

Chapter 2

Carbon-Dot Synthesis

The first report on the production of Carbon-Dots, quite tellingly, featured an almost “accidental” discovery of fluorescent carbon nanoparticles through an unrelated synthetic pathway—a byproduct in arc-discharged soot generated for the synthesis of carbon nanotubes [1]. Intriguingly for the researchers who carried out the experiments, some of the “impurities” identified in the crude nanotube soot were fluorescent (Fig. 2.1), and furthermore different fractions yielded distinct fluorescence wavelengths (e.g., different colors). Analysis of the “fluorescent carbon” as these particles were initially termed indicated that they comprised of very small, nanometer scale, particulates of carbonaceous material, concluded to be small carbon nanotube fragments.

Fluorescent “carbon nanocrystals” were produced, in fact, as side products in other carbon nanotube preparations, and also upon further chemical processing of nanotube samples—both multiwall carbon nanotubes (*MWCNTs*) as well as single-wall nanotubes (*SWNTs*). Figure 2.2, for example, depicts such carbon nanocrystals generated through electrochemical treatment of *MWCNTs*. In the experiment, Z. Ding and colleagues at the University of Western Ontario, Canada, constructed an electrochemical cell in which one of the electrodes comprised of surface-deposited *MWCNTs* [2]. Cycling the cell voltage hundreds of times resulted in gradual disintegration of the *MWCNT* electrode, generating fluorescent Carbon-Dots [still referred to in that work as “carbon nanocrystals”] within the electrolyte solution. The process leading to Carbon-Dot formation was believed to occur through fragmentation of the carbon nanotubes assisted by the electrolyte molecules penetrating into “defect sites” on the nanotubes’ surface. The voltage cycling, in particular, was presumed to contribute to breaking C–C bonds, producing hydroxyl and COOH residues. Furthermore, the electrochemical process likely generated hydroxyl and/or oxygen radicals in water which could subsequently react with the nanotubes and promote their cleavage.

While those studies detected Carbon-Dots as a side-product of carbon *nanotubes*, the realization that the “fluorescent carbon” contained new carbon nanostructures has attracted growing interest and led to research aimed at specific synthesis of the new

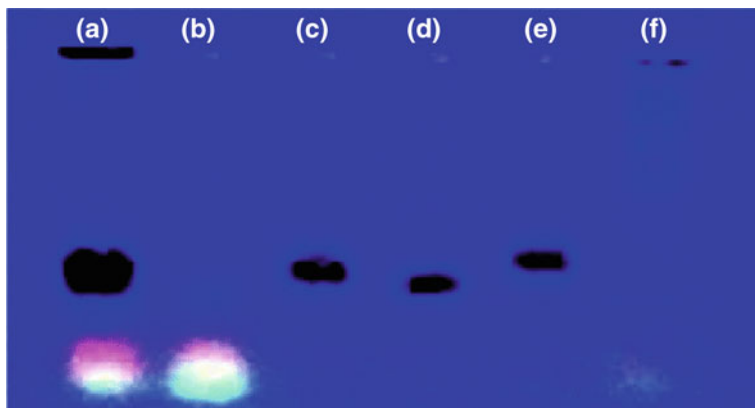


Fig. 2.1 “Fluorescent carbon” nanoparticles identified in agarose gel. The fluorescent fragments were identified in suspensions of single-wall nanotubes (SWNTs). Shown is an agarose gel image under 365 nm illumination. **a** Crude SWNT; a fluorescent band is apparent; **b** purified fluorescent carbon; **c–e** carbon nanotubes; **f** fragmented SWNTs. Reprinted with permission from Xu et al. [27]. Copyright (2004) American Chemical Society

carbon nanoparticles, later termed “carbon quantum dots.” Early synthesis procedures mostly used “brute-force” experimental schemes, using high energy impact upon a carbon source thereby generating the fluorescent carbon nanoparticles. Later studies laid the groundwork for more broadly applicable strategies of Carbon-Dot synthesis. Simply put, the stages of many early synthesis approaches for Carbon-Dot production comprised of *fragmentation* of the macroscopic carbon source, inducing (or retaining) the *crystalline organization* of the carbon cores of such (nanoparticle) fragments, and *surface functionalization* of the Carbon-Dots which in most cases has been a prerequisite for the unique photoluminescence properties of the carbonaceous nanoparticles. The diverse Carbon-Dot synthesis schemes discussed below illuminate these aspects.

A representative early example of a brute force approach to construct Carbon-Dots was through *laser ablation* [3]. Laser ablation has been routinely used to produce inorganic nanoparticles from solid substrates; the high energy delivered by the laser beam causes ablation, or removal, of particulates from the target solid substrate, and the substances thus removed have been often found to exhibit nanoscale dimensionalities. This phenomenon was also the case in one of the first direct demonstrations of Carbon-Dots as reported by Y-P Sun and colleagues at Clemson University [3] (in fact, that paper was among the first publications referring to the newly discovered nanoparticles as “carbon-dots”). The researchers prepared a carbon target through high-temperature treatment of a graphite powder/cement mixture and then applied laser ablation (using the widely employed Nd:YAG laser). High temperature (900 °C) was also required to generate the carbon nanoparticles.

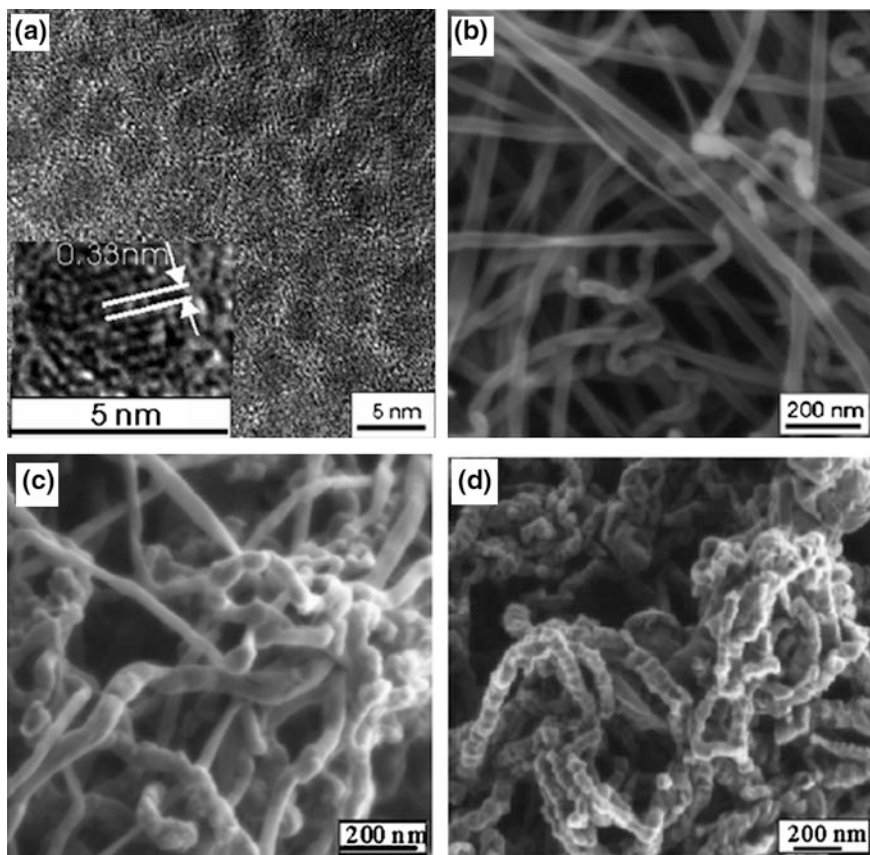


Fig. 2.2 “Carbon nanocrystals” generated upon electrochemical processing of multiwall carbon nanotubes (MWCNTs). **a** High-resolution transmission electron microscopy (HRTEM) of the nanocrystals; **b–d** scanning electron microscopy (SEM) images of the MWCNTs. Pristine sample (**b**), and after 100 voltage cycles (**c**) and 1000 cycles (**d**). The corrugated surface producing the carbon nanocrystals is apparent after voltage cycling. Reprinted with permission from Zhou et al. [2]. Copyright (2007) American Chemical Society

The report by Y-P Sun and colleagues highlights another fundamental aspect of Carbon-Dot synthesis and Carbon-Dot research in general: the realization that Carbon-Dots’ *surfaces* have a central role in affecting the fluorescence properties of these nanoparticles. Specifically, the Carbon-Dots described above, produced through laser ablation, were *not fluorescent*, even after purification and treatment with a strong acid. However, as depicted in Fig. 2.3, surface functionalization (or “passivation”) with hydrocarbon chains (specifically polyethylene glycol, PEG, in that study) was necessary in order to make the Carbon-Dots photoluminescent. This observation, in fact, crystallizes a fundamental difference between Carbon-Dots and other photoluminescent nanoparticles, particularly semiconductor quantum dots

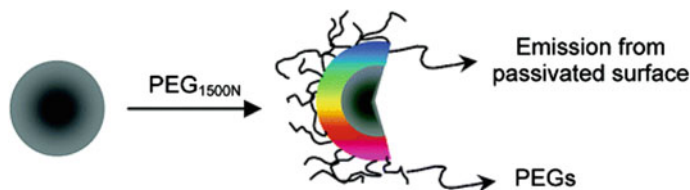


Fig. 2.3 Functionalization of Carbon-Dot surface with polyethylene glycol (PEG). Surface passivation is required to make the Carbon-Dots luminescent. Reprinted with permission from Sun et al. [3]. Copyright (2006) American Chemical Society

(Qdots). In Qdots, the fluorescence emission has been traced to the “quantum effect” in which the nanometer scale of the semiconductor particle dictates coalescence of energy levels allowing excitation of electrons from the valence band into the conducting band in discrete energies. In contrast, a large body of work indicates that the fluorescence properties of Carbon-Dots are associated with the particles’ *surface*, specifically “surface defects” responsible for light absorbance in specific wavelengths, i.e., different colors (see detailed discussion in Chap. 3). Accordingly, synthesis schemes for modification of the Carbon-Dots’ surface play a central role in the field.

Passivation of Carbon-Dots’ surface with varied molecular species other than PEG has been carried out. Y-P Sun and colleagues have observed that other polymers, such as propionylethylenimine-co-ethylenimine (PPEI-EI), generated photoluminescent Carbon-Dots similar to PEG [4]. In fact, surface passivation played an additional important role in the proliferation of Carbon-Dot studies, as it could make the Carbon-Dots *hydrophilic*—thus soluble in water and available for biological applications, particularly bioimaging. Indeed, the varied synthetic routes for coupling functional moieties to Carbon-Dots’ surfaces are among the central features contributing to the growth of Carbon-Dot research.

Surface passivation of Carbon-Dots has taken many forms using a variety of molecular constituents. While the significant majority of early studies have employed reactions of Carbon-Dots surfaces with varied organic residues, *inorganic* elements have been examined as well. Y-P Sun and colleagues, for example, showed that doping of the Carbon-Dots with *semiconductor salts* such as ZnS and ZnO prior to surface passivation could enhance the quantum yield of the particles (e.g., their brightness) [5]. Figure 2.4 reveals the formation of the ZnS lattice on the surface of the Carbon-Dots following the doping process, and the dramatic fluorescence of the composite nanoparticles. It should be noted that the luminescence properties in that system were somewhat difficult to explain; the semiconductor salts presumably promoted formation of surface “defects” which contributed to the photoluminescence. While doping with inorganic salts and its effect upon Carbon-Dots’ luminescence is interesting from a synthetic standpoint, this line of research has not noticeably progressed because one of the more prominent “selling points” of Carbon-Dots is their production from *organic* building blocks, thus making these nanoparticles supposedly less toxic than inorganic nanoparticles.

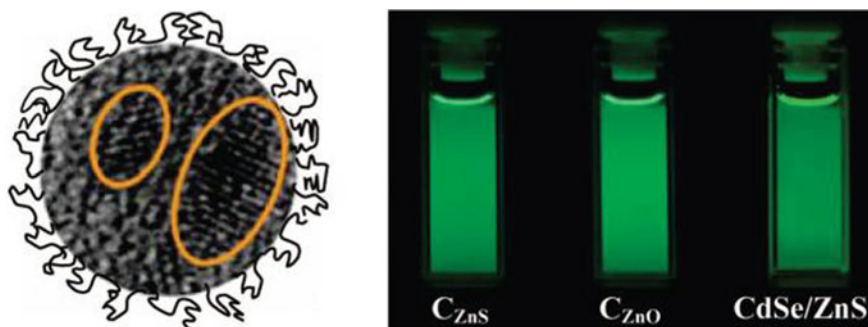


Fig. 2.4 ZnS-doped Carbon-Dots. *Left* Portion of a high resolution TEM (HRTEM) image showing the ZnS lattice planes within the Carbon-Dot (circled). Surface functionalization of the Carbon-Dot is illustrated. *Right* photographs of solutions containing the Carbon-Dot/semiconductor composites upon UV irradiation; fluorescence is apparent in all samples. Reprinted with permission from Sun et al. [5]. Copyright (2008) American Chemical Society

Soon after the first reports on production of photoluminescent Carbon-Dots appeared in the literature, a major advance in the synthetic routes for making these intriguing nanoparticles had been achieved. In particular, Carbon-Dot synthesis was demonstrated using readily available precursors, obviating the elaborate preparation processes of the starting materials as described above. Numerous carbon-containing substrates have been successfully utilized as building blocks for construction of Carbon-Dots, including organic solvents, various saccharides, amino acids, proteins, and others. Notably, the underlying feature in most Carbon-Dot preparation schemes is the proposition that formation of the graphitic nanoparticles is thermodynamically (and/or kinetically) favored, regardless of carbon precursor used.

Figure 2.5 depicts a laser-based scheme for production of Carbon-Dots using *toluene*—a common organic solvent—as the carbon precursor. The preparation scheme, demonstrated by X. Li and colleagues at Huazhong University of Science and Technology, China, relied on irradiating the toluene sample with *non-focused* pulsed laser—different than the high power laser irradiation employed in ablation

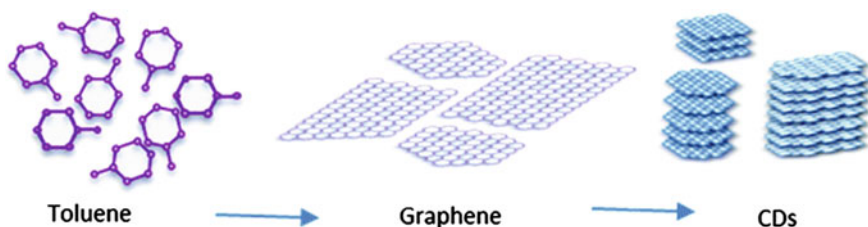


Fig. 2.5 Synthesis of Carbon-Dots using toluene as the starting material. The proposed process consists of formation of graphene sheets through pulse-laser irradiation, followed by fragmentation to yield the Carbon-Dots. Reproduced from Yu et al. [6], with permission of the Royal Society of Chemistry

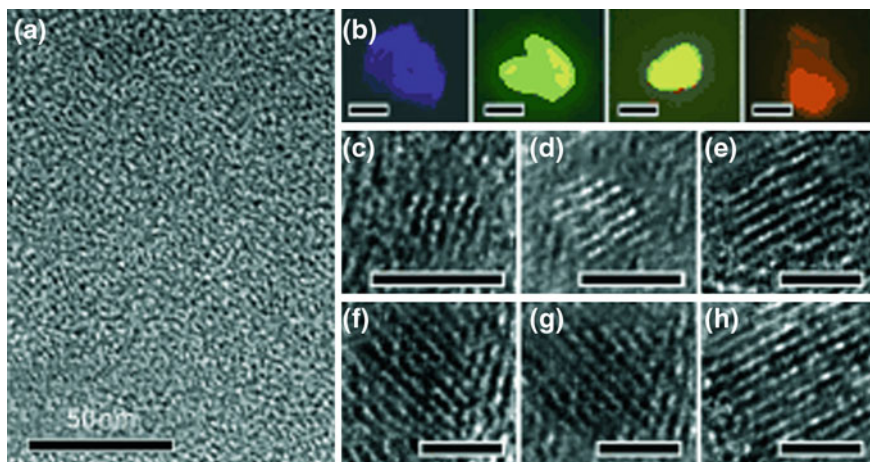


Fig. 2.6 Carbon-Dots produced through an electrochemical method. **a** TEM image of the Carbon-Dots (exhibiting small < 5 nm diameters); **b** photoluminescence images recorded upon excitation at different wavelengths; **c–h** high resolution TEM images showing the crystalline graphite lattice planes. Scale bars correspond to 2 nm. Reprinted from Li et al. [7], with permission from John Wiley & Sons (2010)

processes discussed above [6]. Remarkably, as outlined in Fig. 2.5, irradiation by the non-focused laser beam appeared to have induced transformation of toluene into *graphene* sheaths, which subsequently produced fluorescent Carbon-Dots. The researchers, in fact, achieved certain tuning of the Carbon-Dots *sizes* through modulating the laser power, observing rather surprisingly an *inverse relationship* between laser power and carbon nanoparticles' sizes.

Electrochemical methodologies have been also demonstrated for Carbon-Dot synthesis. S.-T. Lee and colleagues at Hong Kong S.A.R., for example, utilized graphite electrodes as carbon source [7]. Specifically, the researchers employed graphite rods as both cathode and anode in an electrochemical cell setup, with NaOH/ethanol as the electrolyte solution. Passage of current through the electrochemical circuit resulted in “chipping” of the graphite rods, producing Carbon-Dots exhibiting different colors (i.e., luminescence wavelengths). While the Carbon-Dots generated in this experiment *did not* possess uniform spherical morphologies (Fig. 2.6), distinct luminescence colors were observed, ascribed to variations in particle sizes and surface defects. The high-resolution TEM images in Fig. 2.6 confirm that the nanoparticles could indeed be referred to as “Carbon-Dots,” as they exhibit the typical graphitic crystalline cores.

Electrochemistry has been implemented by other researchers to produce Carbon-Dots since the technique is easy to carry out and the product yield is usually high. Figure 2.7 presents an experimental setup of an electrochemical cell designed to utilize a graphite electrode as a carbon source for Carbon-Dots, and illustrates the visual progression of the reaction. This electrochemical cell approach, developed by K.P. Loh and colleagues at the National University of Singapore, employed an *ionic*

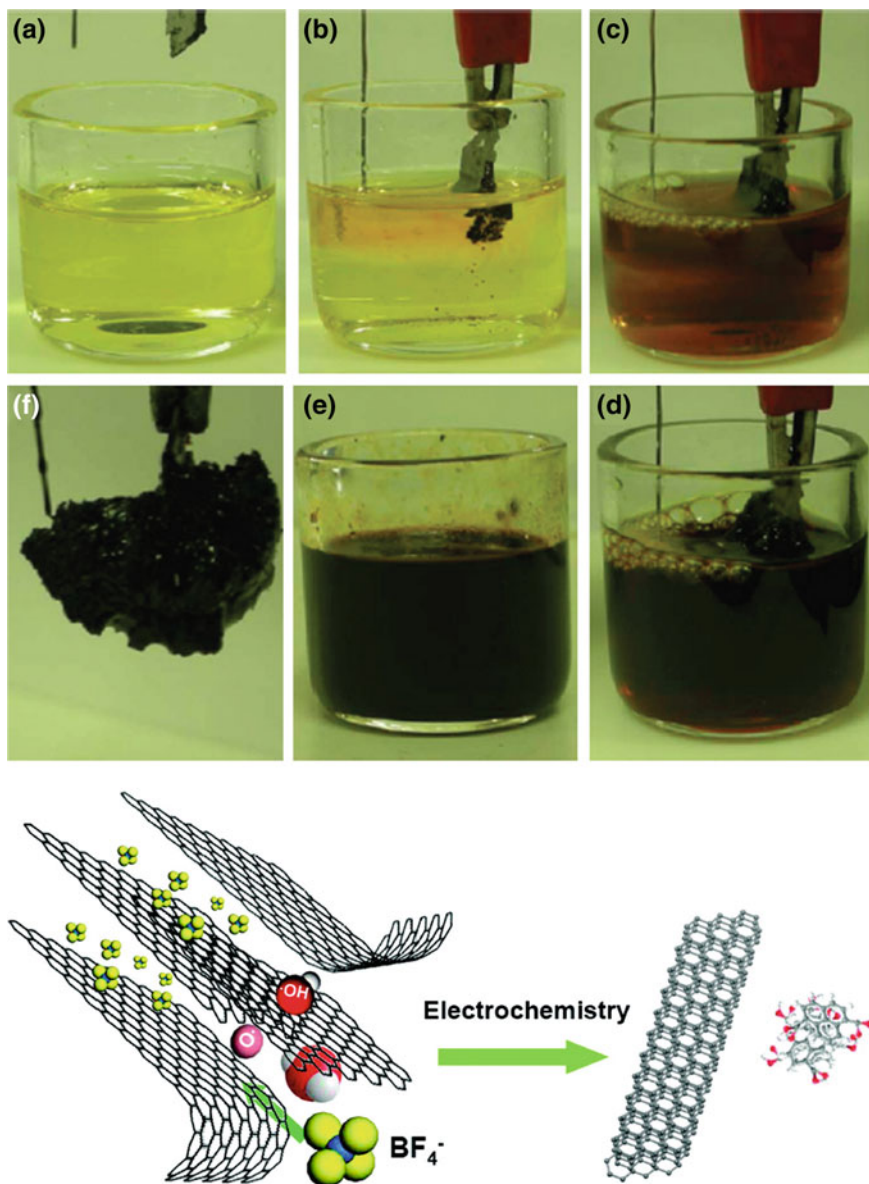


Fig. 2.7 Production of Carbon-Dots through exfoliation of graphite in ionic liquids. *Top* photographs showing the progression of the electrochemical reaction in which the graphite anode is placed in an electrolyte solution comprising the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]). The *brownish* color corresponds to carbon nanoparticles. Panel **f** shows the appearance of the graphite electrode after the reaction. *Bottom* an illustration of the proposed mechanism: the ions (originated from the ionic liquid) penetrate between the graphite sheets, generating carbon nanotubes and Carbon-Dots. Reprinted with permission from Lu et al. [8]. Copyright (2009) American Chemical Society

liquid (IL) as the electrolyte [8]. Ionic liquids have been used as “green” substitutes for organic solvents and could possess powerful solvation capabilities. In the context of the Carbon-Dot fabrication process described in Fig. 2.7, the ionic liquids, specifically the positive *imidazolium ion*, had dual roles. First, the imidazolium ions could transform into reactive *radicals* upon accepting electrons from the anode in the electrochemical cell; the radicals reacted with, and induced “fraying” of the graphite sheets, giving rise to the small carbon fragments. Second, as shown in Fig. 2.7b, the ions inserted into the graphite layers, thereby enhancing the exfoliation process. An apparent limitation, however, of many electrochemistry-based Carbon-Dot synthesis schemes such as the experiment in Fig. 2.7 has been the rather broad distribution of nanoparticle sizes and morphologies, necessitating further separation and purification steps.

Numerous other synthetic routes have utilized “wet chemistry” to construct Carbon-Dots. Figure 2.8 outlines a typical solution-based strategy for Carbon-Dot synthesis. The process, developed by R. Liu and colleagues at the Max-Planck-Institut für Polymerforschung, Germany, was based upon embedding the carbon source (phenol/formaldehyde resin) within porous silica colloids acting as host matrix [9]. A high-temperature carbonization process (e.g., pyrolysis) generated Carbon-Dots which were subsequently released through dissolution of the silica scaffold; further surface passivation of the dots gave rise to the typical luminescence properties. While pyrolysis was the main driving force for Carbon-Dot production, the porous silica carriers were instrumental in preventing

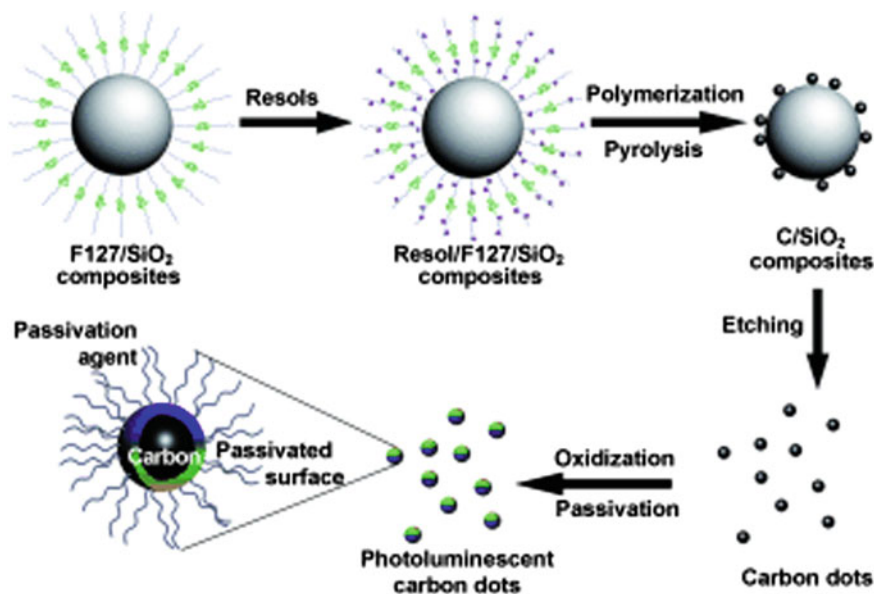
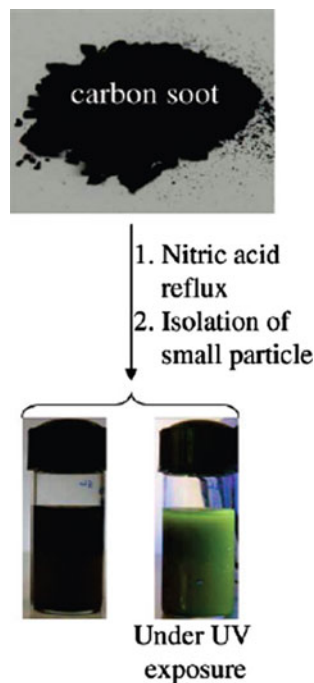


Fig. 2.8 Synthesis of Carbon-Dots within a silica matrix. Reprinted from Liu et al. [9], with permission from John Wiley & Sons (2009)

aggregation of the nanoparticles. It is notable that the synthesis scheme in Fig. 2.8 presumably yielded *amorphous* Carbon-Dots rather than Carbon-Dots comprising *crystalline* graphitic cores, albeit exhibiting strong, multicolor luminescence. This result lends support to the proposed relationship between the luminescence properties of Carbon-Dots and putative *surface defects* (see Chap. 3).

As expected in a young and evolving scientific field, proliferation of studies led to development of rather simple synthesis schemes. In particular, Carbon-Dots can be readily produced even without the use of structure-directing matrixes such as the colloidal silica host (e.g., Fig. 2.8). Carbon *soot*, generated in numerous carbon-processing reactions, has been found to be a useful precursor substance for Carbon-Dots. S.C. Ray and colleagues at the Indian Institute for the Cultivation of Science have shown that soot produced by candle burning could be a source of Carbon-Dots, generated simply through refluxing the soot in a strong acid (such as nitric acid), followed by size separation of the smaller nanoparticles (Fig. 2.9) [10]. The strong oxidation properties of the acid were crucial for dissolution of large carbon aggregates in the soot; the acid further reacted with the carbon colloids to produce the oxygen- and nitrogen-containing surface defects associated with the fluorescence emission of the particles. Such soot-based techniques, however, yielded Carbon-Dots exhibiting relatively low brightness (e.g., low quantum yield), likely because of the large particles produced and the broad size distribution. Other soot-based methods for production of Carbon-Dots were introduced, employing

Fig. 2.9 Preparation of Carbon-Dots by acid treatment of carbon soot. Candle-generated soot was refluxed in a strong acid, producing Carbon-Dots. Following purification, the Carbon-Dot solution exhibited fluorescence (bottom photograph). Reprinted with permission from Ray et al. [9]. Copyright (2009) American Chemical Society



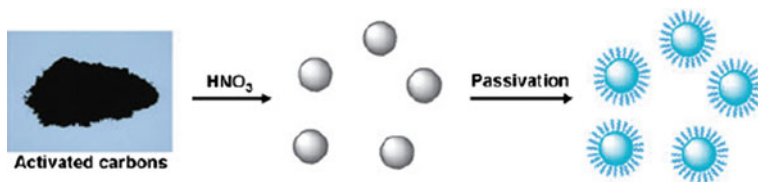


Fig. 2.10 Synthesis of Carbon-Dots from activated carbon. Reproduced from Qiao et al. [12], with permission of the Royal Society of Chemistry

acid treatment of soot generated from varied carbon reactions like combustion of natural gas [11].

Figure 2.10 outlines another procedure for production of Carbon-Dots using a natural carbon source [12]. In that important work, Q. Huo and colleagues at Jilin University, China, successfully prepared Carbon-Dots through acid-induced oxidation of *activated carbon* (i.e., carbon from natural sources such as wood, which following physical treatment—usually application of hot gas—becomes highly porous or “active”). After purification of the Carbon-Dots produced by the chemical treatment, surface passivation was carried out using different amine-terminated organic agents yielding water-soluble luminescent Carbon-Dots.

The study outlined in Fig. 2.10 represents an important leap in Carbon-Dot research, since it showed that the carbon nanoparticles could be produced (in large quantities) from readily available reagents through easily applicable synthetic schemes and with no need for sophisticated and/or expensive instrumentation. It is safe to say that the synthetic progress accomplished by Q. Huo and others constituted a major driving force for the significant growth of activity and applications of Carbon-Dots.

In parallel with the proliferation of “chemical oxidation” techniques starting around 2010 for production of Carbon-Dots [generally involving reaction of carbonaceous substances with strongly oxidizing acids] other solution-based Carbon-Dot synthesis strategies have been developed. In particular, *hydrothermal treatment* has likely become the most common procedure for production of the Carbon-Dots. This generic approach is quite striking in its simplicity and versatility, generating Carbon-Dots from varied carbon sources. The crux of hydrothermal synthesis of Carbon-Dots is a process in which high temperature induces condensation of the carbonaceous building blocks and crystallization of the graphitic core. Another important feature of hydrothermal synthesis schemes has been the observation that residues from the carbon reagents are still retained upon the *surface* of the crystalline cores, thereby bestowing the nanoparticles varied, and chemically controllable, functionalities and optical properties.

Figure 2.11 illustrates a proposed mechanism for assembly of Carbon-Dots through hydrothermal treatment [13]. This particular process, developed by S.P. Lau and colleagues at the Polytechnic University of Hong Kong, was carried out via microwave heating of glucose as the carbon source. According to the experimental model (Fig. 2.11), the Carbon-Dots were assembled through

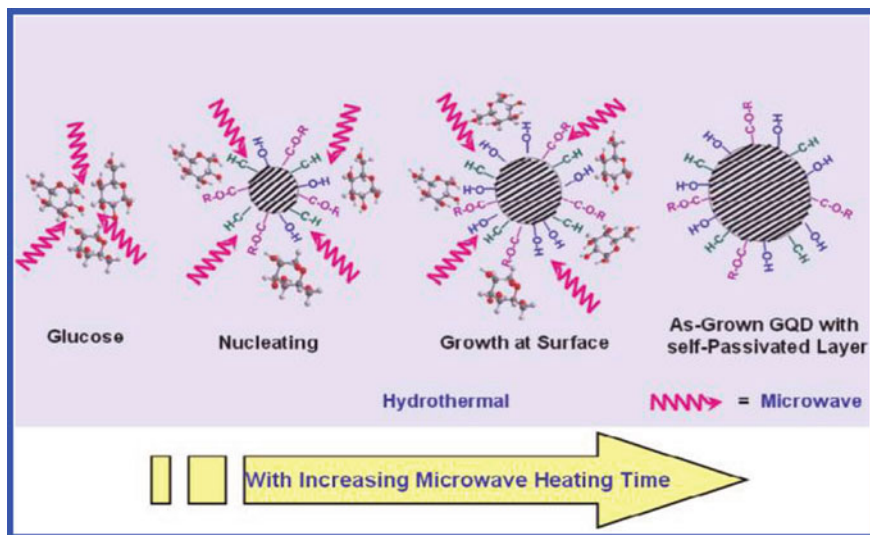


Fig. 2.11 Hydrothermal synthesis of Carbon-Dots using glucose as a carbon source. A model for nucleation and growth of Carbon-Dots induced by microwave heating of glucose solution. Reprinted with permission from Tang et al. [13]. Copyright (2006) American Chemical Society

a nucleation process, leading to gradual growth of the crystalline nanoparticle core and formation of a “self-passivated” layer comprising functional fragments of the glucose building blocks. Intriguingly, these microwave-generated Carbon-Dots featured excitation/emission in the deep blue spectral range, a rather unique property (as the large majority of reported Carbon-Dots emit at longer wavelengths).

Microwave-based synthesis has been employed in other Carbon-Dot fabrication routes. Figure 2.12 illustrates a scheme for preparing Carbon-Dots doped with nitrogen atoms (e.g., N-doped Carbon-Dots) through microwave treatment of calcium citrate and urea. Notably, this simple synthetic route, developed by Y. Zhang and colleagues at Shanghai Jiao Tong University, China, presented a *heterogeneous* synthesis process utilizing a mixture of a *powder* (calcium citrate) and *solution* (urea) [14]. The resultant Carbon-Dots emitted high luminescence both in solution and in the solid phase, a somewhat unique property in Carbon-Dot systems (as Carbon-Dots generally exhibit fluorescence *quenching* in solid phases).

High-temperature carbonization for fabricating Carbon-Dots has been carried out in solvents other than water. M. Kreiter, C-Y. Liu, and colleagues at the Max-Planck-Institut für Polymerforschung showed that heat treatment of carbon sources such as citric acid dispersed within *noncoordinating solvents* [i.e., non-polar, organic solvents] produced highly luminescent Carbon-Dots [15]. The approach was actually inspired by synthesis pathways developed for production of *inorganic quantum dots*, in which nonpolar solvents were believed to promote assembly and transformation of the nanoparticles’ building blocks into crystalline

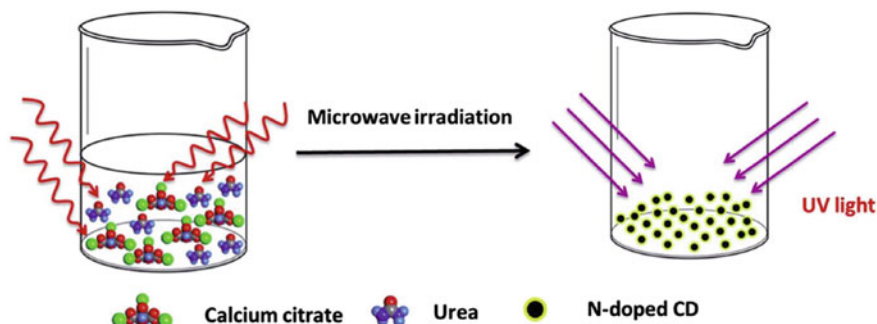


Fig. 2.12 Generation of N-doped Carbon-Dots through microwave heating. Synthesis was carried out upon microwave irradiation of a heterogeneous mixture of calcium citrate (powder) and urea (solubilized). Reproduced from Xu et al. [14], with permission of the Royal Society of Chemistry

colloids. In case of the Carbon-Dots, the simple one-step synthesis scheme reported by Kreiter and his colleagues was particularly successful in increasing the luminescence (i.e., quantum yield) of the particles, an observation that might be related to more effective surface passivation by amine derivatives co-added to the reaction mixture; in that regard, the nonpolar solvents likely enhanced the reactivity between the Carbon-Dots and the amine residues.

Several synthetic pathways have led to fabrication of Carbon-Dots exhibiting somewhat unusual luminescence properties. H. Lin and colleagues at the Chinese Academy of Sciences synthesized N-doped Carbon-Dots via a simple procedure involving triaminobenzene as the carbon source (Fig. 2.13) [16]. The resultant Carbon-Dots contained a relatively high abundance of nitrogen-containing functional groups, including amines, amides, and other carbon-nitrogen units. Intriguingly, these N-doped Carbon-Dots exhibited a strong emission in *yellow*, i.e., around 600 nm—a rare observation as the majority of Carbon-Dots reported thus far had maximal emission in shorter wavelengths (i.e., green-blue). Similarly, in contrast to other studies of Carbon-Dots, no excitation-dependent emission was apparent. These distinct photophysical properties most likely reflect modulation of the Carbon-Dots' surface states of by the nitrogen-containing functional groups (via mechanisms that are still unresolved).

Fig. 2.13 Yellow Carbon-Dots from triaminobenzene. The simple synthesis scheme produced Carbon-Dots emitting in *yellow*. Reprinted with permission from Jiang et al. [16]. Copyright (2015) American Chemical Society

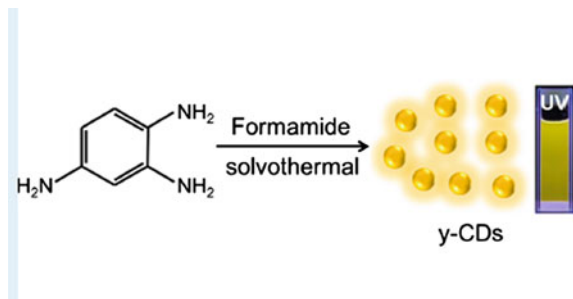
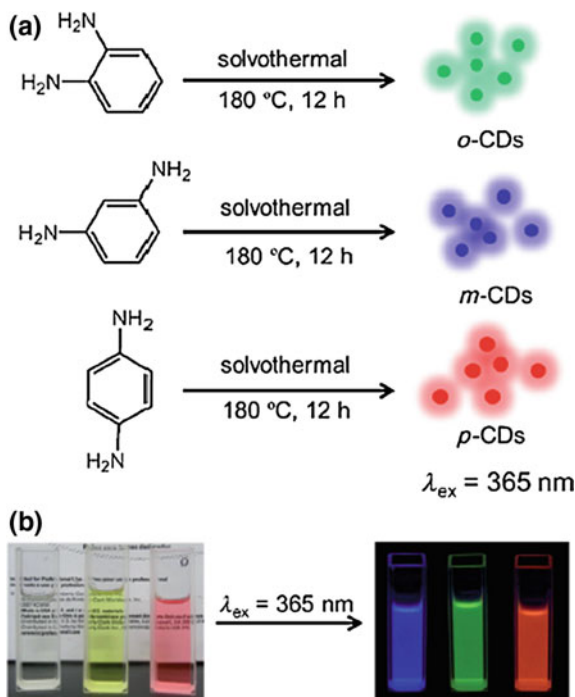


Fig. 2.14 Carbon-Dots emitting different colors from phenylenediamine isomers.

a Specific colors of Carbon-Dots generated from the *ortho*, *meta*, and *para* isomers. **b** Photographs showing the solution colors in regular light (*left*) and upon UV irradiation (*right*). Reprinted from Jiang et al. [28], with permission from John Wiley & Sons (2015)



That same research group has shown that different *isomers* of phenylenediamine produced Carbon-Dots displaying distinct colors (Fig. 2.14) [16]. Remarkably, as shown in Fig. 2.14, the three isomers *para*-phenylenediamine, *ortho*-phenylenediamine, and *meta*-phenylenediamine, gave rise to the three “basic” colors red, green, and blue (i.e., “RGB”), upon excitation by UV light. This observation was presumably related to the different nitrogen contents (and sizes) of the carbon nanoparticles. Importantly, the full RGB range generated by the Carbon-Dots could be exploited for the production of films exhibiting different predesigned colors by doping polymer films with specific Carbon-Dot compositions.

Numerous methods have been devised to prepare Carbon-Dots from *natural sources*, and it is fair to say that the huge variety of carbon-containing substances will continue to inspire researchers to develop new synthesis schemes using common and readily available carbon materials. Figure 2.15 illustrates an experiment in which *waste frying oil* was used to produce Carbon-Dots [17]. In fact, the simple synthetic scheme, demonstrated by J.S. Yu and colleagues at Nanjing University, China, generated Carbon-Dots that were also doped with *sulfur* atoms. The S-doped Carbon-Dots were used for cell imaging, and their luminescence properties closely depended upon the solution pH, presumably affecting the degree of protonation of the carboxyl residues upon the Carbon-Dots’ surface. In a broader context, the system depicted in Fig. 2.15 is an example of the widely-used synthetic pathways for Carbon-Dot *doping* using different precursors.

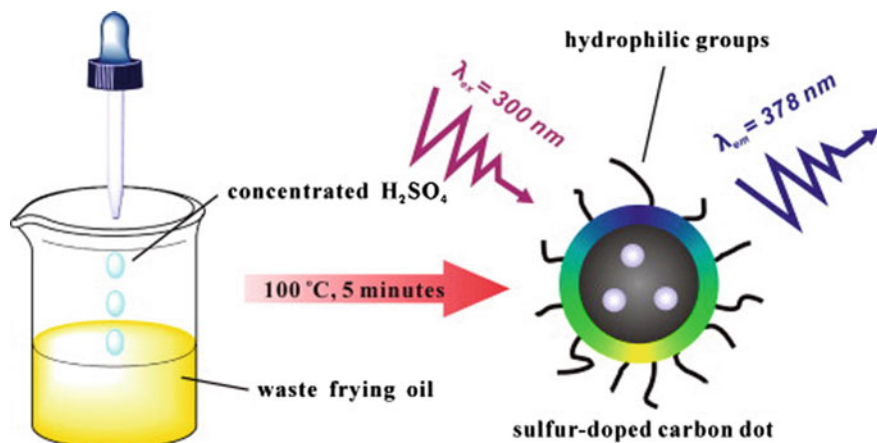


Fig. 2.15 Preparation of sulfur-doped Carbon-Dots from waste frying oil. Reprinted from Hu et al. [17], Copyright (2014), with permission from Elsevier

Sugars have been obvious candidates for Carbon-Dot synthesis and indeed many reports have described synthetic routes utilizing basic sugars, such as glucose, fructose, and others. However, the use of building blocks other than simple hydrocarbons has yielded in many instances Carbon-Dots exhibiting more interesting properties compared to simple sugar units. J. Tang and colleagues at the Chinese Academy of Sciences, for example, synthesized Carbon-Dots from *bovine serum albumin* (BSA), a widely used and commercially available protein [18]. The one-pot synthesis scheme involved hydrothermal treatment of the protein in the presence of an amine derivative (serving as the surface passivation agent); the pyrolysis reaction initiated by the high temperature gave rise to Carbon-Dot formation, exhibiting bright blue emission. This simple process also highlights the use of *proteins* as potential carbon sources in Carbon-Dot synthesis. The wide variety of proteins, availability in large quantities in many instances, and water solubility (for most proteins) point to their use as versatile starting materials in Carbon-Dot synthesis.

Figure 2.16 presents a straightforward strategy for construction of Carbon-Dots from *folic acid* as the carbon source [19]. The choice of folic acid in that study aimed to make the Carbon-Dots selective toward the *folate receptor* which is overexpressed in many cancer cells. The Carbon-Dots were synthesized in a single-step hydrothermal process without the need to first synthesize Carbon-Dots and subsequently conjugating the as-prepared Carbon-Dots with folic acid. Indeed, the folic acid-derived Carbon-Dots could selectively stain cancer cells through honing onto the folate receptors on the cell surfaces. This study represents the seemingly endless variability of Carbon-Dot synthesis pathways, reflecting the realization that any carbon-containing compound might be used in practice to produce Carbon-Dots.

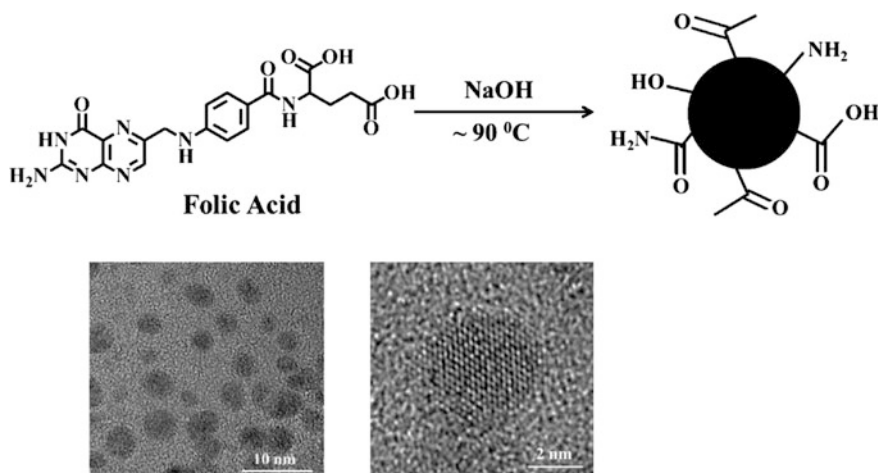


Fig. 2.16 Carbon-Dot preparation from folic acid. *Top* Scheme of the thermal process for generation of the Carbon-Dots in basic aqueous solution. *Bottom* High-resolution TEM of the Carbon-Dots showing the crystalline graphitic core structure. Adapted from Bhunia et al. [19]

In some instances, the carbonaceous reagents employed for synthesis of the Carbon-Dots had multiple functions—not only serving as the carbon source. R. Zboril and colleagues at Olomuc University, Czech Republic, have used *surfactants* as the starting materials in Carbon-Dot synthesis [20]. The synthetic route comprised of hydrothermal treatment of a commonly used surfactant, cetylpyridinium chloride monohydrate (Fig. 2.17), which yielded relatively uniform Carbon-Dot samples. Intriguingly, the luminescence of the Carbon-Dots was found to be sensitive to *solvent polarity*, producing different solvent-dependent colors upon UV excitation (Fig. 2.17, bottom). The surfactants in that Carbon-Dot system served not only as the carbon source, but also as stabilizers of the carbon nanoparticles, promoting their solubilization in different solvents, and affecting the “surface states” responsible for the luminescence properties of the particles.

Among the varied synthesis schemes for production of Carbon-Dots, some techniques stand out as seemingly serendipitous. This description fits the strategy depicted in Fig. 2.18, in which Carbon-Dots were prepared by mixing two ubiquitous chemicals—acetone and sodium hydroxide—and incubating the mixture for a few days [21]. The experiment, carried out by X. Ji and colleagues at South Central University, China, unexpectedly generated Carbon-Dots, presumably through the well-known aldol reaction, undergone in the case here by acetone in the alkaline solution environment (Fig. 2.18a). The unsaturated ketone formed by the reaction might have further polymerized, producing oligomeric chains which condensed into the Carbon-Dots. While the researchers reported that the Carbon-Dots exhibited the typical excitation-dependent photoluminescence spectra, the carbon cores of the nanoparticles appeared *amorphous* rather than the usual crystalline organization. Another interesting feature of the system was the formation

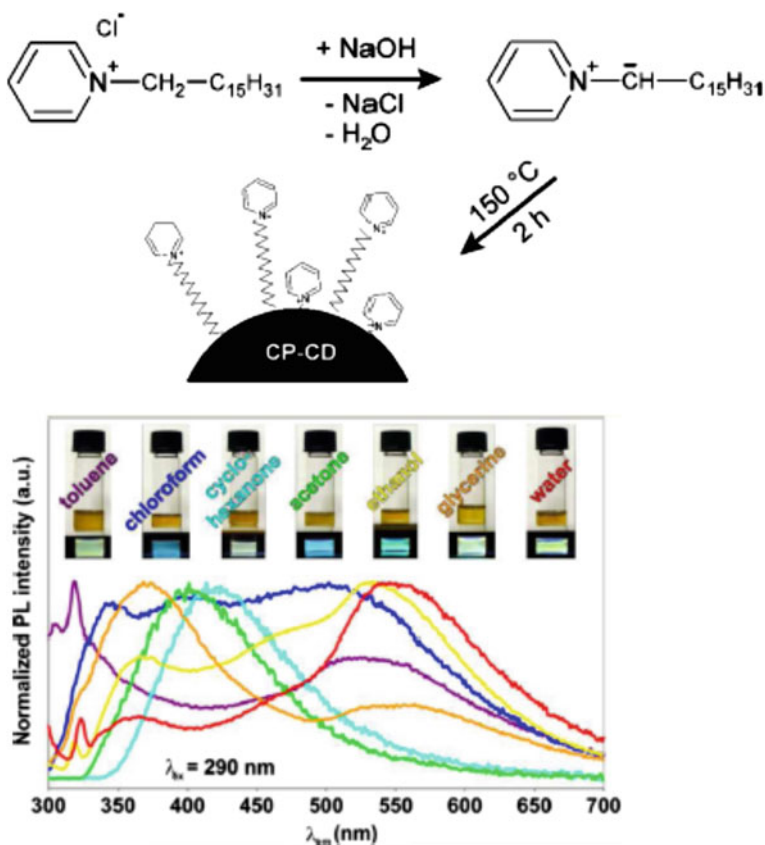


Fig. 2.17 Surfactant-generated Carbon-Dots exhibiting solvent-dependent colors. *Top* Scheme of the Carbon-Dot synthesis starting from cetylpyridinium chloride monohydrate; *bottom* Carbon-Dot solution colors and emission spectra in the indicated solvents. Reprinted with permission from Kozák et al. [20]. Copyright (2013) American Chemical Society

of a *porous carbon network* following high-temperature ($800\text{ }^\circ\text{C}$) calcination of the Carbon-Dots, which served as an excellent storage medium in sodium ion batteries.

In parallel with the rapidly proliferating reports on *Carbon-Dots*, many studies have focused on **graphene quantum dots (GQDs)** (Fig. 2.19). While GQDs have been perceived as distinct morphological entities, their structural and photophysical properties are in many respects similar to those of Carbon-Dots, reflecting the nanoscale dimensions, crystalline organization of the graphitic cores, and surface modification as a primary factor affecting the luminescence wavelength. The main distinction between GQDs and Carbon-Dots concerns the overall shape of the nanoparticles; Carbon-Dots likely constitute isotropic [spherical] nanoparticles, while GQDs are believed to adopt “disk-like” structures, comprising few graphite/graphene layers (i.e., thickness of a few nanometers) (Fig. 2.19).

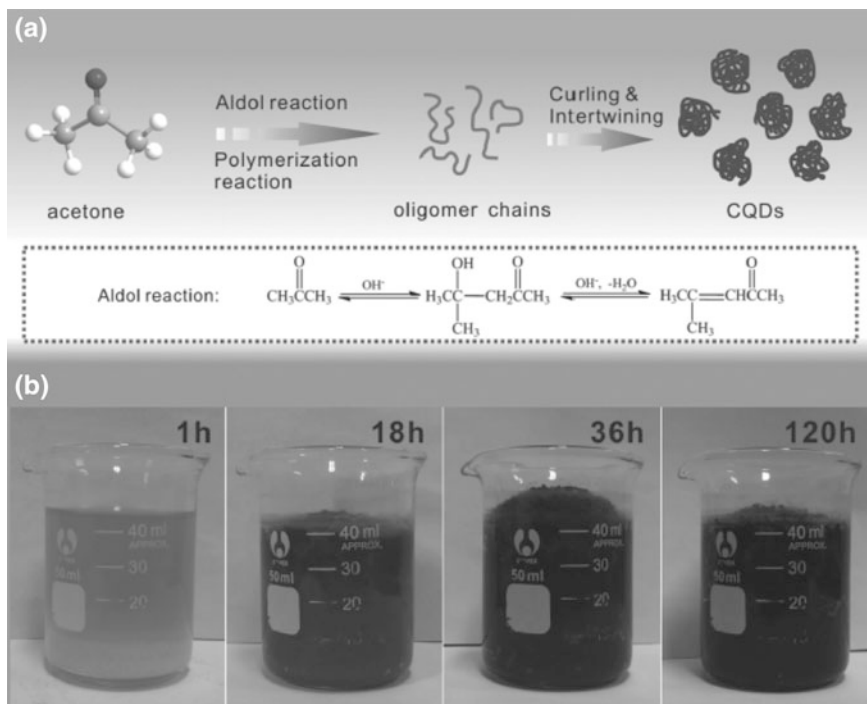


Fig. 2.18 Carbon-Dot synthesis from acetone in NaOH solution. **a** Proposed scheme for synthesis of the Carbon-Dots through the aldol reaction of acetone; **b** the reaction mixture after different incubation times. Formation of the condensed Carbon-Dot suspension is apparent after few days. Reprinted from Hou et al. [21], with permission from John Wiley & Sons (2015)

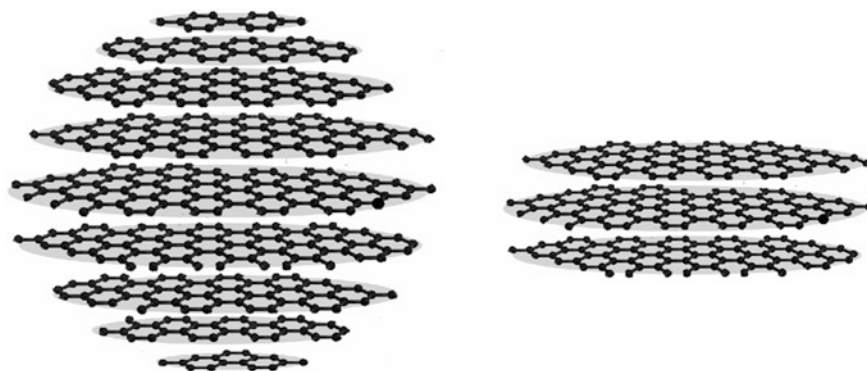


Fig. 2.19 Structural features of carbon-dots and graphene quantum dots. Generic structures of Carbon-Dots (left) and GQDs (right). Carbon-Dots are generally perceived as spherical aggregates, while GQDs comprise fragments of graphene layers

While some researchers consider GQDs a “special case” of Carbon-Dots, their fabrication and applications have followed, in fact, somewhat different paths. The first reports on GQDs referred to the “dots” as nanometer-scale domains of two-dimensional graphene fabricated through nanolithography (for example high-resolution electron beam lithography [22]). Several studies highlight the difference between the mostly *top-down* methods (such as lithography) for fabrication of GQDs, in comparison with *bottom-up* chemical synthesis techniques employed in the case of Carbon-Dots [and specifically discussed in this Book]. Obviously, precise particle dimensions that can be obtained via lithography have allowed investigation of the unique physical phenomena associated with GQDs.

GQDs have been fabricated also via “wet chemistry” methods similar to techniques described above in case of Carbon-Dot synthesis. K. Mullen and colleagues at the Max-Planck-Institut für Polymerforschung, Germany, reported synthesis of discoidal GQDs using a coronene derivative as the starting material [and carbon source] (Fig. 2.20). The preparation method involved initial self-assembly of the coronene in solution, followed by high-temperature transformation (pyrolysis) which generated graphite-like aggregates; subsequent exfoliation-through-oxidation and surface functionalization of the reaction products yielded GQDs exhibiting thickness of 2–3 nm (corresponding to 2–3 graphene layers) and diameters of tens

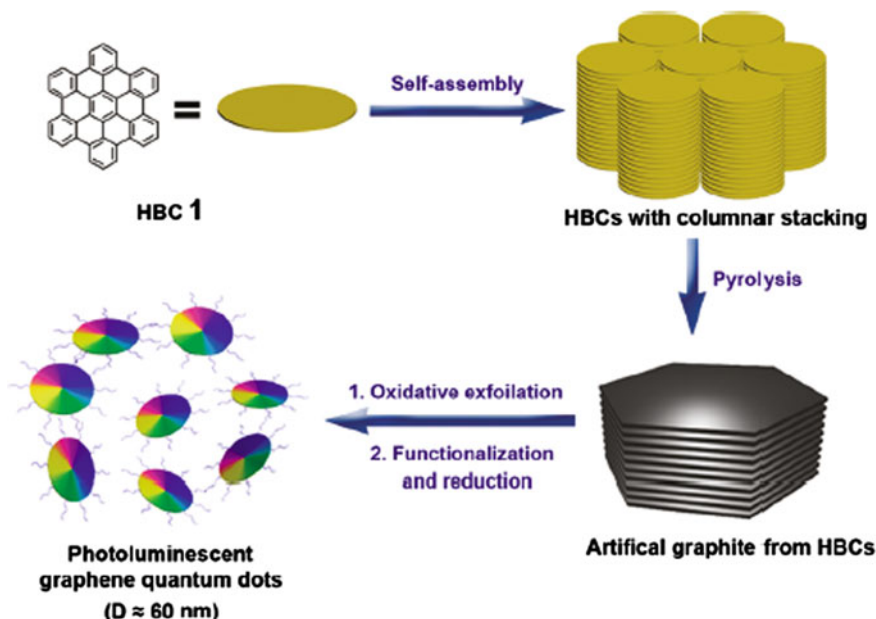


Fig. 2.20 Graphene quantum dots from coronene as the starting material. A scheme depicting the bottom-up synthesis process of the GQDs, likely originating from pyrolysis of the stacked layers of hexabenzocoronene (HBC). Reprinted with permission from Liu et al. [29]. Copyright (2011) American Chemical Society

of nanometers. The formation of GQDs in this case was attributed to the anisotropic rigid structure of the coronene building block, leading to assembly of the initial stacked columns that were subsequently fragmented, forming the GQDs (Fig. 2.20). It should be noted that the synthetic procedure yielded surprisingly uniform dispersion of the GQDs, highlighting the potential of “bottom-up” synthetic techniques to produce anisotropic carbon nanostructures in a controlled manner.

The study depicted above in Fig. 2.20 utilized a specific organic molecule for assembly of organized structures, ultimately generating the crystalline carbon cores of the GQDs. In many instances, however, GQDs have been synthesized from widely used carbon materials that already exhibit supramolecular ordering, such as carbon nanotubes or graphite “flakes”. Figure 2.21, for example, depicts a synthetic pathway in which carbonaceous assemblies such as multiwall carbon nanotubes (MWCNTs) or graphite fragments were reacted with potassium atoms to yield GQDs [23]. The study, carried out by S. Zhang and colleagues at Sheffield University, UK, revealed intercalation of the potassium atoms within the layered structures of the MWCNTs and graphite-promoted exfoliation and disintegration upon exposure to air [due to the high reactivity of the electron-donating potassium]. The fragmentation and oxidation processes associated with the combustion reaction between potassium and oxygen gave rise to GQDs comprising mostly a *single* graphite monolayer in relatively high yields.

Many published schemes for synthesis of GQDs employed *graphene oxide (GO)* as the starting material. Such strategies have taken advantage of the layered sheet organization of GO, obviating the need for initial assembly processes such as presented above (e.g., Figs. 2.20 and 2.21). Indeed, the use of building blocks which already employ graphene layers distinguishes *GQDs* from *Carbon-Dots*, as GQDs generally retain the few-layered organization of graphene. In such GO-based techniques, GQDs are essentially produced through disintegration/fragmentation of the GO sheets by varied experimental means, complemented by surface functionalization to generate photoluminescence. An example of such a GQD synthetic

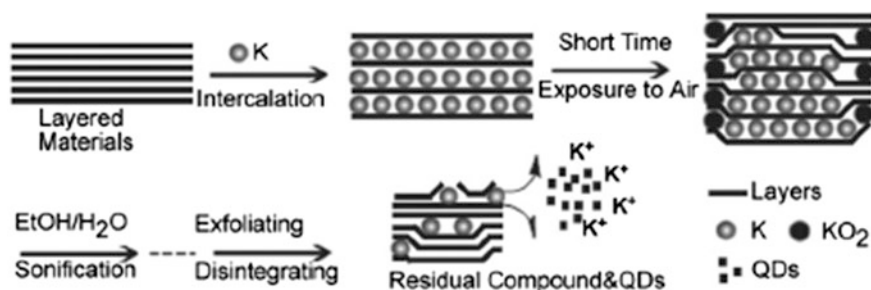


Fig. 2.21 Synthesis of GQDs through potassium-induced exfoliation of carbonaceous layered materials. The scheme shows insertion of the potassium atoms within the carbon layers; subsequent oxidation resulted in fragmentation of the layered materials and formation of GQDs. Reproduced from Lin et al. [23], with permission of the Royal Society of Chemistry

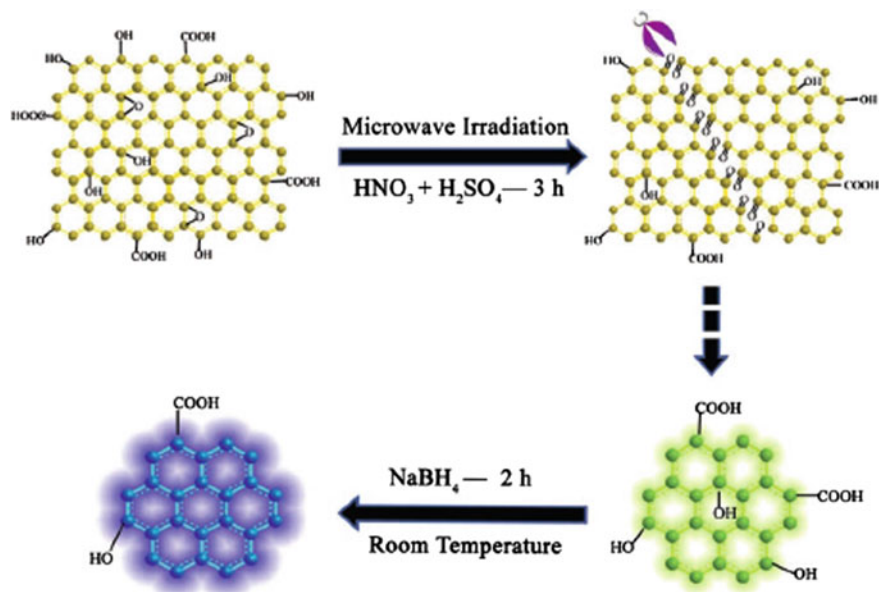


Fig. 2.22 Synthesis of GQDs via combined oxidation in strong acids and reduction. Reprinted from Li et al. [24], with permission from John Wiley & Sons (2012)

route, developed by J-J Zhu and colleagues at Nanjing University, China, is depicted in Fig. 2.22 [24]. The “one-pot” process combined microwave heating of GO and treatment with a strong acid to cleave the GO sheets. Similar to Carbon-Dot preparation schemes, the ubiquitous oxidation step is important for breaking the C–C bonds within the (graphene) starting materials, yielding small nanoparticles exhibiting OH and COOH surface residues. Notably, while acid oxidation produced GQDs exhibiting *green* luminescence, further reaction with sodium borohydride (NaBH₄), a commonly used reducing agent, transformed the GQDs’ color to *purple*, ascribed to modulation of the surface residues on the nanoparticles.

Other methodologies have been developed for producing GQDs from GO as the starting material. Similar to the above procedure, the main synthetic challenges consist of identifying reaction schemes that are not too harsh to carry out, yielding uniform carbon nanoparticle products in a controlled manner, and utilizing readily-available reagents. Figure 2.23 depicts a facile oxidation/fragmentation method based upon the “Fenton” reaction [25]. The Fenton reaction employs iron ions and hydrogen peroxide to generate hydroxide radicals which constitute powerful oxidizing agents. The hydroxide radicals progressively induced breaking of carbon–oxygen and carbon–carbon bonds in the GO sheets, resulting in formation of GQDs. According to the synthesis model proposed by the researchers and outlined in Fig. 2.23, the Fenton reagent initially induced “holes” in the GO network, which expanded and eventually yielded GQDs. Notably, this pathway might also provide means of controlling the concentrations and sizes of the particles produced.

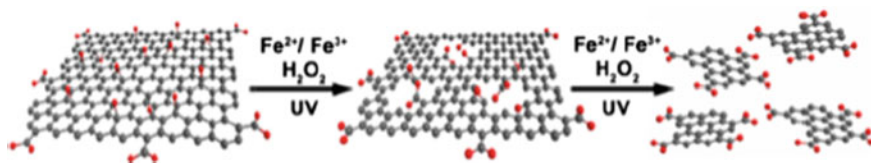


Fig. 2.23 Generation of graphene quantum dots through Fenton reaction of graphene oxide (GO). The scheme shows the fragmentation of the GO sheet following oxidation by the Fenton reagent, ultimately yielding GQDs. Reprinted with permission from Zhou et al. [30]. Copyright (2012) American Chemical Society

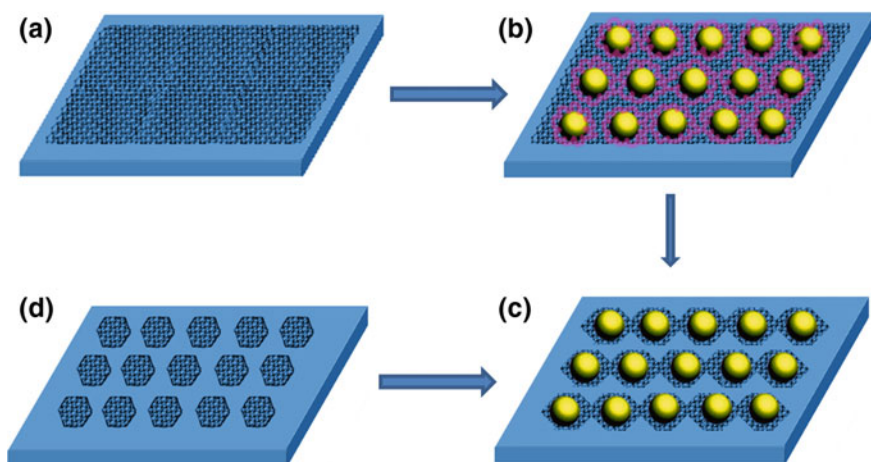


Fig. 2.24 Fabrication of graphene quantum dots using an array of gold nanoparticles and polymer micelles. **a** preparation of a graphene film; **b** an array of polymer micelle-coated Au nanoparticles (NPs) placed upon the film; **c** plasma etching removes the organic substances, leaving behind the Au NPs and graphene fragments underneath; **d** GQDs are produced after removal of the Au NPs. Adapted from Kim et al. [26]

A combined “top-down” and “bottom-up” strategy for production of GQDs is outlined in Fig. 2.24. The methodology, developed by B.H. Sohn and colleagues at Seoul National University, Korea, relied upon placing gold-containing polymer micelles upon a graphene sheet [26]. Following formation of metallic gold nanoparticles within the polymer micelles, the system was subjected to plasma etching (e.g., bombardment with high energy gas molecules). In this scenario, the uniform gold nanoparticles assembled within the polymer “cages” functioned as “shields”—while the plasma treatment removed the unprotected graphene, generating nano-size GQDs underneath the gold particles. Removal of the Au particles subsequently exposed the resultant GQDs. While the approach outlined in Fig. 2.24 involve several steps and appears somewhat elaborate, it enables one to fabricate uniform GQDs in large quantities. Furthermore, control of GQD

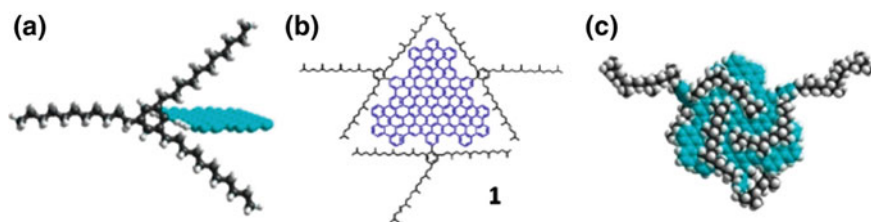


Fig. 2.25 Template-directed synthesis of GQDs. Schemes showing the synthetic concept. **a** A trialkylphenyl residue (*black*) is attached to a graphene sheet (*blue*). Hydrogen atoms involved in stabilization of the GQDs are indicated in *white*; **b** molecular organization of a graphene nanoparticle stabilized by three trialkylphenyl residues; **c** a theoretical calculation depicting the GQD core (*blue*) enclosed by the alkyl chains. Reprinted with permission from Yan et al. [31]. Copyright (2010) American Chemical Society

dimensions is feasible through the choice of polymer “mask” employed, as high-molecular weight polymer substances can generate larger particles and vice versa.

An interesting “templating” synthesis method was developed for production of size-controlled GQDs by L. Li and colleagues at Indiana University (Fig. 2.25). As shown in Fig. 2.25, the researchers “encapsulated” a graphene core within three alkyl-phenyl residues which both determined the dimensionalities of the dots as well as prevented aggregation of GQDs in solution. The resultant GQDs were relatively large (having diameters at around 15 nm), however their uniform sizes gave rise to a defined absorption peak in the visible spectral region, enabling their potential use as light absorbers in solar cells. Moreover, this synthesis strategy makes possible, in principle, tuning of the particles’ sizes by varying the *lengths* of the alkyl chains.

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