Chapter 1
Nanotechnology: Principles and Applications

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Abstract Nanotechnology is one of the leading scientific fields today since it combines knowledge from the fields of Physics, Chemistry, Biology, Medicine, Informatics, and Engineering. It is an emerging technological field with great potential to lead in great breakthroughs that can be applied in real life. Novel nano- and biomaterials, and nanodevices are fabricated and controlled by nanotechnology tools and techniques, which investigate and tune the properties, responses, and functions of living and non-living matter, at sizes below 100 nm. The application and use of nanomaterials in electronic and mechanical devices, in optical and magnetic components, quantum computing, tissue engineering, and other biotechnologies, with smallest features, widths well below 100 nm, are the economically most important parts of the nanotechnology nowadays and presumably in the near future. The number of nanoproducts is rapidly growing since more and more nanoengineered materials are reaching the global market The continuous revolution in nanotechnology will result in the fabrication of nanomaterials with properties and functionalities which are going to have positive changes in the lives of our citizens, be it in health, environment, electronics or any other field. In the energy generation challenge where the conventional fuel resources cannot remain the dominant energy source, taking into account the increasing consumption demand and the CO_2 emissions alternative renewable energy sources based on new technologies have to be promoted. Innovative solar cell technologies that utilize nanostructured materials and composite systems such as organic photovoltaics offer great technological potential due to their attractive properties such as the potential of large-scale and low-cost roll-to-roll manufacturing processes The advances in nanomaterials necessitate parallel progress of the nanometrology tools and techniques to characterize and manipulate nanostructures. Revolutionary new approaches in nanometrology

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will be required in the near future and the existing ones will have to be improved in terms of better resolution and sensitivity for elements and molecular species. Finally, the development of specific guidance for the safety evaluation of nanotechnology products is strongly recommended.

1.1 Introduction

The term nanotechnology comes from the combination of two words: the Greek numerical prefix nano referring to a billionth and the word technology. As an outcome, Nanotechnology or Nanoscaled Technology is generally considered to be at a size below 0.1 μm or 100 nm (a nanometer is one billionth of a meter, 10^{-9} m). Nanoscale science (or nanoscience) studies the phenomena, properties, and responses of materials at atomic, molecular, and macromolecular scales, and in general at sizes between 1 and 100 nm. In this scale, and especially below 5 nm, the properties of matter differ significantly (i.e., quantum-scale effects play an important role) from that at a larger particulate scale. Nanotechnology is then the design, the manipulation, the building, the production and application, by controlling the shape and size, the properties-responses and functionality of structures, and devices and systems of the order or less than 100 nm [1, 2].

Nanotechnology is considered an emerging technology due to the possibility to advance well-established products and to create new products with totally new characteristics and functions with enormous potential in a wide range of applications. In addition to various industrial uses, great innovations are foreseen in information and communication technology, in biology and biotechnology, in medicine and medical technology, in metrology, etc. Significant applications of nanosciences and nanoengineering lie in the fields of pharmaceutics, cosmetics, processed food, chemical engineering, high-performance materials, electronics, precision mechanics, optics, energy production, and environmental sciences.

Nanotechnology is an emerging and dynamic field where over 50,000 nanotechnology articles have been published annually worldwide in recent years, and more than 2,500 patents are filed at major patent offices such as the European Patent Office [3].

Nanotechnology can help in solving serious humanity problems such as energy adequacy, climate change or fatal diseases: “Nanotechnology” Alcatel-Lucent is an area which has highly promising prospects for turning fundamental research into successful innovations. Not only to boost the competitiveness of our industry but also to create new products that will make positive changes in the lives of our citizens, be it in medicine, environment, electronics or any other field. Nanosciences and nanotechnologies open up new avenues of research and lead to new, useful, and sometimes unexpected applications. Novel materials and new-engineered surfaces allow making products that perform better. New medical treatments are emerging for fatal diseases, such as brain tumours and Alzheimer’s disease. Computers are built with nanoscale components and improving their performance depends upon shrinking these dimensions yet further" [4].

Nanomaterials with unique properties such as: nanoparticles carbon nanotubes, fullerenes, quantum dots, quantum wires, nanofibers, and nanocomposites allow completely new applications to be found. Products containing engineered nanomaterials are already in the market. The range of commercial products available today is very broad, including metals, ceramics, polymers, smart textiles, cosmetics, sunscreens, electronics, paints and varnishes. However new methodologies and instrumentation have to be developed in order to increase our knowledge and information on their properties. Nanomaterials must be examined for potential effects on health as a matter of precaution, and their possible environmental impacts. The development of specific guidance documents at a global level for the safety evaluation of nanotechnology products is strongly recommended. Ethical and moral concerns also need to be addressed in parallel with the new developments.

Huge aspirations are coupled to nanotechnological developments in modern medicine. The potential medical applications are predominantly in diagnostics (disease diagnosis and imaging), monitoring, the availability of more durable and better prosthetics, and new drug-delivery systems for potentially harmful drugs. While products based on nanotechnology are actually reaching the market, sufficient knowledge on the associated toxicological risks is still lacking. Reducing the size of structures to nanolevel results in distinctly different properties. As well as the chemical composition, which largely dictates the intrinsic toxic properties, very small size appears to be a dominant indicator for drastic or toxic effects of particles. From a regulatory point of view, a risk management strategy is already a requirement for all medical technology applications [5–7].

In order to discuss the advances of nanotechnology in nanostructured materials, we presented first in Sect. 1.2 the methods and principles of nanoscale and nanotechnology, and the relevant processes. The impact of nanotechnology in the field of electronics is presented in Sect. 1.3. Energy harvesting and clean solar energy are presented in Sect. 1.4 focusing in a new emerging technology of plastic photovoltaics which is based on nanostructured materials. The techniques and the tools which are currently used to characterize and manipulate nanostructures are presented in Sect. 1.5. In Sect. 1.6, the future perspectives as well as the increasing instrumentational demands are discussed.

1.2 Methods and Principles of Nanotechnology

1.2.1 What Makes Nanostructures Unique

The use of nanostructured materials is not a recently discovered era. It dates back at the fourth century AD when Romans were using nanosized metals to decorate glasses and cups. One of the first known, and most famous example, is the Lycurgus

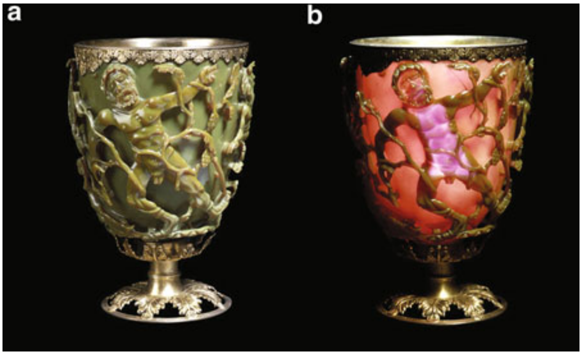

Fig. 1.1 The Lycurgus cup in reflected (**a**) and transmitted (**b**) light. Scene showing Lycurgus being enmeshed by Ambrosia, now transformed into a vine-shoot. Department of Prehistory and Europe, The British Museum. Height: 16.5 cm (with modern metal mounts), diameter: 13.2 cm. The Trustees of the British Museum [8]

cup (Fig. 1.1) [9], that was fabricated from nanoparticles (NPs) from gold and silver that were embedded in the glass. The cup depicts King Lycurgus of Thrace being dragged to the underworld. Under normal lighting, the cup appears green. However, when illuminated from within, it becomes vibrant red in color. In that cup, as well as in the famous stain glass windows from the tenth, eleventh, and twelfth centuries, metal NPs account for the visual appearance.

To shed light to the changes in visual appearance of gold, from the usual yellowish color to the reddish one that appears in the Lycurgus cup a comparison between differences of absorption spectra from a bulk gold metal film and a gold colloidal film (Fig. 1.2). The thin, bulk gold metal film absorbs across most of the visible part of the electromagnetic spectrum and very strongly in the IR and at all longer wavelengths. It dips slightly around 400–500 nm, and when held up to the light, such a thin film appears blue due to the weak transmission of light in this wavelength regime. On the contrary, the dilute gold colloid film displays total transparency at low photon energies (below 1.8 eV). Its absorption becomes intense in a sharp band around 2.3 eV (520 nm) This sharp absorption band is known as surface plasmon absorption band. Metals support SPs that are collective oscillations of excited free electrons and characterized by a resonant frequency. They can be either localized as for metal NPs or propagating as in the case of planar metal surfaces. Through manipulation of the geometry of the metallic structure, the SPR can be tuned depending on the application. The resonances of noble metals are mostly in the visible or near infrared region of the electromagnetic spectrum, which is of interest for decorative applications. Because of the plasmonic excitation of electrons in the metallic particles suspended within the glass matrix, the cup absorbs and scatters blue and green light – the relatively short wavelengths of the visible spectrum. When viewed in reflected light, the plasmonic scattering gives the cup a greenish hue, but if a white light source is placed within the goblet, the glass

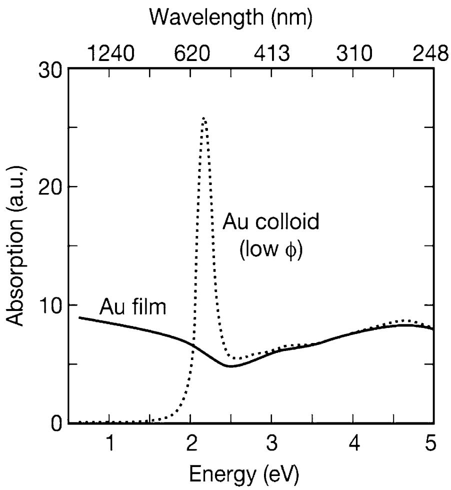

Fig. 1.2 Absorption spectra of a gold nanocrystal film which absorbs only above 1.8 eV like a semiconducting material due to the quantum confinement effect and a thin, bulk gold metal film of equivalent thickness which absorbs like a typical metal in the infrared energy region. ϕ is the volume fraction of gold in the sample [10]

appears red because it transmits only the longer wavelengths and absorbs the shorter ones [10].

1.2.2 Size Dependence

The aforementioned ability of gold as well as of other noble metals and semiconductors relies on quantum confinement which is a very successful model for describing the size dependent electronic structure of nanometer sized materials According to this theory electrons are confined in all three dimensions causing matter to behave completely different in terms of its optical and electronic properties. When the dimension of a material approaches the electron wavelength in one or more dimensions, quantum mechanical characteristics of the electrons that are not manifest in the bulk material can start to contribute to or even dominate the physical properties of the material [11].

Besides quantum size effects, the nanomaterials behavior is different due to surface effects which dominate as nanocrystal size decreases. Reducing the size of a crystal from 30 to 3 nm, the number of atoms on its surface increases from 5% to 50% beginning to perturb the periodicity of the "infinite" lattice. In that sense, atoms at the surface have fewer direct neighbors than atoms in the bulk and as a result they are less stabilized than bulk atoms [11]. The origin of the quantum size effects strongly depends on the type of bonding in the crystal.

1.2.3 Metal NPs

For metals, the electron mean free path (MFP) determines the thermal and electrical conductivity and affects the color of the metal. For most of the metals, MFP is of the order of 5–50 nm. Reducing further this threshold, the electrons begin to scatter off the crystal surface, and the resistivity of the particles increases. For very small metal particles, the conduction and valence bands begin to break down into discrete levels. For gold particles, this causes a change in color from red to orange at sizes around 1.5 nm.

1.2.4 Quantum Dots

In a bulk semiconductor electrons can freely move within an area from a few nanometers to a few hundred of nanometers as defined by the Bohr radius. Thus continuous conduction and valence energy bands exist which are separated by an energy gap. Contrary, in a quantum dot, where excitons cannot move freely, discrete atomic like states with energies that are determined by the quantum dot radius appear.

The effect of quantum confinement has a great technological interest from semiconductors and optoelectronics to biological applications. As depicted in Fig. 1.3, by changing the particle size the emitting color of quantum dots can be

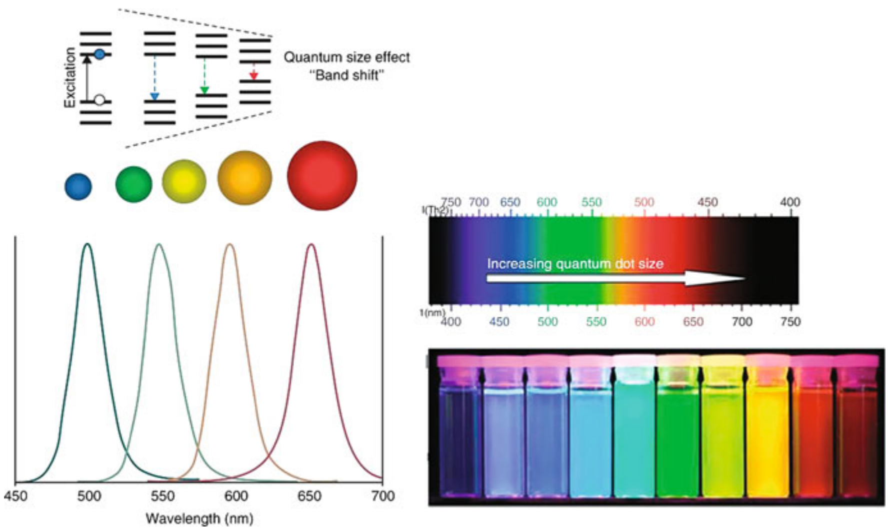

Fig. 1.3 Schematic drawing representing the changes on optical behavior of nanoparticles associated with their size. *Top*: Electronic structure of QDs with “blue shift” due to quantum confinement [12]

tuned. Shorter quantum dots emit shorter wavelength of light and bigger quantum dots emits longer wavelengths of light. The energy band gap E_g is correlated with size: as the dimension of particles decreases, the energy increases.

$$E_g^{Qd} = E_g^{b} + \left(\frac{h^2}{8R^2}\right)\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \left(\frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R}\right),$$

where $E_{g,b}$ and $E_{g,QD}$ are the bandgap energies of the bulk solid and quantum dot, respectively, R is the quantum dot radius, m_e is the effective mass of the electron in the solid, "e" is elementary charge of the electron, "h" is Planck's constant, the m_h is the effective mass of the hole in the solid, and " ε" is the dielectric constant of the solid. The middle term on the right-hand side of the above equation is a 'particle-in-a-box-like' term for the exciton, while the third term on the righthand side of the equation represents the electron–hole pair Coulombic attraction, mediated by the solid [12]. Some of new applications of quantum dots are memories, transistors, detectors, and lasers and quantum computers.

1.2.5 Nanotechnology Imitates Nature

When a droplet of water lands on the lotus leaf, it beads up, rolls off the leaf surface without leaving a trace of water behind, and washes away any dirt along its way. This self-cleaning property fascinated scientists for a long time until recently, when scientists realized that this peculiar behavior is due to the nanostructures present on the surface of the lotus leaf. They term this as super-hydrophobicity. These can be integrated in numerous parts of the building infrastructure. New developing nanostructured surfaces behave like the lotus leaf and stay dry when water lands on them. Such degree of water repellency exceeds even that of one of the most well-known hydrophobic materials, polytetrafluoroethylene (PTFE) or Teflon [13].

The natural technology of gecko foot-hairs can provide biological inspiration for future design of remarkably effective adhesives. Since gravity plays a negligible role at nanoscale, the van der Waals forces become very important. The van der Waals energy per unit area, E/α, between two infinite parallel surfaces is:

$$\frac{E}{a} = -\frac{A}{12\pi D^2},$$

where A is the Hamaker constant which is a constant that depends on the material properties (and can be positive or negative depending on the intervening medium) and D is the distance between the surfaces. The feet of a Gekko gecko contains approximately one billion spatulae that can provide a sufficiently large surface area in close contact with the substrate for adhesion to be the result of van der Waals forces [14] (Fig. 1.4).

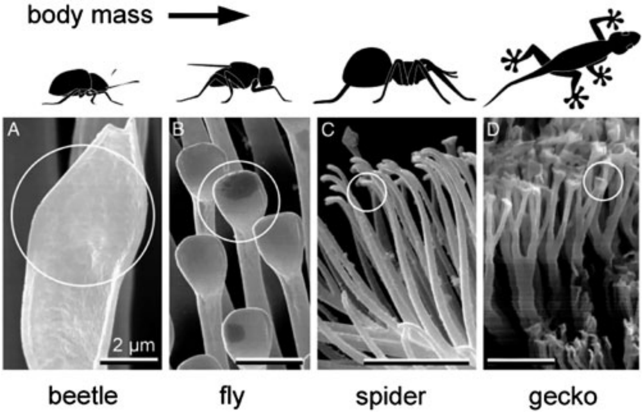

Fig. 1.4 Terminal elements (*circles*) in animals with hairy design of attachment pads. Note that heavier animals exhibit finer adhesion structures [15]

Different methods for the synthesis of nanoengineered materials and devices can accommodate precursors from solid, liquid, or gas phases and encompass a tremendously varied set of experimental techniques. A detailed presentation of these is beyond the scope of this review. In general, however, most synthetic methods can be classified into two main approaches: "*top-down*" and "*bottom-up*" approaches and combinations of them (Fig. 1.5). "*Top-down*" (photolithography, microcontact printing) techniques begin with a macroscopic material or group of materials and incorporate smaller-scale details into them, whereas "*bottom-up*" (organic-synthesis, self-assembly) approaches begin by designing and synthesizing custom-made molecules that have the ability to self-assemble or self-organize into higher order mesoscale and macroscale structures. Bottom-up approach aims to guide the assembly of atomic and molecular constituents into organized surface structures through processes inherent in the manipulated system [16].

One example of the bottom-up approach is self-assembly. Self-assembly is the fundamental principle which generates structural organization on all scales from molecules to galaxies. It is a method of integration in which the components spontaneously assemble, until a stable structure of minimum energy is reached. Furthermore, self-assembly is not limited to nanoscaled molecules but can be carried out on just any scale, making it a powerful bottom-up method for Nanotechnology. Self-assembly of colloidal nanoparticles on surfaces is extensively discussed in Chap. 10 by Koutsos et al. An alternative example of bottom-up approach uses scanning probe microscopes to position molecules at the desired position on surfaces.

One the most common self-assembled monolayers (SAMs) preparation methodology is that of alkanethiols on gold which was first reported in 1983 by Nuzzo and Allara [17]. The preparation of SAMs typically involves immersing a gold-coated substrate in a dilute solution of the alkanethiol in ethanol as shown Fig 1.6. A monolayer spontaneously assembles at the surface of the substrate over the next

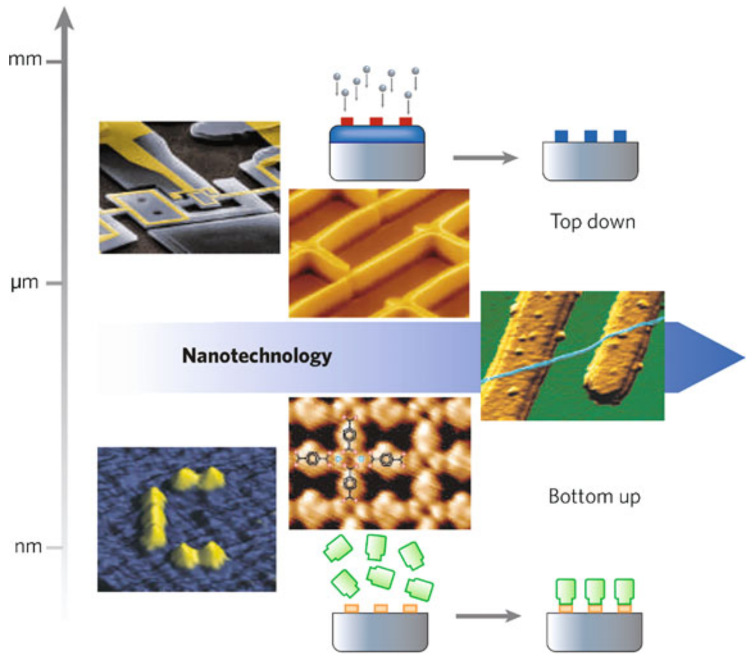

Fig. 1.5 Two approaches to control matter at the nanoscale: shown (clockwise from top) are an electron microscopy image of a nanomechanical electrometer obtained by electron-beam lithography, patterned films of carbon nanotubes obtained by microcontact printing and catalytic growth, a single carbon nanotube connecting two electrodes, a regular metal–organic nanoporous network integrating iron atoms and functional molecules, and seven carbon monoxide molecules forming the letter "C" positioned with the tip of a scanning tunneling microscope [16]

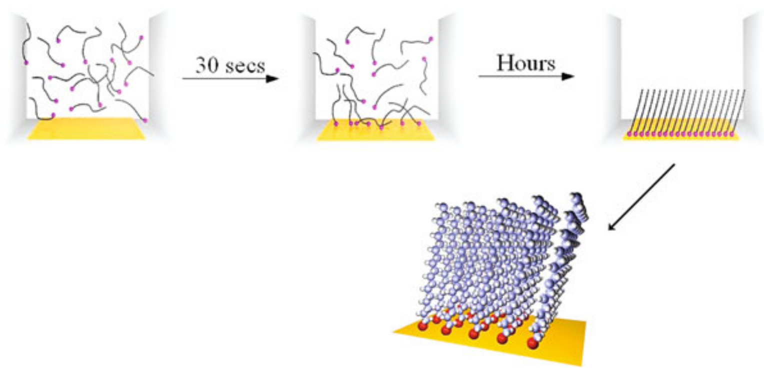

Fig. 1.6 Schematic representation of the self-assembly process. Initially alkanethiols come down onto the gold surface. As more alkanethiols come to the surface, the layer begins to organize and pack into an ordered monolayer [18]

1 to 24 h. Initially, within a few seconds to minutes, a disordered monolayer is formed. Within this early time frame, the thickness reaches 80–90% of its final value. As the layer continues to form, van der Waals forces between the hydrocarbon chains help pack the molecules into a well-ordered, crystalline layer. During this ordering phase, contaminants are displaced (for example, adventitious hydrocarbons on the gold), solvents are expelled from the monolayer, and defects are reduced while packing is enhanced by increased packing of the alkanethiols [18].

1.3 From Microelectronics to Nanoelectronics and Molecular Electronics

In 1965, Intel co-founder Gordon Moore forecasted the rapid pace of technology innovation. His prediction, popularly known as "Moore's Law," states that transistor density, that is the number of transistors in an integrated circuit or chip on integrated circuits, doubles about every two years (Fig. 1.7). The first microprocessor was introduced by Intel in 1971 (4004) and contained 2,300 transistors. In 2004, Intel's fastest processor (Intel® Itanium® 2 processor, 9 MB cache) contained 592,000,000 transistors. In 2010 Intel's processor exceeded 2,000,000,000 transistors [20]. However, this development is now reaching a wall so that smaller is no longer any faster. The prime reason for the limitation the semiconductor electronics experiences is its power dissipation and thus heat [21].

Figure 1.8 shows the evolution miniaturization of the conducting channel between the two other contacts, the source and the drain of a transistor. The channel length which is made of n- or p-doped silicon was reduced from 50 nm in 2003 to 10 nm today (2011). However technical factors limit the top-down development of microelectronics, the non-scalability of the MOS transistor below a critical size

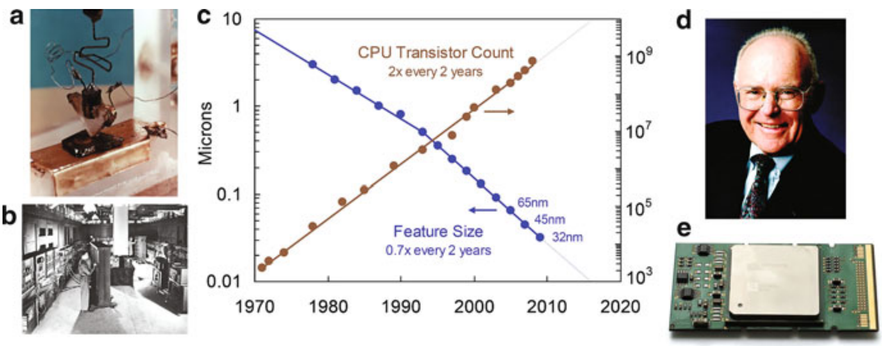

Fig. 1.7 (**a**) The first, point-contact transistor invented by John Bardeen and Walter Brattain in December 1947. Photo courtesy of Alcatel-Lucent. (**b**) Electronic Numerical Integrator and Computer, ENIAC conceived and designed by John Mauchly and J. Presper Eckert in 1946. (**c**) Transistors per microprocessor history [19]. (**d**) Gordon Moore. (**e**) Intel Itanium 2 processor

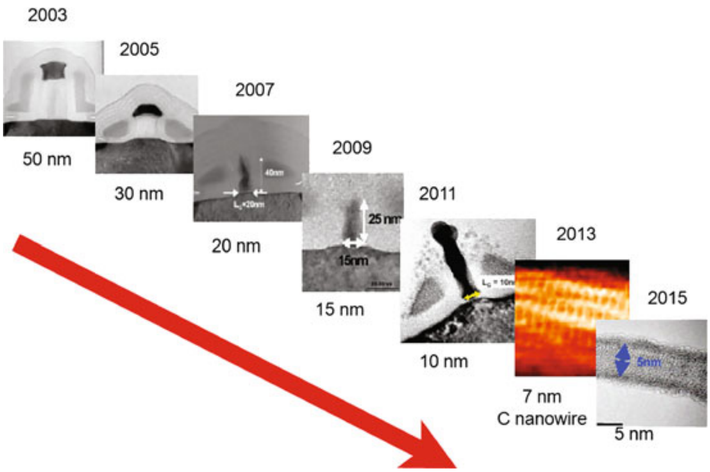

Fig. 1.8 Scaling history of the transistor channel length. The channel length was reduced from 50 nm in 2003 to 10 nm today. Future perspectives incorporate the use of nanowires in OFETs [20]

L_{phys} (the physical limit) or the impossibility of batch defining, using proximity masks, feature sizes below a critical one L_{litho} (the lithographic limit) [22]. At the IC (integrated circuit) level, the channel length (L) of the transistor is very critical because as this length decreases we have: (a) increase in the number of the transistors of the IC, thus then more "logic gates", so more "processing" power and (b) decrease in the "responding time" of the "logical operations". At the transistor level, the channel length (L) of the transistor is included in the basic equation of the gain factor β.

$$\beta = \frac{\mu_{\varepsilon}}{t_{\text{OX}}}\left(\frac{W}{L}\right).$$

That means, when the length L decreases, we have: (a) increase in the gain factor β of the transistor and (b) better directivity of electrons in the channel path [23].

Organic field-effect transistors (OFETs) are an alternative technology with high technological potential due to the possibility of low-cost and large-area manufacturing processes. An OFET uses an organic semiconductor in its channel and can be prepared either by vacuum evaporation of small molecules or by solution-casting of polymers or small molecules. It has been demonstrated that single-walled carbon nanotubes (SWNTs) can be used as quasi-one-dimensional (1D) electrodes to construct organic FETs with molecular-scale width ($\sim$2 nm) and channel length (down to 1–3 nm) [24].

Ultra-dense integrated circuits with features smaller than 10 nm would provide enormous benefits for all information technologies, including computing, networking, and signal processing. The top-down route of the silicon technology has indeed been relatively easy to run until its basic step (optical lithography) has met its physical limits (minimum feature size around the light wavelength). To overcome this limit, shorter wavelengths are required, such as in extreme ultraviolet lithography. X-ray lithography is currently the leading technology in the drive to replace photolithography as a large-scale production tool because it uses masks, which are suited to high-volume production.

Nanoelectronics research is currently looking not only for the successor to CMOS processing but also for a replacement for the transistor itself. On the scale of 10 nm dimensions, components have a wavelength comparable to that of an electron at the Fermi energy. The confinement and coherence of the electron gives rise to gross deviations from the classical charge transport found in conventional devices. Quantum-mechanical laws become increasingly dominant on the nanoscale, and it is probable that nanoelectronics will operate on quantum principles [25].

Molecular electronics, i.e., the information processing at the molecular-scale, becomes more and more investigated and envisioned as a promising candidate for the nanoelectronics of the future. More than a possible answer to ultimate miniaturization problem in nanoelectronics, molecular electronics is foreseen as a possible way to assemble a large number of nanoscale objects (molecules, nanoparticles, nanotubes, and nanowires) to form new devices and circuit architectures [26].

The difference between molecular- (nano) and micro-electronics is not the size (dimensionality), but the profoundly different device- and system-level solutions, the device physics, and the phenomena, fabrication, and topologies/organizations/architectures. Three-dimensional topology molecular and nanoelectronic devices, engineered from atomic aggregates and synthesized utilizing *bottom-up* fabrication, exhibit quantum phenomena and electrochemomechanical effects that should be uniquely utilized. Given technological advancements, molecular electronics proponents believe purposeful bottom-up design will be more efficient than the top-down method, and that the incredible structural diversity available to the chemist will lead to more effective molecules, thus approaching optional functionality for each application. A single mole of molecular switches, weighing about 450 g and synthesized in small reactors (a 22-L flask might suffice for most steps of the synthesis), contains 6×10^{23} molecules – a number greater than all the transistors ever made. While we do not expect to build a circuit in which each single molecule is both addressable and connected to a power supply (at least not in the first few generations), the extremely large numbers of switches available in a small mass illustrate one reason molecular electronics can be a powerful tool for future computing development [27].

1.4 Nano in Energy and Clean Energy

Energy is one of the most challenging needs of humanity, and is highest on the list of priorities and requisites for human welfare [28]. According to the International Energy Agency (IEA), World's primary energy demand will increase by 36% between 2008 and 2035. Electricity demand is expected to grow by 2.2% per year between 2008 and 2035. Taking in account the CO_2 emissions and the global climate change impact on life and the health of the planet renewable energy sources will have to play a central role in moving the world onto a more secure, reliable, and sustainable energy path [29].

Solar energy is the most abundant, inexhaustible and clean of all the renewable energy resources till date. The power from sun intercepted by the earth is about 1.8×10^{11} MW, which is many times larger than the present rate of all the energy consumption. Photovoltaic technology is one of the finest ways to harness the solar power [30].

Figure 1.9 shows the history of confirmed "champion" laboratory cell efficiencies. The performance of conventional solar cells is approaching a plateau; only incremental improvements have been accomplished in the last decade despite dedicated R&D effort.

Tandem solar cells based on III–V materials have achieved the highest efficiencies of any present photovoltaic device exceeding 40% recently However, the cost of these devices is very high, limiting their application to space applications [32]. The efficiencies reached with commercial solar cell modules are significantly lower than those of the best laboratory cells due to losses incurred during scaleup. The typical size of "champion laboratory cells" is in the square centimeter range or even below, facilitating the collection of photocurrent. High efficiency multijunction solar cells with finely-tuned quantum wells are presented in Chap. 5 by Varonides.

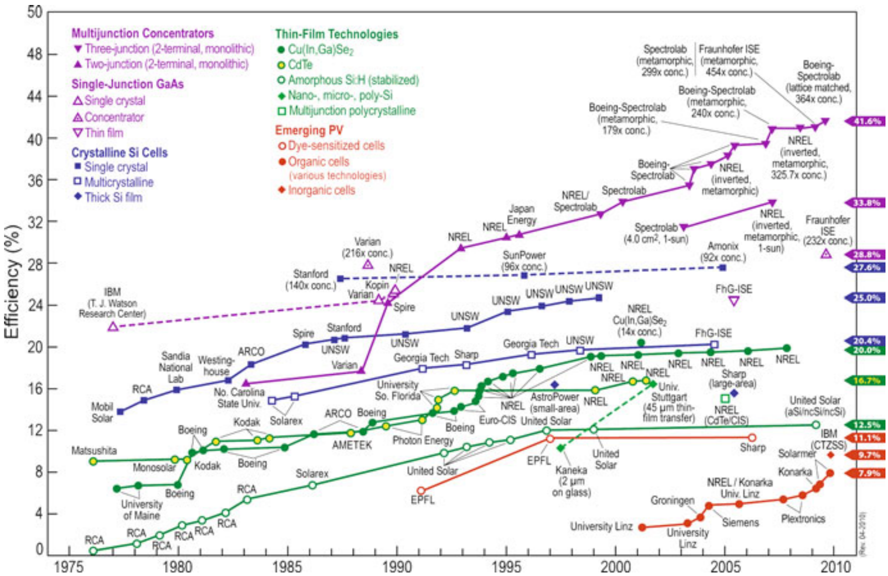

Fig. 1.9 Historic summary of champion cell efficiencies for various PV technologies. Tandem solar cells based on III–V materials present the highest efficiencies of any present photovoltaic device exceeding 40% [31]

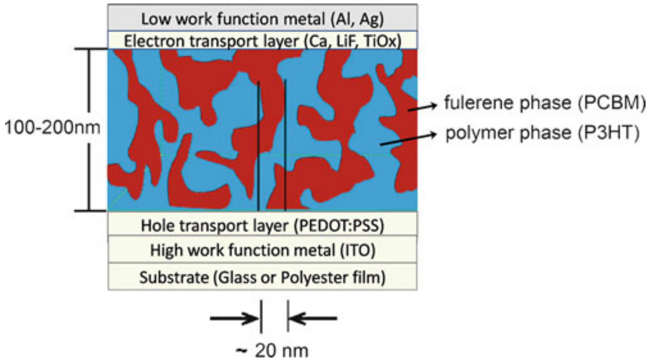

Fig. 1.10 Schematic structure of a typical organic solar cell device

Although inorganic semiconductors (silicon, amorphous silicon, gallium arsenide, and sulfide salts) have been the primary focus, the photosensitivity and the photovoltaic effects in devices made with organic materials have also been explored because of the advantages such as the potential of large-scale and low-cost roll-to-roll manufacturing processes. More specific, organic photovoltaics offer great technological potential as a renewable energy source due to their mechanical flexibility, low weight of plastic materials and easy thin-film casting technology [33–37].

Plastic electronics technologies are aimed at producing significant improvements in device efficiency-to-cost ratios. This necessitates significantly improving efficiency or reducing cost or ideally both. To realize these goals, many of these technologies will need to utilize nanostructured materials and composite systems that can be tailored to have optimized electronic and optical properties [38, 39]. For example, as shown in Fig. 1.10, an organic solar cell consist of a multilayered structure made of thin films each one of which has a certain functional property. The most common architecture consists of a transparent substrate which can be either glass or a polyester film such as poly(ethylene terephthalate) PET or poly(ethylene naphthalate) PEN. A highwork function metal electrode such as indium tin oxide (ITO) serves as an anode for collecting holes and a lowwork function metal such as aluminum serves as the cathode collecting the electrons which are produced in the active layer. Additional buffer layers such as hole transport layers (PEDOT:PSS) or electron transport layers (Ca, LiF, and TiO_x) are placed between the electrodes and the active layer to provide better energy level alignment and better ohmic contact between the organic layer and the metal electrodes.

The most successful active layer up to date consists of a bulk heterojunction (BHJ) that is formed by a p-type semiconductor (electron donor), such as poly(3-hexylthiophene) (P3HT) with an n-type semiconductor (electron acceptor), such as methanofullerene derivatives (PCBM). Due to the low dielectric constant in organic components ($\sim$3) photoexcitation leads to a strongly bound exciton, which needs to be dissociated into free carriers. This dissociation can take place in a strong electric field or at the donor–acceptor interface. Then, free carriers need to be transported to the corresponding electrodes via drift and diffusion processes, where they are collected, giving rise to an electric current. The morphology of the active donor–acceptor film is critical for charge generation and transport, strongly influencing device performance. Despite the rapid increase in device performance observed recently, much effort is still required to understand the fundamental processes of photovoltaic energy generation, in particular to elucidate the complex relationship between nanoscale morphology/electronic properties and device performance and to further develop the appropriate nanometrology needed to address this interplay [40].

1.5 Nanotechnology Tools: Nanometrology

The great development in Nanotechnology has given birth to the need of knowing of the dimensions that characterize its nanostructure. This lead to the appearance of a new scientific field called Nanometrology. Nanometrology is the science and practice of measurement of functionally important, mostly dimensional parameters and components with at least one critical dimension which is smaller than 100 nm. Success in nanomanufacturing of devices will rely on new nanometrologies needed to measure basic materials properties including their sensitivities to environmental conditions and their variations, to control the nanofabrication processes and materials functionalities, and to explore failure mechanisms. In order to study and explore the complex nanosystems, highly sophisticated experimental, theoretical, and modeling tools are required [41]. Especially, the visualization, characterization, and manipulation of materials and devices require sophisticated imaging and quantitative techniques with spatial and temporal resolutions on the order of 10^{-6} and below to the molecular level. In addition, these techniques are critical for understanding the relationship and interface between nanoscopic and mesoscopic/macroscopic scales, a particularly important objective for biological and medical applications [42]. The need for better characterization at the nanoscale derives from the correlation between the macroscopic functional properties with the nanoscale structural characteristics of nanomaterials which is a prerequisite for the development of emerging low-cost manufacturing technological fields such as organic electronics. These include organic solar cells (OPVs), organic light emitting diodes (OLEDs) and organic field-effect transistors (OFETs), and others. Insights on the nanomorphology as well as the conduction mechanisms at the various interfaces that exist in these multilayered devices are crucial for the development of the plastic electronic technology and the construction of better products. Examples of important tools available at the moment include highly focused synchrotron X-ray sources and related techniques that provide detailed molecular structural information by directly probing the atomic arrangement of atoms; scanning probe microscopy that allow three-dimensional-type topographical atomic and molecular views or optical responses of nanoscale structures; in situ optical monitoring techniques that allow the monitoring and evaluation of building block assembly and growth; optical methods, with the capability of measuring in air, vacuum, and in liquid environment for the study of protein and cells adsorption on solid surfaces, they have been employed to discriminate and identify bacteria at the species level and it is very promising for analytical purposes in biochemistry and in medicine [43–45].

The nanometrology methods need measurements that should be performed in real-time to allow simultaneous measurement of properties and imaging of material features at the nanoscale. These nanometrology techniques should be supported by physical models that allow the de-convolution of probe–sample interactions as well as to interpret sub-surface and interface behaviors. *Ellipsometry* is a key-technique meeting the aforementioned demands. It can be applied during the nanofabrication processes and provide valuable information concerning the optical, vibrational, structural, and morphological properties, the composition as well as the thickness and the mechanisms of the specimen under growth or synthesis conditions in nanoscale. Further correlation between optical and other physical properties can lead to a more complementary characterization and evaluation of materials and devices [46–49]. Additional information about the possibilities and application of this technique are given in Chap. 7 by Laskarakis et al. *X-ray photoelectron spectroscopy (XPS)* is one of the most quantitative techniques to determine both atomic concentration and the chemical environment of the species at the surface of a sample. XPS has a high potential for non-destructive depth profiling (<10 nm from the surface) in angle resolved mode or by using synchrotron radiation for variable excitation energy XPS. *Secondary ion mass spectroscopy (SIMS)* is a highly sensitive technique that may be used to determine the composition of a material, typically at or near the surface. Deduced from specific calibrations, a quantity of atoms as a function of their mass charge ratios is measured as a function of depth. Detection limits for trace elements are typically between 10^{12} and 10^{16} atoms per cm^3 [50]. *X-ray reflectivity (XRR)* is also a powerful tool for investigating monolithic and multilayered film structures. It is one of the few methods that, with great accuracy, not only allows information on the free surface and the interface to be extracted but also the mass density and the thickness of very thin film of the order of a few nanometers along the direction normal to the sample surface to be determined. XRR is able to offer accurate thickness determination for both homogeneous thin films and multilayers with the same precision, as well as densities, surface, and interface roughness of constituent layers. In addition, other promising nanometrology techniques include the *tip-enhanced-Raman-spectroscopy (TERS)* [51–53]. TERS combines the capabilities of Raman spectroscopy that has been used for many years for the single layer and even single molecule detection in terms of its chemical properties, with the advantages of an atomic force microscopy tip that is put close to the sample area that is illuminated by the Raman laser beam. In this way, a significant increase in the Raman signal and in the lateral resolution by up to nine orders of magnitude takes place. Thus, TERS can be used for the chemical analysis of very small areas and for the imaging of nanostructures as well as of other materials such as proteins and biomolecules (Fig. 1.11) [56, 57].

Another important nanometrology method is *nanoindentation* that has rapidly become the method of choice for quantitative determination of the mechanical properties (as hardness and elastic modulus) of thin films and small volumes of material. In Fig. 1.12a, b the nanoindentation load–displacement curve coming from nanoindentation test to amorphous carbon thin film grown on silicon (001) substrate and the imprint of the Berkovich diamond indenter on the surface of aluminum is presented. More information about this technique are provided in Chap. 6 by Kassavetis et al.

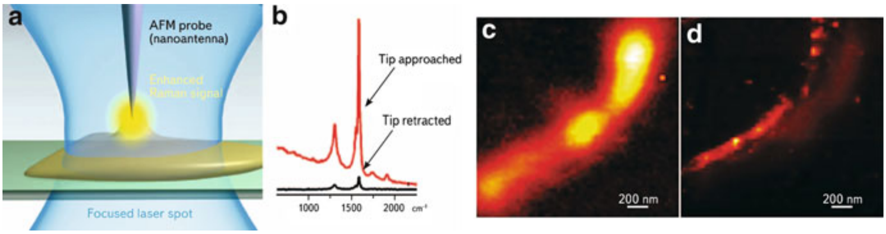

Fig. 1.11 (**a**) A specially prepared AFM probe (metalcoated cantilever or etched metal wire is precisely positioned inside a tightly focused laser spot. (**b**) Intensity of carbon nanotube G- and D-Raman bands increases by several orders of magnitude when the special AFM probe is landed and positioned over a small (5 nm height) nanotube bundle – the effect of Tip Enhanced Raman Scattering (TERS). (**c**) "Conventional" confocal Raman image of the nanotube bundle, the observed width of the bundle is ~250 nm (diffraction limit of confocal microscopy, laser wavelength – 633 nm). (**d**) TERS image of the same bundle – now the observed width is ~50 nm. In this example, TERS provides more than four-times better spatial resolution as compared to confocal microscopy [54, 55]

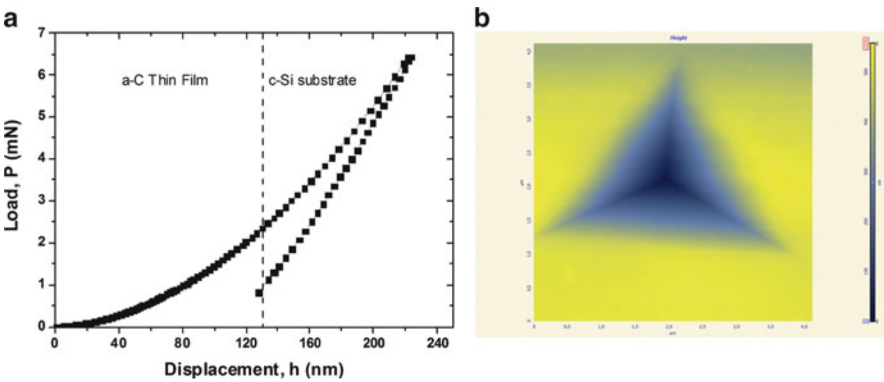

Fig. 1.12 (**a**) Nanoindentation load–displacement curve and (**b**) the imprint of the Berkovich type diamond indenter on aluminum

Finally, *scanning probe microscopes (SPMs)* are standard instruments at scientific and industrial laboratories that allow imaging, modifications, and manipulations with the nanoobjects. They permit imaging of a surface topography and correlation with different physical properties within a very broad range of magnifications, from millimeter to nanometer-scale range. Atomic force microscopy (AFM) and AFM related techniques (e.g., scanning near-field optical microscopy – SNOM) have become sophisticated tools, not only to image surfaces of molecules but also to measure molecular forces between molecules. This is substantially increasing our knowledge of molecular interactions. Electrical scanning probe microscopy (SPM) techniques have already made a number of important contributions to the field of organic electronics. Conductive atomic force microscopy (c-AFM), electrostatic force microscopy (EFM), scanning Kelvin probe microscopy (SKPM), and similar variants were successfully used to elucidate charge injection/extraction, transport, trapping, and generation/recombination in organic devices [58].

1.6 Future Perspectives

Nanotechnology is distinguished by its interdisciplinary nature. As investigations at the nanolevel are occurring in a variety of fields, it is expected that the results of this research are going to have a significant impact on a broad range of applications [59] Nanomaterials with tailored unique properties have limitless possibilities in materials science Products where the addition of a relatively small amount of functionalized nanoparticles or carbon nanotubes leads to a major change in the properties are going to revolutionize many commercial technologies.

It is believed that nanotechnology can greatly contribute to the evolution of modern medical approaches and practices. Nanoscale constructs are already used in therapeutical applications against cancer and pathogens mostly by acting as drug carriers. Also either in-vivo or ex-vivo engineered scaffolds and tissues are implanted in patients whose own organs and tissues are damaged or lost. Furthermore, specific nanostructures are widely used as imaging and detection agents in diagnostic procedures. The ideal goal is to improve health by enhancing the efficacy and safety of nanosystems and nanodevices while at the same time use nanomedicine in order to cure diseases that remain incurable or the conventional therapeutical approaches against them are either expensive or inefficient.

The advances in fundamental nanosciences, the design of new nanomaterials, and ultimately the manufacturing of new nanoscale products and devices all depend to some degree on the ability to accurately and reproducibly measure their properties and performance at the nanoscale. Therefore, nanometrology tools and techniques are both integral to the emerging nanotechnology enterprise and are two of the main areas critical to the success of nanotechnology. Decades of nanoscience research have led to remarkable progress in nanotechnology as well as an evolution of instrumentation and metrology suitable for some nanoscale measurements.

Consequently, today's suite of metrology tools has been designed to meet the needs of exploratory nanoscale research. New techniques, tools, instruments and infrastructure will be needed to support a successful nanomanufacturing industry.

The currently available metrology tools are also beginning to reach the limits of resolution and accuracy and are not expected to meet future requirements for nanotechnology or nanomanufacturing. Novel methods and combinations, such as the TERS technique, achieve much higher resolution values since they provide a significant increase in the Raman signal and in the lateral resolution by up to nine orders of magnitude. This combination overcomes the difficulties that originate from low signal since the Raman systems have limit in lateral resolution of 300 μm and require high laser power for surface investigation because the measured Raman intensity is six orders of magnitude lower than the excitation power. Thus, TERS is a promising technique and we can see it in the near future to be used for probing the chemical analysis of very small areas and for the imaging of nanostructures and biomolecules such as proteins. New approaches have to be developed and existing ones based on XPS, X-ray absorption spectroscopy, SPM and SIMS have to be improved in terms of better spectral and spatial resolution, better contrast and better sensitivity for elements and molecular species. Ideally new methods should have capabilities to work in situ, at ambient air and/or in liquid surroundings.

However, clever new approaches need to be developed. For this, it is required to understand the fundamental mechanisms by which the probes of the nanometrology measuring systems interact with the materials and objects that are being measured. Also, it is important to develop standard samples and to construct standardized procedures for measurements in nanometer scale, which enable the transfer of the properties and response of the unit from the nanometer to macroscopic scale without any appreciable loss of accuracy, for certifying, calibrating, and checking nanometrology instruments. Finally, even with the vast array of current tools available, the important question is whether or not they are providing the required information or reams of inconsequential data. Revolutionary approaches to the nanometrology needed may be required in the near future and therefore, revolutionary and not just evolutionary instrumentation and metrology are needed.

1.7 Summary

Nanotechnology is an emerging technology with applications in several scientific and research fields, such as information and communication technology, electronics, energy, biology, medical technology, etc. Novel nano- and biomaterials, and nanodevices are fabricated and controlled by nanotechnology tools and techniques, which investigate and tune the properties, responses and functions of living and non-living matter, at sizes below 100 nm.

Nanotechnology is a science with huge potential and great expectations. The daily announcements of new discoveries and breakthroughs are going to influence all aspects of human society. Nanomaterials bring new possibilities by tailoring the optical, the electronic the mechanical, the chemical, and the magnetic properties. In the last few years there was a rapid progress in the fabrication and processing of nanostructures. As a result nanophase materials and applications are already in the market and a large volume of new applications is expected over the next several years. However, the development and commercialization of products containing nanomaterials raises many of the same issues as with introduction of any new technology, including concerns about the toxicity and environmental impact of nanomaterial exposures. Despite the extensive research of the last decade the literature on toxicological risks of the application of nanotechnology in medical technology is scarce.

In order to investigate in depth the complex nanosystems, highly sophisticated nanoscale precision metrology tools are required. The advances in nanomaterials necessitate parallel progress of the nanometrology tools and techniques. Examples of important nanometrology tools as they have been discussed above include: ellipsometry, highly focused X-ray sources and related techniques, nanoindentation and scanning probe microscopies. The above described nanometrology methods contribute towards the understanding of several aspects of the state-of-the-art nanomaterials in terms of their optical, structural, and nanomechanical properties. The nanoscale precision and the detailed investigation that these nanometrology techniques offer, give them an enormous potential for even more advanced applications for the improvement of the quality of research and of the everyday life.

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