reviews, the majority of the researches used clay nanoparticles; nevertheless, other

types of reinforcing elements like carbon nanotubes (CNTs), metals, nanoparticles and biobased nanofillers such as starch nanoparticles and biodegradable cellulose nanowhiskers have been applied. The latter biobased nanofillers offer more advantages like generating fully biobased formulations and edibility since they can be made of food hydrocolloids (Le Corre et al. 2010).

The usefulness of using nanostructures in food industry as presented in (Lagaron and Lopez-Rubio 2011; Gemili et al. 2010; Mastromatteo et al. 2010) includes:

- Controlled and/or burst release of substances in active and functional food packaging technologies and intelligent food packaging.
- Formulation of active packaging technologies based on bioplastics such as more efficient antioxidant, oxygen scavenging or antimicrobial biopackaging, which has more direct implications in increasing packaged foods quality and safety.
- Important issues associated with the use of bioplastics, such as the non-intended migration of plastic components to foods, can also be potentially reduced by the use of nanoparticles.

While significant progress has been made in the area of nanobiotechnology, there are still many issues left to resolve before clinical use of these materials can be realized. Before nanostructures can be utilized for human body, several important properties need to achieve. The nanostructures must be nontoxic, non-immunogenic, stable in blood, biodegradable and applicable to various biomolecules. From commercial and engineering points of view, the nanostructures also must possess scalable and inexpensive manufacturing process. Technical, regulatory and legal challenges, however, exist along the road to implement nanotechnology in the fields of medical pharmaceutical and food industry. A great challenge is realizing the long-term impact of nanostructures on human health and their interactions (Papazoglou and Parthasarathy 2007). The other issue is lack of knowledge about the stability of nanostructures during processing. However, the use of natural additives like clay nanoparticles and nanocellulose may help to overcome this problem because of their biocompatibility.

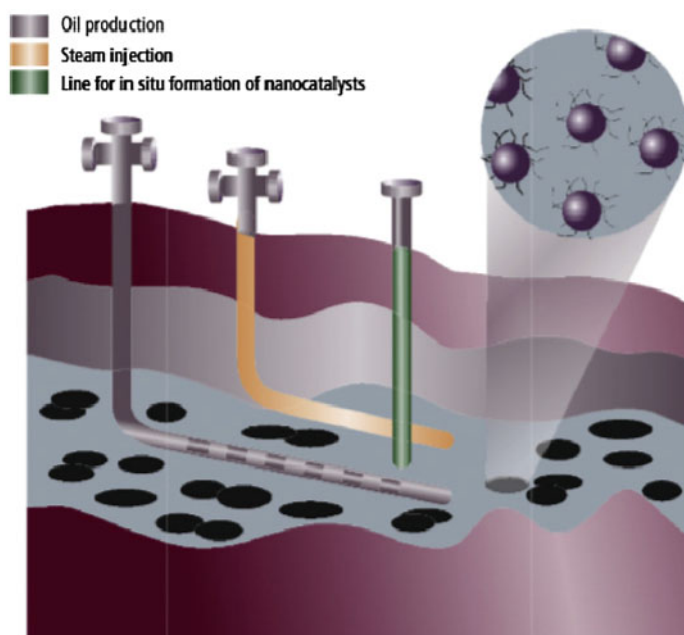
### **2.1.1.2 Nanotechnology in Petroleum Industries**

Nanotechnology is offering new and improved methods in different areas of the oil and gas industries from exploration and well drilling to refining and distribution. Properties of nanostructures such as lightness, corrosion resistance and mechanical strength make them significant elements to be used in the oil industry machines, specially drilling machines (Singh et al. 2010). Nanotechnology represents breakthrough elements, thanks to the development of innovative monitoring techniques and smarter nanosensors. Conventional sensors and other measuring tools are unreliable in hostile high-temperature and high-pressure conditions. Improved performance sensors for imaging, measuring and controlling reservoirs and oilfields will improve all activities in the area of oil industry, from exploring oil well and drilling to oil transporting and reserving (Matteo et al. 2012). Besides the potential

applications enumerated for nanotechnology in oil and gas industry, nanostructures can provide extraordinary opportunities to develop more cost-effective and environmentally friendly upgrading and recovery enhancement of heavy feedstocks (Krishnamoorti 2006; Nassar et al. 2011; Almao 2012). Nanostructures were used for reduction in the viscosity of heavy oil, thus benefiting the oil exploitation and upgrading transportation. Using nanostructures in catalysts provides several advantages that ultimately increase the economics of the upgrading process. The catalyst-improved characteristics include (Hashemi et al. 2014):

- (a) High surface area-to-volume ratio, which results in improved catalytic performance for processing purposes
- (b) Increased probability of contacts between reactants because of their high mobilization inside the reactor
- (c) Long run times for conversion as there is no need of catalyst replacement because of nanocatalysts implementation inside the medium
- (d) Stable long-term high activity

Another promising advantage is possibility of in situ preparation of catalyst. Figure 2.4 illustrates the in situ preparation of nanocatalyst for upgrading and recovery of bitumen during the steam-assisted gravity drainage (SAGD) process (Nassar et al. 2011). In this method, nanocatalysts are introduced into the porous



**Fig. 2.4** In situ heavy oil upgrading and recovery (Nassar et al. 2011)



media through a line to perform upgrading inside the reservoir to convert bitumen to lighter products. The ultra-dispersed nanocatalysts will aid the SAGD process, and light oil is produced at the surface, whereas heavy molecules, solids and minerals stay subsurface. Successful in situ processing will reduce the operating costs as well as environmental concerns; however, there is a long way and extensive works are needed to commercialize the proposed method (Hashemi et al. 2014).

Other emerging applications of nanotechnology in oil industry include development of:

- New generation membranes for gas separation.
- New types of smart fluids for water shutoff and improved/enhanced oil recovery (Matteo et al. 2012).
- Nanocatalyst (Pour et al. 2010; Gharibi et al. 2012).
- Unconventional petroleum exploration and exploitation (Caineng et al. 2012).

### 2.1.1.3 Nanotechnology in Material Science

Nanocomposites are broadly defined as nanofillers bonded to a matrix (Paul and Robeson 2008). Nanocomposites of ceramic, metallic and polymer matrixes have shown outstanding properties in comparison with composites of the same material but using microstructures (Gao et al. 2007; Thostenson et al. 2005; Esawi and Farag 2007; Pezzin et al. 2011). The benefits encompass improved mechanical properties, scratch resistance, barrier properties, fire resistance and dimensional stability. Moreover, a small amount of nanofillers can cut weight and reduce cost compared with the usual loading of conventional fillers (Thostenson et al. 2005). Nanocomposites can be classified as structural or functional depending on the role of the nanofiller in each situation (Pezzini et al. 2011). For structural composites, the mechanical properties of the nanoparticle, such as high Young's modulus, tensile strength and elongation at break, and the ability to resist compression and distortion can be used to produce lightweight structural materials. On the other hand, in functional composites, other interesting properties are exploited, such as high electrical and thermal conductivity, required in the development of thermal resistant materials, sensors, electrical conductors, photoemitters, electromagnetic shields or energy accumulators. Polymer nanocomposites enable substantial improvements in material properties such as shear and bulk modulus, yield strength, toughness, scratch resistance, optical properties, electrical conductivity, gas and solvent transport, with a small loading of nanostructure dispersed in the polymer matrix (Paul and Robeson 2008). Nanostructures also increase the temperature at which the polymer will start to acquire a softened state, and hence, they have been extensively used in synthesis of thermoplastic polymers. Using natural nanostructures to develop thermoplastic polymers is a promising route toward producing sustainable products (Cyras et al. 2008; Schlemmer et al. 2010; Aouada et al. 2011). Nanocellulose, nanostructured minerals (like clay hallo site nanotubes, modified bentonites and montmorillonites), organic-inorganic hybrid nanomaterials and



polymer matrix clay-reinforced nanocomposites are some of the examples of nanostructured natural materials. These natural nanostructures have been also examined for other applications. For example, nanoceramic coatings have been developed that can be applied in household appliances or automobiles instead of coatings made from hazardous materials like chromium and toxic heavy metals (Nentwich and Greßler 2012). A small amount of nanoclay (less than 5 wt%) indicated a great enhancement in polymer properties regarding the mechanical and thermal resistance (Powell and Beall 2007; Choudalakis and Gotsis 2009; Meneghetti and Qutubuddin 2006; Du et al. 2010). Nanocellulose is another example of natural nanostructures that have wide applications in producing moldable lightweight and high-strength materials, medical implants, electrodes for fuel cells, barrier film for packaging applications (keeping oxygen from spoiling food), composites for construction, vehicles and furniture (Klemm et al. 2009; Siró and Plackett 2010). Cellulose is abundant, has high strength and stiffness, low weight and biodegrade ability.

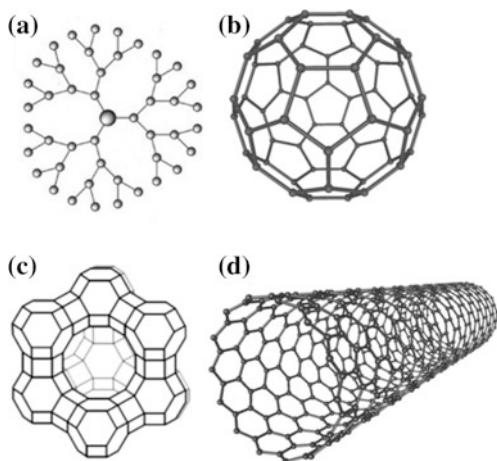
#### 2.1.1.4 Nanotechnology in Environmental Science

Nanotechnology innovations have also raised great applications in the environmental sector. Nanostructure-based materials are aimed to improve the environment through direct applications in detecting and removing pollutants from soil and groundwater. Nanosensors capable of detecting a low concentration of toxic gases are imperative for environmental monitoring and chemical safety as well as control of chemical processes and agriculture. Nanoadsorbents and nanomembranes indicated their effective role in water and air purification as well as wastewater treatment by removal of various types of pollutants including heavy metals, synthetic dyes and biological contaminants (Lu et al. 2005; Yang et al. 2007; Liao et al. 2008; Savage and Diallo 2005; Kwon et al. 2008; Kuo 2009; Diallo 2009; Li et al. 2013; Hu et al. 2009; Mishra et al. 2010; Yao et al. 2010; Bora and Dutta 2014). Nanostructures act as an adsorbent or photocatalyst and have indicated high sensitivity, selectivity and efficiency for removal of these contaminants. Common nanostructures with potential applications for adsorbing pollutants include dendrimers, zeolites and CNTs (Diallo 2009). Different structures of these materials are depicted in Fig. 2.5.

There are also some nanostructures with photocatalytic activity, like Zinc Oxide, applied for the treatment of environmental pollution (Sung et al. 2010). The nanomembranes, nanoadsorbents and nanostructures with photocatalytic activity can be used to purify indoor air volumes or to separate out contaminants in automobile tailpipes and factory smokestacks and prevent these contaminants entering the atmosphere.

Another excellent application of nanotechnology in the water sector is for water desalination. As the fresh water resources become increasingly scarce due to overconsumption and contamination, scientists have begun to consider seawater as

**Fig. 2.5** Typical structures of nanomaterials with potential applications for adsorption: **a** dendrimer, **b** fullerene, **c** zeolite, **d** carbon nanotube



another source for drinking water. However, the seawater has too much salt for human consumption, and desalination is required for removing the salt to create new sources of drinking water. Desalination is an expensive method, and nanomembranes have the potential to reduce its cost (Mansoori et al. 2008; Kar et al. 2012).

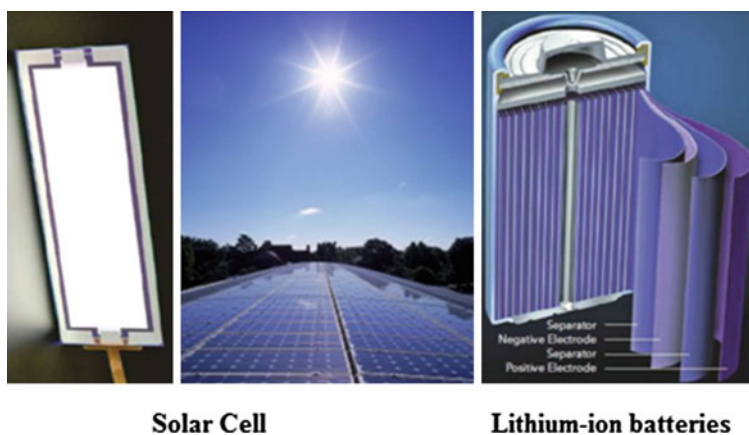
Besides their role in environment remediation, nanostructure-based products, based on their special properties, have the potential to make products or production processes more environmentally friendly (Yuan 2004). Although positive environmental effects are rarely the reason for using nanobased products, such an influence is an acknowledged side effect. They contribute to environmental and climate protection by saving the raw materials and energy sources. For example, using nanocomposites increases the durability of the products against mechanical and thermal stresses or weathering and thus increases the useful life of a product. It was indicated that adding nanostructures, like nanosilica or carbon nanofiber or tubes, to tires reduce rolling resistance, which leads to fuel savings (Sun et al. 2012a, b; De et al. 2013; Chandra and Bhandari 2013). Nanocomposites also can reduce weight of the vehicle and hence fuel consumption that save energy during transport. Nanocoatings, which are resistant to dirt or easy-to-clean, do not need to be cleaned so often and hence help energy and water saving in facility cleaning. Novel insulation materials in the constructions, in which nanostructures have been used, improve the energy efficiency of buildings and reduce the energy needed to heat and cool buildings.

One of the outstanding roles of nanotechnology is improving energy and resource efficiency in the chemical industry. The explosion and developments in nanotechnology have exhibited significant impacts on the understanding, practice and applications of catalysis. Nanocatalysts can be used to increase the yield of chemical reactions and reduce the amount of environmentally damaging side products. Catalysis provides controls over the rates at which chemical bonds are

broken and formed. Therefore, it is the key to energy conversion and environmental protection in chemical manufacturing and transportation. In the chemical industry, nanocatalysts with improved properties boost energy and resource efficiency. High hopes are placed in nanotechnologically optimized products and processes for energy production and storage. Novel lighting materials with nanoscale layers of plastic and organic pigments enhance conversion rate from energy to light (Chang et al. 2013).

### 2.1.1.5 Nanotechnology in the Energy Sector

The world demand for energy is expected to become about 30 terawatts by the year 2050. Compounding this challenge is to protect our environment by increasing energy efficiency and developing clean energy sources. Solutions require scientific breakthroughs and truly revolutionary developments. Within this context, nanotechnology presents exciting and requisite approaches for addressing these challenges. Those areas that nanotechnology helps to improve efficiency of energy sources have been described as its positive effect in environment (previous section). Another application of nanostructure in the energy sector is for energy production, distribution and storage. For example, electrodes comprising CNTs have been used to produce high-power lithium batteries, solar cells, fuel cells and several other electrochemical applications (Lee et al. 2010; Lota et al. 2011; Liu et al. 2012; Zhang and Dai 2012). Lithium-ion batteries (LIB) consisting of nanostructures also indicated improved storage capacity as well as an increased lifespan (Landi et al. 2009). LIB (Fig. 2.6) have several applications, ranging from portable electronics to electric vehicles, due to their superior energy density over other rechargeable battery technologies. Using nanostructure also offers LIB of smaller size and lower weight that may attract more attentions. Another example of positive effect of



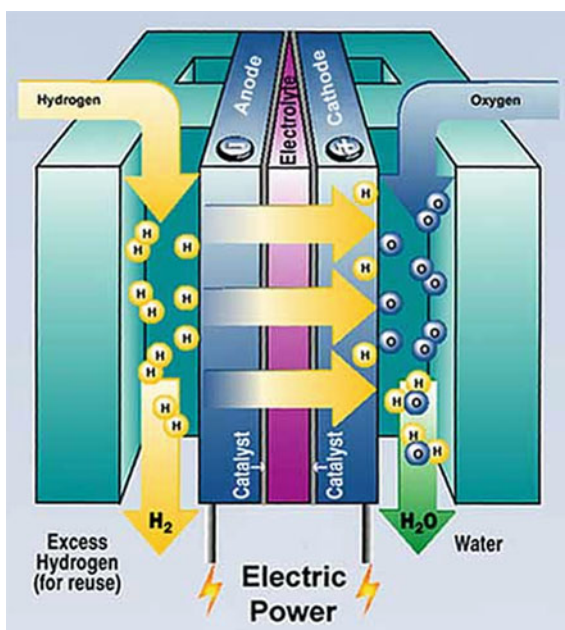
**Fig. 2.6** Solar cell and lithium-ion batteries (LIB)

nanotechnology is their application in solar cells (Fig. 2.6). For example, solar cells with nanoscale semiconductor materials have been developed by mimicking natural photosynthesis in green plants (Anandan et al. 2006). Solar energy is nowadays considered as a promising renewable source of energy. The benefits of nanotechnology in solar cells include reducing costs of materials, processing and installation and achieve reaching higher efficiency levels compared to traditional ones.

A fuel cell is an electrochemical device consisting of an electrolyte, an anode and a cathode which directly and continuously converts the chemical energy of a fuel into electrical energy (Hoogers 2002). Fuel cells may replace fossil fuels to power automobiles and reduce our reliance on petroleum; however, their efficiency still needs to be improved. The efficiency of fuel cells is determined by the rate of electron transfer at electrodes. The main factors that determine efficiency of a fuel cell involve the catalysts and electrolyte used and the operating temperature, since they influence the reaction kinetics and the ionic transportation in the cell (Kirubakaran et al. 2009). The performance of fuel cells with nanostructures has been found to be superior to other common electrodes in terms of their efficiency and reversibility. Nanotechnology researches offer more efficient catalyst in fuel cell through specific design of catalyst.

Hydrogen is the most abundant element in the universe, and its molecule can store a great amount of chemical energy, which can be used to generate electricity. This is the base of developing hydrogen fuel cells, in which chemical oxidation of hydrogen to water produces electricity (Fig. 2.7). Hydrogen fuel cells can be used to power the vehicle or power plants, in place of fossil fuels. A great priority of

**Fig. 2.7** Hydrogen fuel cell  
(Source EnLIST Chemistry  
Workshop, University of  
Illinois, 2010)



hydrogen fuel cells is that they do not contribute to air pollution. The first step in developing fuel cells is to enhance the hydrogen storage. Hydrogen can be compressed and reversibly stored in tanks through chemical or physical bonding of hydrogen with storage material. Nanotechnology has offered great possibility in improving storage materials; high porous materials able to adsorb hydrogen in their porous or complex hybrids reversibly bound with hydrogen in their lattice structure (Sakintuna et al. 2007; Zubizarreta et al. 2009). Carbonaceous structures (activated carbon, carbon nanofiber and CNTs) are leading adsorbent candidates for gases including hydrogen (Lee et al. 2000; Panella et al. 2005; Zubizarreta et al. 2009; Ioannatos and Verykios 2010). The properties that make carbon materials attractive include their morphology, in the form of a fine powder, with high porosity and the existence of specific interactions between the carbon atoms and the gas molecules.

Supercapacitors are energy-storage devices that store energy directly and physically as charge, whereas batteries store energy in chemical reactants capable of generating charge (Izadi-Najafabadi et al. 2010). They have application in small-scale energy-storage devices in stationary electronics, such as memory backup devices and solar batteries with semipermanent charge–discharge cycle life (Jurewicz et al. 2001). Supercapacitors compared to the other energy-storage devices are able to store and deliver energy rapidly and efficiently for a long life cycle via a simple charge separation process. In addition, their wide range of power capability makes it possible to hybridize them with other energy-storage devices, such as batteries and fuel cells. The performance of supercapacitors have been further improved by using nanostructures (Frackowiak et al. 2006; Cheng et al. 2011; Kong et al. 2013; Hahm et al. 2012; Kim et al. 2012). It is worth mentioning here that carbon nanostructures compared to the other types of nanostructures have been preferred to be used in the electrode materials. Conventional carbon materials have been extensively used in energy-storage systems due to their good chemical stability and high electrical conductivity. Carbon nanostructures, besides the advantages mentioned for conventional carbon materials, have unique electrical and electronic properties, a wide electrochemical stability window and a highly accessible surface area (Kim et al. 2012).

### 2.1.1.6 Nanotechnology in Other Specific Fields

Different nanostructures (nanoparticles, nanotubes, nanocrystals) contribute to the fabrication of gas sensors (Comini 2006; Lupan et al. 2010; Sun et al. 2012a, b; Moloney and Barrera 2013; Chow et al. 2013; Benkstein et al. 2014). The main advantage of these sensors is the nanoscopic size of the sensing element and the corresponding nanoscopic size of the material required for a response. In addition, the mechanical robustness of the sensing elements and its low buckling force increase the sensor lifetime. As an example, the electrical resistivity of single-wall nanotubes has been found to change sensitively on exposure to gaseous ambient containing  $\text{NO}_2$ ,  $\text{NH}_3$  and  $\text{O}_2$ . Nanosensors' response is at least an order of magnitude faster than those currently available, and they could be operated at room

temperature or at higher temperatures for sensing applications (Lupan et al. 2010; Chow et al. 2013; Sharma et al. 2013).

The correspondence between mechanical response and electronic transport has been proven potential applications of nanostructures in such applications as nano-electro-mechanical sensors (NEMs). Besides their wide application in life science, NEMs are now being researched for their use in automotive industries (Esashi 2009; Hema 2013). A tiny sensor would be able to monitor and report tire pressure to the driver while being able to withstand extreme temperatures and vibrations. NEMs also provide opportunities for smart airport pavement instrumentation and health monitoring by long-term, continuous, real-time response measurement of transportation infrastructure systems (Yang et al. 2014).

Nanostructures can be also applied in scanning probes of high-resolution imaging instruments, such as scanning tunneling microscope (STM), atomic force microscope (AFM) and electrostatic force microscopes. More detailed explanations on these instruments can be found in Sect. 2.1.3. They can be also used for surface manipulation. For example, on an AFM tip, they can be controlled like tweezers to pick up and release nanoscale structures (Takekawa et al. 2005). Nanotweezers also have great application in life science (Hashiguchi et al. 2003; Roxworthy and Toussaint 2013). Nanostructures are also considered for improving the catalysts performance, either as active element or as support (Akia et al. 2014; Shen and Yoshikawa 2013).

Applications of nanotechnology-based products are not limited to those addressed in this section, and some unique applications are being developed. A unique role of nanostructure is in the area of controlled release of an element. Besides sustained release of drugs, food additives and fragrances, explained in the field of biotechnology application, they are applied for controlled release of anti-corrosion agents as well as sustained release of herbicides, insecticides, fungicides and antimicrobials. Another imperative application of nanostructures is in developing antibacterial products. Silver nanoparticles have been extensively used in both antibacterial and biocidal fabric and agent. These products have biomedical applications (YeonáLee et al. 2007; Choloupla and Malam 2010) and can be applied as preservatives in wood, paints, etc. (Nowack et al. 2011). Nanoparticulate titanium dioxide ( $\text{TiO}_2$ ) is another nanostructure used in synthesis of antimicrobial products (Chung et al. 2008). This nanostructure has found more applications such as in synthesis of flame retardants (Chen and Wang 2010; Kiliaris and Papaspyrides 2010), mineral UV filter in sunscreens (Popov et al. 2005; Sadrieh et al. 2010) and self-cleaning products (tiles, windows and textiles) like antifogging car mirrors and dental mirror surfaces (Funakoshi and Nonami 2007; Veronovski et al. 2009). Another emerging application of nanostructure is in the field of refractory technologies, for example, in the steel and cement industries (Kuznetsov et al. 2010; Antonovič et al. 2010).

Despite vast application of nanostructures, there are some uncertainty about their side effects on human health and environment. Accordingly, a great attempt toward developing healthier and more efficient and sustainable nanotechnology-based products is conducting. In this respect, natural and modified natural nanostructures

are preferred. Their applications are as wide as refractories, textiles, energy, biomedical, functional barriers and environmental fields. The most common natural nanostructures are nanoclays (hallo site and kaolin clays), montmorillonite, nanocellulose and nanostarch.

### ***2.1.2 Nanostructured Materials Synthesis, Concepts and Design***

Nanostructures defined as materials with at least one dimension of their structure in the nanometer scale. Nanostructures possess new and unique chemical and physical properties compared to their corresponding bulk or isolated atoms and molecules. Nanostructures have a limited number of atoms (or molecules) in which their arrangement can be controlled during synthesis. Therefore, their chemical, mechanical, optical, electronic and magnetic properties of nanostructures can be significantly altered. For example, the color or absorption spectrum changes dramatically with size when the size is small compared to the de Broglie wavelength or the Bohr excitation radius of the electron (Cao 2004). When a metal particle such as gold is smaller than 10 nm, it essentially exists in a state that is neither liquid nor solid. When a common liquid such as water is confined to a space that is only a few nanometers in dimension (for example, when water flows in a nanochannel), its properties are significantly different from those of the liquid water and solid ice that we are familiar with (Cao 2004).

The technological importance of these nanostructures is well demonstrated in various applications, including in catalytic process, biotechnology, medical and biomedical, photonic, energy-storage, etc. It is worth mentioning that the nanostructures properties are dependent not only on size but also on morphology and spatial organization. Factors like microstructures of nanoparticles, their size distribution, order of orientation, presence of defects and contaminants also significantly change the suitability of a nanostructure for integration of any material or devices. Accordingly, the feature size, shape of nanostructures and its purity need to be well controlled to attain the properties and functions that have been already established. Consequently, besides fabulous potential applications of nanostructures in different areas, their fascinating properties still remain the main motivation for further discovery and exploration.

#### **2.1.2.1 Synthesis Technologies and Challenges**

Referring to their wide range of applications, synthesis and manufacturing of nanotechnology-based products is one of the most active fields in nanoscience and nanoengineering. Nevertheless, advances in this field mainly depend upon the ability to synthesize nanostructures of controlled properties. It is well recognized



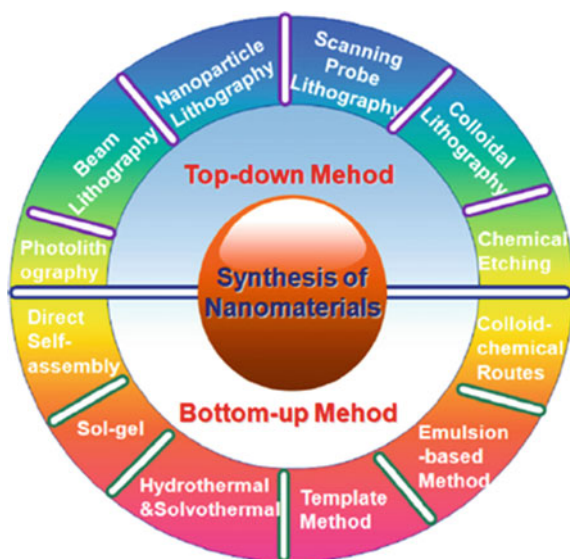
that properties of nanostructure materials greatly depend on the size, shape, composition, morphology and its crystalline structure. Accordingly, various approaches have been developed to control these parameters and, therefore, meet the requirements for diverse applications. Despite numerous technologies for fabrication of nanostructures, typically, there are two drastically different approaches, top-down and the bottom-up. The top-down approach is analogous to making a stone statue which is starting from bulk size and getting nanosize. A bulk piece of solid materials is taken and modified by milling, carving or cutting to create the desirable shape and size. The top-down process involves material wastage and is limited by the resolution of the tools employed. The smallest sizes of the structures made by these techniques are also restricted. Anyway, the top-down approaches have been practiced with great success by the electronics industry in fabrication of integrated circuits (Cao 2004).

Examples of this kind of approach include the various types of lithographic techniques (such as photo-, ion beam, electron or X-ray-lithography) and solid treatment such as milling, cutting, etching and grinding. The bottom-up approach for creating nanostructure involves starting from unit base of material (atom or molecule) and getting the bulk size with controlling the unit base arrangement. This approach can be analogous to building a house. Lots of building blocks are taken and put in a specific place to make final bigger structure. There is less wastage in this technique; however, it is limited in how big the structures can be made. Producing nanostructures is generally carried out through chemical reaction, and strong covalent bonds will hold the constituent parts together. This approach is the more preferred and efficient method for fabricating a wide variety of nanostructures with controllable size and properties. Chemical synthesis, self-assembly and molecular fabrication are all examples of bottom-up techniques (Texter and Tirrell 2001). A good example of bottom-up approach can be found in nature; all cells use enzymes to produce DNA by taking the component molecules and binding them together to make the final structure. In addition to these two main approaches, there are some special methods that cannot be classified in these two categories, as depicted in Fig. 2.8.

As explained in the section of nanotechnology applications in different fields, nanostructures have the potential to provide greatly enhanced performance and customer benefits at very low volume use. The practice of large volume manufacturing for bulk chemicals is unlikely to be the way for development of manufacturing processes for nanostructures. Instead of large footprint plants, smaller, portable, modular and integrated manufacturing systems will be desirable for nanostructures production (Zhao et al. 2003; Stephanopoulos et al. 2005). The major challenge for development of such systems is their scale-up. Scale-up of manufacturing processes for nanostructures to technological scales has not been pursued to an appreciable degree yet.

Another important issue is the matter of kinetics. Bottom-up approach is grounded in processes that tend toward desirable equilibrium structures. Chemical processes generally should go as fast as possible, consistent with product quality. It is difficult to envision the processing research fruitfully without data on the rates of

**Fig. 2.8** Schematic illustrations of the synthesis methods of nanomaterials (Qiao et al. 2011)



formation process. For design and development purposes, it is required to fully understand the trajectories, through time and structural intermediates, of the processes. This needs research in reaction kinetics, and the related issues of mechanisms have several facets. As the complexity and number of components in these processes increase, predictive models will become more important tools in process and product design. Thorough understanding of chemical bonding, reaction mechanisms, pathways and kinetics is crucial for reactor design. Practical processes must be controlled to produce nanostructures that possess intricate internal structure. Structural analyses present instrumental challenges, i.e., techniques capable of measuring with reasonable resolution are needed; informative, online measurement is also prerequisite for process control; characterization of defects is particularly important for the applications envisioned (Wang 2000a, b; Gommers et al. 2004; Puretzky et al. 2005; Gancs et al. 2008; Schlemmer et al. 2010; Chow et al. 2013). Moreover, barriers like environmental protection issues and human society safety must be applied to the development of nanostructures fabrication in the commercial sector.

### Top-down Methods

Synthesis of nanomaterials by means of top-down approaches is generally physical or mechanical approach. The top-down strategies are mainly based on milling, machining and lithography. A categorized diagram of these methods is depicted in Fig. 2.9.



**Fig. 2.9** Classification of the common top-down methods for nanostructural material synthesis or production

Photolithography, in which the entire surface is simultaneously patterned at once, is the most common top-down technique. This technique is cost-effective and relatively fast; however, its resolution is limited to typically 0.2–0.5  $\mu\text{m}$  because of the optical diffraction effects. Electron and ion-based lithography, in contrast, provide creation of ordered arrays of nanostructures with high resolution of about 50 nm (Qiao et al. 2011). Since they have line-by-line generation pattern, better control over shape and spacing of nanostructures is achieved but at slower rate compared to photolithography. Dip pen lithography (DPN) is a process in which the tip of an AFM is “dipped” into a chemical fluid and then used to “write” on a surface, like an old-fashioned ink pen onto paper. DPN is also serial technique, and hence, it is not suitable for high-volume manufacturing technologies. Nanoimprint

lithography (NIL) is a process for creating nanoscale features by “stamping” or “printing” them onto a surface. In soft lithography, patterns of small features are stamped and lines at a width nanometer can be printed. These patterns become micro-channels for analysis of nucleic acids, proteins or cells in a lab-on-a-chip or lab-on-a-system devices. Other top-down techniques include scanning tunneling microscopy (STM), micro-contact printing (mCP) and NIL (Liu et al. 2008).

Another branch of top-down method in the nanostructure material synthesis is milling. Milling is generally a conventional method to size reduction in solid. It theoretically can use to reduce size of the powder to nanosized range, but in the practice, this method has several limitations. Milling is a routine method for producing nanocrystalline powder, which is named powder metallurgy. Besides conventional mills, today new generation of mills, planetary mill, produces submicronized powder with the nanosized crystalline. This method is also using in the mechanical alloying.

Generally, mechanical milling has proved to be an effective and simple technique without involving high-temperature treatment for the production of nanopowder and nanocrystalline powders, with the possibility of obtaining large quantities of materials with modified properties. In this technique, starting powder particles are trapped between highly kinetic colliding balls and the inner surface of the vial, which causes repeated deformation, re-welding and fragmentation of premixed powders resulting in the formation of fine, dispersed particles in the grain-refined matrix. During the milling operation, two essential processes affect the particle characteristics. First, the cold welding process leads to an increase in average particle size of the composite. The second, fragmentation, process causes the breaking up of composite particles. Steady-state equilibrium is attained when a balance is achieved between these processes after a certain period of milling (Salah et al. 2011). Another type of nanostructure synthesis is micromachining. In this type of operation, usually a mechanical machining such as drilling, cutting, turning and so on is done in nanoscale using special apparatus such as laser beam, ion beam, X-ray beam and chemical or electrochemical methods.

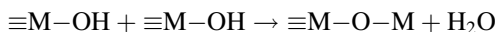
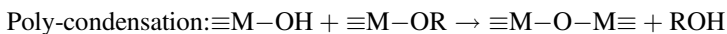
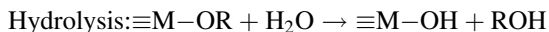
## Bottom-up Methods

The bottom-up approach is a self-assembly of molecular species, with controllable chemical reactions. This approach involves the creation and utilization of functional materials, devices and systems with novel properties and functions achieved in the forms of control of matter, atom by atom, molecule by molecule or at the macromolecular level. This fact causes the synthesis to be carried out in a fluid phase, while the top-down methods were done in the solid phase. Compared to top-down approach, this technique is more efficient and flexible to synthesis vast variety of nanomaterials with well-controlled shape, size, morphology, structure, surface properties conveniently.

Generally, the bottom-up approach to synthesis of nanostructural materials can be divided to two main methods which are synthesis in liquid phase and gas

(or vapor) phase. In most of these methods, chemical reactions take place, and in the others, physical events (such as vaporization, condensation or precipitation) occur. In any case, the unit base of the nanostructure product (atom or molecule) is generated in the mobile phase (fluid phase). Then, nanostructure is created with controlling of unit base mobility and also their deposit arrangement in an expected pattern. This controlling of deposit arrangement is the art of nanotechnology. In other words, when the synthesis condition (such as temperature, pressure, atmosphere, initial concentration, reactant type, resident time, type and concentration of additives and so on) is controlled and leads sensitively, different nanostructure shapes such as hollow sphere, filled sphere, core-shell, tube, rod, plate, horn shape and any other one-, two- and three-dimensional shape with desirable composition and crystallinity are achievable even in the mass production.

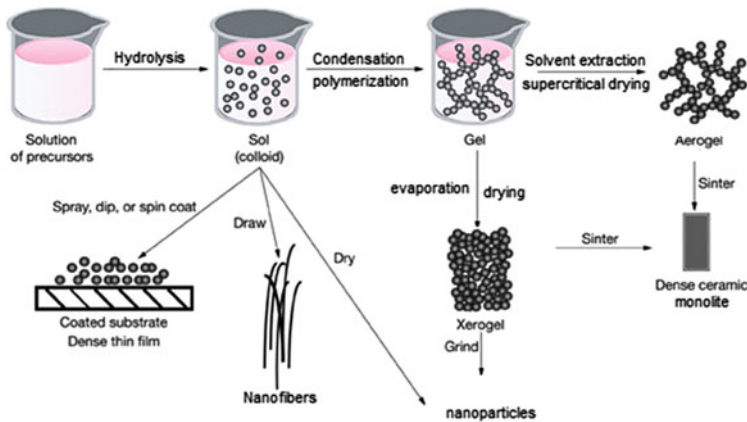
Examples for synthesis in liquid phase are precipitation, sol-gel, hydrothermal, microemulsion and electrochemical deposition (anodizing and cathodizing). The most common types of bottom-up synthesis procedures in the liquid phase are those based on the use of sol-gel method. Sol-gel method is referred to a large group of synthesis methods where sol is obtained from solution through hydrolysis followed by gel formation through poly-condensation reactions. Sol-gel methods are mostly based on controlled hydrolysis of metal alkoxides in aqueous or organic medium where there are two distinct reactions: hydrolysis of the alcohol groups and poly-condensation of the resulting hydroxyl groups as follow:



Metal alkoxides are denoted as  $\text{M}(\text{OR})_x$  where M is symbol of a metal and R is hydrocarbon chain.

The first step in sol-gel processes leads to the formation of a colloidal solution of monomers (in dimension about 0.1–1  $\mu\text{m}$ ) where only the Brownian motions are present, named as sol. Increasing bulk concentration of the dispersed phase or any changes in pH and/or solvent substitution result in formation of strong contacts between particles, and thus, monolithic gel, a solid network containing liquid components, is formed. In gel state, liquid and solid are dispersed in each other, where molecules of solvent are enclosed in a flexible, but fairly stable, three-dimensional grid formed by solid particles. Concentration of sols that leads to gel formation is carried out by evaporation at relatively low temperatures, extraction, dialysis or electrodialysis and/or ultra-filtration. Sol-gel processes are generally applied for synthesis of a wide range of nanotechnology-based products such as nanoparticles, thin films, nanofibers. The sol-gel process for synthesis of thin films usually consists of four steps:

- The desired colloidal particles once dispersed in a liquid to form a sol.
- The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.



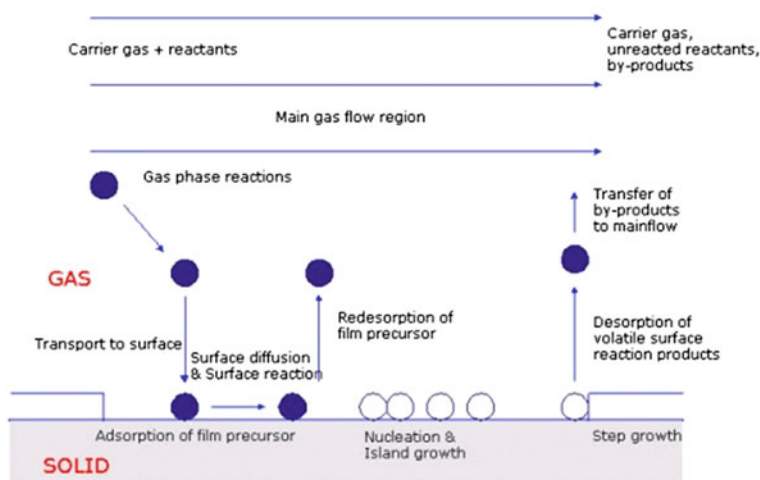
**Fig. 2.10** Schematic diagram of sol-gel method and its nanomaterials products

- The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.
- The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

After gel formation, the solvent needs to be removed from the gel. Different types of dried gel (aerogels, xerogels, ambigels, cryogels) can be produced depending on the method of drying (super critical drying, ambient drying, freeze drying, etc.). The final product (dried gel), pronounced quasi-one-dimensional structure, includes the nanostructures whose bulk density can vary by hundreds of times with sufficiently high surface area (hundreds of  $\text{m}^2/\text{g}$ ). When drying causes shrinking in the gel, xerogels are formed, and in case no shrinking happens in the gel, aerogels are obtained. Shrinking and gel shape deformation depend on the conditions applied for drying; for example, ambient drying will result in xerogels, and super critical drying will get aerogels. Figure 2.10 illustrates the consequences of sol-gel process to produce different types of dried gel and nanostructures.

Examples for synthesis in gas phase, based on bottom-up approach, are chemical vapor deposition (CVD), chemical vapor synthesis (CVS), physical vapor deposition (PVD), light scattering, laser ablation. CVD as a symbol of gas-phase synthesis procedure is a technique which is used to produce solid nanomaterials, typically CNT and thin films. In this process, substrates are heated to high temperatures and exposed to precursor materials in the gaseous state. The precursors react or decompose on the substrate surface to yield a coating of the required material. CVD has been found subsequently to be an excellent, scalable method for the production of high-quality material. The CVD growth of carbon nanomaterials consists of several stages:

- Substrate heating/conditioning
- Growth
- Substrate cooling



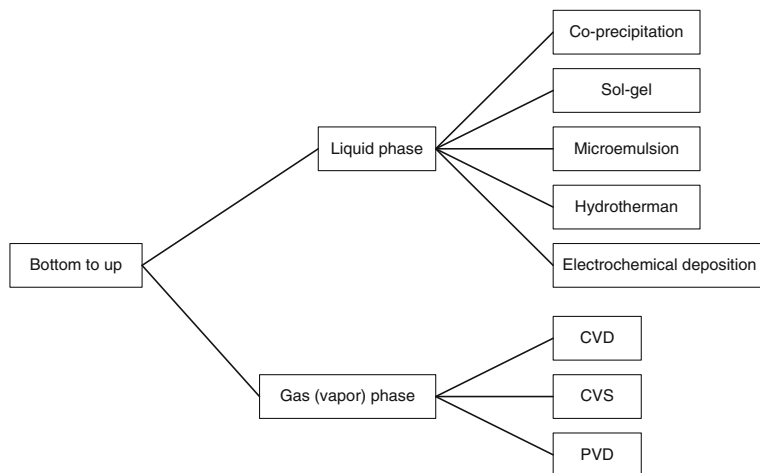
**Fig. 2.11** Events take place in the CVD process (<http://postechlocal.k2web.co.kr/user>)

To start, substrates are heated to the growth temperature. During heating, it is common to flow gases appropriate for substrate conditioning (i.e., for removal of surface oxides and contamination). After a certain time period, precursor gases are introduced into the reaction chamber. Given appropriate system conditions (temperature, pressure, etc.), these precursors lead to the formation of films of surface-bound material. Growth is carried out for a certain period of time, after which precursor supply is terminated. Heating is then switched off and the substrate cooled to a temperature at which it can be safely removed. During these stages, several events take place on the precursor and product atoms (molecules) and these events affect the product properties. These events are illustrated in Fig. 2.11, which are as follows:

- Precursor bulk flow
- Precursor adsorption
- Surface and gas-phase reactions
- Surface diffusion of precursor and product
- Precursor and product desorption
- Nucleation and growth of product

For graphene synthesis, CVD processes are typically carried out using metal substrates, methane feedstock, low pressures (1–50 Torr) and temperatures of 900–1000 °C. In addition to methane, other process gases, such as argon and hydrogen, may be present. Common substrates include copper and nickel. Copper substrates are particularly attractive, since growth is then dependent on precursor-substrate contact. In this case, growth stops after graphene formation (as opposed to continuing on to form thick, nonuniform graphitic material).





**Fig. 2.12** Schematic diagram of categorized methods in the bottom to up procedure in the nanomaterials synthesis

Recently, researchers have shown that CVD formation of graphene may be possible at reduced temperatures. This work has involved the use of room temperature liquid precursors, e.g., toluene, introduced into CVD systems in vapor form. Reduced growth temperatures should enable CVD processes to become compatible with more substrate types. Other work has also demonstrated the formation of graphene material from solid precursors, e.g., PMMA.

CVD growth of CNTs is very different. Rather than metal films or foils, CNT synthesis requires inert surfaces decorated with metallic nanoparticles. For these, transition metals such as iron, nickel and cobalt are commonly used. The metals are applied to substrates directly in nanoparticle form (e.g., from suitable liquid dispersions) or as thin films, prior to growth. For the latter case, the heating/conditioning step involves nanoparticle formation through thermal film coalescence. During the subsequent growth stage, nanoparticles are exposed to feedstocks. Typical feedstocks include methane, ethylene and alcohol vapors. These thermally decompose to yield carbon at nanoparticle sites that is catalytically assembled into CNT structures. These CNTs “sprout” out of the nanoparticles as growth continues. The classification of bottom to up methods in nanostructural materials synthesis is shown in Fig. 2.12. It should be noticed that there, other methods not mentioned in this chart. Only, the general methods are categorized in this chart and each mentioned method can be divided into several detailed methods that follow the same general route. In addition, those methods that are important in the chemical engineering view point are mentioned.

## Other Special Synthetic Methods

The most important achievements in nanotechnology are the novel techniques by combining the methods of lithography and self-assembly, such as lab-on-a-chip and system-on-a-chip. There are other special methods, including microwave irradiation, photochemical synthesis and bioinspired synthesis. Some of these techniques are:

- Biomimetic and Bioinspired Methods
- Photochemical and Radiation chemical Methods
- Ultrasonic-assisted Synthetic Methods
- Microwave Synthetic Methods
- Ionic liquid-assisted Synthesis Methods
- Electrochemical Synthesis

### ***2.1.3 Routine Tests for Characterization of Nanostructures***

To determine the success of the nanotechnology-related processing, the key objective is to characterize the structural feature as well as chemical and physical properties of nanostructured system. Numbers of characterization techniques for both individual and bulk nanostructured systems have been adopted and developed. High-resolution techniques offer the possibilities to study individual nanostructures, while bulk characterization methods do not provide information of individual nanoparticles. The properties and behaviors observed and measured by these techniques are typically group characteristics. Properties of nanomaterials can be substantially different from that of their bulk encounters. However, bulk characterization techniques are essential complement to other high-resolution methods, which provide rather detailed information on only a few particles. Since most nanostructures have uniform chemical composition and structures, bulk methods are extensively used in the study of some properties of nanostructures, like mechanical, electronic and optical properties. Nevertheless, all nanostructures properties are size dependent, and thus, their properties can be considerably tuned by adjusting the size, shape or extent of agglomeration (Cao 2004). For example, the optical absorption peak of metal particles can shift by hundreds of nanometers via particle size and shape. Recall that both techniques are complementary in the study of nanostructures. This section presents the basic principles of those characterization methods mostly applied in nanotechnology researches. Full explanation of all characterization techniques, their technical details, operation procedures and instrumentations are beyond the aim of this text, and readers interested to obtain more detailed information can refer to the special books and handbook like (Settle 1997; Wang 2000a, b; Wilkening and Koenders 2006).

### 2.1.3.1 Microscopes

The first step in characterization of nanostructures is to visualize their morphology. Under ideal conditions, the smallest object that the eye can resolve is about 0.07 mm. This limit is related to the size of the receptors in the retina of the eye. Microscopes are employed to improve our capacity for observing the objects in more details. These instruments allow us to observe a magnified image with greater details as they effectively bring the object closer to the eye and hence magnify the image falling on the retina. The best distance that one can resolve with optical microscope is of the order of 0.25  $\mu\text{m}$ , and hence, this type of microscope is not applicable for nanostructure visualization. For characterization and manipulation of individual nanostructures, it becomes essential to measure at a nanometer scale and resolution of the order of atomic distances or even smaller. High-resolution techniques can provide resolution at nanoscale and thus local information on the nanometer scale. High-resolution microscopes are categorized into scanning probe microscopes and electron microscopes (EM).

#### Scanning Probe Microscopy

Scanning probe microscopy (SPM) covers a broad group of quantitative measuring instruments applied for topographical imaging as well as quantification of chemical and physical properties of surfaces at a resolution down to nanometers (Bonnell 2001; Meyer et al. 2004). In SPM, a probe of nanometer dimension is used to trace the surface of the sample. A sharp tip (3–50 nm radius of curvature) mounted on a flexible cantilever scan across the object surface. Due to flexibility of cantilever, tip can follow the surface profile and as a result produce topographic image of a surface with atomic resolution in all three dimensions (Chi and Röthig 2000). The resolution of an image obtained by SPMs depends on the sample, movement control of the tip on sample and the inherent nature of the data. The mechanism presented and the scanning of a nanoscale probe forms the basis of all scanning probe instruments. Depending on the physical interactions used to probe the surface, the scanning probe microscopes have different names. Atomic force microscopy (AFM) and STM are the most common SPM used in study of nanostructures.

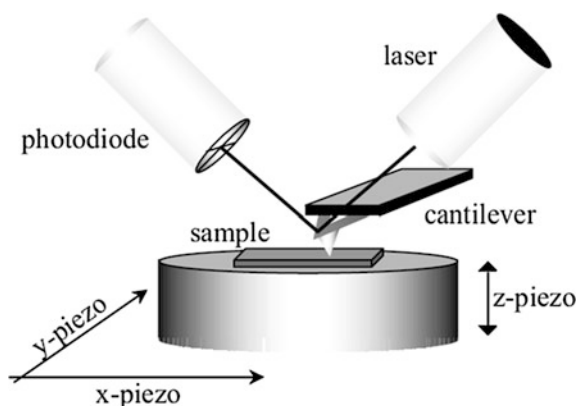
Generally speaking, AFMs use interatomic or intermolecular forces, while STMs are based on the quantum mechanical tunneling effect. Almost all solid surfaces, whether hard or soft, electrically conductive or not, can all be studied with STM and AFM. Although SPM is a surface image technique, combining with appropriate instruments, they have found a much broadened range of applications, such as nanoindentation, nanolithography and patterned self-assembly. SPM techniques are also used in biotechnology researches, for example, study of biomolecule imaging and proteins unfolding, antibody–antigen binding, binding forces of complimentary DNA strands, etc. (Gaboriaud and Dufrêne 2007; Wei and Liu 2010; Murty et al. 2013). Furthermore, SPM has recently entered the production and quality control environment of semiconductor manufacturers (Magonov et al. 2011).

## Atomic Force Microscopy

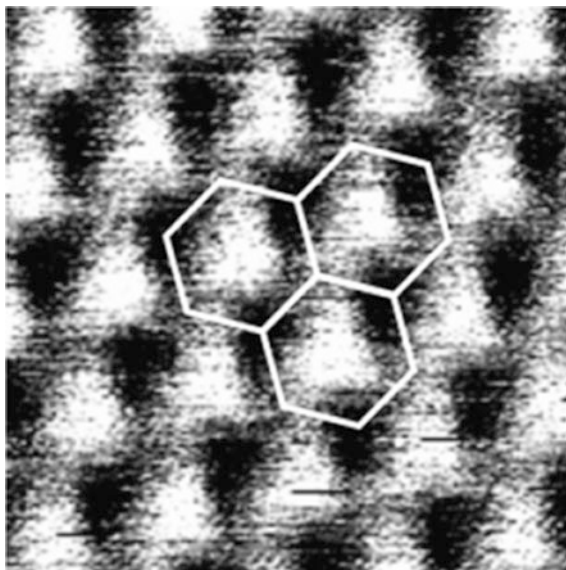
Atomic force microscopy (AFM) is one type of SPM used to image surface structures. In addition, as its mechanism depends on the force of attraction between molecules, it is also possible to measure surface forces, i.e., attractive or repulsive forces between tip and sample (Magonov and Alexander 2008). In AFMs, the probe is a tip at the end of a cantilever which bends in response to the force between the tip and the sample. Figure 2.13 illustrates a simple schematic of an AFM. A sample is positioned on a piezoelectric scanner. A microscopic tip (curvature radius of  $\sim 10\text{--}50\text{ nm}$ ) attached to a cantilever spring moves across the surface of the sample, and deflections are detected by measuring the cantilever's vertical displacement using reflections from a laser beam. When the cantilever flexes, the light from the laser is reflected onto the split photodiode and position of the reflected beam changes depending on the cantilever deflection. A photodetector converts this change in an electrical signal, and a displacement map of the surface is depicted that allows visualization of surface structure at the nanometer scale or even subnanometer scale (Wang 2000a, b). Since AFMs provide three-dimensional images of a sample surface, it probes the sample and makes measurements in three dimensions,  $x$ ,  $y$  and  $z$ . A resolution in the  $x$ – $y$  plane ranges from 0.1 to 1.0 nm and in the  $z$  direction is 0.01 nm (atomic resolution) (Chatterjee et al. 2010).

AFM does not require any special sample, and no current flows between the AFM tip and sample. The later makes AFM suitable for studies of nonconductors. Accordingly, this technique is widely employed for studies and the detection of atomic scale features of insulating surfaces including ceramic materials, biological samples and polymers. These microscopes can be used in either an ambient or liquid environment, and it does not need a vacuum environment. With all these advantages, AFM is capable of measuring topography, surface energy and elasticity of samples at the nanometer, even molecular scale, and it has significantly impacted the research fields of materials science, physics, chemistry, biotechnology, polymers and the specialized field of semiconductors (Magonov et al. 2011). The AFM microscope is capable of imaging all kinds of surfaces under atmospheric

**Fig. 2.13** Schematic diagram showing AFM principles (Chi and Röthig 2000)



**Fig. 2.14** AFM topography of a graphite surface (Hölscher et al. 2000)



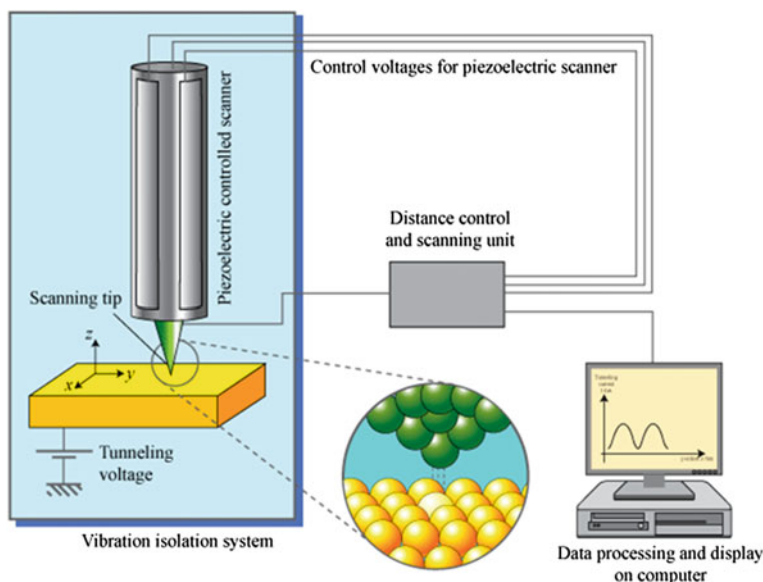
conditions without the need of special sample preparation. One of the best images obtained from AFM scans is topography of a graphite surface as illustrated in Fig. 2.14. A good top view image of graphite indicates the graphene lattice in the white lines, and different shading of carbon atoms results from the different situation in the atomic layer underneath (Hölscher et al. 2000).

### Scanning Tunneling Microscopy

Scanning tunneling microscopies (STM) are addressed as the first instrument to give real-space atomic resolution images (Binnig et al. 1982). STM relies on the electrical conductivity of the sample, and a weak electrical current flowing between tip and conductive sample is measured using tunneling (exponential) current. In STM, electrical charges pass from the surface of an object to the point of the microscope without there being any contact. The current varies strongly with distance. The movement of the point of the microscope is controlled with a specific current value in order to follow exactly the surface of the sample. Figure 2.15 illustrates a schematic of STM.

### Electron Microscopes

Electron microscopy (EM) is the most powerful technique for structural research and characterization of nanoparticles. With this technique, several important features of nanostructures such as size, presence of defects or contamination and



**Fig. 2.15** Schematic diagram showing STM principles ([http://www.virlab.virginia.edu/VL/easyScan\\_STM.htm](http://www.virlab.virginia.edu/VL/easyScan_STM.htm))

surface quality can be observed (Li 2002; Gommès et al. 2004). Similar to light microscopy where a light source is used to produce an image of higher magnification from a specimen, in EM, an electron source is used for the same purpose. In order to prevent overheating inside the instrument due to collisions between the electrons and gas molecules, the inner compartments of the EM are maintained in a vacuum. EM, like light microscope, contains a number of diaphragms that restrain the dispersion of the electron beam, and lenses that deflect electrons. Similar to light microscope, a condenser lens concentrates the beam, and an objective lens focuses the beam on the object.

An EM, which uses the wave nature of the electron to capture an image, is capable of imaging at a significantly higher resolution and magnification than light microscopes (Egerton 2005; Goodhew et al. 2000). This enables the instrument's user to examine specimen at nanoscale, thousands of times smaller than the smallest resolvable object in a light microscope. Electron microscopy has a major role in elucidating those micro- and nanostructures in which the reflections in reciprocal space are not sharp and spread out along lines or planes. Examples of these structures are fullerenes and related molecular structures like CNTs (Tendeloo and Amelinckx 2000; Gommès et al. 2004). Electron diffraction technique is able to produce useful structural information, mainly because the electron-sample interaction is very strong (Tendeloo and Amelinckx 2000). In electron microscopy, electrons are source of illuminating the sample. The lenses used in EM are electromagnetic lenses, which are widely different from glass lenses, though similar

**Fig. 2.16** Scanning electron microscopy (SEM) machine



principles apply in both cases (Pradeep 2007). There are two important types of electron microscopy, namely scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The schematic of SEM and TEM machines is illustrated in Figs. 2.16 and 2.17, respectively, and the principal elements of them are presented in the following sections.

### Scanning Electron Microscopy

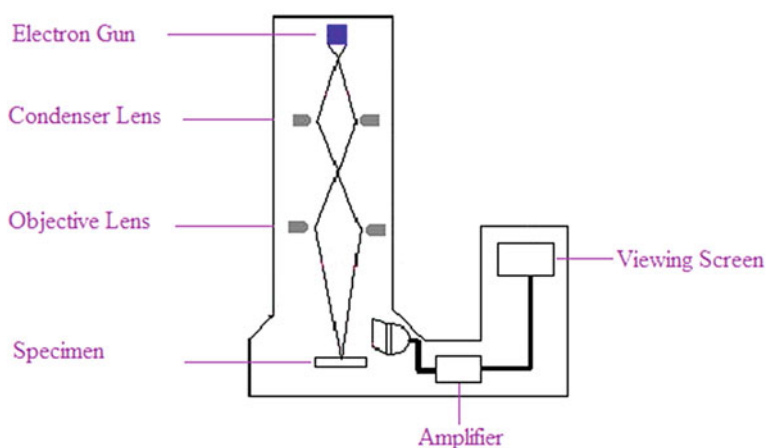
Main parts of Scanning electron microscopy (SEM) include an electron gun, lenses (a condenser lens, an objective lens, stigmator lenses), coils for the  $x$ - $y$  scan movement, specimen chamber and detection device for image formation (Fig. 2.18). An electron gun in SEM provides a stable beam of electrons, and the surface of solid is scanned with a focused beam of electrons (Goodhew et al. 2000). The electrons interact with atoms in the sample and produce various signals that contain information about the physical nature, sample's surface topography and chemical composition of it. Specimens can be observed in high vacuum, in low



**Fig. 2.17** Transmission electron microscopy (TEM) machine

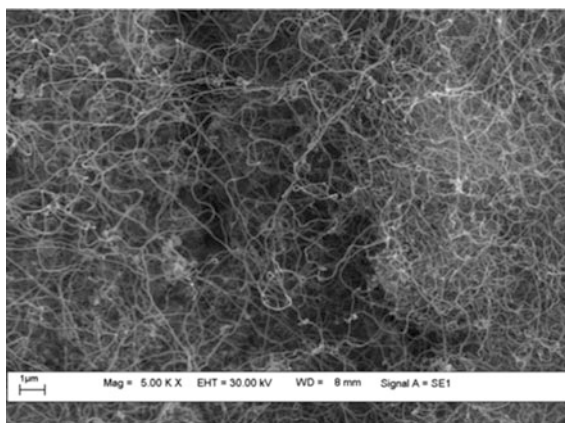


vacuum and (in environmental SEM) in wet conditions. SEM is the most widely used electron microscopy because of its versatility, its various modes of imaging, ease of sample preparation, possibility of spectroscopy and diffraction, as well as easy interpretation of the images (Pradeep 2007). Another advantage of SEM is that a very wide range of magnification is available which facilitates the visualization of virtually every detail. Some SEMs can obtain image resolutions even smaller than 1 nm (around 0.5 nm). No special sample preparation and no limitation for sample size are other benefits of this type of microscopy. The resolution of the SEM approaches a few nanometers, and the instruments can operate at magnifications over 1000 (Egerton 2005). Figure 2.19 shows SEM observation of bundles of CNTs with 5000 magnification.



**Fig. 2.18** Schematic diagram showing the main components of a SEM

**Fig. 2.19** SEM monograph  
CNT 5000 magnification

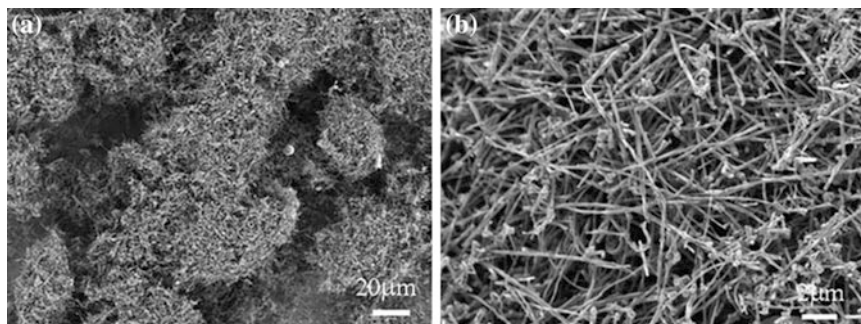


### Field Emission Scanning Electron Microscopy (FESEM)

A field emission cathode, a thin and sharp tungsten needle (tip diameter 0.1–0.01  $\mu\text{m}$ ), in the electron gun of a SEM can liberate narrower probing electron beam. The beam is accelerated in the direction of the column by a voltage gradient. The electron beam produced by the field emission source is about 1000 times smaller than in a common SEM that causes improved spatial resolution as well as minimized sample charging and damage (Li 2002). Therefore, quality of images captured by FESEM is markedly better (clearer and less electrostatically distorted) compared to images obtained from SEM. Field emission necessitates an extreme vacuum ( $\sim 10^{-11}$  atm) in the column of the microscope. However, in contrast to a conventional tungsten filament used in SEM, a field emission tip lasts theoretically for a lifetime, provided the vacuum is maintained stable. For ultra-high magnification imaging, like advanced coating thickness and structure uniformity determination, FESEM is the most suitable device. Small contamination feature geometry and elemental composition measurement are also possible with FESEM. The resolution of SEM is limited to about 1 nm, whereas FESEM can achieve higher resolutions (Bhushan 2010). Figure 2.20 shows FESEM observation of CNT using different magnifications.

### Transmission Electron Microscopy

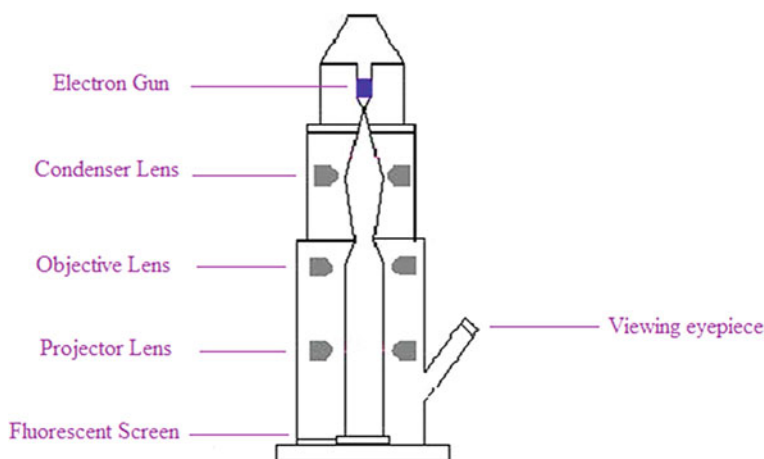
Transmission electron microscopy (TEM) is an EM technique used to obtain nanostructural information by diffraction and imaging from an ultra-thin specimen (Wang 2000a, b). It can provide image of higher magnification with better resolution compared to SEM. A schematic diagram for a common type of TEM is shown in Fig. 2.21. A beam of electrons is transmitted through specimen, interacting with the specimen as it passes through the sample. An image is formed from the interaction of the electrons transmitted through the specimen. The image can be



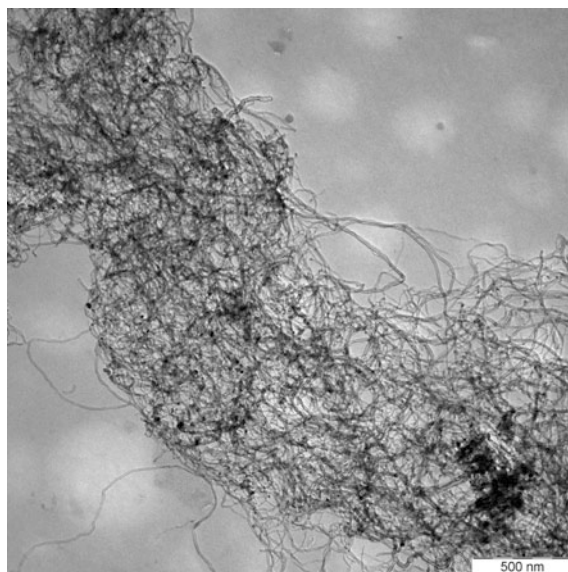
**Fig. 2.20** FESEM images of CNTs at different resolutions (Kim et al. 2006b)

magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a CCD (charge-coupled device) image sensor. Comparing the TEM diagram with SEM diagram depicted in Fig. 2.19, two clear distinctions can be found. First, there is an additional projection lens (beneath the objective lens) to project the image on a screen. The second one is the location of the object for observation. As depicted in Fig. 2.19, the specimen chamber in SEM is located below the column, while in TEM the specimen chamber is located about half way the column (Fig. 2.22). Difference in position of specimen relates with the specific mode of image formation in either TEM or SEM.

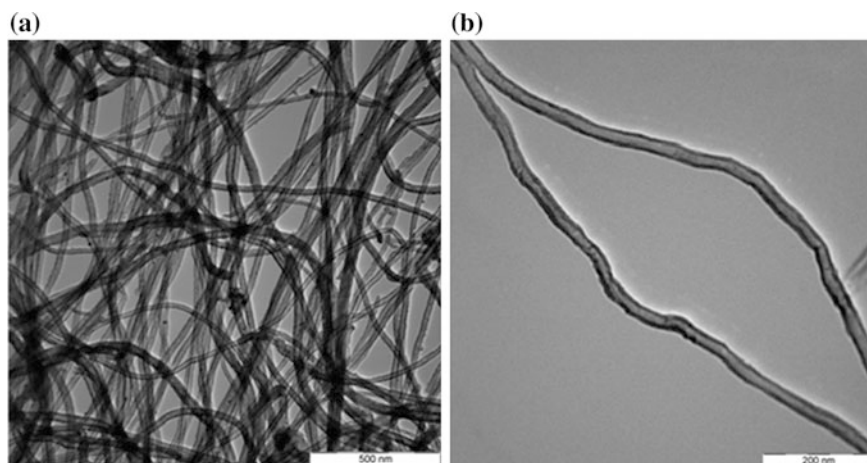
Having fine TEM observations, thin samples should be prepared due to the important absorption of the electrons in the material. A modern TEM is capable of producing a fine electron probe of smaller than 2 nm, allowing direct identification the local composition of an individual nanostructure. Figures 2.22 and 2.23 illustrate TEM observation on a CNTs sample using different magnifications.



**Fig. 2.21** Schematic diagram showing the main components of a TEM



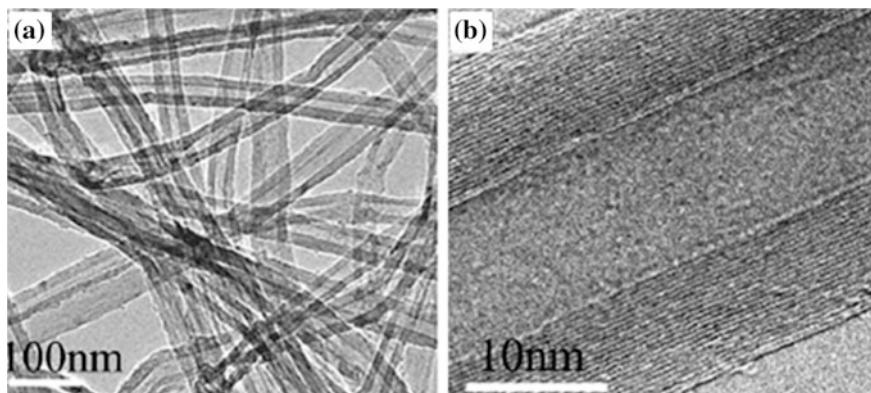
**Fig. 2.22** TEM monograph CNT at magnification of 20,000



**Fig. 2.23** TEM monograph CNT at magnification of **a** 70,000 **b** 150,000

### High-Resolution TEM

Conventional TEM uses only the transmitted beams or some of the forward-scattered beams to create a diffraction contrast image. High-resolution TEM (HRTEM) uses the transmitted and the scattered beams to create an interference image (Tendeloo and Amelinckx 2000). This technique is a powerful tool to study properties of materials



**Fig. 2.24** TEM **a** and HRTEM **b** image of MWCNT (Yu et al. 2006)

on the atomic scale like the surface and inner crystallinity, surface and planar defects (Gancs et al. 2008; Williams and Carter 2009). The morphology and size distribution of the nanostructures are most easily obtained by TEM (Fig. 2.25a), whereas their purely morphological features such as shape, diameter and length and their internal structure can be obtained by HRTEM (Fig. 2.24b). HRTEM can be also used to determine the 3D shape of small particles (Wang 2000a, b).

### 2.1.3.2 X-ray Diffraction Analysis

X-ray diffraction analysis (XRD) is an important crystallographic method that has long been used to obtain all information related to the crystalline phase present in the solid sample. This information includes lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. (Cullity and Stock 2001). In this technique, a collimated and rather monochromatic beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å, is incident on a specimen. Interaction of X-rays with crystalline matter leads its diffraction produced by the reticular planes that form the atoms of the crystal. A crystal diffracts an X-ray beam passing through it to produce beams at specific angles depending on the X-ray wavelength, the crystal orientation and the structure of the crystal. In the macroscopic version of X-ray diffraction, a certain wavelength of radiation will constructively interfere when partially reflected between surfaces (i.e., the atomic planes) that produce a path difference equal to an integral number of wavelengths (Zanchet et al. 2000). X-ray diffraction by crystal structure is described by the Bragg law:

$$2d \sin \theta = n\lambda \quad (2.1)$$

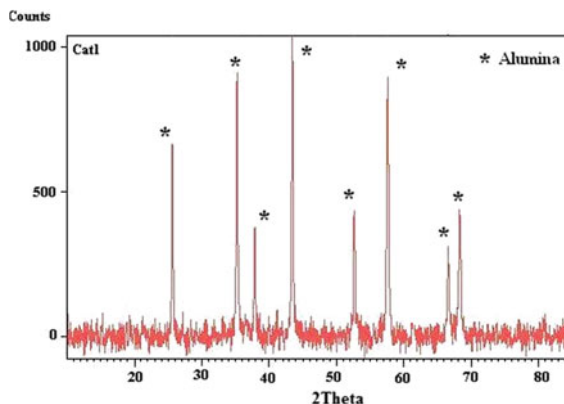
where  $n$  is an integer,  $\lambda$  is the wavelength of the radiation,  $d$  is the spacing between atomic planes in the crystalline phase and  $\theta$  is the angle between the radiation and the surfaces. The intensity of the diffracted X-rays is measured as a function of the diffraction angle  $2\theta$  and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties. XRD is nondestructive and does not require elaborate sample preparation, which partly explains the wide usage of XRD method in materials characterization (Cullity and Stock 2001). In general, the diffraction pattern of crystalline nanoscale materials exhibits broadened and shifted peaks as compared to bulk, and these changes are associated with both size and strain (Souza Filho and Fagan 2011).

This relation demonstrates that interference effects are observable only when radiation interacts with physical dimensions that are approximately the same size as the wavelength of the radiation. Since the distances between atoms or ions are on the order of 1 Å, diffraction methods require radiation in the X-ray region of the electromagnetic spectrum or beams of electrons or neutrons with similar wavelength. Accordingly, through X-ray spectra one can identify and analyze any crystalline matter. Each crystalline powder gives a unique diffraction diagram, which is the basis for a qualitative analysis by X-ray diffraction (Belin and Epron 2005). Identification is practically always accompanied by the systematic comparison of the obtained spectrum with a standard one (a pattern), taken from any X-ray powder data file catalogues, published by the American Society for Testing and Materials (JCPDS). X-ray diffraction is generally used for catalyst characterization in CNT synthesis research (Tran et al. 2007; Hsieh et al. 2009; Philippe et al. 2007), since the crystalline structure of transition metals is not active for CVD reaction. In other words, crystalline configuration of nanostructures cannot catalyze the CNTs growth reaction. On the other hand, XRD is not basically used for CNTs analysis as this method can just reveal the graphitized structure of carbon and there is no difference between CNT and graphite in the spectrum (Belin and Epron 2005).

Another example of using XRD is to study the suitability of heterogeneous catalyst for CNT formation through CVD method. The suitable heterogeneous catalyst for CNT production involves a well dispersion of transition metal(s) in a suitable support. Monometallic and bimetallic catalytic particles with the same amount of metal are compared. Transition metals are the active elements, and they must be in the form of nanoparticles. Transition metals do not act as catalyst for CNT formation if aggregation of metal particles in the form of crystalline structure is observed. The XRD diffractogram for bimetallic catalytic particles indicates an intense peak just for alumina (Fig. 2.25). The indicated peaks in diffractogram at  $2\theta$  identical to 25.56, 35.12, 37.75, 43.32, 52.52, 57.47, 66.47 and 68.17 degree have relatively high intensity and symmetry. These peaks correspond to the crystalline structure of alumina (Tran et al. 2007; Hsieh et al. 2009; Philippe et al. 2009). Hence, the predominant species on these samples are only alumina, which obviously comes from the catalyst support particles. Accordingly, as there are no detectable peaks for metals, and just intense peaks corresponding to the alumina are observed, the following conclusions can be inferred. The crystallinity of the samples was mainly due to the alumina used as a support but not due to the presence of



**Fig. 2.25** Diffractogram obtained by XRD for catalytic particles comprising iron and cobalt with mass ratio of 8–8 %



any metallic phases. In other words, there is no accumulation of metals (iron or cobalt) or metal compounds in the bimetallic catalytic samples, and the small particles of metals were well dispersed in the support.

### 2.1.3.3 Particle Characterization

Gas sorption (both adsorption and desorption) at the clean surface of dry solid powders is the most popular method for determining the surface area of the fine powders and porous materials as well as their pore size distribution (Lowell 2004; Condon 2006). In gas sorption methods, the specimen is first heated and degassed by vacuum force or inert gas (such as nitrogen, krypton, or argon) purging to remove adsorbed foreign molecules. The sample is then placed in a vacuum chamber at a constant and very low temperature (usually at the temperature of liquid nitrogen,  $-195.6\text{ }^{\circ}\text{C}$ ), and subjected to a wide range of pressures, to generate adsorption and desorption isotherms (Xu 2001). The amounts of gas molecules adsorbed or desorbed are determined by the pressure variations due to the adsorption or desorption of the gas molecules by the adsorbent (the sample). Knowing the area occupied by one adsorbate molecule (for example, nitrogen) and using an adsorption model, the total surface area of the sample can be determined. The most well-known and most widely used adsorption model is the BET equation for multilayer adsorption (Brunauer et al. 1938):

$$\frac{P}{n(P_s - P)} = \frac{1}{cn_m} + \frac{c - 1}{cn_m} \frac{P}{P_s} \quad (2.2)$$

In Eq. 2.2,

$P$  is adsorption pressure

$P_s$  is saturation vapor pressure

$C$  is a constant (so-called) BET constant

$n$  is the amount adsorbed (moles per gram of adsorbent) at the relative pressure

$n_m$  is the monolayer capacity (moles of molecules needed to make a monolayer coverage on the surface of one gram of adsorbent).

By plotting the quantity on the left of this equation,  $P/[n(P_s - P)]$  against  $(P/P_s)$ , versus  $P/P_s$ , the terms  $C$  and  $n_m$  can be determined through the slope and intercept of this plot. The specific area,  $S$ , can then be derived:

$$S = N_A n_m \sigma \quad (2.3)$$

In Eq. 2.3,  $N_A$  is Avogadro's number and  $\sigma$  is the area occupied by one adsorbate molecule.

The most common adsorbate used is nitrogen with the value  $\sigma = 16.2 \text{ \AA}$  (Xu 2001).

Note that, the plot should be taken over the 0.05–0.35  $P/P_s$  range, since beyond these values the linearity of the plot breaks down. Other parameters, identified through gas sorption method, are the porosity in terms of pore size, pore volume and pore size distribution. The range of pore sizes that can be measured using gas sorption is from a few angstroms up to about half a micron. Pore size of porous materials and its distribution are determined using adsorption/desorption isotherm based on an assessment model, such as the t-plot, the MP method, the Dubinin–Radushkevich method and the Barrett–Joyner–Halenda (BJH) model, etc. (Condon 2006).

#### 2.1.3.4 Chemical Analysis

Chemical characterization involves determining the surface and interior atoms and compounds as well as their spatial distributions (Cao 2004). According to the principle, different substances produce distinctive spectral lines, and spectroscopy techniques have been developed. Spectroscopy is a general methodology based on principle of interaction of electromagnetic radiation on materials. In addition to wavelength, other characteristics of the light, such as its intensity, can also provide useful information, and thus, spectroscopy has been adapted in many ways to extract the information required. In X-ray spectroscopy, for example, when X-rays bombard a substance, the electrons in the inner shells of the atoms are excited and then de-excite emitting radiation. This radiation comes out at different frequencies, depending on the atom and chemical bonds present. Accordingly, with spectroscopic techniques, it is possible to determine what elements in what quantities and what chemical bonds are present. Different spectroscopic techniques operate over different, limited frequency ranges within this broad, depending on the processes and magnitudes of the energy changes. A vast number of spectroscopy techniques have been developed that makes hard to have exact classification for them. Spectroscopy techniques are basically different in terms of nature of energy source utilized, type of interaction between the energy and the material and type of measurement.



### 1. Nature of energy source utilized, for example

- Optical spectroscopy
  - X-ray photoelectron spectroscopy (XPS)
  - UV-vis spectroscopy
  - Fourier transform Infrared spectroscopy (FTIR)
  - $\gamma$ -ray spectroscopy (Mossbauer spectroscopy)
- Electron spectroscopy
  - Energy Dispersive Spectroscopy (EDS)
  - Auger Electron Spectroscopy (AES)
  - Mass Spectroscopy (MS)
- Ionic spectroscopy
  - Rutherford backscattering spectrometry (RBS)
  - Ion scattering spectroscopy (ISS)

There are some spectroscopy techniques classified as electron spectroscopy, in which the kinetic energy of electrons emitted from a substance is measured. In electron spectroscopy, the substance is bombarded with ionizing radiation, and thus, electrons are excited by absorbing photon energy from an initial low-energy state to a higher-energy state. When an electron is ejected from an inner shell of an atom, the resultant vacancy can be filled by either a radiative (X-ray) or nonradiative (Auger) process. Because the energy of these electrons is approximately equal to the difference between the two shells, X-rays or Auger electron can be a characteristic of the element from which it was released and the shell energy of that element. The famous examples of this technique include energy dispersive X-ray spectroscopy, electron energy loss spectroscopy, X-ray photoelectron spectroscopy and Auger electron spectroscopy.

### 2. Type of interaction between the energy and the material

- Emission
- Absorption
- Vibration (infrared spectroscopy, Raman spectroscopy)

Absorption and emission spectroscopy determines the electronic structures of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground states (emission). Emission spectroscopy can be fluorescence (emission from excited electronic singlet states) or phosphorescence (emission from excited electronic triplet states). Fluorescence spectroscopy is commonly used in biology and medicine, as its damaging effects are less than other methods and because some organic molecules are naturally fluorescent.

Vibrational spectroscopy is employed to derive information on the vibrational excitation of molecules. Atoms are spherically symmetric, but molecules have shapes which permit them to vibrate and rotate. A substance can be thought of as systems of balls (atoms) connected by springs (chemical bonds). These balls

(atoms) can vibrate or rotate with frequencies determined by their mass (atomic weight) and by the stiffness of the springs (bond strengths). These oscillations induced provide new energy levels that can be quantized to extract information about chemical bonds in the detecting samples (Cao 2004). Vibrational energies are much smaller as compared to the chemical bond energies; therefore, even minute changes in the local atmosphere of a sample are reflected in the spectra (Pradeep 2007).

### 3. Type of measurement

Infrared spectroscopy is known as Fourier transform infrared spectroscopy (FTIR), because a Fourier transform (a mathematical process) is required to convert the raw data, intensity-time output, into the actual spectrum (intensity-frequency). FTIR is a powerful technique for identifying the identities, surrounding environments or atomic arrangement, and concentrations of the chemical bonds in the sample.

Due to great development and improvement in spectroscopy techniques, they are now employed for obtaining wide range of information including energies of electronic, vibrational, rotational states, structure and symmetry of molecules, dynamic information. The most common spectroscopic techniques employed in characterization of nanostructures are presented:

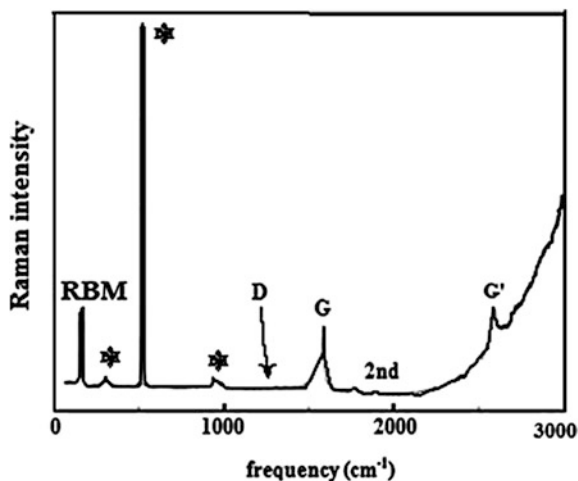
#### **UV-Vis Spectrophotometer**

A UV-Vis spectrophotometer measures the amount of light absorbed at each wavelength of the UV and visible regions of the electromagnetic spectrum. In a standard UV-Vis spectrophotometer, a beam of light is split; one half of the beam (the sample beam) is directed through a transparent cell containing a solution of the compound being analyzed; and one half (the reference beam) is directed through an identical cell that does not contain the compound but contains the solvent. UV-Vis spectrophotometry is a powerful technique to obtain useful information about optical properties of nanostructure and their size (Burda et al. 2000). For example, reduction in the silver ion to silver nanoparticles (SNPs) results the visual change of color from yellow to red. The UV-Vis spectrum of the SNPs indicates an absorption band at 420–430 nm as a result of surface plasmon vibrations SNPs (He et al. 2004).

#### **Raman Spectroscopy**

Raman spectroscopy is based on the inelastic light scattering by the lattice vibrations (phonons). In bulk materials, the scattering obeys the momentum selection rule which states that only the phonon wave vector equal to zero is allowed (Souza Filho and Fagan 2011). Raman spectrum is very sensitive to the lengths, strengths and arrangements of chemical bonds in a material, but less sensitive to the chemical composition (Cao 2004). A promising application of Raman spectroscopy is for structural analysis of CNTs. Different types of CNTs, single-wall, double-wall and multi-wall CNTs, can be distinguished by Raman spectroscopy (Dresselhaus et al. 2005). The various forms of CNT can be distinguished by the position and the line

**Fig. 2.26** Raman spectrum of one SWNT taken over a broad frequency range (Dresselhaus et al. 2002)

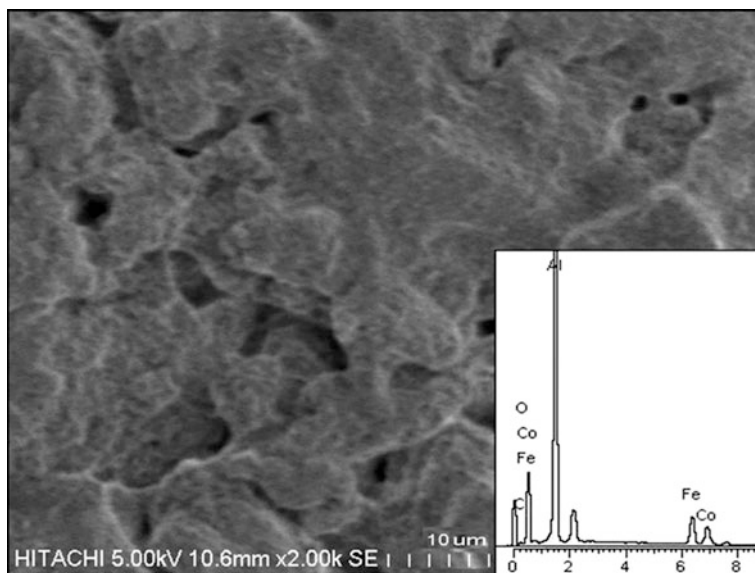


width of the frequency bands in the Raman spectrum. Figure 2.26 demonstrates a Raman spectrum of one SWNT taken over a broad frequency range.

Breathing mode (RBM) is usually located between 75 and 300  $\text{cm}^{-1}$  from the exciting line; an illustration of the spectrum resulting from this mode is displayed in the figure. The frequency of the RBM is directly linked to the reciprocal of the nanotube diameter. Basically, D band position at 1285–1300  $\text{cm}^{-1}$  and a linewidth of 10–30  $\text{cm}^{-1}$  are characteristic of SWNTs, while MWCNTs form has a typical position of 1305–1330  $\text{cm}^{-1}$  and a width of about 30–60  $\text{cm}^{-1}$  (Belin and Epron 2005). The D band is expected to be observed in multi-walled carbon nanotube (MWCNT). However, when it is observed in single-walled carbon nanotube (SWNT), it is assumed that it is due to defects in the tubes. Raman spectroscopy has also provided a powerful tool to study the vibrational properties and electronic structures of SWCNT (Lefrant 2002). The position, width and relative intensity of the bands in the Raman spectrum are modified according to the type of CNT. For example, the Raman line shape differs between metallic and semiconductor nanotubes and thus allows distinguishing the two types.

### Energy Dispersive Spectroscopy

Quantitative analysis of chemical composition for a specimen can be obtained by X-ray energy dispersive spectrometry (EDS), sometimes is referred as EDX. In this technique, a specimen is excited by the incident electrons. The X-rays emitted from the sample atoms represent the characteristics of the elements, and their intensity distribution represents the thickness-projected atom densities in the specimen (Wang 2000a, b). EDS is generally a complementary tool with EM, SEM or TEM. For example, in order to understand heterogeneous catalysis, information about the nature and structure of the upper atomic layers is required (Hagen 1999). SEM image combined with EDS spectrum of a catalytic sample can be provide information about the morphology, structure and composition of it. EDS analysis can



**Fig. 2.27** SEM/EDX illustration of catalyst surface (Fe–Co: 2.5–2.5 %)

qualify and quantify the presence of metal elements on the surface of the catalytic particles, and EM observation indicates surface morphology. Figure 2.27 shows SEM/EDX analysis result for a catalyst sample made from iron and cobalt as active elements supported on alumina. With SEM/EDX, both topographical information and knowledge about elemental composition are obtained.

### Electron Energy Loss Spectroscopy (EELS)

Electron energy loss spectroscopy (EELS), which is another common spectroscopy technique available on many EM, is often spoken of as being complementary to EDS.

A proper application of EELS can provide additional information which is not possible in the case of EDS. For example, EELS is capable of measuring atomic composition, chemical bonding, valence and conduction band electronic properties, surface properties and element-specific pair distance distribution functions (Wang 2000a, b; Egerton 2005). With EELS, it is possible to differentiate different forms of carbon, diamond, graphite, amorphous carbon and “mineral” carbon (such as the carbon appearing in carbonates). The spectra of 3d transition metals can be also analyzed to identify the oxidation states of the atoms transitions. EELS is based on the inelastic collisions of a monochromatic beam of electrons and the study of the kinetic energy of the electrons. The energy loss of the sample corresponds to excitations in the sample (Bhushan 2010).

### Auger Electron Spectroscopy

Auger electron spectroscopy (AES) derives its name from the effect, first observed by Pierre Auger, a French Physicist (Hawkins 1977). Under the impact of an incident electron, the electrons bounded to the atoms may be excited, either to a free electron state or to an unoccupied energy level with a higher energy. The quantum transitions associated with these excitations will emit photons (or X-rays) and electrons such as secondary electrons, Auger electrons and ionized electrons. By discriminating between Auger electrons of various energies, quantitative chemical and electronic structural analysis can be obtained (Olsson et al. 1997). AES, which utilizes the emission of low-energy electrons in the Auger process, provides elemental analysis of surface layers of a specimen with high sensitivity (typically ca. 1 % monolayer) for all elements except H and He (Chourasia and Chopra 1997). AES is based on three basic steps, atomic ionization, electron emission and analysis of the emitted Auger electrons. A specimen atom, excited by the incident electron, emits some of the energy by one of the higher level electrons coming down, by emitting a second electron with a characteristic energy. The elements with higher Auger electron yields have lower X-ray emission and vice versa. Thus, the AES is more sensitive to light elements, while EDS is to heavier elements (Wang 2000a, b).

### X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is based on detecting photoelectrons ejected by X-rays. This technique provides determination of the chemical bonding of species present on the surface of solid materials. XPS, like AES, is applicable to detecting almost all the elements in the Periodic Table, with few exceptions, whereas EDS can only detect elements with  $Z > 11$ . XPS, and to a much lesser extent AES, is capable of readily providing information on the nature of chemical bonding and valence states (Brune et al. 1997; Wang 2000a, b). XPS is an important tool in materials engineering with applications such as corrosion, embrittlement of metals and powder metallurgy. In polymer technology, XPS is widely used for analysis of functional groups and determination of thickness and distribution of thin liquid film on a substrate (Bhushan 2010).

### Ionic Spectroscopy

When a beam of ions hits the surface of a material, a part of projectiles will be scattered back into the vacuum after one or more collisions. Measuring the energy of back-scattered particles can be used to identify the mass of these atoms, which is the base of ISS. The technique is classified depending on the energy of the primary ion beam:

- Low-energy ion scattering (LEIS) spectroscopy is referred to primary energies in the range of 100 eV–10 keV,
- medium-energy ion scattering (MEIS) to a range from 100 to 200 keV and
- high-energy scattering (HEIS) to energies between 1 and several MeV.

Often the LEIS technique is called ISS, while HEIS technique is best known as Rutherford backscattering spectroscopy (RBS). RBS is quantitatively a precise

technique for analysis of chemical composition, and it is a popular thin film characterization technique. However, RBS is restricted to only selected combinations of elements whose spectra do not overlap. LEIS (or ISS) has some advantages and disadvantages depending on the specific problem being examined. The quantification analysis using LEIS is impeded by the uncertainty of the inelastic losses and the neutralization rate depending on ion trajectories. The practical use of ISS is determined by its extreme sensitivity to only the top surface or two monolayers. It is necessary to note that ISS is strongly affected by surface contamination and elements of similar molecular mass cannot be differentiated. For example, in a system comprising iron and cobalt, these two elements cannot be distinguished because their molecular masses are so close to each other (Taglauer 1991).

### Mass Spectroscopy

Mass spectrometry is based on slightly different principles to the other spectroscopic methods. Mass spectroscopy determines the mass/charge ratio ( $m/z$ ) in the vapor phase of a specimen. With mass spectroscopy, it is possible to determine exact molecular mass and structure of the molecule (Downard 2004). The physics behind mass spectrometry is that a charged particle passing through a magnetic field is deflected along a circular path on a radius proportional to the mass/charge ratio. Bombardment of a sample surface with a primary ion beam followed by mass spectrometry of the emitted secondary ions constitutes secondary ion mass spectrometry (SIMS) (Benninghoven et al. 1987). Today, SIMS is widely used for analysis of trace elements in solid materials, especially semiconductors and thin films. The SIMS ion source is one of only a few to produce ions from solid samples without prior vaporization. The SIMS primary ion beam can be focused to less than 1  $\mu\text{m}$  in diameter. Controlling where the primary ion beam strikes the sample surface provides for microanalysis, the measurement of the lateral distribution of elements on a microscopic scale (Brune et al. 1997).

#### 2.1.3.5 Thermal Analysis

Thermal analysis is a general name for measurement of certain physical and chemical properties, like enthalpy, heat capacity, mass and coefficient of thermal expansion as a function of temperature. The most common thermal analysis techniques include thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). In DTA and DSC, temperature of a sample is compared with that of an inert reference material during a programmed change of temperature. Thermal analysis techniques have found important roles to play in analysis and development of nanostructures and nanocomposites. TGA is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by measuring the changes in mass of a substance as a function of temperature or time when the specimen is heated. Figure 2.28 shows common schematic of machine used for TGA. The measurement is normally carried out in air or in an inert atmosphere, such as helium



**Fig. 2.28** Thermogravimetric analysis device

or argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1–5 %  $O_2$  in  $N_2$  or He) to slow down oxidation.

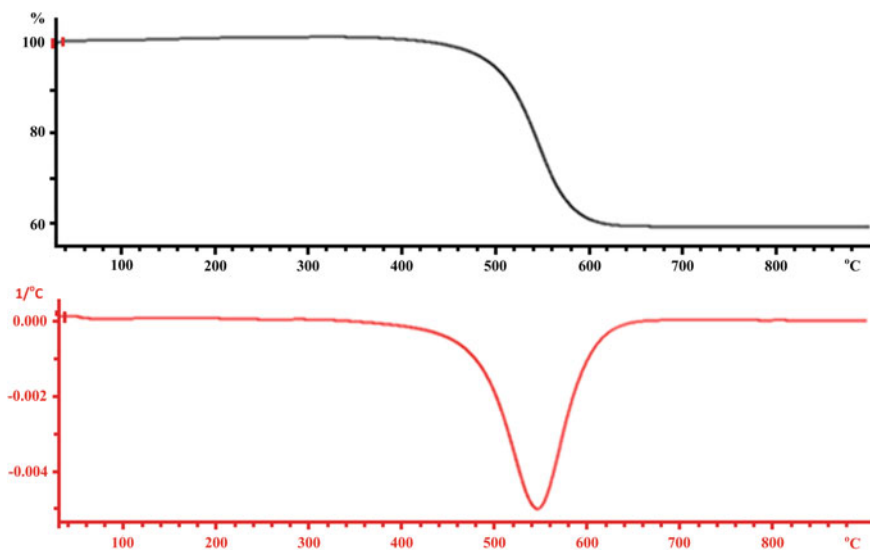
As an example for TGA, this analysis method has been adopted to distinguish the different forms of the carbon deposits (e.g., amorphous carbon and CNTs) according to their different thermal stabilities (McKee and Vecchio 2006). A sample collected from reactor after reaction accomplished involves carbon formed and catalytic particles. Nanotubes have a higher thermal stability than amorphous carbon, and thus, they burn off at higher temperatures. Increasing amorphous carbon contamination in the sample, the temperature corresponding to the peak burn-off rate will shift lower. In addition, after the mass loss has stabilized (after all nanotube and amorphous carbon product have burned off), the remaining mass gives an indication of the original non-carbon content of the sample (typically the mass of the residual catalyst). Figure 2.29 illustrates TGA result of product obtained from CVD of ethanol. To conduct TGA, a ceramic crucible having certain amount of sample is placed on the weighing pan inside the equipment and heated to about 800 °C with the increasing rate of 10 °C/min. The weight loss of the sample for the period of the heating time is automatically recorded and plotted as a function of temperature.

The techniques used for nanostructures characterization are not limited to those presented here, and readers interested to get more information are encouraged to refer the books like Burda et al. (2000), Xu (2001), Cao (2004), Wang (2000a, b). Table 2.1 presents summary of those techniques addressed in this book for better understanding and comparison.

## 2.2 Transforming Nanotechnology into Nanoengineering Through Chemical Engineering Principles

Commercial production and applications of nanostructure materials (nanomaterials) have not yet been completely developed. A great majority of scientists and engineers are attempting to resolve the challenges posed by synthesis, processing,





**Fig. 2.29** TGA illustrations for product obtained from chemical vapor deposition of ethanol using at  $T$ : 600 °C

application, purification and characterization of these new materials. The innovations and developments in these aspects of the nanomaterials are fueled by the progress in all fields of engineering, science and technology. However, development and improvement in the nanomaterials production in large scale lie on engineering principles, in a specific manner on chemical engineering. For instance, design of new manufacturing processes of effective catalysis and improved separation and purification methods will pave the road for commercial production of nanostructures. In addition, simulation and modeling of processes help to understand and hence to optimize the process including chemical reactions and regeneration cycle systems. Although processes applied for synthesis of nanostructures are somehow complicated, these complex processes can be dynamically simulated and optimized with the aid of computer. The key parameters of processes determined from models can be applied in practice to control the process, for instance, to produce even more quality in the end products. Accordingly, development of theoretical framework as well as advanced engineering knowledge to increase understanding of structures and behaviors of nanostructures is strongly required. Besides, a practical framework capable of new process design and improvement in the performance or controlling the existing processes are vital. In this respect, an integrated program comprised of theoretical model accompanied with numerical or analytic solution of the model equations, and comparison with experimental data on both dynamics and structure of such systems is essential. In conclusion, it is fair to note that nanotechnology should be transferred to nanoengineering that means engineering-based effort like transport phenomena must be considered.

**Table 2.1** Summary of common techniques employed for nanostructure analysis

Technique	Characterization parameter	Type of information
AES	Auger Electron energy spectrum	Elemental composition, layer thickness
AFM	Local van der Waals force	Surface topography map, elasticity, magnetic and electrostatic properties
BET	Gas adsorption desorption	Surface area and porosity
EDS	Electron scattering	Elemental composition
EELS	Electron scattering	Elemental composition, chemical bonding, electronic properties
FESEM	Electron scattering	Morphology, size, defects
FTIR	Atom vibration	Elemental composition, chemical bonding, functional groups, molecular composition
HRTEM	Electron transmission	Morphology, crystalline structure, size, defects
ISS	Scattered ion energy and angle	Elemental composition, surface structure, atomic distances
Mossbauer spectroscopy	Resonant absorption of $\gamma$ -ray	Elemental composition, chemical bonding, crystallinity, magnetic properties
Raman spectroscopy	Atom vibration	Chemical bonding
RBS	Energy spectrum of scattered MeV-ions	Elemental composition, layer thickness
SIMS	Mass of sputter-ejected ions	Elemental composition, mass spectra determination of trace elements in ppb
SEM	Distribution and energy of scattered electrons	Morphology, constituent phases
STM	Spatial variation of electron tunneling current	Surface topography, surface electronic structure, constituent phases
TEM	Electron transmission	Morphology, size, defects
TGA	Weight loss of a sample due to temperature increasing in predetermined atmosphere	Thermal stability, volatile component
UV-vis spectroscopy	Absorption or reflectance of light in the ultraviolet-visible wavelength	Elemental composition, particle size, optical property
XPS	Photoelectron energy	Elemental composition, chemical bonding, layer thickness
XRD	Scattered and diffracted X-ray distributions	Crystalline structure, space groups, atomic positions and profiles, layer thickness

### ***2.2.1 Nanotechnology in Support of General Science and Engineering***

It is essential to explain interrelation of nanotechnology with the other conventional technologies and sciences at first. There are differences between nanosciences and nanotechnology. These differences are related to how the nanoconcepts and

nanoproducts are used. In other words, nanoscience discusses basic concepts and description of related phenomena to change of materials structure and behavior when one of their characteristic dimensions is in nanosize. For example, in the physics view point, it is important to understand why quantum properties of a semiconductive materials change when its size is around the nanorange. As another example, variation of suspension color (such as gold particles in the water) is a nanophenomenon when the size of particle situates in the nanosize. This variation of size of a material can also cause variation of chemical properties (such as catalytic effect), and this represents an attractive nanophenomenon for many chemical applications.

In contrast, nanotechnology is different than nanoengineering from the view point of nanophenomena and their process description. In fact, rule of technology word in the nanotechnology slang causes that description of nanophenomena gives applied and processed results and therefore gives new products with new properties with optimum consideration, but in a descriptive manner in contradistinction to nanoengineering which is more quantitative. As an example, one of the most important and commercial production methods of carbon nano-tubes (CNTs) is CVD. General description of this method is thermal or catalytic decomposition of a hydrocarbon to hydrogen and carbon molecules and then control of deposition arrangement of carbon atoms to a regular structure named tube. Nanoengineers interest to produce this product in the large scale and also to find new materials with improved properties using CNT, while distinguish and determination of effective molecular scale mechanisms in synthesis of CNT as a nanostructures material to find its kinetic are interesting for chemists.

There is an increasing emphasis on the development of systems for nanostructures production, which require different aspects of chemical engineering such as transport phenomena, kinetic, thermodynamic process modeling and simulation and so on. In a system or process related to nanomaterials synthesis or production, distribution of sizes, shapes and their purity relates to their capacity to execute diverse functions in specific applications (Rolando 2007). Fundamentals associated with production of nanomaterials are complicated, and conventional principles are not able to predict and optimize the systems at nanoscale. As mentioned, when systems scale down to the nanoscale, the fundamental theory used in larger-scale systems breaks down because of fundamental differences in the physics. The behavior of materials and thus their properties at nanoscale are difficult to predict.

It is well known that almost all physical and chemical properties of systems in the nanometer region become size dependent. For example, color of a piece of gold remains golden until it has size of microns. However, this golden color changes to red when the size of gold reaches regime of nanometers. Interparticle forces such as van der Waals (attraction) and electrostatic (repulsion) also affect the behavior of suspension consisting nanoparticles. For example, the attractive van der Waals force may cause particles to aggregate. At the small scale, forces such as friction and surface tension often dominate over forces such as gravity. Another example is

in selecting a material for energy conversion. The suitability of a thermoelectric material for energy conversion is based on the figure of merit  $Z$ , defined as (Faghri and Zhang 2006)

$$Z = \frac{\alpha^2}{R_e k} \quad (2.4)$$

where

$\alpha$  is the Seebeck coefficient

$R_e$  is electrical resistivity and

$k$  is thermal conductivity

Materials with a high value of “ $Z$ ” are difficult to find in bulk form, and thermoelectric materials at nanoscale indicate good energy conversion. However, to manipulate the nanostructures of certain materials, the electron and phonon thermoelectric transport must be first understood. In this respect, Boltzmann transport theory can be applied to describe transport of electrons and electron–lattice interaction to yield the two-step heat conduction model at nanoscale and heat transfer (Chen et al. 2004). Quantum Boltzmann equation explains how particles are kicked into or out of phase-space elements due to collisions. According to the examples mentioned, classical physics alone fails in describing the phenomena at nanoscale to predict the behavior of nanostructures, and thus, classical physics begins to give way to quantum physics in terms of description of physical phenomena. When electrons are confined to nanosized objects, their energy levels change that cause altering the electronic and optical properties of the material (Shong et al. 2010). Nanostructures properties, such as their conductivity, magnetism and so on, can be explained through properties of electrons. To describe the properties of electrons, the quantum mechanical wave description of matter is applied.

Another imperative difference of dealing with nanostructures compared to other conventional materials is the strong coupling between structure and flow that necessitates a more microscopic view of transport phenomena in such systems. In nanotechnology, systems mostly deal with mixing and dispersion of nanoparticles and/or nanoparticle growth in fluids that show interaction between nanostructure and flow that determines the final properties and also behavior of the system. Full understanding of relation between nanostructure and flow is a key issue to manipulate and control ultimate properties of such systems. Nanofluids, dilute colloidal suspensions of nanoparticles, can be addressed as one of the most popular nanoscale systems. Nanofluids can be transparent, semitransparent and opaque depending on the properties and concentration of the dispersed particles, and they may contain a certain amount of surfactants or dispersants to enhance their stability. The popularity of the topic of nanofluids is pertained to observations of enhanced properties and behavior in heat transfer (Choi and Eastman 2001), mass transfer (Krishnamurthy et al. 2006; Olle et al. 2006) and antimicrobial activities (Zhang et al. 2007). To interpret the experimental observations, a number of mechanisms

have been proposed (Yu and Choi 2003; Wang et al. 2007; Prasher et al. 2006a, b; Keblinski et al. 2002).

The laws of physics are certainly legitimate at the nanoscale, and many physical phenomena can be adequately described with classical physics (Shong et al. 2010). However, it is vital to obtain structural information of nanoparticle, which can be fed to the conventional effective medium theories to give predictive models for nanofluids behavior. The reasons are: first, new phenomena observed when novel materials and devices at the nanoscale are made, and second, nanoparticle structuring is a dominant mechanism for explanation and prediction of their behaviors in a fluid. For example, theory of Brownian motion has been examined for explanation and prediction of nanofluid behavior. The random movement of a small particle (about one micron in diameter) suspended in a fluid is called Brownian motion. Based on classical physics, Brownian motion is described in terms of diffusion processes. Since diffusion depends on temperature, it is fair to note that Brownian motion is related to the thermal motion of molecules. When a particle is falling down in a fluid (Fig. 2.30), terminal velocity for a particle is defined as

$$v_t = \frac{2}{3} \frac{mg}{\pi \mu D} \quad (2.5)$$

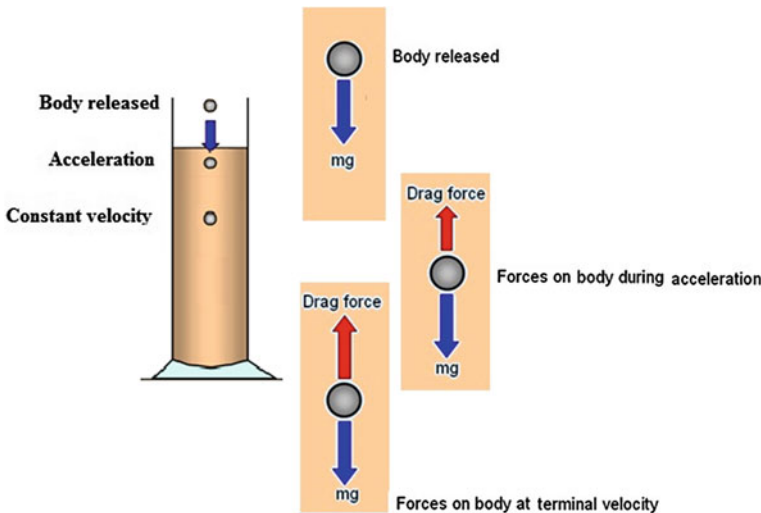
where

$m$  is mass of particle (kg)

$D$  is its diameter (m) and

$\mu$  is fluid viscosity (kg/m s) and

$g$  is gravitational acceleration (9.8 m/s<sup>2</sup>)



**Fig. 2.30** A particle is falling through a fluid

mass of particle can be written in terms of its density and volume, then

$$m = \rho \left( \frac{\pi D^3}{6} \right) \quad (2.6)$$

By substituting  $m$  in Eq. 2.5:

$$v_t = \frac{1}{9} \frac{\rho g D^2}{\mu} \quad (2.7)$$

$$v_t \propto D^2 \quad (2.8)$$

Note that the above treatment is only valid for small particles that flow in streamline with low velocities. This condition is met when the Reynolds number ( $Re$ ) is less than about 2000, where  $Re$  is a nondimensional quantity that describes the type of flow in a fluid defined by:

$$Re = \frac{\rho v D}{\mu} = \frac{\rho v}{(\mu/D)} = \frac{\text{Inertial forces}}{\text{Viscous forces}} \quad (2.9)$$

where

$\rho$  is fluid density

$\mu$  is fluid viscosity

$v$  is relative velocity of particle and solid and

$D$  is particle diameter

Since the terminal velocity is proportional to the diameter squared (Eq. 2.7), it is clear that small particles fall very much more slowly. As size decreases, the ratio of inertia forces to viscous forces within the fluid decreases and viscosity dominates. Hence, nanoscale objects moving through fluids are dominated by viscous forces, and their motion is characterized by a low Reynolds number. This means that nanoparticles sense the viscosity of the fluid much more than particles having fairly large diameter. To give a quantitative example, consider a gold sphere (density 19,300 kg m<sup>-3</sup>) with diameter of 1 mm is falling through water (viscosity = 0.01 kg/m s). It has a terminal velocity calculated from Eq. 2.7 of about 2 ms<sup>-1</sup>. If the sphere is now 1 μm in diameter, its terminal velocity becomes about 2 μms<sup>-1</sup>. If its radius is further reduced to 1 nm, its terminal velocity drops to 2 pm/s.<sup>1</sup> Furthermore, at the nanoscale, the effects of individual molecules in the fluid impact significantly the Brownian motion of nanoparticle.

Time evolution of the position of a Brownian particle is best described using the Langevin equation. Langevin equation is a stochastic differential equation in which two force terms have been added to Newton's second law (Langevin 1908). One

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<sup>1</sup>Pico meter per second.

term represents a frictional force due to viscosity, and the other one is random force associated with the thermal motion of the fluid molecules.

In general, Newton's law of motion in one direction, considering presence of an external force ( $F_{\text{EXT}}$ ), Brownian diffusive force ( $F_{\text{B}}(t)$ ) and viscosity ( $\mu$ ) of the fluid, can be written as Eq. 2.10 below. Since friction opposes motion, the first additional force is proportional to the particle's velocity ( $v$ ) and is opposite in direction. This equation needs to be solved to describe the complete motion of an object in a fluid.

$$F_{\text{EXT}} + F_{\text{B}}(t) - 3\pi\mu Dv = m \frac{dv}{dt} \quad (2.10)$$

Substituting  $m$  as a mass of a spherical particle with diameter  $D$  and velocity as  $v = dx/dt$ , gives:

$$F_{\text{EXT}} + F_{\text{B}}(t) - 3\pi\mu D \frac{dx}{dt} = \left(\frac{\pi}{6}\rho D^3\right) \frac{d^2x}{dt^2} \quad (2.11)$$

When particles of nanosize are dispersed in a solution, Brownian motion ensures that the particles will move about constantly colliding with each other. Due to these collisions and intense affinity of nanoparticles, aggregation is expected in system consisting nanoparticles. To obtain a stable dispersion, DLVO theory, named after Derjaguin and Landau, Verwey and Overbeek, can be found useful (Derjaguin and Landau 1993; Verwey and Overbeek 1999). This theory explains the aggregation of aqueous dispersions quantitatively and describes the force between charged surfaces interacting through a liquid medium. When two particles move close to each other, their electrical double layers overlap, and thus, a repulsive electrostatic force develops. According to DLVO theory, if there is a balance between the repulsive interactions of the double layers on neighboring particles and the attractive interactions arising from van der Waals forces between the molecules in the particles, there is a well dispersion of particles in a fluid. In case of having a well dispersion of nanoparticles, Brownian model has been used for explanation and prediction of enhancement in thermal properties of nanofluids (Kebllinski et al. 2002; Evans et al. 2006). Brownian motion of particles contribute to the enhancement of thermal convection in a system through two ways, the first is direct contribution due to motion of particles that transports heat, and the second is indirect contribution due to micro-convection of fluid surrounding individual particles. However, both direct and indirect contributions of Brownian motion for nanoparticles were theoretically proven to be negligible. Besides, nanoparticles are often in the form of agglomerates and/or aggregates, so the Brownian motion is not expected to play a significant role. Moreover, the enhancement of thermal conductivity in nanoscale systems was found independent of temperature. Weak dependence of nanoparticles thermal conductivity on temperature and base liquid viscosity suggests that the Brownian motion of nanoparticles cannot be a dominant mechanism for the enhanced thermal conductivity of nanofluids (Ding et al. 2007).



The relationship between convective heat transfer behavior of nanofluids and their rheological behavior has been extensively studied (Kwak and Kim 2005; Prasher et al. 2006a, b; Ding et al. 2006; He et al. 2007; Namburu et al. 2007; Chen et al. 2007, 2009a, b; Saeedinia et al. 2012; Yang et al. 2012; Hachey et al. 2014). In these studies, nanofluids exhibited either Newtonian or both Newtonian and non-Newtonian behavior depending on particle size and shape, particle concentration, base liquid viscosity, solution chemistry-related surface layer and electro-viscous effects.

For shear-thinning nanofluids (pseudo-plastic), the shear viscosity approaches a constant at high shear rates. Such a constant is termed the high shear viscosity and is very relevant to the convective heat transfer applications where heat transfer fluids are often in vigorous motion and subjected to very high shear.

In high shear rate regions where the shear viscosity approaches a constant value (called high shear viscosity), the viscosity scales with temperature in a similar fashion to that of the base liquid. The experimental results also show that both the high shear viscosity of nanofluids and the base liquids follow well the classical Vogel–Tammann–Fulcher (VTF) Eq. 2.12, which describes temperature dependence of viscosity (Bird et al. 2002). However, the relative increment in high shear viscosity at a given particle concentrations is almost independent of temperature (Chen et al. 2007, 2009a, b).

$$\log \mu = A + B/(T - T_0) \quad (2.12)$$

where

$T$  is temperature ( $^{\circ}\text{C}$  or  $\text{K}$ )

$\mu$  is fluid viscosity

$A$ ,  $B$ , and  $T_0$  are constants

The presence of nanoparticles in fluids increases the high shear viscosity, and the extent of increment depends on nanoparticle shape and volume fraction. Given other conditions, the high shear viscosity of nanofluids containing rod-like particles is much higher than those containing spherical nanoparticles. The experimentally observed rheological behavior of nanofluids containing rod-like particles cannot be explained purely by the shape effect, and particle aggregation should be considered. Nanofluids containing spherical nanoparticles are less complicated than rod-like nanoparticles. Regression of the measured high shear viscosity of nanofluids containing spherical nanoparticles gives a binomial relationship (Chen et al. 2007):

$$\mu = \mu_0 \left( 1 + 10\phi + (10\phi)^2 \right) \quad (2.13)$$

where  $\mu$  and  $\mu_0$  are the shear viscosity of nanofluids and base liquids, respectively. These authors classified nanofluids as:

*Dilute* nanofluids ( $0 < \varphi < \sim 0.001$ ) containing well-dispersed nanoparticles with no discernible shear-thinning behavior. Shear viscosity can be described by the Einstein equation.

*Semi-dilute* nanofluids ( $\sim 0.001 < \varphi < \sim 0.05$ ) containing aggregates of nanoparticles with no obvious shear-thinning behavior.

*Semi-concentrated* nanofluids ( $\sim 0.05 < \varphi < \sim 0.10$ ) containing aggregates of nanoparticles with clear shear-thinning behavior.

*Concentrated* nanofluids ( $\varphi > \sim 0.10$ ) have interpenetration of aggregates.

The concentrated nanofluids are out of the normal range of nanofluids for heat transfer applications.

Comparing the results of these studies shows that convective heat transfer coefficient was enhanced or deteriorated depending on the nanofluids characteristics including the shape and size of nanoparticles and viscosity of fluid. Nanofluids containing tubular or rod-like nanoparticles often give a higher enhancement of convective heat transfer coefficient in comparison with spherical or disk-like nanoparticles. Nanofluids made of less viscous liquids give a higher heat transfer coefficient in comparison with those made of highly viscous liquids. For cases where heat transfer enhancement is observed, the convective heat transfer coefficient generally increases with increasing flow rate or increasing particle concentration, and the enhancement may exceed the extent of the thermal conduction enhancement. No clear trend has been found in the effect of particle size on the convective heat transfer coefficient of nanofluids. If nanofluids are non-Newtonian, then the analysis that leads to the constant Nusselt number is invalid. Nusselt number, a dimensionless quantity, describes the ratio of conductive thermal resistance to the convective thermal resistance of the fluid (Eq. 2.14).

$$\text{Nu}(l) = \frac{\text{Convective Heat Transfer}}{\text{Conductive Heat Transfer}} = \frac{hx}{k} \quad (2.14)$$

where

$x$  is the characteristic length (m)

$k$  is the thermal conductivity of the fluid (W/m K)

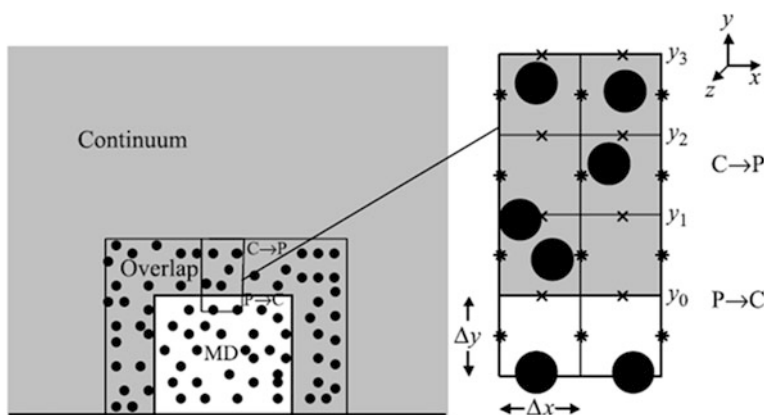
$h$  is the convective heat transfer coefficient of the fluid (W/m<sup>2</sup> K)

As discussed earlier, even very dilute nanofluids can be non-Newtonian, particularly for the water-based nanofluids. Given a nanofluid and pipe geometry, heat transfer enhancement in the turbulent flow regime is less significant than that in the laminar flow regime. No sufficient quantitative information, however, is available in the literature that can be used to infer the dominant mechanisms for heat transfer enhancement/deterioration under convective and boiling heat transfer conditions, where many controversies remain and require further research. The effect of temperature depends on the relative importance of the Brownian diffusion and the shear

flow convection. At low shear rates and high temperatures, the Brownian diffusion can be stronger in comparison with the convection; a stronger shear-thinning behavior is expected (Chen et al. 2007).

Current approach for modeling transport phenomena is based on continuum states, the materials are assumed to be continuous, and the fact that matter is made of atoms is ignored (Bird et al. 2002). However, traditional Navier–Stokes equation and the energy equation based on the continuum assumption have failed as the spatial scale of flows approaches the molecular mean free path, and hence, this approach is not valid for systems at nanoscales (Faghri and Zhang 2006). The discreteness of those systems that involve flow in micrometer- and nanometer-scale channels is important (Nie et al. 2004). For example, continuum approaches can describe fluid motion in nanoporous solids using hydrodynamic models and applying the appropriate boundary conditions; however, the precise relation between the fluids motion in nanopores and the details of the interactions of the fluid with the pore wall is still an open problem. A key parameter characterizing the applicability of the continuum equations, Navier–Stokes equation, is the Knudsen number, defined as the ratio of the molecular free path to the transverse dimensions of the system (Quirke 2006). A thorough understanding and modeling of molecular transport through nanostructures are essential to the logical design of new materials and devices for various purposes like separation processes, nanofluidics, and high-throughput characterization, analysis and sequencing. Non-continuum modeling of transport phenomena, based on atomistic descriptions, such as molecular dynamics (MD) simulations, is an appropriate approach for describing molecular transport through nanostructures. Nie et al. (2004) developed a hybrid method, in which continuum fluid dynamics and molecular dynamics are combined, for describing fluid dynamic at nanoscale. The continuum Navier–Stokes equation was used in one flow region and atomistic molecular dynamics in another. The spatial coupling between continuum equations and molecular dynamics is achieved through constrained dynamics in an overlap region (Fig. 2.31).

In a practical application of using nanosystems in blood, the motion of these systems in a fluid is complex and difficult to control that makes design of the propulsion system a major engineering challenge. Brownian motion would cause a constant random shaking, and surface forces at the nanoscale are significant, resulting in sticking of the system to any surface that it comes into contact with. Nevertheless, these effects can be useful by getting insight into the nature. Living organisms with nanodimension, like viruses, are able to find their way into cells. If molecules with sticky and non-sticky areas are designed, then the agitation caused by Brownian motion will eventually lead to molecules sticking together in very well-defined ways to form rather complex macromolecular structures (Shong et al. 2010). This mode of assembly is known as self-assembly, as discussed before in Sect. 2.1.1.2. The complications of interactions between nanostructures and flow, as addressed in this section, offer difficult challenges that necessitate knowledge and experiences of who is familiar with the material processing and engineering principles through fluid mechanics, i.e., chemical engineer. In general, the laws of traditional physics describe our macroscopic world. The laws of quantum physics



**Fig. 2.31** Schematic of the hybrid method. The continuum description is used in the shadowed region and the atomistic description is used in the dotted region. In  $C \rightarrow P$ , continuum solutions provide boundary conditions for MD simulations, and in  $P \rightarrow C$ , atomistic solutions provide boundary conditions for continuum simulations (Nie et al. 2004)

give a universal image of our world. These laws are essential to our understanding of the nanoworld.

### 2.2.2 An Industrial Perspective Research Challenges in Nanotechnology

Nanotechnology is not a single industry or one a new phenomenon, like the Internet, but offers new possibilities which will likely take place at industrial giants. Any activity in the field of nanotechnology falls in one of the areas addressed below,

1. Synthesis of nanoscale building blocks, named nanostructures like nanoparticles, nanotubes and nanofibers
2. Fabrication and/or processing of nanoscale building blocks for a desired purpose like nanofluids
3. Incorporating nanoscale building blocks into final product, like nanocomposites, nanodevices and nanosensors.

The first two types can be viewed as individual industries where the products coming from them are the substrates for the industries in the third group. In the following, products obtained from each of these three groups are called nanotechnology-based products. Each process involved in producing nanotechnology-based products is strongly required to be commercialized regarding producing commodity with unique performance and customer benefits at a reasonable cost. For example, CNTs have been found a wide range of applications as

addressed in Sect. 2.1.1. Nevertheless, its commercial synthesis and its using as building blocks to produce new materials are still an open problem (Homma 2014; Oueiny et al. 2014; Mehra et al. 2014). CNTs can be produced via different routes; however, CVD has been found as a commercial method. Although large number of research works conducted on synthesis of CNTs using CVD method, the controllable procedure is still under observation. Synthesis of CNTs is categorized in the first group, and when CNTs are dispersed in a liquid, a nanofluid is produced (second group). Nanofluids containing CNTs have been indicated enhanced thermal heat transfer; however, the effects of parameters, including viscosity of fluid, dispersion pattern of nanotubes, etc., are still under study (Aravind et al. 2011; Walvekar et al. 2012; Leong et al. 2014). The nanofluid then can be used in preparing nanocomposites applicable in various applications, for example, in high heat-generating system (Jajja et al. 2013) or as a reinforcement of cement slurry (Nasiri et al. 2013). Preparing nanocomposites is categorized in third group and according to the recent articles, it still needs improvement toward full commercialization (Liu and Kumar 2014). An essential key to commercial production of CNT itself and the products made from CNTs, it is vital to reduce the operation costs as well as control the basic properties of the end products during the manufacturing processes. Academic scientists, engineers and industry visionaries have been keen to prospect for novel strategies and fabrication methods of nanotechnology-based products, in the hope to transform the strategies from a laboratory-scale approach into a mainstream process. However, for realization of wide industrial applications, much research work is required to achieve controlled and large-scale synthesis of nanostructures with reasonable price. The most challenging issues for commercialization of nanotechnology-based products include:

A. Development of robust methods for industrial manufacturing of certain nanostructures

Chemical engineering unit processes have significantly contributed to successful commercialization of many discoveries in the chemical industry. Examples include well-known industrial petrochemical and polymers like Nylon, Teflon<sup>®</sup>, and many other industrial materials improved peoples' lifestyle around the world. Unit operations will be equally important for the commercial production of nanotechnology-based products. Unit operations mostly used in production of nanotechnology-based products include milling, mixing and reaction. For example, gold nanoparticle is commonly synthesized in mixing-reaction system (Yang et al. 2010; Zhao et al. 2013), FePt nanoparticles were produced by high-energy ball milling (Velasco et al. 2012) and nanosilicon carbide-reinforced aluminum was produced by high-energy milling (Kollo et al. 2011). In industrial manufacturing, it is basically impractical to get a product from raw materials by just carrying out a single unit process. It is essential to make the raw materials ready for the main process through upstream processes (pre-treatment), and the materials after main process generally need to go through downstream processes (post-treatment) for the desired product(s) to be separated from unwanted materials. The pure main product in required form is obtained after downstream processes. Process design, including

all upstream, main and downstream process, describing how a product, including nanotechnology-based products, is produced, can be addressed as the first step toward industrialization of the process. The research activities conducted in the laboratories are prerequisites, but the scale is small to obtain appropriate parameters for the design of commercial units. Promising laboratory works will take time to scale up and bring costs down; however, scale-up requires a leap in manufacturing technology. For example, in commercial production of nanostructures, like CNTs, nanogold, nanosilver, as a building block of other products, it is essential to control the size and morphology of these nanostructures. In this regard, size-controlled synthesis of nanoparticles has been developing (Yang et al. 2010; Wei and Liu 2010).

Other limitations pertaining to large production of nanotechnology-based products include low efficiency of process and extensive energy consuming. For example, synthesis of nanostructures using CVD needs temperature above 600 °C (Danafar et al. 2009). Development of micro-unit processes and then advanced technologies for obtaining reliable predictive information are under intense investigation to reduce unwarranted development costs (Ehrfeld et al. 2000; Hessel et al. 2006).

#### B. Active control of the structure and composition of the product with desired macroscopic properties

As mentioned above, the great challenge in synthesis of nanotechnology-based products is how to produce nanostructures with the properties that can be predicted, tailored and tuned beforehand. For example, there is an explosive growth in production of nanocomposites with enhanced or novel properties like high thermal composites, scratch-resistant coating and self-cleaning coating; however, the end-use property of composite strongly depends on the nanostructure properties used as well as processing conditions applied for producing the nanocomposite. To get deeper insight, let's mention the famous example of CNTs, which can have either conductive or semiconductive property according to the configuration of carbon atoms. Depending on the chirality of single-wall CNTs, they may exhibit either metallic or semiconducting properties. Generally, the percent fraction of each type can be affected by growth conditions. However, the electrical characteristics of nanotubes are neither controllable nor selectable on a manufacturing scale. Small changes of the experimental parameters, specifically nature and concentration of the reactants and temperature, lead to considerable alteration of the resulting molecular assemblies. In the next step, nanocomposite preparing well dispersion of nanotubes is critical to reach the desired properties. Proper control of the properties and response of nanotechnology-based products need a comprehensive understanding of mechanisms involved in product synthesis. From an industrial standpoint, it is significant to be able to describe the systems/operations used in the chemical industries and predict their behavior if any change is applied to the system. The diversity of nanotechnology-based products means that there is not going to be a single answer. However, developments of simulation methods at the molecular and atomic level may allow a better understanding of phenomena at nanoscale.

They provide powerful tools to interpret interparticle forces as well as predict nanostructures behaviors, as described in Sect. 2.2.2. Although all results obtained from modeling and simulation have to be experimentally validated, with the increase in computing power and software development, they are providing real reduction in time and cost in development and commercialization of nanotechnology (Uddin et al. 2012). Accordingly, the processes involved in producing nanostructures need sensing and actuation of matter at the nanoscale. Such a delicate control requires advanced smart sensing and characterization systems.

### C. Development of process instrumentation

Online measurement and control of process parameters are a prerequisite for obtaining high production yields of the desired product properties. This task becomes more complicated due to complexity of processes involved in the formation of nanostructures and dependence of end-use properties of nanostructure with their size, atomic configuration and chirality. For example, spherical nanoparticles in a fluid indicated different thermal conductivity and thermal diffusivity compared to the presence of cylindrical nanoparticles in the same fluid (Zhang et al. 2007). A nanostructured filler with different size influences the morphologies and properties of membrane (Yang et al. 2007). Different size of nanoparticles in Fe/Cu/La catalyst showed different product distribution and kinetic parameters in Fischer–Tropsch synthesis (Pour et al. 2010). In this regard, knowing process kinetics and the related issue of mechanisms are a necessary prelude to model and control changes in progress (Texter and Tirrell 2001). Observing the evolution of processes necessitates acquisition of accurate kinetic data in real time, and hence, researchers put their attention toward developing in situ measurement of nanostructure during their formation process to observe and control changes in progress (Zhao et al. 2003; Poretzky et al. 2005; Li-Pook-Than et al. 2010). The acquisition of such data will impel development of a sophisticated instrumentation that provides informative, online measurement to observe and control changes in progress.

### D. Characterization of nanostructures

Bulk characterization of processing materials, in which length scale of meters to micrometer is measured, is not sufficient for processes involved in production of nanotechnology-based products. Properties and characteristics of nanostructures, specially, cannot be based on averaged bulk properties, and in-depth characterization of the materials at the atomic and molecular scale configurations is vital. According to the type of nanotechnology-based products, characterization can be classified into three main levels:

1. Primary characteristics of nanostructures like particle size distribution, defects and impurity in nanostructure, morphology and surface of nanostructure
2. Interfaces and boundaries such as interparticle forces, boundary defects
3. End-use properties like electrical, mechanical, thermal, antimicrobial.



Without truthful structural information, products comprising nanostructures cannot be engineered. Properties of nanoscale building blocks determine end-use performance of the product. For instance, controlling and manipulating conformation and position of polymer molecules with nanometric resolution on surface represent a major industrial challenge in sensors or controlled molecular assemblies. Fabrication of reliable, high-performance product requires an increased understanding of the role played by the microstructure and the surface. Presence of defects and impurity is particularly important for the envisioned applications of the nanotechnology-based products. Therefore, there is a strong demand to develop new tools of characterization that provide accurate and reliable structural information. The use of online size measurement and control of today's particulate products manufacturing processes will be essential to control nanoparticle formation. Online nanocharacterization tools must be used, and therefore, their development needs to be actively pursued. In this framework, instrumentation in all its forms (laser, molecular beams, NMR, TAP, X-ray diffraction, mass spectrometry, tomography, trajectography, computers, etc.) should be of great help in obtaining an accurate picture of chemical transformations and in understanding cellular mechanism.

#### E. Sustainability, environmental, health and safety aspects

It is important for environmental health and safety to keep up with the rapid growth of the nanotechnology industry. A major contemporary industrial challenge is manufacturing products while eliminating or substantially reducing the detrimental environmental consequences of the processes adopted. Nanotechnology has great potential to transform science and industry in the fields of energy, material, environment and medicine. However, in socioeconomic viewpoints, a great challenge for nanorelated industries is to ensure that their new products are safe in the human body and in the environment. Accordingly, novel and sustainable approaches for commercial production of nanostructures should be taken into account. In this regard, economic and environmental impacts of the process are well examined and understood. The transparency of health, safety and environmental impacts of nanotechnology in living systems should be at the forefront. Toxicity of nanostructures is in doubt and reliable and standardized methods for rapid assessment of their toxicity under various exposure, dosing and biological conditions are strongly required. Effective methods must be established among researchers, developers and regulatory bodies to facilitate transfer of research results that reliably assess toxicity of a nanostructure to ensure product safety for industrial and medical users. Regulatory standards should be developed which ensure that precautions are taken in any commercialization development to provide a consistent, quality product to the market with no disadvantage to any group of people. Pure research is more suitable to universities or governmental organizations that the results of research activities are open to the public. On the other hand, improved activities may be more efficiently performed by the sectors motivated by profit and based on the principle of nondisclosure of results. However, the real outcomes of industry must be tested in real society through trial and error.

Our surroundings are rapidly changing with the developments in science and technology. Already, safety and a sense of security cannot be obtained without consciousness, that is, consciousness and investment have become indispensable. The expectations from science and technology for constructing a peaceful society are very huge. In order to solve the problem related to the peace of mind at a higher level, it is necessary to consider the safety provided by science and technology and the need for a sense of security together. Therefore, many sciences must work together. The inclusion of psychology, which regards the sense of security and the probability terms, could be one such joint initiative.

### **2.2.2.1 Chemical Engineering Approaches to Nanostructured Materials Manufacturing**

Chemical engineers are playing impressive roles in developing a new science based on phenomena, structures and potential applications where understanding at nanometer length scales is crucial. The areas in nanotechnology that chemical engineers are making major contributions are addressed as:

- Development of new and novel products like
  - Catalysts
  - Multicomponent composites
  - Natural nanostructures
  - Sorbents for environmental contaminants
- Innovation in processes for synthesis of nanotechnology-based products (Recall that nanotechnology-based products include both synthesis of nanostructures and incorporation of these nanostructures to produce new products like nanocomposites and nanosensors)
- Process optimization for nanotechnology-based products
- Mathematical modeling, kinetic study and thermodynamic study of processes involved in synthesis of nanostructures
- Transport phenomena investigation

Whether this new science base leads to important technological developments depends even more on chemical engineers. Many laboratories have demonstrated controllable methods based on bottom-up approaches as a manufacturing procedure for nanomaterials. The high level of scientific activity in this field has created several kinds of major opportunities for chemical engineering research. The overall opportunity is a shift from laboratory techniques and provocative demonstrations of structure to practical, larger-scale, applied processing methods. This move requires several achievements in chemical engineering, including the precision manufacturing of precursors, expansion of chemical engineering ideas of molecular chemistry to supermolecular chemistry from a bonding, kinetics and mechanistic point of view and a focus on self-assembly processes that can be scaled up to

interesting levels. This leads to a rich array of research and process development issues for chemical engineers.

Understanding and controlling nanotechnology unit operations will be equally important for the commercialization of nanotechnology. Platforms and process technologies in engineering nanotechnology laboratories consist of synthesis of nanostructures and incorporate these nanostructures as building blocks into final products like coatings, sensors and drug delivery systems (Roco 2004).

Engineering research and education, including chemical engineering, play a key role in nanomaterials manufacturing, and this role will even expand in the future because of its integrative, system approach-oriented and transforming characteristics. As the degree of complexity of systems increases at the nanoscale, and various disciplines of science and engineering converge, chemical engineers role will be more critical. The rudimentary capabilities of nanotechnology today for systematic control and manufacture at the nanoscale are envisioned to evolve in four overlapping generations of new nanotechnology products with different areas of R&D focus (Roco 2004).

#### 2.2.2.2 Kinetic Approaches of the Reaction

Kinetics of chemical reaction is a quantitative description for the rate of chemical reaction occurred and the rules of affecting parameters on this rate. The kinetics of a chemical reaction is presented as mathematical correlations that show fundamental aspects of the reaction pathways. This concept increases our ability to develop new and better ways of achieving desired chemical reactions, improve the yield of desired products or even develop a better catalyst for a specific reaction. From the chemical engineering viewpoint, the kinetic of chemical reaction is an essential tool to design chemical reactors as help the chemical engineer to optimize the reactor size by adjusting the reaction rate. Generally, the size of reactor is related to the amount of reactant consumption and the rate of this consumption (or amount of the product and the rate of product generation via the chemical reaction). The quantitative description of the kinetic is provided by several theoretical manners such as physical chemistry rules and even quantum mechanics or molecular dynamics. With today's powerful computers, however, the kinetic studies have to be performed experimentally to find a simple description of the rate and/or verifying the theoretical reaction rate (Missen et al. 1999).

In experimental activities for kinetics study of a reaction, a chemical reactor is used to carry out the reaction and to obtain the rate of the chemical reaction. Mathematical description of the chemical reaction rate is usually equation that describes functionality of the rate with the various factors such as the components concentration and temperature. In chemical reaction engineering (CRE), the information obtained from kinetics is a means to determine size of reactor as well as other aspects such as equilibrium, product distribution and thermal effect. Kinetics, however, does not provide all the information required for this purpose, and heat, mass and momentum balances are also needed to describe the effects of other

factors and problems such as mixing, heat treatment, diffusion and mass transfer diffusion.

A system may be considered in three levels of size to compare the nature of kinetics. These levels are as follows:

1. Microscopic or molecular

A large set of reactant molecules characterized by a definite value of concentration, temperature, pressure and density at any time;

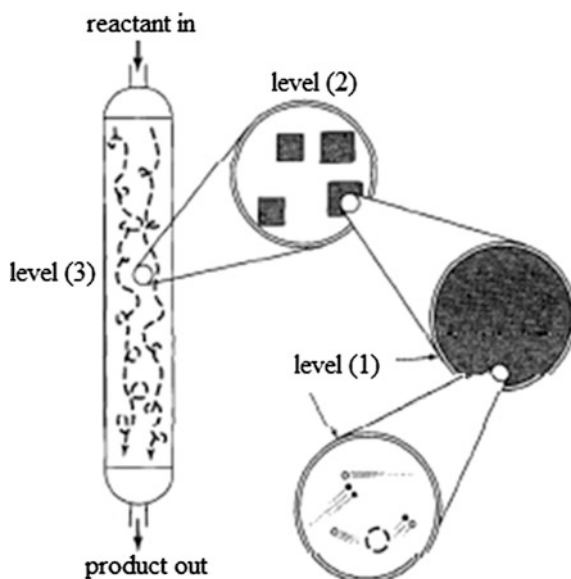
2. Local macroscopic—for example, one solid particle reacting with a fluid, in which gradients of component concentration, temperature, etc., within the particle are detectable.

3. Global macroscopic—for example, in reaction of a fluid with a collection of particles as a bed, in addition to local gradients within each particle, there may be global gradients throughout a bed of the reactor, from particle to particle and from point to point within the fluid.

These levels are illustrated in Fig. 2.32. Levels (1) and (2) are domains of kinetics in the sense of focusing on the mechanism and the rate of reaction connected to the stoichiometric and equilibrium constraints. The level (3) provides sufficient information about overall behavior of the reactor in this level. This information is required to make decisions about design and operation of reactors from the economical view point. In spite of this matter, it is possible under certain ideal conditions at level (3) to make the required decisions based on information available at level (1), or at levels (1) and (2) combined.

At the molecular or microscopic level (Fig. 2.32), chemical change involves only chemical reaction. At the local and global macroscopic levels, other processes may

**Fig. 2.32** Different levels in kinetic analyses of a system (Missen et al. 1999)



be involved in change of composition. These are diffusion and mass transfer of species as a result of differences in chemical potential between points or regions, either within a phase or between phases. The term “chemical engineering kinetics” includes all of these processes, as may be required for the purpose of describing the overall rate of reaction. Yet another process that may lead to change in composition at the global level is the mixing of fluid elements as a consequence of irregularities of flow (nonideal flow) or forced convection. Still other rate processes occur that are not necessarily associated with change in composition: heat transfer and fluid flow. Consideration of heat transfer introduces contributions to the energy of a system that are not associated with material flow, and helps to determine  $T$ . Consideration of fluid flow for our purpose is mainly confined to the need to take frictional pressure drop into account in reactor performance. Further details for quantitative descriptions of these processes are introduced as required.

The rate of reaction is defined for a component involved in a reaction either as a reactant or as a product. The situation of a reaction may vary from a system to another system. The situation of a reaction system is defined as the reaction phase (single or multiple) and/or constant of variable properties (e.g., component concentration, pressure, temperature and density) is changed with respect to position at any given time.

The reaction rate is negative if it is described based on consumption of a reactant component, and it is positive if it is based on a product. The rate of reaction with respect to a component (for example,  $A$ ), denoted as  $R_A$ , is an extensive factor rate of formation of  $A$ . The intensive form of the reaction rate (denoted as  $r_A$ ) is the rate referred to a specified normalizing quantity such as the reactor volume or the mass (or surface) of catalyst. Since the rate  $r_A$  does not depend on the size of system, it may be considered to be the “point” or “intrinsic” rate at the molecular level (level 1). The two rates are related by the system size (such as the reactor volume as normalizing quantity) where for a uniform system (such as well-stirred tank)  $R_A = r_A V$  and for a nonuniform system (such as tubular plug flow)  $dR_A = r_A dV$ .

The rate of chemical reaction with respect to any other component involved in the reaction is related to  $r_A$  directly through reaction stoichiometry for a simple, single-phase system, or it may require additional kinetics information of a complex system.

## General Rules

The rate law of chemical reaction is a function of a number of parameters. The most important ones are:

1. The nature of the species involved in the reaction
2. The component concentrations (reactant or product), the reaction rate is improved with increasing the reactant concentration and decreasing the product concentration usually.

3. Temperature, usually temperature increase causes faster reaction rate. Although there is exception such as the oxidation of nitric oxide to produce nitric acid, in this case, the rate decreases as  $T$  increases.
4. Catalytic activity, the rates of many industrial reactions are improved with using the desirable catalyst.
5. Nature of contact of reactants: The mixing of the reaction system causes the better contact of the components. Sometimes, the intimacy of contact of reactants can affect the rate of reaction oppositely.
6. Presence of foreign exciting factor: Today using the foreign source of energy to excite the reaction is an interesting subject in many researches. The rate of chemical reaction is affected with irradiation of the reaction media with macro-wave, ultrasonic wave, infrared or ultra-violet light, etc.

Dependency of the chemical reaction rate to the mentioned factors is expressed mathematically in the form of a rate law, as following general form of  $r_A = r_A$  (concentration, temperature, catalyst activity, etc.)

The exact derivation of this relation is too complex and is a multidiscipline activity which is related to different fields such as thermodynamic, transport phenomena, physical chemistry and kinetic. This causes to use approximate expressions which have to valid with the experimental data. Fortunately, rate of most of the reactions obeys simple mathematical functionality which is semi-experimental–semi-theoretical relation (such as power law functionality), but derivation of parameters of this simple relation needs specific experimental data.

### Kinetic Model for a New Process

The concept of kinetic in a process indicates rate of the process as a function of the state variables. When a reaction takes place in a process (a system), generally the main step defining the process rate is the chemical reaction. Therefore, kinetic of chemical reaction is an important topic in the study of any system. In a process involved for the synthesis of a nanomaterial via chemical reaction in both gas and liquid phase, multiple reactions, as main and side reactions, usually take place. In these systems, beside the chemical reactions, there are other steps affecting the rate of nanoprodukt synthesis. This means that synthesise rate of the nanoprodukt is too complex to be discovered and determined in single step. Several scientists and researchers have tried to find the mechanisms involved in the nanomaterial synthesise. Although several variables affect the kinetics of nanomaterial formation, they can be divided into three types such as the three levels mentioned earlier (Fig. 2.32):

- Type 1: reactant transfer from bulk to surface, mechanism involves the material to come from bulk to surface by a mechanism such as diffusion, adsorption and film transfer. These mechanisms are observed on transfer of the product (and also the reactants) from the surface to the bulk phase. There is a global

macroscopic viewpoint to consider these mechanisms. Generally, the mass transfer phenomena can define these mechanisms and their rates.

- Type 2: conversion of reactant to product, mechanism of chemical reaction. A local macroscopic level describes this type of mechanism.
- Type 3: atom/molecules of product move to produce nanostructure, mechanisms of surface phenomena such as nucleation, growth, agglomeration and sintering take place. A microscopic level of consideration is involved in these mechanisms.

Figure 2.33 shows these mechanisms schematically.

Many investigations have been focused on the determination of kinetic of each steps and influence of the conditions on the rate steps. Comparison of the investigation results shows that many parameters have effect on the rate functionality and the rate constants. In other word, it is impossible to relate a definite kinetic law to a nanostructure synthesis system without giving special attention to its specific conditions. The main parameters affecting the kinetic law can be classified as following groups:

- Type, size and structure of nanostructure
- The operating conditions: such as temperature, pressure, time and concentrations of reactants
- The catalyst properties such as composition, surface chemistry and structure
- The synthesis process and type of reactor
- Type and concentration of the raw materials.

This variety of parameters affecting the synthesis kinetics is because of multiple and complex mechanisms involved in the synthesis. It is commonly accepted that the thermogravimetric analysis combined with mass spectroscopy (TGA-MS) is a powerful coupling technique to study the growth kinetic of CNTs in situ, because variation of the sample weight, temperature and enthalpy with time during the reaction can be collected as the experimental measurement results online in TGA.

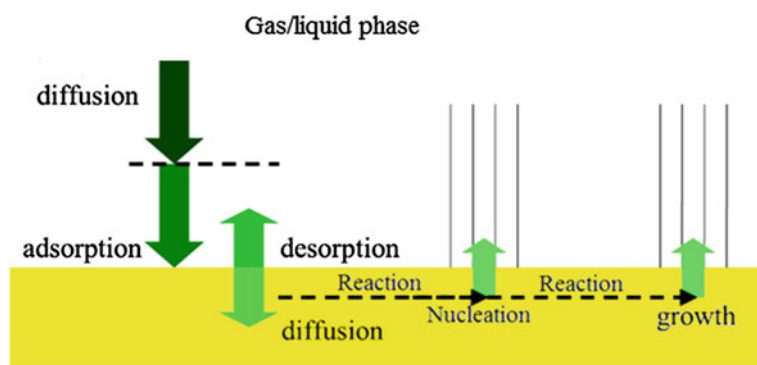


Fig. 2.33 Different mechanisms affecting on the nanomaterial synthesis



Then, the MS instrument indicates variation of type and composition of the gaseous outlet stream with time online. These data can be analyzed using models to find the kinetic law of the reaction (Zhang et al. 2014).

### Some Examples on Kinetic Study

To find the explanation, let us discuss this concept using an example. The CNTs synthesis process is one of the most important processes in nanotechnology that attracted a great number of attentions to discover facts about its synthesis. To realize various applications of CNT, it is necessary to control the structure of the CNTs. CVD is considered as one of the techniques that enable control of structure of CNTs. Experimental data suggest that different parameters affect the morphology of the resulting carbon products as well as parameters of the CNTs. Though numerous attempts to control CNT structure have been made, the effect of these parameters on the yield and structure of CNTs are still not clear, and the observed dependences need to be explained. Many attempts are focused on finding the kinetics of CNT synthesis to find effect of the different parameters on the CNT properties.

There are several main steps from carbon of hydrocarbon precursor in the bulk phase to carbon of CNT on the catalyst surface. These steps are mentioned below, respectively.

1. Mass transfer of the hydrocarbon gas from bulk to the external surface of catalyst support
2. Intraparticle diffusion of the hydrocarbon gas within the catalyst
3. Adsorption of the hydrocarbon gas onto the catalyst surface (active site)
4. Reaction on the catalyst surface to produce carbon molecules
5. Dissolution of carbon molecules in the catalyst
6. Supersaturation of the catalyst with carbon
7. Nucleation and growth of CNT
8. Desorption of hydrogen and other gaseous products from the catalyst surface
9. Diffusion of the gaseous products from the catalyst surface to the external surface of catalyst support
10. Mass transfer of gaseous products from support to the bulk phase

Each step mentioned above has individual rate affecting the overall formation rate of CNT. Comparison of rate of these steps helps us to neglect some of steps. The generally accepted main steps of CNT synthesis in catalytic CVD process include the following steps:

- (a) Adsorption/desorption, diffusion and gas-phase transformation of precursor molecules on the catalyst surface,
- (b) Decomposition of precursor on the catalyst surface or in the gas phase,
- (c) Diffusion of carbon through the catalyst surface,
- (d) Nucleation and growth of CNTs.

Theoretically, any hydrocarbon is able to be used for CNT synthesis. This may have been show generally as following overall relation:

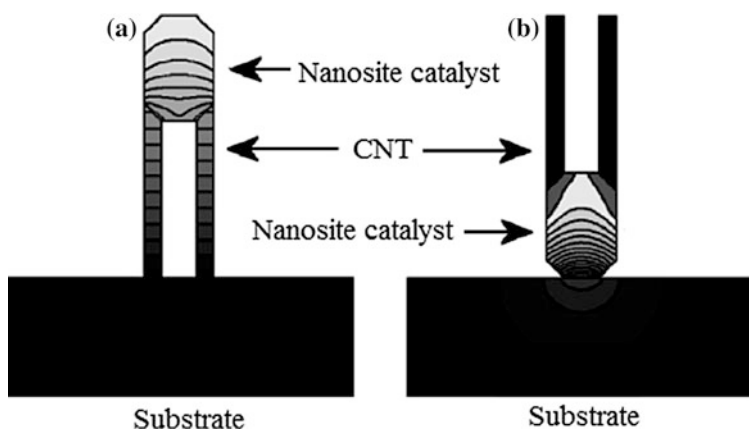


Since different hydrocarbons are characterized by different sticking coefficients and decomposition energies, the carbon supply rate onto the catalyst surface can be changed (Lebedeva et al. 2011). It is generally accepted that the growth is more important to control and predetermine the CNT structure. It is not clear whether the growth kinetics can be modeled as transport limited or reaction limited. Transport limitations can be further classified into factors such as the supply of carbon to the catalyst from the gas phase, the diffusion of carbon through catalyst particles and the diffusion of carbon over the nanotube surface. Extensive efforts have been made to study the dependence of CNT growth on various parameters such as temperature, pressure, time, carbon source and catalyst system. Numerous aspects of growth and nucleation are not well understood, such as critical diameter, growth termination and root-growth versus tip-growth mechanisms (Kwok et al. 2010). The later factor is shown graphically in Fig. 2.34.

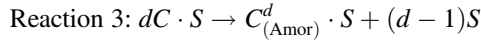
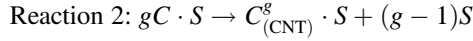
For example, decomposition of ethanol on catalyst active site (S) of  $F_2O_3/MgO$  to form CNT is represented as (Kwok et al. 2010):



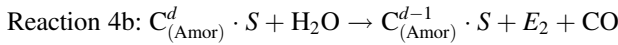
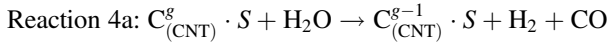
As a simple model of CNT growth, in the first possible reaction,  $C \cdot S$  reacts with the root carbon of the CNT to increase the number of crystalline carbons on the nanotube chain by one (reaction 2). This reaction shows mechanism of CNT growth on the catalyst surface. In the second,  $C \cdot S$  may react with any carbon along the chain to increase the mass of amorphous carbon (reaction 3). These reactions are shown as:



**Fig. 2.34** Comparison of tip-growth (a) and root-growth (b) mechanisms of CNT growth



In these equations, an arbitrary  $g$  number of nanotube carbons and  $d$  number of amorphous carbons are shown as  $C_{(\text{CNT})}^g$   $C_{(\text{Amor})}^d$  and , respectively. In the etching step, water from the decomposition of ethanol can react with any form of carbon in the system to produce  $H_2$  and  $CO$ :



The chemical reaction rates of these reactions are defined as the power law kinetic.

$$R_1 = K_1 C_{C_2H_5OH} C_S^2 \quad (2.15)$$

$$R_2 = K_2 C_{C,S}^2 \quad (2.16)$$

$$R_3 = K_3 C_{C,S} (C_{C,S} + C_{\text{CNT}} + C_{\text{AMOR}}) \quad (2.17)$$

$$R_4 = K_4 C_{H_2O} (C_{\text{CNT}} + C_{\text{AMOR}}) \quad (2.18)$$

The kinetic parameters of these reactions are calculated and reported in Table 2.2 using the Arrhenius functionality ( $K = A \exp^{-E/RT}$ ).

To define variation of the components concentration during the reactions, we can write the mole balance on the components and obtain following relations:

$$dC_{C,S}/dt = 2k_1 C_{C_2H_5OH} C_S^2 - K_2 C_{C,S}^2 - K_3 C_{C,S} (C_{C,S} + C_{\text{CNT}} + C_{\text{AMOR}}) \quad (2.19)$$

$$dC_{\text{CNT}}/dt = K_2 C_{C,S}^2 - K_4 C_{H_2O} C_{\text{CNT}} \quad (2.20)$$

$$dC_{\text{AMOR}}/dt = K_3 C_{C,S} (C_{C,S} + C_{\text{CNT}} + C_{\text{AMOR}}) - K_4 C_{H_2O} C_{\text{AMOR}} \quad (2.21)$$

where  $C_{S0} = C_S + C_{C,S} + C_{\text{CNT}} + C_{\text{AMOR}}$  and  $C_{S0}$  is constant. The concentration of water and ethanol ( $C_{C_2H_5OH}$  and  $C_{H_2O}$ ) is controllable by adjusting concentration of

**Table 2.2** Kinetic parameters of the reactions 1–4 (Kwok et al. 2010)

Reaction	Activation energy ( $E$ ) $KJ/mol$	Pre-exponential factor ( $A$ ) $M^6/mol \text{ min}$
1	$128 \pm 12$	$10^{2.0 \pm 0.6}$
2	$243 \pm 3$	$10^{12.7 \pm 0.6}$
3	$254 \pm 5$	$10^{12.1 \pm 0.6}$
4	$260 \pm 80$	$10^{14.8 \pm 2.0}$

these components in feed stream of the reactor. It is important that the number of catalyst active sites ( $C_S$ ) is decreased because of amorphous/structured carbon coverage. This is a concept of catalyst deactivation. Basically, the concentration of catalyst active site ( $C_S$ ) can be defined as:

$$C_S = C_{S0} \cdot a(t) \quad (2.22)$$

where  $a$  is activity of the catalyst surface. A simple model can be defined as only considers catalyst deactivation by formation of the coke that covered the active sites. This coke can be partially removed from the catalyst surface by gasification with the hydrogen present in the reaction atmosphere. Consequently, the rate of catalyst deactivation is expressed as (Pérez-Cabero et al. 2004)

$$-da/dt = k_d a - k_r(1 - a) \quad (2.23)$$

where  $k_d$  and  $k_r$  are the deactivation and regeneration kinetic constants, respectively. These constants are function of temperature with Arrhenius functionality. The Arrhenius parameters of these constants are presented in Table 2.3. Solution of this equation will give:

$$a(t) = K_s + (1 - K_s)\exp^{-k_G t} \quad (2.24)$$

where  $k_G = (k_d + k_r)$  and  $K_s = k_r/k_G$ . Using this expression and replacing in Eq. 2.22, the variable concentration of catalyst will drive with time as following:

$$C_S = C_{S0}(K_s + (1 - K_s)\exp^{-k_G t}) \quad (2.25)$$

Now, this relation can be used to define effect of catalyst deactivation on the CNT synthesis (Eq. 2.20).

To discuss the rate law of diffusion of carbon through the catalyst surface, the Fick's first law is used correctly as (carbon atoms) (Klinke et al. 2005):

$$J_p = -D\Delta C \quad (2.26)$$

where  $C$  the concentration and  $D$  is the diffusion constant which is given by Arrhenius equation as

$$D = D_0 \cdot e^{-E/RT} \quad (2.27)$$

**Table 2.3** Arrhenius parameters of the activity rate constants ( $k_d$  and  $k_r$ ) (Pérez-Cabero et al. 2004)

Rate constant	Activation energy (E) $k_j/\text{mol}$	Pre-exponential factor (A) 1/min
$k_d$	69.1	$4.46 \times 10^2$
$k_r$	187.2	$2.8 \times 10^6$

where  $E$  is the activation energy and  $D_0$  is diffusion factor. The typical amount of these parameter are  $D_0 = 2.2 \text{ cm}^2/\text{s}$  and  $E = 1.27 \text{ eV}$  in the case of carbon diffusion in Fe (fcc). Thus, the diffusion coefficient at temperature 923 K will be  $D = 2.533 \times 10^{-11} \text{ m}^2/\text{s}$ . Following the iron–carbon diagram, the maximal solubility of carbon in iron at 923 K is  $S = 65 \text{ ppm}$  (weight). Exceeding this amount leads to the formation of iron carbide  $\text{Fe}_3\text{C}$ . This limit determines the maximal concentration gradient  $\Delta C$ . Therefore, the amount of  $\Delta C$  can be calculated as:

$$|\Delta C| = \frac{S}{d_{\text{diff}}} \frac{MW_{\text{Fe}}}{MW_{\text{C}}} \frac{1}{V_{\text{Fe}}} \quad (2.28)$$

where  $d_{\text{diff}}$  is the diffusion distance (usually  $d_{\text{diff}} = 0.5d_{\text{particle}}$ ),  $MW_{\text{Fe}}$  and  $MW_{\text{C}}$  are molecular weight of Fe and carbon, respectively, and  $V_{\text{Fe}}$  is molar volume of Fe ( $=7.093 \times 10^{-6} \text{ m}^3/\text{mol}$ ). One obtains:

$$|\Delta C| = 42.63 \frac{1}{d_{\text{diff}}} \frac{\text{mol}}{\text{m}^3} \quad (2.29)$$

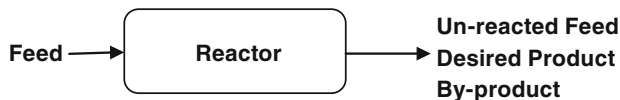
In this case, we have:

$$J_P = 1.079 \times 10^{-9} \frac{1}{d_{\text{diff}}} \frac{\text{mol}}{\text{m s}} \quad (2.30)$$

This will get the maximum flux of carbon diffusion into Fe catalyst structure at  $T = 923 \text{ K}$ .

### 2.2.2.3 Chemical Reactors

A chemical reactor is the heart of chemical processes, and it is a device in which the feedstock (reactants) is converted to the desired product by chemical transformations or chemical reactions (Fig. 2.35). Reactors are not only involved in producing chemical products but also in energy production like combustor and in certain electrochemical cells like fuel cells (Missen et al. 1999). There are different types of reactors and various factors that need to be taken into account in selecting chemical reactors for specific task. In addition to economic considerations, the appropriate selection of reactor will give the highest yields and purity for desired product, while minimize pollution (Coker 2001). Three important parameters, conversion (Eq. 1.10),



**Fig. 2.35** Reactor transforms feed into desired product and by-product

yield (Eq. 1.12) and selectivity (Eq. 1.14), describe the performance of a chemical reactor.

Reactor design embodies many different facets and disciplines like mechanical design of equipment, instrumentation and process control, economic and socio-economic (environmental and safe operation). However, reactor design in chemical engineering discipline means is analysis of performance of an existing reactor. The term “reactor performance” may refer to the operating results achieved by a reactor, particularly with respect to fraction of reactant converted or product distribution for a given size and configuration, or the size and configuration for a given conversion or distribution (Missen et al. 1999). In any case, reactor performance depends on rates of processes involved and fluid characteristics of the system. The rates of processes depend on the reaction occurred, heat and mass transfer characteristics of the system and equilibrium limitations. Fluid characteristics of the system correlate with the motion and relative motion of fluid elements (both single-phase and multiphase situations) and solid particles. Flow characteristics include residence-time distribution (RTD), mixing characteristics for elements of fluid in the reactor and the level of segregation (Missen et al. 1999). Lack of sufficient information on any of these characteristics is a major impediment for complete design of a reactor.

Information about the composition and temperature at each point of the reactor enables the designer to describe the behavior of a chemical reactor. Concentrations of species at any point may change due to either chemical reaction or mass transfer. The temperature at any point of the reactor may also change because of the heat absorbed or released by chemical reaction or heat transfer. The rate of the chemical reaction as well as the rate of mass and heat transfer influences the concentration and temperature of a given section of the system. Concentration, temperature and molecular properties determine the reaction rate (Missen et al. 1999). This process occurs through kinetic properties that affect the outcome of the process through the kinetics of heat and mass transfer. The rates of mass and heat transfer depend on the properties relative to the reactor, such as size of the reactor, size and speed of the impeller, and the area of heat exchanging surfaces (Coker 2001).

Temperature is the most important parameter that influences kinetics and qualitative characteristics of the reaction products. The deviation from optimal reaction temperature involves uncontrollable change of reaction rate, which negatively affects selectivity of chemical processes. The exact control of temperature, which is a driving force for heat exchange, is the central factor for determining other parameters in a process. In order to provide an optimal progress of a chemical reaction, different conditions must be achieved in the reactor: First, a nearly ideal mixing of the reactants should be ensured, linked with the generation of an extended phase interface in multiphase reactions. Afterward, the required response time must be guaranteed by a residence time with preferentially narrow RTD. Finally, the reactor heat necessary for the reaction must be supplied or carried off. In this connection, control of temperature, pressure, time of reaction and flow velocity is important (Reschetilowski 2013).

Reactor design and selection are among the most important task in the whole process design. Reactors produce both wanted products and unwanted by-products. The unwanted by-products lead to loss of revenue and environmental problems. The chemical reactor is designed and dimensioned to get the required yield and conversion of the raw material to desired product. Good performance of a reactor is then imperative in both determining the economic viability of the overall process and its environmental impact. Reactor design that intends to predict the performance of a reactor for specified requirements necessitates both experimental and theoretical endeavors (Prud'homme 2010). The first step in reactor design for a certain product is to make a decision regarding the reaction path, as there are sometimes different routes to produce a specific material. Besides commercial and technical factors that must be considered here, the preferred reaction path is the one that use the cheapest raw materials and produce the smallest quantities of by-products. It is worth mentioning that, at this early stage of design, all consequences of the selected reaction path are not predictable; however, some of them are clear (Smith 2005). The next step will be to choose the catalyst, if catalyst is needed, and then determination of ideal characteristics (like type, size configuration) and operating conditions (like temperature and pressure in the reactor, feeding condition) for the reaction system (Missen et al. 1999). Some of the parameters considered when selecting a reactor for chemical reactions are the number of phases involved, the differences in the physical properties of the participating phases, the post-reaction separation, the inherent reaction nature (stoichiometry of reactants, the intrinsic reaction rate, isothermal/adiabatic conditions, etc.), the residence time required, and the mass and heat transfer characteristics of the reactor (Reschetilowski 2013). To get through the best selection for reactor, there are several questions that should be first answered (Coker 2001; Prud'homme 2010; Smith 2005):

- What is expected from the reactor?
- What are requirements imposed by the reaction mechanisms? For example, what is the rate expression, and the required production capacity? What are reaction heat and reaction rate constant?
- What is the nature of chemical reaction (or reactions) that occur in reactor? For example, is the reaction homogeneous or heterogeneous? or is the reaction is catalytic or non-catalytic?
- What are the reaction conditions including temperature of the heat transfer medium, temperature of the inlet reaction mixture, inlet composition and instantaneous temperature of the reaction mixture?
- What is the thermodynamic state and deviation from thermodynamic equilibrium?
- What are the governed principles of transport phenomena in the reactor? What are the values of heat and mass transfer coefficient?

Besides these factors related to the nature and kinetics of the reactions and transport phenomenon in the reactor, the optimum design relies on review of some information about type of reactor and its mode of processing (Smith 2005; Coker 2001). For example:

Is process preferred to be batch or continuous?

Is combination of reactors in series or parallel required?

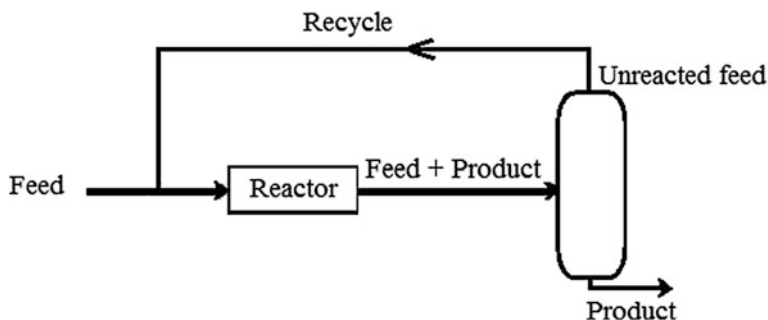
What is the mode of operation is it an isothermal (i.e., constant temperature) or an adiabatic (i.e., heat does not exchange with the surroundings) condition?

Can the desired degree of conversion of the raw feedstock be obtained by a single pass operation best, or recycling is needed? Incomplete conversion in the reactor requires a recycle for unconverted feed material, as depicted in Fig. 2.36 (Smith 2005).

After answering to the questions addressed above, a good approximation is approaching as nearly as possible the ideal condition. Ideal reactors are often a good approximation to real cases, and their studying can be used as a good approach for real reactor design (Prud'homme 2010). Ideal reactors are either perfectly insulated from the viewpoint of mass and heat transfer (adiabatic) or at equilibrium with the surroundings (Coker 2001). More details for reactor selection according to the reactions can be found in Smith 2005.

### Batch Reactors

A batch reactor is a vessel that has no input or output during the time reaction proceeds. In batch reactors, the reactants are loaded into the reactor at the beginning of the operation and the reaction is initiated by heating the contents to reaction temperature, adding a catalyst and so on. The reaction is allowed continuing for a predetermined time, and finally, the products are discharged. The time that reaction



**Fig. 2.36** Feed recycling to send the feedstock conversion

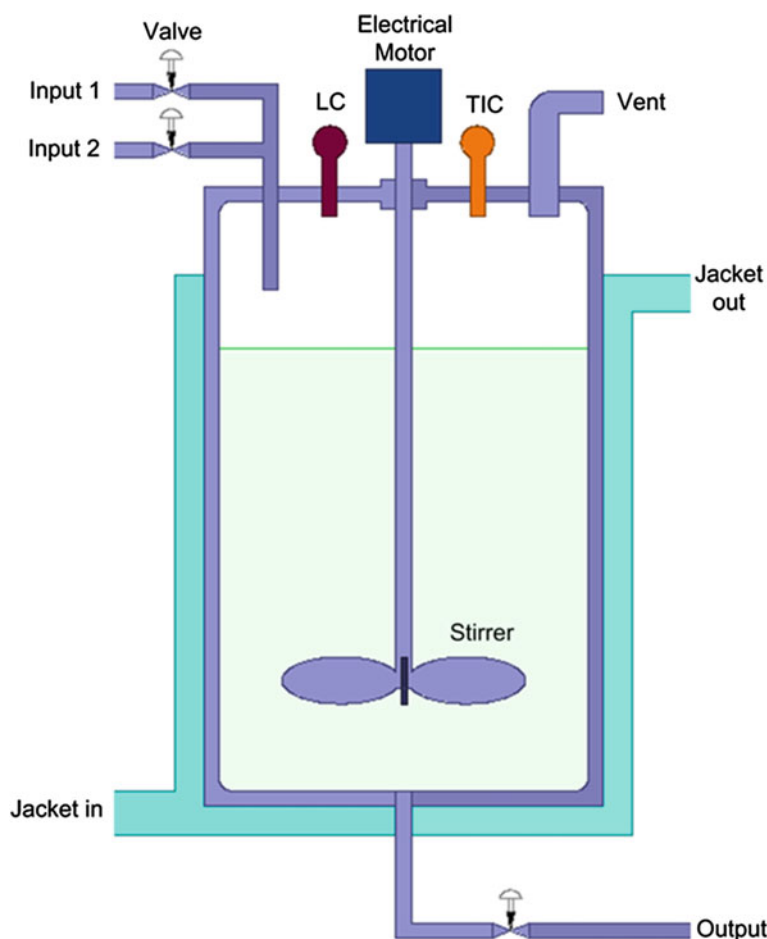


let to be proceeded is the required time to achieve a given conversion. A good example of batch reactors is small flasks and beakers usually used in laboratory-scale setup. Here, reactants are added and brought to reaction temperature. A batch reactor is addressed by the following characteristics (Missen et al. 1999; Coker 2001).

1. Batch reactor is a closed system that means the total mass is fixed. Although the total mass in the reactor is constant, the volume or density of each batch may vary as reaction proceeds. If a batch reactor is used for a liquid-phase reaction that the volume and density can be assumed constant, but this assumption is not valid when there is a gas-phase reaction.
2. The energy of each batch may vary (as reaction proceeds). Heat exchangers are usually used to control temperature.
3. The operation of the reactor is inherently unsteady state. The extent of reaction and properties of the reaction mixture (for example, batch composition) change with time
4. The reaction (residence) time for all elements of fluid is the same.

Batch reactors have several advantages, which make them attractive for many commercial operations. The most important ones are being economical for small-volume production and being flexible. These parameters make them multi-purpose equipment for production of a variety of products at different rate of production. Batch reactors are also preferred for those industrial purposes that equipment needs regular cleaning and sterilization (Smith 2005), like pharmaceutical and biotechnology products. Besides the application of batch reactors in manufacturing processes, they are extensively applied in the laboratory research. A general illustration of a batch reactor for liquid-phase reaction is depicted in Fig. 2.37. Feed streams are introduced through input lines, and then, valves fitted in the input lines are closed. To make the liquid-phase homogenous and provide better contact among reactants, a stirrer is used. Depending on the type of reaction (being exothermic or endothermic), reactor needs to be cool down or warm up using the jacket. Temperature and level of materials are controlled by temperature indicator controller (TIC) and level controller (LC). When the reaction is accomplished, the valve fitted on the output line is opened to collect the materials including main product, by-products and reactants not to be participated in the reaction.

The performance of batch reactors is influenced by several factors. The important ones are contacting pattern and operating condition (Smith 2005). There are different contacting patterns to enhance the mass transfer. Agitated tank and moving bed are good example of contacting mode for batch reactors. In the ideal-batch model, the content of the reactor is subjected to perfect mixing. Concentrations change with time, but the perfect mixing ensures that at any instant, the composition and temperature throughout the reactor are uniform (Missen et al. 1999; Smith 2005). Operating conditions of batch reactors are described by both fixed and dynamic variables. Batch cycle time and total amount of reactants are optimized values fixed for a given batch reactor system. Nevertheless, values for temperature,



**Fig. 2.37** Batch reactor (*LC* level controller, *TIC* temperature indicator controller)

pressure, rate of feeding and product takeoff change through the batch cycle time. If the profile of these dynamic variables (temperature, pressure and rates for feeding and product takeoff) is known, a simulation of the reactor can be carried out in the time interval considered.

One of the main drawbacks for batch reactor is its limitation in mass production, because the characteristics and properties of product may vary from a batch to another batch. Nevertheless, they are particularly useful for investigation of the kinetics of a chemical reaction (Prud'homme 2010) since the time is the main variable in this system and sampling in different times can provide information about concentration variation with time which is necessary for kinetic study. In addition, when a researcher aims to study an unknown reaction and tries to find the effects of parameters such as temperature, pressure and concentration on the

reaction characteristics, this type of reactor is usually preferred. These capabilities of batch reactor are important from the nanotechnology viewpoint, and therefore, the batch reactors are generally selected. However, a challenge in using a batch reactor for rate determination is the ability to obtain good conversion data as a function of time (Denn 2011).

For example, synthesis of nanoparticles in a hydrothermal system is a batch reactor. In this system, the reactor vessel is loaded with the reactant. Then, the vessel (which is a pressure vessel) is heated to the high temperature that causes high-pressure condition in the vessel volume. In this condition, a specific reaction takes place and the monodispersed nanoparticles are formed with full control of the particle size.

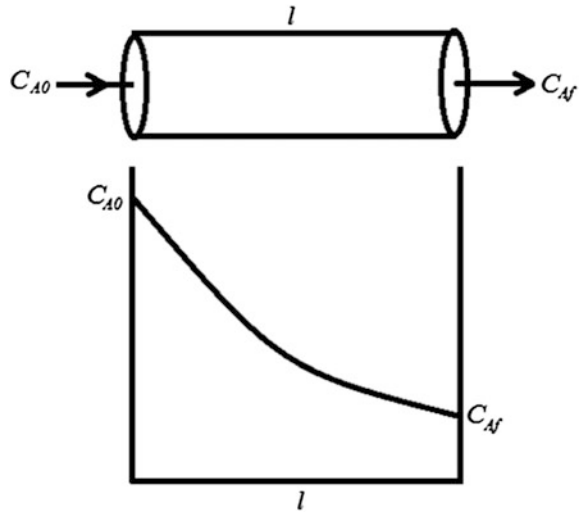
## Continuous Reactors

In continuous reactors, feeding and product takeoff are both continuous, but not necessarily at a constant rate. Referring to Fig. 2.37, both input and output lines are opened during reaction. Not the total mass inside the vessel or the density of the stream is constant with time, and the system may operate at steady state or at unsteady state (Missen et al. 1999). An ideal model for continuous reactors is continuous stirred tank reactor (CSTR). In this model, a stirrer is installed in the vessel that perfectly mixes the reactor contents (Fig. 2.37). As a result of this well mixing, the composition and temperature of the reaction are homogeneous in all parts of the vessel (Coker 2001). CSTRs are used both in a laboratory and on a large scale. They are preferred for the laboratory investigation of gas-phase reactions, particularly when solid catalysts are involved (Missen et al. 1999). They are also employed in a series arrangement. A good example of this application is for the continuous copolymerization of styrene and butadiene to make synthetic rubber. An important disadvantage of the CSTR is that for a given conversion, it requires a large inventory of material, which is not desirable if the reactants or products are hazardous (Nauman 2008). The residence time of individual fluid elements in the CSTR reactor is not constant and varies (Smith 2005).

Plug-flow reactors (PFR) are another type of ideal continuous reactor. A PFR is similar to a CSTR in being a flow reactor, but is different in its mixing characteristics. In PFR, the flow in the vessel is plug flow, i.e., there is no mixing in the direction of flow. An example for PFR reactors is large cylindrical tubes used in the petrochemical industry for the cracking of hydrocarbons. This process is continuous with reactants in the tubes and the products obtained from the exit. The extent of reaction and properties, such as composition and temperature, depends on the position along the tube and does not depend on the time (Coker 2001). The former is illustrated in Fig. 2.38, in which concentration profiles are also shown with respect to position in the vessel. Each element of fluid has the same residence time  $t$  as any other, that is, there is IZO spread in  $t$ .

Due to complete mixing in the plane perpendicular to the direction of flow, the properties of the fluid, including its velocity, are uniform in this plane (Missen et al. 1999). In the plug-flow model, due to steady movement of flow only in one

Fig. 2.38 Plug-flow models



direction, a steady uniform movement of the reactants is assumed, with no attempt to induce mixing along the direction of flow. Like the ideal-batch reactor, the residence time in a plug-flow reactor is the same for all fluid elements. Plug-flow operation can be approached by using a number of mixed-flow reactors in series. The greater the number of mixed-flow reactors in series, the closer is the approach to plug-flow operation (Smith 2005). PFRs are used for both laboratory-scale investigations of kinetics and large-scale production. They are preferred when (Nauman 2008):

- Careful control of residence time is important, as is the case where there are multiple reactions in series.
- High rates of heat transfer are required as PFRs offer a high ratio of heat transfer surface area to volume.
- High pressure is required. Under high-pressure conditions, a small-diameter cylinder requires a thinner wall than a large-diameter cylinder.

PFRs are not useful for multiphase reactions since it is often difficult to achieve good mixing between phases, unless static mixer tube inserts are used (Nauman 2008). The most important results obtained for ideal reactor models are summarized in Table 2.4

Table 2.4 Summary of model for ideal reactors

		Batch reactor	PFR	CSTR
Reactor model		$\frac{dC_A}{dt} = -r_A$	$\frac{dC_A}{d\tau} = -r_A$	$\frac{\Delta C_A}{\Delta \tau} = -r_{Af}$
Reactor parameter		$t$ (residence time)	$\tau = \frac{V}{q}$ (space time)	$\tau = \frac{V}{q}$ (space time)
Concentration determination	$n = 1$	$C_A = C_{A0}e^{-kt}$	$C_{Af} = C_{A0}e^{-k\tau}$	$C_{Af} = \frac{C_{A0}}{1+k\tau}$
	$n \neq 1$	$C_{A0}^{1-n} - C_A^{1-n} = (n-1)kt$	$C_{A0}^{1-n} - C_{Af}^{1-n} = (n-1)k\tau$	$k\tau C_{Af}^n + C_{Af} = C_{A0}$

Many industrial reactors operate in the continuous mode. The main reason of common usage of these reactors is their ability in mass production of many products in any condition. These reactors are designed in the no-mixing status (PFR) or perfect mixing status (CSTR) at any conditions such as isothermal or non-isothermal, homogeneous or heterogeneous, steady state or unsteady state, constant volume or variable volume, or any other conditions. As an applied example, in the catalytic reactions, contact of the reactants with the catalyst surface is a key parameter of the reactor operation. Tank vessel is an example for CSTR, where fixed bed is an example for PFR in heterogeneous reactors. An improved contact can be achieved in reactors like fluidized bed, moving bed, trickle bed, rotary drum. In the nanotechnology field, many nanostructure materials mainly in the gas phase are produced via catalytic reactions. However, controlling these reactions to achieve the best conditions is too complex and necessitates special arrangement of the phases contacting. For example, in CNT synthesis via CVD, the fluidized bed reactor is a suitable choice in which mass production and preset properties of the product are achievable. In such system, the fluid phase continuously flows in the reactor as plug and the solid (catalyst) is perfectly mixed.

### Semi-batch reactor

A semi-batch reactor is an intermediate of the batch and continuous conditions. This type of reactor is a vessel where a feed stream inlets to the reactor continuously, while there is no output stream (rarely with a continuous product stream without input stream, such as decomposition reaction of a liquid and gas releasing which the gas product has to exit from the reactor environment during the reaction). When multiple reactant components are involved in a complex reaction, the semi-batch reactor is appropriate choice to control the concentrations and therefore to control the reaction progress. Consider the reaction  $aA + bB \rightarrow cC$  takes place in a batch reactor. The components *A* and *B* initially are in contact with each other at a predetermined concentration, but after a while, the concentration of each component varies uncontrollably. On the contrary, the reaction in progress can be simply controlled if one of the components *A* or *B* is added to the other gradually. This is the principle of semi-batch state where an input stream (containing one of the reactant component) inlets to the reactor (containing another one of the reactant) while there is no output stream. Semi-batch reactors can operate in the steady-state condition with adjusted rate of the input stream. It should be noticed that the controlling of the reactant concentration during the reaction is one of the advantages of the semi-batch system. This system facilitates different purposes such as temperature controlling, pH controlling, diluter or additive adding.

The semi-batch state generates excellent condition for synthesis of a number of nanomaterials. As an example, consider reduction in Ti cations in a liquid phase that the component  $\text{TiO}_2$  is produced and precipitated as a solid based on precipitation method (the precipitation method will be explained in the next section). The reaction is:



A vessel is first loaded with one of the reactants (for example,  $\text{TiOCl}_4$ ), and then, the other reactant (for example,  $\text{NH}_4\text{OH}$ ) is gradually added to the vessel. As the reaction proceeds, no stream leaves the vessel. Rate of the reaction and thus rate of the solid formation can be simply controlled by controlling the input rate of the reactant. This ability is imperative in synthesis of solid particle with nanosize (Namin et al. 2008).

### Micro- and Nano-reactors

Micro-reactors are reactors with the small dimensions, which do not exceed 1 mm (Ehrfeld et al. 2000). They are miniaturized chemical reaction systems, which contain micro-channels, in which fluid flows continuously and chemical reactions take place (Jensen 2001). The main difference of micro-reactors from the common continuous-flow reactors consists in a laminar flow regime of the fluids (Hetsroni et al. 2005). Since the ratios of viscous force to inertial force and of interfacial force to inertial force in micro-channels are several orders of magnitude higher than that in regular equipment, laminar flow always happens in such systems. The small dimensions of channels also lead to relatively large surface area-to-volume ratios ( $10,000\text{--}50,000 \text{ m}^2/\text{m}^3$ ) and shorter diffusion paths compared to conventional reactors ( $100 \text{ m}^2/\text{m}^3$ ), and thus, transport process is improved (Ehrfeld et al. 2000; Capretto et al. 2011). As a result of laminar flow, molecular diffusion dominates the transport phenomena, and hence, time taken to enable mixing across a micro-channel can be approximated according to molecular diffusion theory, in which the rate of transfer is directly proportional to the surface area (Reschetilowski 2013). Accordingly, heat and mass transfer in micro-reactors is some orders of magnitude higher than that in usual reactors. For example, the mass transfer coefficient for micro-reactor could be  $K_{La} \approx 5\text{--}15 \text{ s}^{-1}$ , which is two orders of magnitude larger than those for macroscopic reactors,  $K_{La} \approx 0.01\text{--}0.08 \text{ s}^{-1}$  (Jensen 2001). Thermal diffusivities are high enough (up to  $41,000 \text{ W}/(\text{m}^2 \text{ K})$ ) that the micro-reactors will be approximately isothermal (Kockmann 2006; Watts and Wiles 2007). In comparison with traditional reactors on the macroscale, higher rates of heat and mass transfer facilitate fast and accurate control of temperature and concentration in the reactor and therefore improve selectivity and productivity of reaction, and also allow reactions to be performed under more uniform conditions (You-qi 2008; Jensen 2001).

Another outstanding advantage of micro-reactors is their capability to be employed at high pressure. In the cylindrical vessels, the most allowable pressure is inversely proportional to the diameter of a capillary. Therefore, micro-channels provide the chance to use micro-reactors at high pressure, about 400 bar and above. Despite such high pressure in the micro-reactor, it can be carried out more safely compared to conventional large-scale reactors (Reschetilowski 2013).

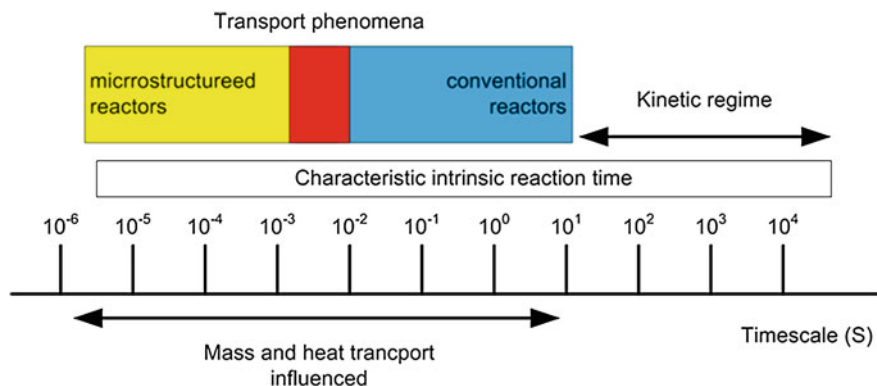


Fig. 2.39 Timescale of chemical and physical processes

Consequently, micro-reactors are supreme for conducting operations even with highly exothermic reactions or under supercritical conditions (Nauman 2008; Benito-Lopez et al. 2008; Marre et al. 2012). Besides all processing benefits for micro-reactor, the axial dispersion effects associated with the parabolic flow profile of typical micro-channel contribute to a broader RTD (Chang 2013). Design techniques for micro-reactors are generally identical to those for macroscale reactors with laminar flow (Nauman 2008). Figure 2.39 shows timescale of different reactor scale and the related phenomena.

Keeping in mind all the benefits presented, the main motivations for employing micro-reactors are the gain in economy, safety and ecology impacts. Micro-reactors, due to their small dimension, contribute to the minimization of raw material and energy consumption as well as waste production and thus improve its economics (Jensen 2001). This feature is significant both in the laboratory research activity and during scale up to the pilot plant or large-scale production. The small quantity of substances in the reactor also minimizes the potential of thermal explosion by dangerous reactions. This feature is particularly important for strongly exothermic reactions and reactions dealing with toxic or explosive materials.

Despite all exceptional advantageous of micro-reactors, there are some practical considerations that need to be taken into account. For example, in liquid phase, the rate of diffusion may not be as high to prevent lateral diffusion if liquid reactions proceed very fast. In this case, mixing can be used to reduce diffusive barriers (Hoffmann et al. 2010). It is worth mentioning here that turbulence is not induced on the microscale even if mechanical or magnetic stirrers are used (Reschetilowski 2013). Another obstacle can be the pressure loss with higher throughputs, which can lead to a restriction of the flow in a micro-reactor. This problem can be also avoided by using a series of continuous micro-reactors with equal dimensions that operate in parallel or in series (Kashid and Kiwi-Minsker 2009). Micro-reactors can be scaled to meet demands for large-scale production by numbering up the micro-reactors and running them for longer times. This strategy makes it feasible to go from microgram

to kilogram quantities without additional chemistry modifications or reactor engineering (Jensen 2001).

Micro-reactors have been finding various applications in either conventional or modern technology. For example, in the field of biotechnology, they are applied for diagnostic applications, sometimes called lab-on-a-chip and production of designer molecules. They are employed in combinatorial chemistry and kinetic studies for effective and fast optimization of investigated reactions (Reschetilowski 2013). For example, they are promising candidates for characterization of catalyst performance, such as kinetics, selectivity and deactivation, with the purpose of high-throughput screening of catalysts (Jensen 2001). Due to their outstanding practical benefits, micro-reactors are preferable for up to 70 % of all chemical reactions and in particular for heterogeneous reaction systems (Roberge et al. 2005; Nauman 2008). Fast reactions with a large heat effect, which is not possible in macroscale reactors, can be carry out in micro-reactor since they allow for nearly isothermal conditions at high reactant concentrations (Chang 2013). In this respect, they have been extensively employed in synthesis of polymers, nanoparticles, as well as bio-, electro- and photocatalysis process.

Since the emphasis of this book is on the nanoengineering, the following sentences will emphasis on this subject. Chemical synthesis of nanostructures using micro-reactors has offered unique capabilities in the advancement of nanotechnology (Yen et al. 2005; Song et al. 2006; Karnik et al. 2008; Duraiswamy and Khan 2009; Marre et al. 2012; Jin et al. 2010; Lazarus et al. 2010; Zhao et al. 2011; Ishizaka et al. 2012; Eluri and Paul 2012). Micro-reactors have indicted the potential to overcome some of the technical challenges in nanomaterial production. The important challenge in synthesis of nanostructure is having control over the size and size distribution of nanostructures that these characteristics depend on several processing parameters, most importantly the residence time and temperature and their distribution. In conventional large-scale reactors, fluctuations in temperature and concentration are difficult to correct because of large response time; e.g., any alteration requires time to have an effect on the whole system. In comparison, changes on the microscale are observed almost immediately (Reschetilowski 2013). The possibility of rapid mixing of reactants and fast heating and cooling of the system enables precise control of the reaction parameters, thus improving the process yield as well as quality of nanostructure, e.g., composition, size and shape of nanostructures. It becomes necessary to directly address the particulate nature of matter for nanoreactor design. On the nanoscale, the diffusion times and Reynolds numbers shown in Table 2.5 become rather meaningless. Instead, the models must address the behavior of individual molecules. Thus, an alternative definition of the nanoscale is the scale at which continuum models must be replaced by molecular models (Smith 2005). The miniaturization of length scale causes significant effects on transport properties and acting forces, as shown in Table 2.5 (Mae 2007).



**Table 2.5** Scaling effect of transport properties (Mae 2007)

Property	nm	$\mu\text{m}$	mm	m
Length (L)	$10^{-9}$	$10^{-6}$	$10^{-3}$	1
Surface area ( $L^2$ )	$10^{-18}$	$10^{-12}$	$10^{-16}$	1
Volume ( $L^3$ )	$10^{-27}$	$10^{-18}$	$10^{-9}$	1
Specific surface area ( $L^{-1}$ )	$10^9$	$10^6$	$10^3$	1
Rate ( $\propto L$ )	$10^{-9}$	$10^{-6}$	$10^{-3}$	1
Inertial force ( $\propto L^4$ )	$10^{-36}$	$10^{-24}$	$10^{-12}$	1
Viscous force ( $\propto L^2$ )	$10^{-18}$	$10^{-12}$	$10^{-6}$	1
Interfacial tension ( $\propto L$ )	$10^{-9}$	$10^{-6}$	$10^{-3}$	1
Viscous force/inertial force ( $\propto L^{-2}$ )	$10^{18}$	$10^{12}$	$10^6$	1
Interfacial tension/inertial force ( $\propto L^{-3}$ )	$10^{27}$	$10^{18}$	$10^9$	1

#### 2.2.2.4 Health, Safety and Environmental Issues

As explained in the previous sections, nanotechnology has great applications in the fields of energy, material, environment and medicine. The quantity of engineered nanostructures is expected to grow significantly in the next several years (Roco 2011). On the other hand, as nanotechnology progresses toward manufacturing and commercial stages, more concerns are being raised about the potential risky effects of nanostructures on human health and environmental media. For example, CNTs, due to their superior mechanical, electronic and thermal conductive properties, are currently used in consumer and industrial products like sports tool or flexible displays and touch screens. On the other hand, CNTs are likely to be released during the life cycle of CNT-incorporated products through mechanical abrasion and degradation. Some researchers asserted that CNTs are toxic to aquatic organisms, and they can damage the lungs if inhaled. Similar reports have been also published for other nanostructures that they can potentially lead to new hazards or increase risks to the environment (Maynard et al. 2006; Maynard and Pui 2007; Oberdörster et al. 2007). However, all these reports are based on preliminary studies, and exact environmental health and hazard risks associated with the nanostructures productions and their application are not fully known yet. Since large numbers of novel nanotechnology-based products are continuously being introduced, it is vital to develop a robust scientific platform to understand health, safety and environments (HSE) outcomes of these products. Consequently, HSE studies need to keep up with the rapid growth of the nanotechnology. Diversity of nanostructures means that there is not going to be a single answer for all of these systems, and multidisciplinary exercises, which move beyond traditional hazard, exposure and risk assessment models, are critical. A comprehensive study on HSE issues associated with nanostructures will answer and resolve questions and uncertainties asked by toxicologists, the community, regulators. Development of regulations and guidelines for occupational health and safety in the workplace through using data and information acquired by HSE studies will eventually have a

strong influence on public acceptance and the implications of nanotechnology and its sustainability.

The HSE impacts of nanostructures occur when these materials are released into the environment or taken up by human being. To assess the toxicology impact of nanotechnology-based products, a fundamental requirement is to understand which physico-chemical properties of nanostructures are important in toxicity and hazard generation (Maynard et al. 2006; Nel et al. 2006; Oberdörster et al. 2007; Seaton et al. 2010). Accordingly, the ability to measure and characterize nanostructures in a range of media (air, soil, water and all living systems) and to examine their toxicity is critical. In this regard, nanostructures properties, like their morphology, size and size distribution, chemical composition, crystalline structure, surface area, surface chemistry, agglomeration and aggregation, should be well evaluated for their undesired HSE impacts *in vivo* and *in vitro*. There are usually two general procedures for data collection including toxicity studies in animals and epidemiologic studies in humans. However, uncertainties are quit large, and it is more important that the nanostructures to be judged on a case-by-case basis. For each nanostructure, short-term and long-term mode of exposure, such as skin absorption, ingestion and inhalation among others, must be systematically studied to determine any potential for organ or tissue damage, inflammation, a triggering of autoimmune diseases and other health-related consequences.

Nanostructures may enter human body through various pathways, and they may act by reacting with surface receptors or by passing into cells and reacting with intracellular receptors. A general statement notes that nanostructures are toxic and they are too small to be prevented by the cells that normally resist other air contaminant. The size of nanostructures is an important characteristic in governing their inter- and intracellular distributions. Agglomerated nanostructures with dimension about few microns can be only taken up by cells such as macrophages. Nanostructures with size of more than about 50 nm can penetrate cells but not cellular organelles such as the nucleus or mitochondria. Those nanostructures that have dimensions below 20 nm can even enter the latter organelles. Consequently, any interactions between a nanostructure and living system will be size dependent.

Airborne exposure with inhalable uptake is currently viewed as the most critical exposure route. On the other hand, nanostructure agglomerates are pervasive in atmospheric sciences, air pollution and material manufacturing, and it is therefore imperative to study the aerosol behavior of nanostructures. Wang and Pui (2013) studied the relationship between morphology of nanostructures and their aerosol behaviors. Based on modeling and experimental results, they elucidated that the penetration of nanotubes, like CNTs, is less than the penetration for a nanosphere with the same mobility diameter, which is mainly due to the larger interception length of the CNTs. CNTs tend to form bundles due to their geometry and van der Waals forces. Accordingly, when CNTs are provided by manufacturers in the powder form, it consist large agglomerates in the order of microns. In fact, large agglomerates have limited mobility, and they are expected to be handled and transported easier and safer comparing to the nanostructures that exist in form of individual nanoparticles. Agglomeration, however, is a particularly complex issue,

and agglomerates may break down to individual nanoparticles. How tightly the nanoparticles are stuck together in the agglomerates is thus a key factor. CNTs have also tendency to form agglomerates with a bundle-like form in aqueous media because of their geometry and hydro-phobic surface. The mobility of CNTs in surface waters and subsurface environments is dependent on the deposition and release behavior of these nanostructures (Petosa et al. 2010; Chen et al. 2010; Yi and Chen 2014). It has been indicated that, in the aqueous systems, CNTs have limited mobility and can deposit on naturally occurring surfaces, such as sand, rocks and sediments (Jaisi and Elimelech 2009). However, the deposited CNTs may be released from the solid surfaces and reenter the aqueous phase when the solution chemistry changes (Tian et al. 2012; Yi and Chen 2014). Besides understanding the release kinetics of CNTs from a product to various ecosystems, it is crucial to determine their behavior, in term of absorption, desorption, biotic uptake and accumulation in living system. In the next step, the physico-chemical interactions, kinetics and thermodynamic exchanges between CNTs and the biological components must be well recognized. Since any nanostructure has different characteristics and hence different behaviors, all the mentioned issues must be well investigated separately for any nanostructure. Entities engaged in nanotechnology must consider practical and innovative steps to minimize identified risks while managing for unknowns and uncertainties. The first step of prudent practices related to the nanoengineering safety involves creating a comprehensive framework to summarize current scientific knowledge and applications of nanotechnology and to identify possible HSE benefits and HSE risks of nanotechnology. In the next step, recommended methodology for risk characterization of nanostructures, assessment and implementation of reasonably practicable combination of HSE risk management approaches will minimize risks to the workers and the environment. Knowing the source of nanostructures release, a set of “reference” or representative materials must be identified for testing that requires separate consideration for occupational exposure as well as exposure from consumer products and via the environment. It is also necessary to prepare technical documents that assess the appropriateness of recommended risk assessment methodologies for nanostructures and suggest improvements in these methodologies. To guide safe implementation of nanotechnology, generation of an accurate informative database is then critical. Creating such database necessitates time and consensus building, rational decision-making implementation of high-throughput and rapid screening platforms. Exploiting computational methods can assist in risk modeling and hazard assessment. The result of such inclusive study will be a regulatory program for the responsible development, production, use and end-of-life disposal of nanostructures employed by companies and other organizations. It also provides value to the nanotechnology-related businesses by helping focusing on decreasing the risk of products while keeping costs down.

To acquire a practical and suitable guideline for nanostructures, one important duty of engineers and scientists is now to reach an appropriate answer to the following questions:

- What are the social and economic dimensions of nanotechnology-based products?
- What is the rate of degradation for nanotechnology-based products?
- What is the rate of nanostructures release and emission to the ecosystems?
- What is the rate of nanostructures transport through the systems?
- How the nanostructures may damage the ecosystems?
- What are the risky and undesired impacts on HSE?
- What is the rate of nanostructure absorption and accumulation in living systems?
- How the nanostructures that enter living systems may damage the system?
- What is the level of exposure that creates unacceptable hazards for nanostructures?
- What is the interaction of nanostructures with other hazardous?
- How the hazardous structures can be controlled?
- What is the quantity of production waste goes to the environment from processes involved in synthesis of nanotechnology-based product?
- What are the reaction intermediates and by-products formed through the process for synthesis of nanotechnology-based product?

In order to get an appropriate answer to these questions, engineers must

- Develop methods for risk characterization and detection of nanostructures
- Develop methods for evaluating the nanostructures properties in the context of their ignition and explosion potential
- Develop technologies that enable the measurement of exposure to nanostructures in different ecosystems (soil and water)
- Develop instruments capable of fast and online measurement of nanostructures
- Develop methods and instruments that able to differentiate materials in the different environment
- Develop appropriate techniques capable of measuring nanostructures in biological systems
- Develop suitable metrics and methods for data collection and interpretation
- Develop scientific procedures to determine the potential toxicity of nanostructures to human, in terms of all potential modes of exposure to hazardous materials
- Develop standardized, well-characterized reference nanostructures
- Develop MSDS guidelines for nanostructures
- Develop a laboratory safety guideline and manufacturing workplace guideline
- Develop methods for hazard control and abatement of nanostructures released

## Exercises

1. What is difference between nanotechnology and nanoengineering?
2. Give an example for each field that comes at the below and state how knowledge of chemical engineers can help:

Design of sensor/biosensor using nanostructures

Design of smart carriers for controlled release of active component

Design of nanofluids for water shut-off and improved/enhanced oil recovery

Design of nanostructures for reduction of the viscosity of heavy oil

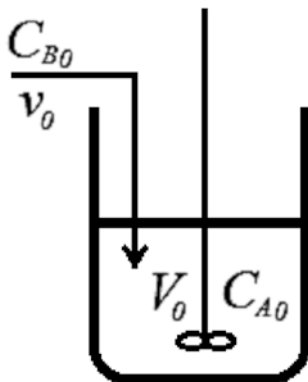
Design of nanocatalyst and usage of these catalyst

Design and application of membranes

Wastewater treatment

Design and application of new energy generator devices

3. What are the two synthesis strategies in nanotechnology? Define each strategy and provide an example for each one.
4. What are the three methods for synthesis of nanostructures using top-down strategy? Find an example for everyone.
5. Explain principles for synthesis of nanoparticles using sol-gel process? How principles of chemical engineering can help in controlling the process?
6. Consider synthesis of carbon nanotubes using CVD process and state how a chemical engineer can develop the process for commercial production?
7. A researcher aims to synthesis catalyst comprising nanoparticles of metal supported on alumina. The prepared catalyst will be used in fluidized bed where the size distribution range of the particles is important. What other characteristics of the catalyst needs to be considered and what are the related characterization methods?
8. A researcher aims to develop a nanocomposite for biosensing. The layer thickness, chemical bonding, and electronic properties of the nanocomposite need to be observed. Which method/s do you recommend?
9. A dilute nanofluid containing spherical nanoparticles of  $\text{Al}_2\text{O}_3$  in water is prepared in a flask with depth of 10 cm. Calculate high shear viscosity of nanofluids.  
How will be the viscosity of nanofluid changes if the nanofluid gets concentrated?
10. A semi-batch reactor is a perfect system for reaction controlling that makes them suitable for nanostructures synthesis. The following figure shows a semi-batch reactor. Consider reaction  $A + B \rightarrow C$  with reaction rate  $-r_A$  (mol/L s) which is the main reaction in synthesis of nanoparticle "C". In order to control the reaction rate for component A, the reactor is first fed by reactant A with initial concentration  $C_{A0}$ . Then, the reactant B is gradually added to the material in the reactor with constant flow rate  $v_0$  and concentration  $C_{B0}$ . Calculate variation of the component concentrations A and B with time. Calculate the concentration of component C if the precipitation rate of component C is  $R_{\text{pre}}$  (mol/L).

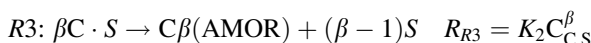
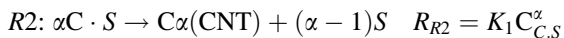


11. In the kinetic example of section “[Some Examples on Kinetic Study](#)” assume that synthesis of CNT via ethanol decomposition as  $\alpha\text{C}_2\text{H}_5\text{OH} + S \rightarrow \text{C}^\alpha(\text{CNT}) \cdot S + 2\alpha\text{H}_2\text{O} + \alpha\text{H}_2$  with the kinetic:

$$R_{\text{CNT}} = dm_{\text{CNT}}/dt = KC_{\text{eth}}C_S$$

where ethanol concentration ( $C_{\text{eth}}$ ) is constant. The amount of active sites vary with time because of catalyst deactivation (Eq. 2.25). Calculate weight of decomposed CNT ( $m_{\text{CNT}}$ ) after time  $\tau$ .

12. Consider parallel reactions R2 and R3 in example of section “[Some Examples on Kinetic Study](#)”:



If carbon nanotube (CNT) is the desirable product and amorphous carbon (amor) is undesirable one, discuss about methods to increase formation rate of CNT compared to the formation rate of amorphous carbon ( $R_{\text{R2}}/R_{\text{R3}}$ ).

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