

Carbon Quantum Dots: Surface Passivation and Functionalization

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Abstract: This review deals with the promising newest carbon-based nanomaterial; Carbon Quantum Dots (CQDs). CQDs demonstrate optoelectronic properties comparable to conventional inorganic semiconductors, however are environmental friendly and benign. They possess complicated structures, particle sizes up to 10 nm and upon surface passivation and/or functionalization their optoelectronic properties are critically improved and tuned. Although there are a few recent reviews on this topic, the majority of them emphasize on CQDs applications or even the synthetic procedures followed to acquire CQDs. In contrary, this review refers in brief to the aforementioned and focuses on the surface passivation and functionalization routes and therefore the functional groups and heteroatoms used for the development of high quality CQDs. Introduction and doping with appropriate heteroatoms is the key point to tailor made features of CQDs and thus organic chemistry provides the vital background for the essential functionalizations.



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Keywords: Carbon quantum dots, surface passivation, organic functionalization, fluorescence, luminescence, optoelectronic properties, synthesis, applications.

1. INTRODUCTION

Graphite, diamonds, activated carbon, charcoal, nanodiamonds, carbon nanotubes, fullerenes, and more recently graphene and carbon quantum dots (CQDs); for sure, carbon always finds its way to be on the spotlight of human's interest. During the past two decades, various carbon nanostructures have enriched the known allotropes and structures of carbon. The tremendous scientific and research interest on them is reflected by two Nobel Prizes (Chemistry 1996, Physics 2010) and one Kavli Prize (Nanoscience 2008). Nowadays, more than ever, countless worldwide research groups focus on these carbon-based nanomaterials. Bonding and hybridization flexibility of carbon atoms, combined with the extraordinary physicochemical properties of these nanostructures, settle them as ideal candidates for state-of-the-art applications.

CQDs represent at the moment the newest class of carbon-based materials. Xu *et al.* on their effort to obtain with electrophoresis purified single-walled carbon nanotubes from arc-discharged soot, isolated, detected and thus accidentally discovered CQDs as a byproduct [1], even though it was Riggs' team that four years earlier had reported strong luminescent soluble carbon nanotubes in a comparable approach by purifying and cutting down nanotubes [2].

From their discovery and up to date, CQDs with critically improved and/or tailored properties have been acquired by numerous research works. The huge number of these reports, along with the growing interest for CQDs has led to a few recent reviews on this topic. However, the majority of them emphasize on CQDs applications or even the synthetic procedures followed to get CQDs [3-13]. In contrary, this review refers in brief to the aforementioned and focuses on the surface passivation and functionalization routes and thus the functional groups and heteroatoms used for the development of high quality CQDs.

On the other hand, organic chemistry is a powerful tool that enables the successful modification of various inorganic substrates and structures, forming hybrids and altering and/or tuning their physicochemical properties. Incorporation of appropriate functional organic groups and heteroatoms leads to desired tailored applicability of the final composites. These features of organic chemistry are greatly exploited in the case of CQDs and this review aims to a comprehensive overview of organic functionalized CQDs.

2. OVERVIEW OF SYNTHETIC METHODS FOR THE PRODUCTION OF CQDS

The very first production of CQDs was achieved in 2004 with arc discharge [1]. In the upcoming years, the potential of additional physical or chemical methods to acquire CQDs was also tested with positive results. In this direction, Sun *et al.* reported the successful fabrication of colorful photoluminescent CQDs by laser ablation of a mixture from graphite powder and cement [14]. A year after chemical approaches were introduced as Liu and colleagues obtained multicolor fluorescent carbon nanoparticles from the combustion soot of candles (Fig. 1) [15]. At the same time, Zhou's team prepared blue luminescent carbon nanocrystals in an electrochemical soaking manner [16]. The aforementioned techniques were further enriched later on with diverse approaches; either according to the top-down route for which final materials derive from a process where matter is broken down, or by the bottom-up route where CQDs are synthesized from suitable molecular precursors.

Thus, Bourlinos and his co-workers produced surface functionalized carbogenic quantum dots in a simple one-step chemical way by thermal decomposition of appropriate molecular precursors [17, 18]. Almost simultaneously in 2009, Peng *et al.* and Liu *et al.* reported aqueous routes for the preparation of CQDs [19, 20]; the former from carbohydrates based on chemical oxidation with strong acids and the latter with supported synthesis from resols by using silica spheres as carriers. The same year, the first microwave-assisted pyrolytic synthesis of CQDs from a poly(ethylene glycol) (PEG-200) and saccharides mixture was reported by the group of

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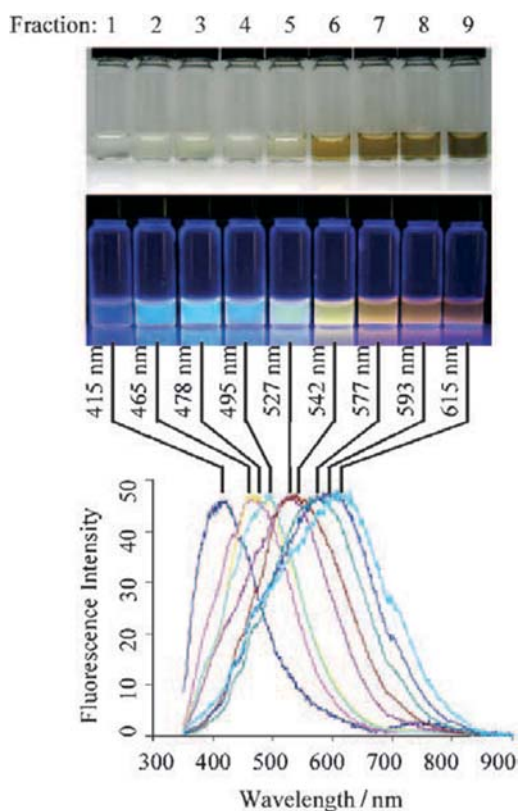


Fig. (1). Optical images of CQDs solutions illuminated under white and UV (312 nm) light, with corresponding fluorescence emission spectra (excitation at 315 nm) and maximum emission wavelengths. (Reproduced with permission from ref. [15]).

Zhu [21]. Jiang and co-workers described a third physical method, after arc discharge and laser ablation, *i.e.* plasma treatment of benzene with ethylenediamine [22], whereas Lu *et al.* managed to formulate CQDs upon ruthenium-catalyzed cage opening of fullerenes [23]. On the other hand, hydrothermal conditions were also employed in order to acquire CQDs with superior optoelectronic properties along with shorter reaction times [24], while Ma *et al.* used successfully ultrasonics [25]. The same year, Kwon and Rhee prepared fluorescent CQDs from microemulsions with the carbonization of sugar allocated in water-in-oil reverse micelles [26]. In addition, there is a lot of effort in the direction of CQDs' fabrication according to green chemistry. As a result, numerous works have been published lately presenting eco-friendly synthetic procedures for CQDs [27, 28], where various low cost abundant carbon-based materials [25, 26, 29-53], or even oil wastes [54] are used as the carbon precursors.

The variety of the applied techniques (physical or chemical, top-down or bottom-up) for the production of CQDs and their diversity imply that there is not a single preparative method gathering most advantages, but rather all approaches exhibit also significant drawbacks with the lack of control over the particle sizes and size distribution being the common disadvantage for most procedures.

3. OVERVIEW OF CQDS PROPERTIES AND APPLICATIONS

CQDs possess a series of attributes which settle them as potential substitutes of conventional semiconducting quantum dots. First of all, they demonstrate strong photoluminescence which can be controlled and tuned by the nanoparticles' size. Their fluorescence

intensity can be further improved upon surface passivation with the formation of thin insulating capping layer. Since they are carbon-based materials that may as well possess oxygen groups, their surfaces can be easily functionalized with organic molecules, introducing various heteroatoms and tailoring their wavelength emission and consequently their applicability. Their hydrophilicity or hydrophobicity is also adjustable and CQDs can be highly soluble in H₂O which is usually desirable. As mentioned earlier, CQDs can be acquired from various cost effective raw materials with diverse methods, while they are environmental friendly and benign. Most CQDs display chemical inertness, high stability and resistivity to photobleaching. Last but definitely not least, CQDs own two additional and very important characteristics; low cytotoxicity and excellent biocompatibility that render them superior compared to conventional semiconducting quantum dots and endow them with the potential of biological use [4-6].

Even though many worldwide research groups have been working on CQDs lately, the exact mechanism of photoluminescence is not yet revealed. This is because of the complicity of CQDs' structure and mainly of their core. For sure, the PL properties are correlated with functionalization and heteroatom doping. Hence, it has been shown that doping with more electronegative elements than C, such as N, drives to blue shift of the photoluminescent emission, while doping with less electronegative atoms as S and Se leads to red shift [55]. It has also been shown that diverse oxygen functionalities or solvents may shift the PL emission wavelength [56]. Recently, there is a trend in CQDs' publications to finally unravel the origin of their PL properties and not just indistinctly link them with functional groups. Thus, experimental and theoretical analyses associate the sp²-hybridized carbon network with the PL emission at short wavelengths and alternative deactivation pathways with red-shifted PL emissions [57]. In addition, the introduction of oxygen functionalities, and more specifically epoxides and hydroxyls, induces more electronic states between the CQDs' bandgap causing red shift in the observed PL emission [58].

Concerning CQDs' applications, it is rational that these revolve around CQDs' main feature, *i.e.* strong photoluminescence. Therefore, fundamental applications regard energy and catalysis. More specifically, CQDs have been employed: for photo-reduction and oxidation [59], as electrochemiluminescent reagents [21, 60, 61], as sensors (Fig. 2) [8, 43, 49, 62-73], as photo- electro- catalysts [25, 74-78], for organic photovoltaic devices [79], as detectors [29, 44, 47, 55, 74, 80-87], for light emitting diodes [88-91], for solar cell devices [92], for ink-free printing luminescent patterns [93], for energy transfer [94], etc. However, based as well on their biocompatible nature, CQDs have been extensively used for bioimaging [8-11, 30, 34, 35, 37, 40, 41, 43, 46, 52, 68, 92, 95-118], but also for theranostic photodynamic therapy [119], as antimicrobial agent [28], as gene nanocarriers [112, 120, 121], for cancer therapy [13, 122], in general as drug delivery systems [33, 123, 124], etc.

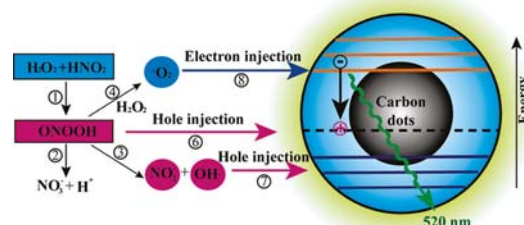


Fig. (2). Schematic illustration of the chemiluminescence mechanism of a carbon dots-based system. (Reproduced with permission from ref. [64]).

4. SURFACE PASSIVATION AND FUNCTIONALIZATION OF CQDS

4.1. Surface Passivation of CQDs

It did not take long from CQDs discovery [1] until the crucial and highly beneficial effect of surface passivation was reported by Sun *et al.* (Fig. 3) [14]. In fact, Sun's group had previously described the formation of strong luminescent water soluble carbon nanotubes with the use of poly-(propionylethylenimine-co-ethylenimine) (PPEI-EI) that bound the nanotubes [2]. Essential linkage for the attachment of the polymer on the carbon nanostructures occurs at surface defect sites [14, 125].

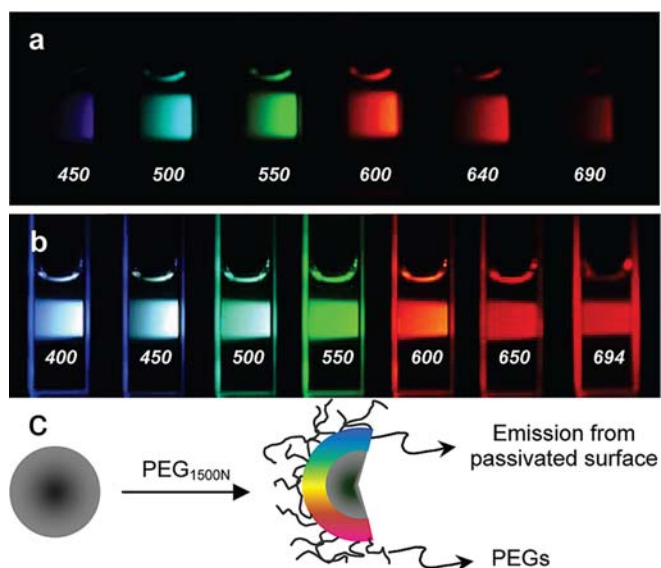


Fig. (3). Aqueous solution of the PEG_{1500N}-attached carbon dots (a) excited at 400 nm and photographed through band-pass filters of different wavelengths as indicated, and (b) excited at the indicated wavelengths and photographed directly. Schematic illustration of a carbon dot passivated with PEG_{1500N} (c). (Reproduced with permission from ref. [14]).

Bare surface of CQDs is not just exposed to contaminants but rather defenseless due to carbon and oxygen endogenous nature to react with organic molecules, which may cause the disappearance of the optoelectronic properties of CDQs. Therefore, a protection layer is vital for the stability and long life usage of CQDs. Surface passivation forms a thin insulating capping layer that shields CQDs from the adhesion of impurities and further improves their fluorescence intensity. Various polymers or organic molecules have been and may be used as surface passivation agents as long as they do not contain visible or near-UV chromophores and therefore are non-emissive at visible wavelengths, leaving intact the observed colorful luminescence emissions of the passivated CQDs [14].

In this direction, Sun *et al.* developed surface passivated CQDs with diamine-terminated oligomeric poly-(ethylene glycol) H₂NCH₂(CH₂CH₂O)_nCH₂CH₂CH₂NH₂ (average $n \sim 35$, PEG_{1500N}). In a typical reaction, PEG_{1500N} was mixed with acid-treated carbon particles and the mixture was heated at 120 °C for 72 h. After the reaction, the mixture was cooled to room temperature (RT) and dispersed in water. Suspension was centrifuged for 30 min resulting to a colored homogeneous supernatant suspension of PEG_{1500N}-passivated carbon dots. Using the same methodology surface passivated CQDs were also acquired using PPEI-EI with EI fraction ~20% [14]. The aforementioned treatment (120 °C for 72 h) has been applied unchanged or slightly modified in numerous works

ever since. In brief, the following passivation agents are used in literature frequently: PEG_{1500N} [14, 20, 53, 59, 76, 90, 96, 97, 126-129], PPEI-EI [14, 90, 95], 4,7,10-trioxa-1,13-tridecanediamine [19, 105, 127], 1-hexadecylamine [89, 130, 131], PEG₂₀₀ [21, 62, 63], PEG₆₀₀ [132], PEG_{900N} [33], PEG₁₅₀₀, PEG₂₀₀₀, PEG₆₀₀₀ and PEG₂₀₀₀₀ [46], PEG_{2000N} [119], PEG₄₀₀₀ [109], poly(ethylenimine)-*b*-poly(ethylene glycol)-*b*-poly(ethylenimine) and 4-arm amine-terminated PEG [98], branched or linear PEI [44, 65, 81, 83, 120, 133], PEG and PEI [115], etc. It is noteworthy that apart from surface passivation, this treatment commonly introduces useful amine groups and therefore also acts as surface functionalization.

4.2. Surface Functionalization of CQDs

Surface functionalization is an intriguing pathway for developing tailor made features on CQDs. The easiest and first applied method for this purpose is the treatment with acid solutions. Refluxing for a few hours with a high concentration nitric acid solution (2-3 N) creates useful surface defects and introduces various oxygen functional groups such as carboxyl, carbonyl, and hydroxyl groups [14, 15, 20].

Nonetheless, acid treatment and in general post-synthetic functionalization, is not the solely approach to insert dopants on CQDs. These can be as well created together with the formation of the CQDs *via* one-step synthetic procedures by using suitable molecular precursors. In addition, by using alkali environment, reduction agents, acylation (alkanoylation) reactions, carbodiimide chemistry, organosilanes, etc. essential functional groups may be grafted on the surfaces of CQDs. The up to date reported in literature techniques for acquiring functionalized CQDs are summarized in Table I and described in detail further below.

One-step Pyrolysis

Pioneers in the one-step formation of functionalized CQDs were Bourlinos and his colleagues who managed to prepare both organophilic and hydrophilic carbon nanoparticles [17, 18]. To achieve this, citric acid [HOOCCH₂C(OH)(COOH)CH₂COOH] was mixed with different amines (R-NH₂) and upon thermal decomposition capped nanoparticles were formed. In this fascinating approach, as citric acid protonates the amines, the relevant ammonium citrate salts are formed through the ionic interaction (-NH₃⁺OOC-). With thermal treatment, the citrate unit serves as the carbon source while the compensating organic ammonium provides the attached surface modifier. This is accomplished as amide linkages (-NHCO-) are created from the thermal dehydration of the ammonium carboxylate moieties (-NH₃⁺OOC-) and bind the organic corona covalently to the cores. In the case of octadecyl ammonium (C₁₈H₃₇NH₃⁺) citrate salt, organophilic nanoparticles are taken, while hydrophilic nanoparticles are obtained with 2-(2-aminoethoxy)-ethanol (OHCH₂CH₂OCH₂CH₂NH₃⁺). Except one-step functionalization, this methodology results to rather uniform monodisperse nanoparticles due to the low melting point of the specific citrate salts and the surface blocking provided by the organic modifiers [17]. If sodium 11-amino-undecanoate [H₂N-(CH₂)₁₀COO⁻Na⁺] is used as the amine precursor, a carboxyl surface modified carbon-based nanoparticle is acquired, which becomes organophilic if sodium is subsequently exchanged with cetyltrimethylammonium [C₁₆H₃₃N(CH₃)₃⁺] [18]. In all cases, after mixing citric acid with the amines, the surface functionalized carbon dots are obtained after pyrolysis at 300 °C.

Similar procedure was followed later on by Wang *et al.* whom oil-soluble CQDs exhibited a maximum quantum yield of 53% and

Table 1. Synthetic routes to functionalized CQDs.

Synthetic Route	Functional Group	Ref.
Acid treatment	Carboxyls, arboxyls, hydroxyls	[14, 15, 20] and many other beyond
One-step pyrolysis	Varied, depended on precursor used	[17, 18, 42, 46, 56, 65-67, 72, 80, 81, 86, 88, 101, 110, 123, 130, 133-142]
Acylation (alkanoylation)	Varied, depended on molecule used	[59, 79, 90, 143, 144]
Carbodiimide chemistry	Varied, depended on molecule used	[49, 62, 87, 98, 101, 119, 124, 145-147]
Organosilanes	Depended on organosilane used	[91, 114, 117, 148, 149]
Hydrothermal	Amines, oxygen-, sulfur-, boron-, phosphorus- and selenium- containing	[32, 34, 35, 37, 38, 40, 41, 44, 47, 48, 51, 55, 68, 70, 71, 73, 84, 115, 116, 118, 121, 150-158]
Solvothermal	Amines, boron-containing	[106, 159]
Alkali treatment	Oxygen-bearing	[75]
Metal attachment	Varied metals	[126, 129]
Post reduction	Hydroxyls, hydrazides, alkyl	[104, 160-163]
Oxidation (plus ammonia)	Amines	[28]
Ultrasonication (plus ammonia)	Nitrogen-bearing groups	[25]
Other	Varied	[22, 29, 39, 43, 50, 54, 74, 77, 82, 85, 92-94, 102, 112, 131, 164-171]

the relative water-soluble CQDs reached a 17% [130]. The same experimental procedure was later adopted by Goh *et al.* that used the citric acid derived CQDs for the bioimaging of hyaluronic acid derivatives [101]. In contrary, Pan and co-workers reported the partial pyrolysis of another precursor, EDTA-2Na-H₂O, at 400 °C under nitrogen atmosphere which resulted to strongly fluorescent CQDs that incorporated carboxyl groups as these were not eliminated [134]. Citric acid together with 11-aminoundecanoic acid was also used by Zhao' team so as to create a plethora of carboxylate moieties on CQDs' surfaces [80]. These groups were further exploited in order to adjust Eu³⁺. The presence of europium may have quenched the fluorescence of CQDs nevertheless an off-on fluorescence detector for phosphates was built. Then, Bourlinos *et al.* modified their original method and prepared quaternized surface functionalized CQDs by pyrolyzing at 250 °C a novel salt precursor made from the acid-base combination of tris(hydroxymethyl) aminomethane (Tris) and betaine hydrochloride [135]. Once again with

the formation of an amide linker, a quaternary ammonium moiety was grafted on the surface. In following years, as referred in Table 1, numerous works have been based on the one-step pyrolysis or co-pyrolysis of various precursors which in many cases were environmental friendly abundant raw materials. This process led to the simultaneous carbonization towards CQDs and incorporation of functional groups with amines and in general nitrogen containing groups being the most common ones. Nevertheless, even though these works are cited in Table 1 (including the microwave-assisted or hydrothermal treatments), many of those are not described further below unless the applied procedure reports something novel compared to previous works [14, 15, 17, 18, 20, 22, 25, 28, 29, 32, 34, 35, 37-44, 46-51, 54-56, 59, 52, 65-68, 70-75, 77, 79-82, 84-88, 90-94, 101, 102, 104, 106, 110, 112, 114-119, 121, 123, 124, 126, 129-131, 133-145, 148-171].

Employment of Organic Reactions

In 2009, Wang *et al.* employed an already applied reaction for the functionalization of carbon nanotubes to modify CQDs and obtained fluorescent derivatives [59]. After refluxing CQDs with aqueous nitric acid, oxidized CQDs were treated with thionyl chloride. The acyl chloride derivative was then reacted with PEG_{1500N} giving carbon dots with surface-attached modifiers. Hence, the covalent bonding of amines on acyl chlorides is a reaction that can be applied in the case of CQDs too [59]. The acyl chloride mediate was also used by Gupta and colleagues in order to attach aniline and methylene blue on the surfaces of CQDs [79]. Pristine CQDs were treated with nitric acid followed by acyl formation in the presence of DMF as catalyst, and acylation reaction with either aniline or methylene blue resulted to covalent conjunction through amide groups' creation. Later on, Anilkumar's team again grafted PEG_{1500N} after thionyl chloride reaction and proceeded further in crosslinking the CQDs with dimethyl pimelimidate [143]. Recently, Wang' group managed to attach an imidazole derivative onto the surface of CQDs according to the same principles [144]. At first, amino-modified CQDs were developed by the co-pyrolysis of citric acid and urea, while 1H-imidazole-4-carboxylic acid was reacted with thionyl chloride. Afterwards, the acylation reaction was employed as the acyl chloride derivative of imidazole was reacted with the amino-modified CQDs at 80 °C for 12 h in THF, leading to the covalent conjugation of imidazole (Fig. 4).

Aiming to targeted cancer cell imaging, Li's team managed to conjugate transferrin on surface passivated CQDs. After being treated with concentrated nitric acid for introducing carboxyl groups and passivated with PEG_{1500N}, or poly(ethylenimine)-*b*-poly(ethylene glycol)-*b*-poly(ethylenimine) or a 4-arm amine-terminated PEG, the CQDs were mixed with transferrin in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) which activated the carboxyl groups of transferrin for coupling with the amine groups of the surface passivation agent to give finally covalent amide bonds [98]. In another similar biological molecule attachment, Gonçalves and her co-workers after acid treatment and passivation with PEG₂₀₀, successfully bound *N*-acetyl-L-cysteine introducing sulfur atoms in the capping layer of the CQDs [62]. The same group under the same protocol tethered mercaptosuccinic acid importing once again useful sulfur atoms in the capping layer [145].

EDC chemistry was applied as well by Huang *et al.* [119]. The carboxyl groups of chlorine e6, also known as talaporfin which is a photosensitizer used in photodynamic therapy, were activated with EDC and *N*-hydroxysuccinimide (NHS) in order to react with the amine groups of passivated with PEG_{2000N} CQDs ending to cova-

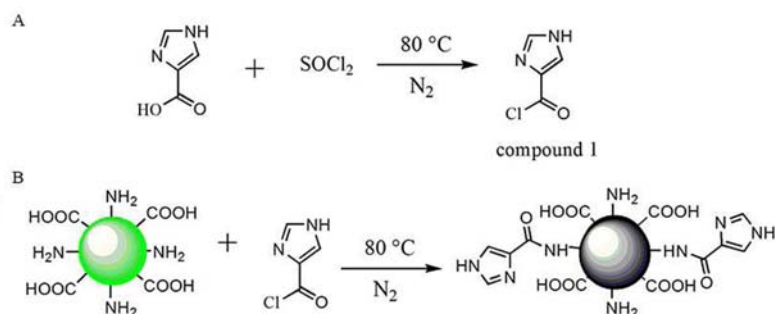


Fig. (4). Schematic illustration for the synthesis of an imidazole derivative (A) and its conjugation on the surface of CQDs (B) based on acylation (alkanoylation) reaction. (Reproduced with permission from ref. [144]).

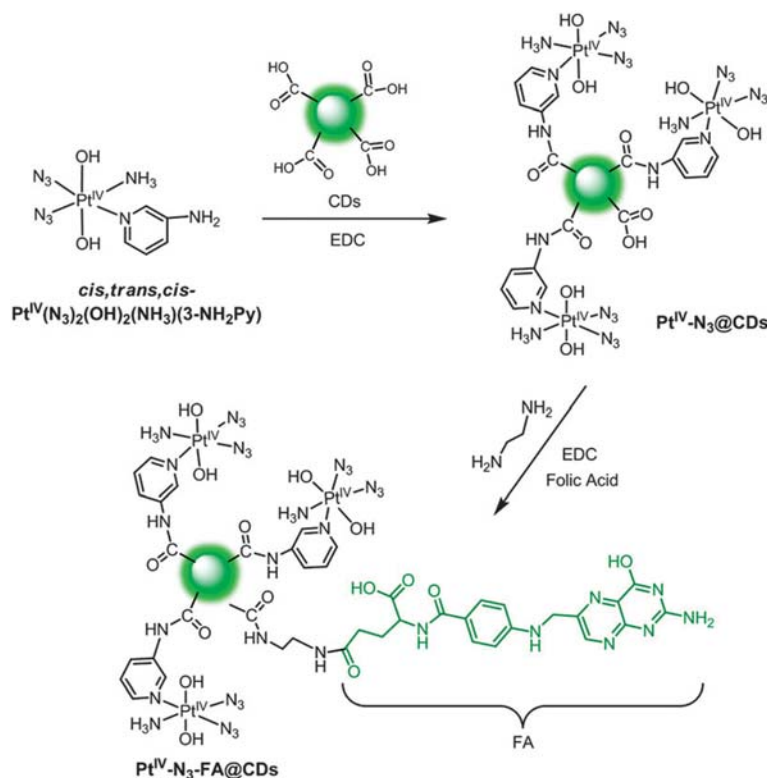


Fig. (5). Schematic representation for the formation of Pt^{IV} -azide-folic acid-functionalized CQDs. (Reproduced with permission from ref. [124]).

lently grafted chlorine e6 through amide bonds. Additionally, Zhang's team achieved to fabricate quinoline derivative-functionalized carbon dots [49]. CQDs were prepared at 160°C from citric acid and branched PEI, while carbodiimide chemistry was employed to covalently conjugate a quinoline derivative onto the surface of the CQDs. The same principals, *i.e.* carbodiimide reactions, were employed for the covalent conjugation of glutamic acid and ciprofloxacin on amino-functionalized CQDs prior formed by the co-pyrolysis of citric acid, glycerin, and PEG diamine at 250°C for 5 h [146]. In 2015, another work by Wang and co-workers was based on EDC chemistry [87]. Carboxyl-modified CQDs were produced from citric acid and ethylenediamine under hydrothermal conditions at 200°C for 5 h. Then, in the presence of EDC and NHS the carboxyl groups were activated and linked covalently to a 10D amino-modified aptamer of *Salmonella typhimurium* after reacting for 1 h with gentle stirring in darkness.

The same synthetic route, EDC/NHS coupling chemistry, was followed by Yang *et al.* who reported the covalent attachment of a nuclear localization signal (NLS) peptide onto the surface of amino-

functionalized CQDs [147]. Pristine N-doped CQDs were fabricated hydrothermally at 60°C for 8 h from citric acid, PEG2000, and ethylenediamine. The conjugation with the *simian virus 40* large T-antigen NLS was achieved with a 48 h long reaction at room temperature in darkness.

Completing the description of reports that lay on EDC chemistry, Yang's group managed to tether a photoactive diazido Pt^{IV} complex on CQDs [124]. Initially, carboxyl-functionalized CQDs were produced from activated carbon by refluxing under oxidative acidic conditions. Then, the Pt^{IV} -azide was conjugated *via* amide bonding between its amino-pyridine groups and the carboxyl groups of CQDs based on EDC coupling. Finally, surplus carboxyl surface groups were treated with an excess amount of ethylenediamine and material was reacted with folic acid (Fig. 5).

Organosilanes

Since organosilanes represent a significant class of functional compounds, their usage in modifying CQDs it was just a matter of time. Hence, in 2011 Wang *et al.* presented the first organosilane-

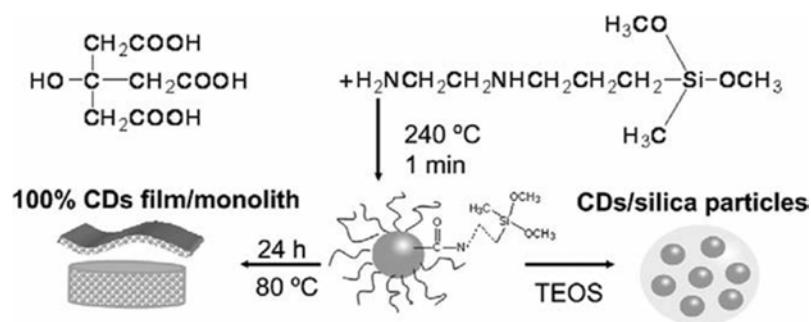


Fig. (6). Schematic illustration for the preparation of photoluminescent CQDs, surface-functionalized with an organosilane *via* one-step process, and further production of flexible CQD film and CQDs/silica particles. (Reproduced with permission from ref. [148]).

functionalized CQDs *via* one-step synthetic route [148]. The group prepared highly luminescent CQDs through the pyrolysis of anhydrous citric acid in *N*-(β -aminoethyl)- γ -aminopropylmethyl-dimethoxysilane (AEAPMS) at 240 °C for 1 min. The fast procedure resulted to ultrasmall CQDs of about 0.9 nm with high quantum yield of up to 47%. CQDs were further processed, whereas the silane presence or its substitution by other silanes deeply expands the variety of the functional groups that can be covalently attached on the surfaces of CQDs and/or the reactions that can be made in additional steps (Fig. 6). Recently, Huang and colleagues employed (3-aminopropyl)triethoxysilane (APS) and applied a one-step simultaneous preparation, passivation, and functionalization of CQDs [114]. Glycerol was used as carbon source and it was reacted with APS at 200 °C for 30 min in a microwave, with the formed CQDs bearing silicate and amine surface functional groups.

The same year, Wen *et al.* mixed 3-(2-aminoethylamino)propyltrimethoxysilane and graphene oxide with ethanol and treated the suspension hydrothermally at 150 °C for 10 h to obtain once again organosilane-surface functionalized CQDs [117]. In 2015, Wang's team carbonized citric acid at 150 °C for 4 h under solvothermal conditions in AEAPMS [149]. Their findings revealed that the organosilane was anchored by both sides onto the CQDs' surfaces, leading to dual long chain surface functional groups with either -NH₂ or -Si(OCH₃)₃ as terminal moieties. In advance, Wang *et al.* achieved the embedment of water-soluble nitrogen/sulfur-co-doped carbon dots into a polyhedral oligomeric silsesquioxane (POSS) matrix [91]. The N,S-co-doped CQDs were prepared from citric acid and L-cysteine upon hydrothermal treatment as described further below in the co-doped CQDs section [150], while the water-soluble octa(tetramethylammonium)-functionalized POSS was used. Hybrid material in powder form emerged by simple mixing of aqueous solutions of CQDs and POSS, followed by solvent slow evaporation at 30 °C for 24 h.

Procedures for Doped with Further than Nitrogen Heteroatoms and Co-doped CQDs

In 2013, the first sulfur-doped CQDs were reported by Chandra *et al.* [92]. For this, thiomalic acid was refluxed for 4 h at 90 °C together with a small amount of concentrated sulfuric acid. Solvent extraction with dichloromethane and ammonium hydroxide addition followed, and finally the S-doped CQDs were formed after the polymerization of the precursor. Malic and succinic acids were also used instead of thiomalic acid in order to evaluate the applicability of the methodology which resulted to high sulfur content as verified by EDX analysis (atomic weight ratio C/S = 5.57/1). Sulfur-doped CQDs were also produced by Kwon and co-workers [131]. Glucose was used as carbon source and thioglycolic acid as sulfur source.

Bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT), water, and decane were used to form a water-in-oil reverse micelles microemulsion solution, whereas hexadecylamine was used as passivation agent. Final materials came from the pyrolysis at 160 °C for 2 h of a mixture of the aforementioned chemicals, while the initial concentration of thioglycolic acid and its ratio to glucose displayed a direct proportion to the sulfur content of the S-doped CQDs. Waste frying oil was used by Hu *et al.* and once again S-doped CQDs were obtained [54]. In a simple and fast reaction, waste frying oil was treated with concentrated sulfuric acid at 100 °C for just 5 min and S-doped CQDs were formed. XPS and FT-IR spectroscopies revealed not only the core doping with thiophene-S groups but also the functionalization of the surfaces with sulfonate groups.

In advance, Dong's team presented the formation of nitrogen and sulfur co-doped CQDs upon hydrothermal treatment of appropriate precursors [150]. The group prepared simple oxygen containing CQDs by heating citric acid monohydrate in an autoclave at 200 °C for 3 h. When glycine was added in the mixture, the same treatment led to the synthesis of nitrogen-doped CQDs. Finally, and as expected, when L-cysteine replaced glycine, CQDs with both nitrogen- and sulfur-bearing groups were acquired. Sulfur- and nitrogen-co-doped CQDs were also developed by Sun and colleagues [39]. Human hair fibers were etched with sulfuric acid and carbonized after heating at various temperatures. Diverse bonding configurations were formed originating from thiophenes, sulfates, and sulfonates for S and pyridinic and pyrrolic groups for N. Experimental findings indicate that higher reaction temperature favors the fabrication of smaller sized doped CQDs with enhanced sulfur content. Sulfur/nitrogen co-doped is also the case of the CQDs prepared by Huang and co-workers shortly after [35]. Hydrothermal treatment of gentamycin sulfate at 200 °C for 1.5 h resulted to a narrow size distribution of nanoparticles with an average diameter of 2.8 ± 0.7 nm. Final CQDs possessed varied kinds of amine and sulfonate groups as confirmed by XPS analysis. In addition, Hu *et al.* fabricated N and S co-doped CQDs with the microwave-assisted co-carbonization of rice and *N*-acetyl-L-cysteine [42]. The process resulted in the formation of N,S-C-dots covered with carboxylic acid, amido and alkyl sulfide moieties as verified by FT-IR and XPS spectroscopies. The N,S-C-dots exhibited tunable and enhanced fluorescence compared to undoped C-dots (derived by the sole pyrolysis of rice) (Fig. 7). Moreover, Wang and co-workers reported a solvent-free synthesis of nitrogen and sulfur co-doped CQDs with the hydrothermal treatment of glutathione at 260 °C for 1 h [47]. The products demonstrated a 16.1% nitrogen and 2.0% sulfur content whereas amine as well as both thiophene-S and sulfide groups were detected implying that the carbon dots' surfaces were successfully functionalized with both heteroatom-based groups.

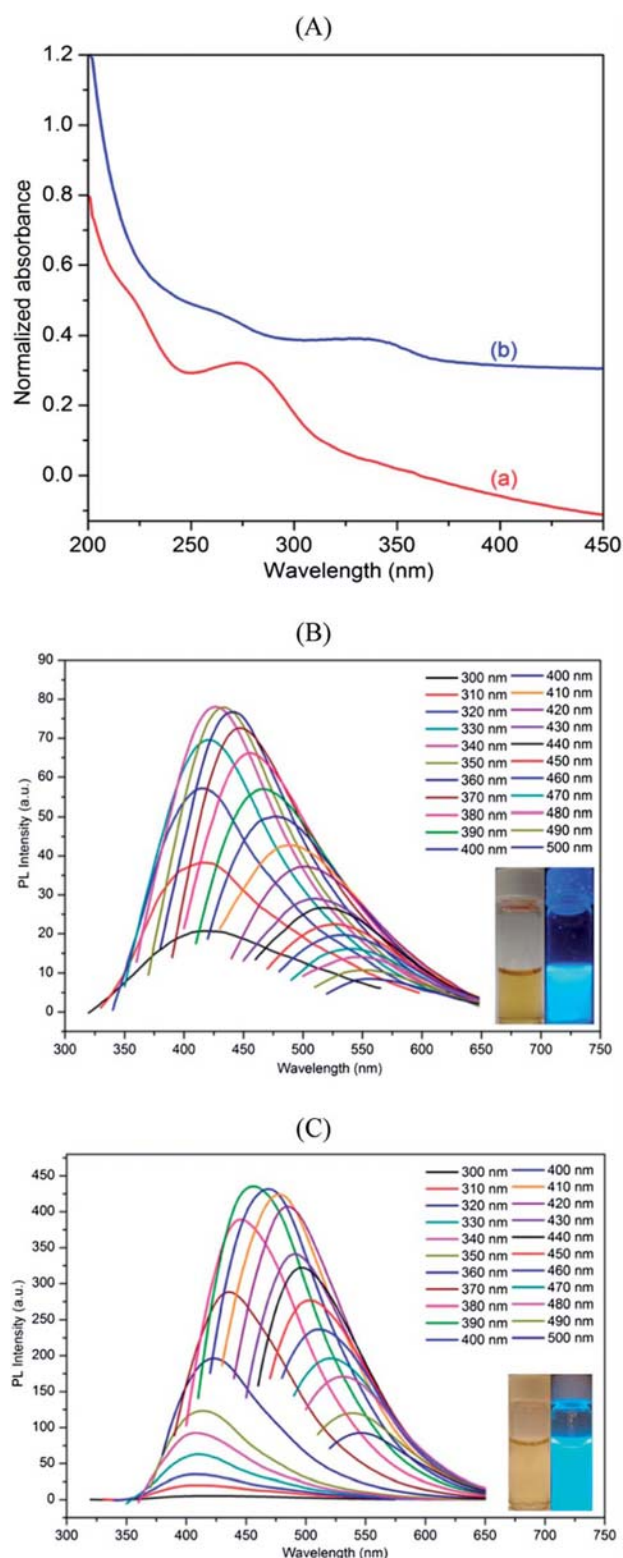


Fig. (7). (A) UV-vis absorption spectra of (a) undoped C-dots and (b) *N,S*-C-dots. Spectra are offset for ease of comparison. (B) and (C) are PL spectra at different λ_{ex} , 300–500 nm of undoped C-dots and *N,S*-C-dots, respectively. The insets display the images of undoped C-dots and *N,S*-C-dots under daylight and UV irradiation. (Reproduced with permission from ref. [42]).

Jahan and co-workers developed on the other hand boron/nitrogen co-doped CQDs [152]. *N*-(4-hydroxyphenyl)glycine

and boric acid (H_3BO_3) were treated hydrothermally at variable temperatures from 150 up to 400 °C for 2.5 h with the final bare CQDs having boron and nitrogen functional groups but carboxyl surface groups as well. EDC/NHS chemistry was further applied for the passivation of the carbon dots with various passivating agents. A year later, Barman *et al.* in a similar way prepared boron/nitrogen but also phosphorus/nitrogen co-doped CQDs [153]. Citric acid and diethylenetriamine were pyrolytically decomposed by hydrothermal treatment at 170 °C for 1 h to form N-doped CQDs. *Ortho*-phosphoric acid in the case of P and boric acid in the case of B were added in the reaction mixture to obtain the co-doped products. Phenylboronic acid was employed by Shen and Xia as the sole precursor for the formation of boron-doped CQDs [70]. CQDs were prepared hydrothermally at 160 °C for 8 h and apart from the incorporation of boron atoms in the core of the nanoparticles, XPS and FT-IR spectroscopies verified the successful surface functionalization with boronic groups. Analogous boron groups were detected in the doped CQDs acquired by Fan *et al.* with the electrolysis of a graphite rod in a borax aqueous solution [170], while Shan's group incorporated boron (5.9 wt.%) into CQDs by the solvothermal treatment of hydroquinone and BBr_3 [159]. Finally, boron/nitrogen co-doped CQDs were synthesized recently by Bourlinos and his colleagues microwave-assisted from citric acid, boric acid, and urea [50].

On the other hand, Yang *et al.* produced the first selenium-doped CQDs [55]. Initially, carbon nanoparticles of an average size 30–50 nm were obtained from Chinese ink upon refluxing for 6 h with HCl aqueous solution, and afterwards were oxidized with a mixture of HNO_3 , H_2SO_4 , and $NaClO_3$ for 1 h at 5 °C and 5 h at 15 °C. Following, NaHSe was added to an aqueous solution of the oxidized CQDs and the mixture was treated hydrothermally at 240 °C for 12 h. With the same methodology and by using NaHS instead of NaHSe, S-doped CQDs may be acquired, whereas if oxidized CQDs were dispersed in DMF/ H_2O (9:1), N-doped CQDs were formed. In all cases, heavy doped (above 10 at.% for heteroatoms) CQDs were obtained and various groups were formed as C-N-C, N-(C), S=O, C-S, Se-Se, and H-Se-C linkages. The high atomic ratios of heteroatoms and the existence of H-Se-C linkages and oxidized S=O groups imply that doping probably was not constricted in the core of the CQDs but in addition functionalized their surfaces too. Furthermore, the findings of the work correlated the electronegativity of the doping heteroatoms with the emitted wavelength of the relevant doped CQDs as blue shift of the fluorescence spectrum was observed for the N-doped CQDs while S or Se doping induces red shift (Fig. 8).

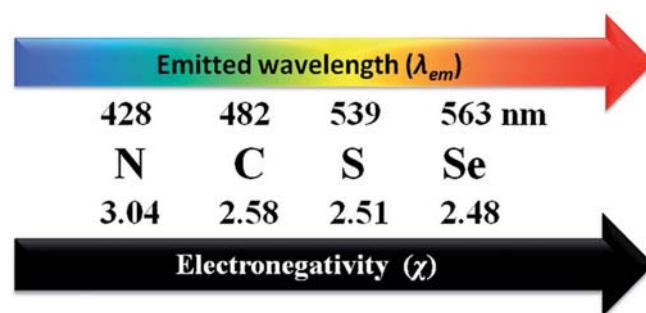


Fig. (8). The relationship between the electronegativity of heteroatoms and the λ_{em} of relevant doped CQDs. (Reproduced with permission from ref. [55]).

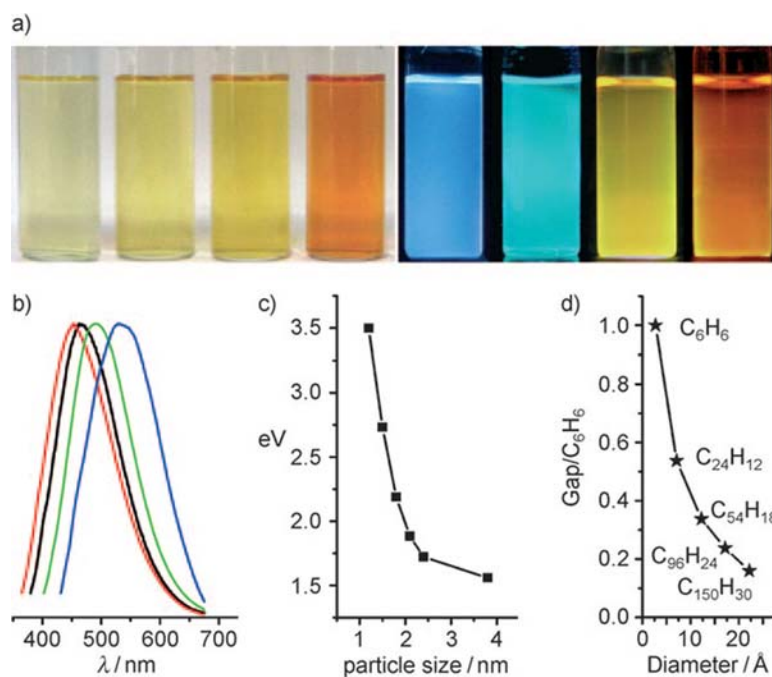


Fig. (9). a) Typical sized CQDs optical images illuminated under white (left; daylight lamp) and UV light (right; 365 nm); b) PL spectra of typical sized CQDs: the red, black, green, and blue lines are the PL spectra for blue-, green-, yellow-, and red-emission CQDs, respectively; c) relationship between the CQDs size and the PL properties; d) HOMO–LUMO gap dependence on the size of the graphitene fragments. (Reproduced with permission from ref. [75]).

Alternative Routes and Recent Advances on One-step Pyrolysis and Hydrothermal Treatment Approaches

Jiang and co-workers described an alternative one-step methodology for developing amino-functionalized CQDs [22]. Synthesis was realized inside a submerged-arc plasma reactor by using benzene as carbon source and ethylenediamine as modifying agent. Plasma generated highly reactive free radical sites that interacted with amines and resulted to final materials with primary amine functionalities.

In a different approach, Anilkumar and colleagues oxidized the surfaces of CQDs with nitric acid, dispersed the oxidized CQDs in DMF and added $Zn(OOCCH_3)_2 \cdot 2H_2O$ under vigorous stirring. Zinc cations were attracted by the negative charge of the surface oxygen functionalities and after slow dropwise addition of an aqueous Na_2S solution, ZnS nanoparticles were formed on a fraction of the CQDs' surfaces [129], relatively to the way Sun's group had developed previously ZnS-doped carbon nanoparticles [126].

On the other hand, Li *et al.* did not go with the flow and used alkali conditions to formulate high quality CQDs with stable photoluminescence and a quantum yield of about 12% (Fig. 9) [75]. CQDs were synthesized electrochemically with a relatively low sodium hydroxide concentration (0.05–0.1 N). Nonetheless, as in the case of acid treatment, the produced CQDs also possess oxygen functionalities at their surfaces as carboxyl, carbonyl, and hydroxyl groups.

In a short time period, Liu's team reported a series of synthetic processes for nitrogen-doped CQDs [29, 74, 165, 166]. At first, the carbon nitride dots as named by the group due to their nitrogen content, were synthesized with the co-polymerization of carbon tetrachloride and 1,2-ethylenediamine either at 80 °C for 60 min, or microwave-assisted for 3.5 min, or solvothermally at 150 °C for 120 min [165]. Subsequently, CQDs were produced by microwave irradiation of N,N-dimethylformamide assisted by acids as chlorosulfonic acid, H_2SO_4 , HCl, or HNO_3 [166]. Then, the same acids

were used to support the CQDs formation with microwave heat-treatment of various organic amines such as dimethylamine, ethylamine or tripropylamine [74]. Finally, a diverse approach was followed in their last work, where the hydrothermal treatment of grass at 180 °C was employed [29]. In all cases, fluorescent CQDs with various nitrogen-containing groups were formed; implying that proper selection of the precursors or applied technique can lead to tuned fluorescent CQDs.

Whereas acid treatment is regularly applied for oxidizing pristine CQDs introducing surface oxygen functional groups, Zheng *et al.* stepped further and performed in addition reduction with sodium borohydride [160]. The reduced CQDs contained also oxygen functionalities only this time there were formed significantly more hydroxyls compared to other groups and to oxidized CQDs. As a result the acid-treated oxidized CQDs exhibited green luminescence attributed to surface energy traps with low quantum yield, while in contrary the reduced CQDs displayed blue luminescence attributed to zig-zag sites with high quantum yield. As confirmed by their results, the enhanced luminescence of the reduced CQDs originated by the high concentration of the surface hydroxyl groups which are known electron-donors. Another conventional reductant, hydrazine hydrate, was employed by Zhang and co-workers for grafting nitrogen containing groups on the surfaces of CQDs [104]. The group prepared CQDs with the electrolysis of graphite rods in NaOH aqueous solution, followed by reduction treatment with hydrazine hydrate for about 500 min. XPS spectroscopy besides the expected decrease of oxygen-bearing groups revealed the formation of hydrazide groups ($O=C-NH-NH_2$).

In advance, Linehan and Doyle prepared lipophilic CQDs by using lithium aluminium hydride ($LiAlH_4$) for the essential reduction [162]. Carbon tetrachloride was dissolved within the hydrophilic interior of a tetraoctyl ammonium bromide reverse micelle and it was reduced with $LiAlH_4$ to form hydrogen-terminated CQDs confined within the micelle interior. The surface of the as-

synthesized CQDs was then modified with dodecane using a platinum-catalyzed process to form C–C bonds, leading to chemically passivated CQDs and minimizing their oxidation. The procedure resulted to highly monodisperse dodecane-capped CQDs with an average diameter of 1.5 ± 0.3 nm. The same synthetic procedure was followed for the production of amine-terminated CQDs by simply substituting dodecane with allylamine, resulting to dispersible in polar solvents CQDs with blue luminescence and a quantum yield of 25% [163].

Contrariwise, Jiang and colleagues used a highly oxidizing agent, namely hydrogen peroxide, to acquire CQDs from graphene oxide (GO). GO was further oxidized and fragmented by H_2O_2 while ammonia was added in the reaction pot so as to introduce amine surface groups. The reaction was carried out for 24 h at 80 °C and resulted to N-doped CQDs with exceptionally high nitrogen content of above 15% as confirmed by XPS analysis. Amide bonds were formed while protonated amines and various oxygen functional groups decorated the CQDs' surfaces [28]. Ammonia as modifying agent and nitrogen source was also used by Ma and co-workers [25]. The group presented a novel method for the one-pot synthesis of water-dispersible CQDs with the ultrasonic treatment of a glucose-ammonia solution for 24 h at RT; obtaining nitrogen-doped CQDs as confirmed by FT-IR and XPS spectroscopies. Nitrogen containing surface groups and mainly amines were once again incorporated in the CQDs produced by Yang *et al.* [32]. Chitosan was used as dual carbon and nitrogen source, and upon hydrothermal carbonization at 180 °C, highly amino-functionalized fluorescent CQDs were acquired through the dehydration of chitosan.

The influence of varied surface oxygen groups in the luminescence of CQDs was studied by Chandra *et al.* [56]. The group prepared three different types of CQDs based on three individual biocompatible and biodegradable polysaccharides, *i.e.* chitosan, alginate, and starch. The chitosan derived CQDs contained a high concentration of primary amine surface groups and almost no carboxyls. In contrast, alginate derived CQDs exhibited high numbers from carboxyl groups, while the starch derived CQDs displayed mainly carbonyl and hydroxyl groups. The differences in the composition of the surface functional groups have an impact to the quantum yields and thus the relevant photoluminescence intensities. In addition, when various organic solvents as triethanol amine and diethylene glycol are present during the synthesis of the three diverse carbon dot materials, their wavelength emission is changed in different ways. Therefore, same solvent may cause blue shift to one sample and red shift to the other. This behavior is also observed with the addition of various divalent metal ions and is attributed to the different concentration of the surface oxygen functional groups between the three types of CQDs. As a consequence, by selecting the appropriate precursor and solvent or cation for post modification, the surface functional groups and the photoluminescence properties may be tuned as desired. The ability to control the lipophilicity/hydrophilicity and photoluminescence of CQDs based on the precursor selection was exploited in advance by Hola and colleagues [140]. Three different alkyl groups (methyl, propyl, and lauryl) were used to produce the relevant esters of gallic acid which were further pyrolyzed at 270 °C for 2 h in air. Findings indicate that not only the size and hydrophilicity of grown CQDs are depended by the alkyl chain length but also their luminescence properties.

Further and advanced studies of the CQDs' luminescence and its origin have been conducted recently. Guldi's group published in 2014 a comprehensive study on the CQDs' photoluminescence

properties by preparing two different types of CQDs; a simple batch was acquired microwave-assisted at ambient pressure while a second batch of CQDs was obtained in a microwave reactor at 15 bar by using in both cases citric acid and urea as precursors [57]. The pressure used for the second batch, forced the gaseous by-products to remain inside the reacting solution, causing a premature termination of the CQDs creation which led to CQDs with narrow and excitation-independent emission. In contrast, if pressure is not applied, the formed CQDs demonstrate broad emission. Experimental and theoretical analyses denote that a sp^2 -hybridized carbon network may be the origin of the intrinsic fluorescent emission of CQDs at short wavelengths, whereas alternative deactivation pathways are responsible for redshifted emissions. Furthermore, the pressurized CQDs may act either as electron donors or as electron acceptors, depending on the substances they are combined with.

In 2015, Hu and colleagues stepped further and managed to prepare a series of CQDs with tunable photoluminescence throughout the entire visible spectrum when excited by white light [58]. CQDs were formed by the pyrolysis at 180 °C of either citric acid or ethylene glycol mixed in both cases with ethylenediamine end-capped polyethylenimine. Accordingly, CQDs with main PL emission peaks at 530-550 nm were acquired. If a reducing agent, *i.e.* $NaBH_4$, was added in the starting reaction system of citric acid, the formed CQDs exhibited blueshifted PL emissions from violet to yellow, depended on the amount of $NaBH_4$ added. In contrast, if a dehydrating agent, *i.e.* H_3PO_4 , was added in the ethylene glycol system, the PL emissions were redshifted from yellow to red. The final CQDs displayed an excitation-independent PL emission which was directly correlated to the oxygen and nitrogen containing groups of the CQDs. Thus, nitrogen content decreases, while oxygen's increases with redshifted PL emission. In addition, the insertion of oxygen functionalities introduces more electronic states between the bandgap leading this way to redshift and decreased quantum yields. Overall, experimental proofs confirmed theoretical calculations and showed that CQDs that emitted from blue to red light possessed gradually more epoxide and hydroxyl groups and less C=O and C-N bonds in this direction, *i.e.* redshifting.

Once again in literature, the low carbonization temperature of citric acid was exploited by Dong *et al.* and it was used as carbon source in a one-step synthesis of passivated/functionalized CQDs [65, 81, 83]. For this reason branched polyethylenimine (BPEI) was also used having the dual role of passivation and functionalization. Synthesis was performed at 200 °C so as BPEI did not degenerate and due to the high amine content of BPEI, the final CQDs correspondingly possessed many amine surface functional groups. By taking advantage of these groups, Dong's team utilized the resulting CQDs as chemical sensors and copper ions detector. On the other hand, Han *et al.* managed to graft polyethylenimine on the surfaces of glucose derived CQDs with a simple reaction at 80 °C for 3 h, with the final functionalized CQDs bearing amine surface groups as confirmed by FT-IR spectroscopy [102]. In addition, Gao and colleagues by using microwaves achieved the preparation of polyamidoamine dendrimers capped-carbon dots [66]. Citric acid was co-polymerized together with polyamidoamine in a microwave oven reaction at 170 °C for 20 min resulting to the amine derivative CQDs. Microwave-assisted and amine-bearing were also the CQDs developed by Qu *et al.* [136] and Niu *et al.* [67]. In both cases, citric acid and urea were heated for a few minutes in a domestic microwave device producing N-doped CQDs.

The one-step pyrolysis was adopted by Guo and co-workers too [88]. By pyrolyzing the photonic crystal poly(styrene-co-

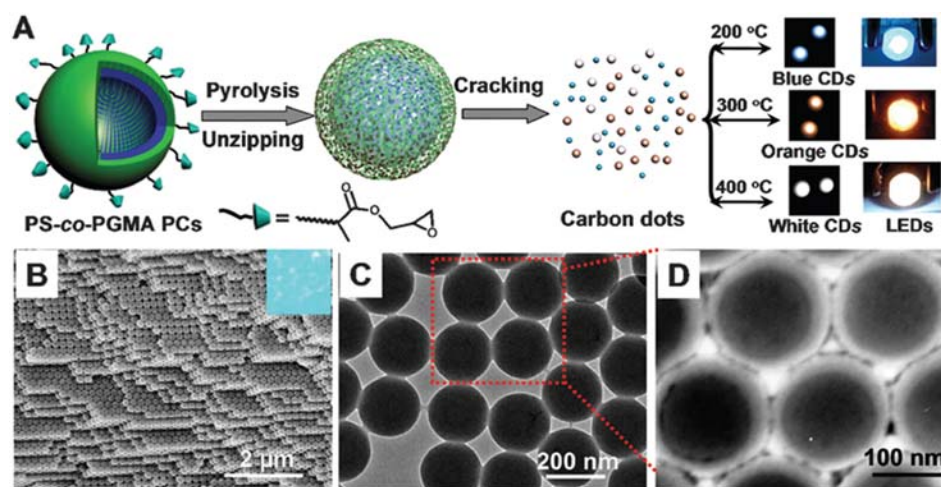


Fig. (10). (A) Schematic representation of the formation of carbon dots from the pyrolysis of photonic crystals. (B) The cross-section SEM image and (C and D) TEM images of PS-co-PGMA core-shell photonic crystals. The inset in (B) is the optical micrograph of the PS-co-PGMA photonic crystal film. (Reproduced with permission from ref. [88]).

glycidylmethacrylate) (PS-co-PGMA) at 200, 300, and 400 °C they managed to acquire CQDs with tunable blue, orange or white photoluminescence emission (Fig. 10). The as-prepared CQDs demonstrated high quantum yields of up to 47% and high solubility in water and organic solvents. Further analysis with characterization techniques revealed that all three types of CQDs possessed carbonyl, hydroxyl but also carboxyl surface groups.

A one-step route was also followed by Zhang *et al.* [167]. By carbonizing at a relatively low temperature carbon tetrachloride in the presence of sodium amide (NaNH_2) as a dechlorination reagent and nitrogen source, a nitrogen-doped CQDs material was obtained, exhibiting nitrogen atoms in a graphite-like structure, pyridinic-like N, pyrrolic-like N, and N-H groups.

In addition, graphene QDs demonstrate small layer dimensions (<10 nm) so as their 1D nature simulates the 0D character of classical carbon QDs. Similarly to CQDs they do exhibit strong fluorescence and thus are also in the research spotlight. In this direction, Li *et al.* employed a bottom-up solution chemistry approach to obtain nitrogen-doped graphene QDs [77]. According to their procedure, CQDs with controlled nitrogen atoms content and defined bonding configurations could be produced. Starting from substituted benzene derivatives such as 2-bromo-5-iodo-3'-(phenylethynyl)-1,1'-biphenyl and phenylboronic acid or from an α,β -diketone and after a series of organic reactions such as Wittig reaction, Suzuki coupling reaction and oxidative dehydrogenation, nitrogen-doped colloidal graphene quantum dots with well-defined structures are formed. At the same time, Li and co-workers presented another N-doped graphene dots material with oxygen-rich functional groups [164]. The group managed to produce the nitrogen containing GQDs *via* an *in situ* electrochemical approach by adding tetrabutylammonium perchlorate as the nitrogen source in the acetonitrile electrolyte solution. XPS spectroscopy verified the presence of amines, hydroxyls, carbonyls and carboxyl groups.

Hydrothermal treatment was also the case of the surfactant-derived amphiphilic CQDs fabricated by Kozák *et al.* [151]. A basic aqueous solution of the cationic surfactant cetylpyridinium chloride monohydrate was heated at 150 °C for 2 h in a Teflon-lined stainless steel autoclave under hydrothermal conditions ending up to the formation CQDs that possessed various nitrogen containing functional groups as N-H and C=N. In a different approach, di-

methylamines were grafted on graphene oxide-derived CQDs as described by Liu *et al.* [106]. Using N,N-dimethylformamide as solvent and nitrogen source, strong two-photon-induced fluorescent N-doped CQDs were fabricated solvothermally at 200 °C for 4.5 h which proved to be both photostable and biocompatible. In a comprehensive work by Qu and co-workers later on, a systematic study of the formation mechanism and optimization for obtaining highly luminescent N-doped CQDs was performed [154]. The group used citric acid as carbon source to form CQDs hydrothermally at 160 °C for 4 h, and employed various precursors as nitrogen source for doping and functionalization. Urea, hexamethylenetetramine, diethylamine, ethanolamine, and ethylenediamine were tested with the latter exhibiting the highest reported photoluminescence quantum yield of 94% for N-doped CQDs.

Recently, Chen *et al.* prepared CQDs with surface carboxyl and amine groups upon the hydrothermal treatment of ethylenediaminetetraacetic acid as carbon source and triethylenetetramine as passivation agent [155]. Both precursors served also as ligands to coordinate with Tb^{3+} ions and chelate them, thus further modifying the surface of the formed CQDs. In advance, Hou and co-workers treated hydrothermally at 200 °C for 5 h citric acid and L-tyrosine methyl ester hydrochloride [156], and *via* polymerization, carbonization and amidation reactions, managed to fabricate CQDs that bear tyrosinate groups on their surfaces.

Contrariwise, Liu's group followed a noncovalent functionalization route for modifying the surface of as-prepared CQDs [157]. Initially, CQDs were developed by the microwave-assisted hydrothermal carbonization of a glucose and poly(acrylate sodium) mixture; and then, folic acid was attached on the surface *via* hydrogen-bond interactions. Lou *et al.* described lately the formation of supra-structures from CQDs based on self-assembly [93]. Nitrogen-doped CQDs were fabricated from citric acid and urea, and further on, the amide surface groups were partially reacted with 1-bromododecane. The incomplete reaction led to amphiphilic CQDs with both hydrophilic amide and hydrophobic dodecyl surface groups. As a result, these CQDs can self-assemble towards supra-CD systems in the form of agglomerates through amphiphilic interactions in toluene exhibiting quenched luminescence.

Lastly, in a totally different, from the aforementioned, approach for surface functionalization, Cheng *et al.* employed polymer sci-

ence chemistry for acquiring modified CQDs for biological applications [112]. The surface functionalized CQDs were prepared *via* surface-initiated atom transfer radical polymerization (ATRP) of a polycation-*b*-polysulfobetaine block copolymer, namely poly[2-(dimethylamino) ethyl methacrylate]-*b*-poly[*N*-(3-(methacryloylamino) propyl)-*N,N*-dimethyl-*N*-(3-sulfopropyl) ammonium hydroxide]. The final dots possessed grafted polymer chains that acted as DNA condensing agents and protective layers from undesired interactions.

Advantages and Disadvantages of Applied Methodologies

The diversity of the applied methodologies for the production of CQDs offers researchers a variety of possible routes aiming the best and desired properties for their CQDs. An ideal procedure would use low-cost abundant raw materials, would be easy, reproducible and cost-effective, fabricating stable CQDs with high quantum yields and excitation-independent PL emission, able to be tailored made, with controllable and narrow size distribution and handy surface functionalization and doping. Apparently, none of the existing approaches gathers altogether the aforementioned advantages. Thus, acid or alkali treatment or in general post-synthetic oxidation or reduction might be easy but the same time costly, not reproducible with low control of the surface functionalization. One-step pyrolysis is again easy but in most cases the photoluminescence and physicochemical (such as size) properties of the obtained CQDs are not predefined as desired but rather their PL emission and properties guide the researchers to find real-world applications. Microwave-assisted, hydrothermal and solvothermal routes offer a true convenience regarding the time needed for preparing CQDs but possess the same disadvantages one-step pyrolysis has. Finally, organic surface functionalization with appropriate molecules and organosilanes may tune significant properties as PL emission wavelength, surface charge, electronegativity, hydrophilicity, etc. but on the other hand might be expensive and as a post-synthetic method it leaves intact the core of the CQDs and probably much of their PL properties and cannot control core's size which means that it should be combined with a synthetic method that controls the abovementioned. Therefore, an advanced approach aiming to high quality CQDs should comprise advantages of probably a hydrothermal or microwave-assisted one-step pyrolysis of appropriate precursors and a post-synthetic organic surface functionalization.

CONCLUSIONS AND PERSPECTIVES

Surface passivation and functionalization of CQDs over the past years has expanded their applicability. Introduction and doping with appropriate heteroatoms is the key point to tailor made features of CQDs and thus organic chemistry provides the vital background for the essential functionalizations. Recently, the significance of CQDs' doping has received the attention that it deserves; however, there are yet some aspects to be addressed. More important is that the CQDs' structure and specifically the dopants-bearing groups are not predefined when doping comes of a one-step pyrolysis of proper precursors that is the most common approach, but rather varied dopant-containing groups are formed which in advance may not functionalize the surfaces but just dope the CDQs' core. On the other hand, since organic chemistry is a powerful tool that enables the successful modification of various structures (among them and CQDs), functionalization and doping of CQDs seems still a virgin field and there are many reactions/modifications that can be made. Attachment of organometallic compounds and consequently of noble metallic centers such as Au and Pt or transition metals as Cu,

Fe and Zn may enhance or reveal new catalytic, sensing or other properties. In addition, covalent bonding of biomolecules or crucial trace elements like N, S and P may create new prospects in bioimaging and biological delivery systems.

CONFLICT OF INTEREST

The author confirms that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

Declared none.

REFERENCES

- Xu, X.; Ray, R.; Gu, Y.; Ploehn, H.J.; Gearheart, L.; Raker, K.; Scrivens, W. A. Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *J. Am. Chem. Soc.*, **2004**, *126*(40), 12736-12737.
- Riggs, J.E.; Guo, Z.; Carroll, D.L.; Sun, Y.P. Strong luminescence of solubilized carbon nanotubes. *J. Am. Chem. Soc.*, **2000**, *122*(24), 5879-5880.
- Lim, S.Y.; Shen, W.; Gao, Z. Carbon quantum dots and their applications. *Chem. Soc. Rev.*, **2015**, *44*(1), 362-381.
- Wang, Y.; Hu, A. Carbon quantum dots: Synthesis, properties and applications. *J. Mater. Chem. C*, **2014**, *2*(34), 6921-6939.
- Li, H.; Kang, Z.; Liu, Y.; Lee, S.T. Carbon nanodots: Synthesis, properties and applications. *J. Mater. Chem.*, **2012**, *22*(46), 24230-24253.
- Shen, J.; Zhu, Y.; Yang, X.; Li, C. Graphene quantum dots: Emergent nanolights for bioimaging, sensors, catalysis and photovoltaic devices. *Chem. Commun.*, **2012**, *48*(31), 3686-3699.
- Baker, S.N.; Baker, G.A. Luminescent carbon nanodots: Emergent nanolights. *Angew. Chem. Int. Ed.*, **2010**, *49*(38), 6726-6744.
- Ding, C.; Zhu, A.; Tian, Y. Functional surface engineering of C-dots for fluorescent biosensing and in vivo bioimaging. *Acc. Chem. Res.*, **2014**, *47*(1), 20-30.
- Luo, P.G.; Yang, F.; Yang, S.T.; Sonkar, S.K.; Yang, L.; Broglie, J.J.; Liu, Y.; Sun, Y.P. Carbon-based quantum dots for fluorescence imaging of cells and tissues. *RSC Adv.*, **2014**, *4*(21), 10791-10807.
- Li, J.; Zhu, J.J. Quantum dots for fluorescent biosensing and bio-imaging applications. *Analyst*, **2013**, *138*(9), 2506-2515.
- Luo, P.G.; Sahu, S.; Yang, S.T.; Sonkar, S.K.; Wang, J.; Wang, H.; LeCroy, G.E.; Cao, L.; Sun, Y.P. Carbon "quantum" dots for optical bioimaging. *J. Mater. Chem. B*, **2013**, *1*(16), 2116-2127.
- Zhao, A.; Chen, Z.; Zhao, C.; Gao, N.; Ren, J.; Qu, X. Recent advances in bioapplications of C-dots. *Carbon*, **2015**, *85*, 309-327.
- Hola, K.; Zhang, Y.; Wang, Y.; Giannelis, E.P.; Zboril, R.; Rogach, A.L. Carbon dots-Emerging light emitters for bioimaging, cancer therapy and optoelectronics. *Nano Today*, **2014**, *9*(5), 590-603.
- Sun, Y.P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K.A.S.; Pathak, P.; Mezziani, M.J.; Harruff, B.A.; Wang, X.; Wang, H.; Luo, P.G.; Yang, H.; Kose, M.E.; Chen, B.; Veca, L.M.; Xie, S.Y. Quantum-sized carbon dots for bright and colorful photoluminescence. *J. Am. Chem. Soc.*, **2006**, *128*(24), 7756-7757.
- Liu, H.; Ye, T.; Mao, C. Fluorescent carbon nanoparticles derived from candle soot. *Angew. Chem. Int. Ed.*, **2007**, *46*(34), 6473-6475.
- Zhou, J.; Booker, C.; Li, R.; Zhou, X.; Sham, T.K.; Sun, X.; Ding, Z. An electrochemical avenue to blue luminescent nanocrystals from multiwalled carbon nanotubes (MWCNTs). *J. Am. Chem. Soc.*, **2007**, *129*(4), 744-745.
- Bourlinos, A.B.; Stassinopoulos, A.; Anglos, D.; Zboril, R.; Karakassides, M.; Giannelis, E.P. Surface functionalized carbogenic quantum dots. *Small*, **2008**, *4*(4), 455-458.
- Bourlinos, A.B.; Stassinopoulos, A.; Anglos, D.; Zboril, R.; Georgakilas, V.; Giannelis, E.P. Photoluminescent carbogenic dots. *Chem. Mater.*, **2008**, *20*(14), 4539-4541.
- Peng, H.; Travas-Sejdic, J. Simple aqueous solution route to luminescent carbogenic dots from carbohydrates. *Chem. Mater.*, **2009**, *21*(23), 5563-5565.
- Liu, R.; Wu, D.; Liu, S.; Koynov, K.; Knoll, W.; Li, Q. An aqueous route to multicolor photoluminescent carbon dots using silica spheres as carriers. *Angew. Chem.*, **2009**, *121*(25), 4668-4671.
- Zhu, H.; Wang, X.; Li, Y.; Wang, Z.; Yang, F.; Yang, X. Microwave synthesis of fluorescent carbon nanoparticles with electrochemiluminescence properties. *Chem. Commun.*, **2009**, (34), 5118-5120.
- Jiang, H.; Chen, F.; Lagally, M.G.; Denes, F.S. New strategy for synthesis and functionalization of carbon nanoparticles. *Langmuir*, **2010**, *26*(3), 1991-1995.
- Lu, J.; Yeo, P.S.E.; Gan, C.K.; Wu, P.; Loh, K.P. Transforming C60 molecules into graphene quantum dots. *Nat. Nanotechnol.*, **2011**, *6*(4), 247-252.
- Wang, Q.; Zheng, H.; Long, Y.; Zhang, L.; Gao, M.; Bai, W. Microwave-hydrothermal synthesis of fluorescent carbon dots from graphite oxide. *Carbon*, **2011**, *49*(9), 3134-3140.

- [25] Ma, Z.; Ming, H.; Huang, H.; Liu, Y.; Kang, Z. One-step ultrasonic synthesis of fluorescent N-doped carbon dots and their visible-light sensitive photocatalytic ability. *New J. Chem.*, **2012**, 36(4), 861-864.
- [26] Kwon, W.; Rhee, S.W. Facile synthesis of graphitic carbon quantum dots with size tunability and uniformity using reverse micelles. *Chem. Commun.*, **2012**, 48(43), 5256-5258.
- [27] Jia, X.; Li, J.; Wang, E. One-pot green synthesis of optically pH-sensitive carbon dots with upconversion luminescence. *Nanoscale*, **2012**, 4(18), 5572-5575.
- [28] Jiang, F.; Chen, D.; Li, R.; Wang, Y.; Zhang, G.; Li, S.; Zheng, J.; Huang, N.; Gu, Y.; Wang, C.; Shu, C. Eco-friendly synthesis of size-controllable amine-functionalized graphene quantum dots with antimycoplasm properties. *Nanoscale*, **2012**, 5(3), 1137-1142.
- [29] Liu, S.; Tian, J.; Wang, L.; Zhang, Y.; Qin, X.; Luo, Y.; Asiri, A.M.; Al-Youbi, A.O.; Sun, X. Hydrothermal treatment of grass: A low-cost, green route to nitrogen-doped, carbon-rich, photoluminescent polymer nanodots as an effective fluorescent sensing platform for label-free detection of Cu(II) ions. *Adv. Mater.*, **2012**, 24(15), 2037-2041.
- [30] Sahu, S.; Behera, B.; Maiti, T.K.; Mohapatra, S. Simple one-step synthesis of highly luminescent carbon dots from orange juice: Application as excellent bio-imaging agents. *Chem. Commun.*, **2012**, 48(70), 8835-8837.
- [31] Wang, J.; Wang, C.F.; Chen, S. Amphiphilic egg-derived carbon dots: Rapid plasma fabrication, pyrolysis process, and multicolor printing patterns. *Angew. Chem.*, **2012**, 124(37), 9431-9435.
- [32] Yang, Y.; Cui, J.; Zheng, M.; Hu, C.; Tan, S.; Xiao, Y.; Yang, Q.; Liu, Y. One-step synthesis of amino-functionalized fluorescent carbon nanoparticles by hydrothermal carbonization of chitosan. *Chem. Commun.*, **2012**, 48(3), 380-382.
- [33] Lai, C.W.; Hsiao, Y.H.; Peng, Y.K.; Chou, P.T. Facile synthesis of highly emissive carbon dots from pyrolysis of glycerol; gram scale production of carbon dots/mSiO₂ for cell imaging and drug release. *J. Mater. Chem.*, **2012**, 22(29), 14403-14409.
- [34] Wang, W.; Lu, Y.C.; Huang, H.; Feng, J.J.; Chen, J.R.; Wang, A.J. Facile synthesis of water-soluble and biocompatible fluorescent nitrogen-doped carbon dots for cell imaging. *Analyst*, **2014**, 139(7), 1692-1696.
- [35] Huang, H.; Lu, Y.C.; Wang, A.J.; Liu, J.H.; Chen, J.R.; Feng, J.J. A facile, green, and solvent-free route to nitrogen-sulfur-codoped fluorescent carbon nanoparticles for cellular imaging. *RSC Adv.*, **2014**, 4(23), 11872-11875.
- [36] De, B.; Karak, N. A green and facile approach for the synthesis of water soluble fluorescent carbon dots from banana juice. *RSC Adv.*, **2013**, 3(22), 8286-8290.
- [37] Li, W.; Zhang, Z.; Kong, B.; Feng, S.; Wang, J.; Wang, L.; Yang, J.; Zhang, F.; Wu, P.; Zhao, D. Simple and green synthesis of nitrogen-doped photoluminescent carbonaceous nanospheres for bioimaging. *Angew. Chem. Int. Ed.*, **2013**, 52(31), 8151-8155.
- [38] Liang, Q.; Ma, W.; Shi, Y.; Li, Z.; Yang, X. Easy synthesis of highly fluorescent carbon quantum dots from gelatin and their luminescent properties and applications. *Carbon*, **2013**, 60, 421-428.
- [39] Sun, D.; Ban, R.; Zhang, P.H.; Wu, G.H.; Zhang, J.R.; Zhu, J.J. Hair fiber as a precursor for synthesizing of sulfur- and nitrogen-co-doped carbon dots with tunable luminescence properties. *Carbon*, **2013**, 64, 424-434.
- [40] Wu, Z.L.; Zhang, P.; Gao, M.X.; Liu, C.F.; Wang, W.; Leng, F.; Huang, C.Z. One-pot hydrothermal synthesis of highly luminescent nitrogen-doped amphoteric carbon dots for bioimaging from Bombyx mori silk - natural proteins. *J. Mater. Chem. B*, **2013**, 1(22), 2868-2873.
- [41] Fan, R.J.; Sun, Q.; Zhang, L.; Zhang, Y.; Lu, A.H. Photoluminescent carbon dots directly derived from polyethylene glycol and their application for cellular imaging. *Carbon*, **2014**, 71, 87-93.
- [42] Hu, Q.; Paau, M.C.; Zhang, Y.; Gong, X.; Zhang, L.; Lu, D.; Liu, Y.; Liu, Q.; Yao, J.; Choi, M.M.F. Green synthesis of fluorescent nitrogen/sulfur-doped carbon dots and investigation of their properties by HPLC coupled with mass spectrometry. *RSC Adv.*, **2014**, 4(35), 18065-18073.
- [43] Huang, H.; Li, C.; Zhu, S.; Wang, H.; Chen, C.; Wang, Z.; Bai, T.; Shi, Z.; Feng, S. Histidine-derived nontoxic nitrogen-doped carbon dots for sensing and bioimaging applications. *Langmuir*, **2014**, 30(45), 13542-13548.
- [44] Liu, Y.; Zhao, Y.; Zhang, Y. One-step green synthesized fluorescent carbon nanodots from bamboo leaves for copper(II) ion detection. *Sensors Actuat. B-Chem.*, **2014**, 196, 647-652.
- [45] Li, Y.; Zhong, X.; Rider, A.E.; Furman, S.A.; Ostrikov, K. Fast, energy-efficient synthesis of luminescent carbon quantum dots. *Green Chem.*, **2014**, 16(5), 2566-2570.
- [46] Teng, X.; Ma, C.; Ge, C.; Yan, M.; Yang, J.; Zhang, Y.; Morais, P.C.; Bi, H. Green synthesis of nitrogen-doped carbon dots from konjac flour with "off-on" fluorescence by Fe³⁺ and L-lysine for bioimaging. *J. Mater. Chem. B*, **2014**, 2(29), 4631-4639.
- [47] Wang, W.; Lu, Y.C.; Huang, H.; Wang, A.J.; Chen, J.R.; Feng, J.J. Solvent-free synthesis of sulfur- and nitrogen-co-doped fluorescent carbon nanoparticles from glutathione for highly selective and sensitive detection of mercury(II) ions. *Sensors Actuat. B-Chem.*, **2014**, 202, 741-747.
- [48] Yang, Z.; Xu, M.; Liu, Y.; He, F.; Gao, F.; Su, Y.; Wei, H.; Zhang, Y. Nitrogen-doped, carbon-rich, highly photoluminescent carbon dots from ammonium citrate. *Nanoscale*, **2014**, 6(3), 1890-1895.
- [49] Zhang, Z.; Shi, Y.; Pan, Y.; Cheng, X.; Zhang, L.; Chen, J.; Li, M.J.; Yi, C. Quinoline derivative-functionalized carbon dots as a fluorescent nanosensor for sensing and intracellular imaging of Zn²⁺. *J. Mater. Chem. B*, **2014**, 2(31), 5020-5027.
- [50] Bourlinos, A.B.; Trivizas, G.; Karakassides, M.A.; Baikousi, M.; Kouloumpis, A.; Gournis, D.; Bakandritsos, A.; Hola, K.; Kozak, O.; Zboril, R.; Papagiannouli, I.; Aloukos, P.; Couris, S. Green and simple route toward boron doped carbon dots with significantly enhanced non-linear optical properties. *Carbon*, **2015**, 83, 173-179.
- [51] Liu, R.; Zhang, J.; Gao, M.; Li, Z.; Chen, J.; Wu, D.; Liu, P. A facile microwave-hydrothermal approach towards highly photoluminescent carbon dots from goose feathers. *RSC Adv.*, **2015**, 5(6), 4428-4433.
- [52] Hsu, P.C.; Shih, Z.Y.; Lee, C.H.; Chang, H.T. Synthesis and analytical applications of photoluminescent carbon nanodots. *Green Chem.*, **2012**, 14(4), 917-920.
- [53] Mao, X.J.; Zheng, H.Z.; Long, Y.J.; Du, J.; Hao, J.Y.; Wang, L.L.; Zhou, D.B. Study on the fluorescence characteristics of carbon dots. *Spectrochim. Acta Mol. Biomol.*, **2010**, 75(2), 553-557.
- [54] Hu, Y.; Yang, J.; Tian, J.; Jia, L.; Yu, J.S. Waste frying oil as a precursor for one-step synthesis of sulfur-doped carbon dots with pH-sensitive photoluminescence. *Carbon*, **2014**, 77, 775-782.
- [55] Yang, S.; Sun, J.; Li, X.; Zhou, W.; Wang, Z.; He, P.; Ding, G.; Xie, X.; Kang, Z.; Jiang, M. Large-scale fabrication of heavy doped carbon quantum dots with tunable-photoluminescence and sensitive fluorescence detection. *J. Mater. Chem. A*, **2014**, 2(23), 8660-8667.
- [56] Chandra, S.; Pathan, S.H.; Mitra, S.; Modha, B.H.; Goswami, A.; Pramanik, P. Tuning of photoluminescence on different surface functionalized carbon quantum dots. *RSC Adv.*, **2012**, 2(9), 3602-3606.
- [57] Strauss, V.; Margraf, J.T.; Dolle, C.; Butz, B.; Nacken, T.J.; Walter, J.; Bauer, W.; Peukert, W.; Spiecker, E.; Clark, T.; Guldi, D.M. Carbon nanodots - toward a comprehensive understanding of their photoluminescence. *J. Am. Chem. Soc.*, **2014**, 136(49), 17308-17316.
- [58] Hu, S.; Trinchi, A.; Atkin, P.; Cole, I. Tunable photoluminescence across the entire visible spectrum from carbon dots excited by white light. *Angew. Chem. Int. Ed.*, **2015**, 54(10), 2970-2974.
- [59] Wang, X.; Cao, L.; Lu, F.; Mezzani, M.J.; Li, H.; Qi, G.; Zhou, B.; Harruff, B.A.; Kermarrec, F.; Sun, Y.P. Photoinduced electron transfers with carbon dots. *Chem. Commun.*, **2009**, (25), 3774-3776.
- [60] Zheng, L.; Chi, Y.; Dong, Y.; Lin, J.; Wang, B. Electrochemiluminescence of water-soluble carbon nanocrystals released electrochemically from graphite. *J. Am. Chem. Soc.*, **2009**, 131(13), 4564-4565.
- [61] Dong, Y.; Zhou, N.; Lin, X.; Lin, J.; Chi, Y.; Chen, G. Extraction of electrochemiluminescent oxidized carbon quantum dots from activated carbon. *Chem. Mater.*, **2010**, 22(21), 5895-5899.
- [62] Gonçalves, H.; Jorge, P.A.S.; Fernandes, J.R.A.; Esteves da Silva, J.C.G. Hg(II) sensing based on functionalized carbon dots obtained by direct laser ablation. *Sensors Actuat. B-Chem.*, **2010**, 145(2), 702-707.
- [63] Gonçalves, H.M.R.; Duarte, A.J.; Esteves da Silva, J.C.G. Optical fiber sensor for Hg(II) based on carbon dots. *Biosens. Bioelectron.*, **2010**, 26(4), 1302-1306.
- [64] Lin, Z.; Xue, W.; Chen, H.; Lin, J.M. Peroxynitrous acid-induced chemiluminescence of fluorescent carbon dots for nitrite sensing. *Anal. Chem.*, **2011**, 83(21), 8245-8251.
- [65] Dong, Y.; Wang, R.; Li, H.; Shao, J.; Chi, Y.; Lin, X.; Chen, G. Polyamine-functionalized carbon quantum dots for chemical sensing. *Carbon*, **2012**, 50(8), 2810-2815.
- [66] Gao, Q.; Han, J.; Ma, Z. Polyamidoamine dendrimers-capped carbon dots/Au nanocrystal nanocomposites and its application for electrochemical immunosensor. *Biosens. Bioelectron.*, **2013**, 49, 323-328.
- [67] Niu, Q.; Gao, K.; Lin, Z.; Wu, W. Amine-capped carbon dots as a nanosensor for sensitive and selective detection of picric acid in aqueous solution via electrostatic interaction. *Anal. Methods*, **2013**, 5(21), 6228-6233.
- [68] Zhu, S.; Meng, Q.; Wang, L.; Zhang, J.; Song, Y.; Jin, H.; Zhang, K.; Sun, H.; Wang, H.; Yang, B. Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging. *Angew. Chem.*, **2013**, 125(14), 4045-4049.
- [69] Howes, P.D.; Chandrawati, R.; Stevens, M.M. Colloidal nanoparticles as advanced biological sensors. *Science*, **2014**, 346(6205), 1247390(1-10).
- [70] Shen, P.; Xia, Y. Synthesis-modification integration: One-step fabrication of boronic acid functionalized carbon dots for fluorescent blood sugar sensing. *Anal. Chem.*, **2014**, 86(11), 5323-5329.
- [71] Zhang, H.; Chen, Y.; Liang, M.; Xu, L.; Qi, S.; Chen, H.; Chen, X. Solid-phase synthesis of highly fluorescent nitrogen-doped carbon dots for sensitive and selective probing ferric ions in living cells. *Anal. Chem.*, **2014**, 86(19), 9846-9852.
- [72] Lu, W.; Gong, X.; Yang, Z.; Zhang, Y.; Hu, Q.; Shuang, S.; Dong, C.; Choi, M.M.F. High-quality water-soluble luminescent carbon dots for multicolor patterning, sensors, and bioimaging. *RSC Adv.*, **2015**, 5(22), 16972-16979.
- [73] Wang, C.; Xu, Z.; Cheng, H.; Lin, H.; Humphrey, M.G.; Zhang, C. A hydrothermal route to water-stable luminescent carbon dots as nanosensors for pH and temperature. *Carbon*, **2015**, 82, 87-95.
- [74] Liu, S.; Tian, J.; Wang, L.; Luo, Y.; Sun, X. A general strategy for the production of photoluminescent carbon nitride dots from organic amines and their application as novel peroxidase-like catalysts for colorimetric detection of H₂O₂ and glucose. *RSC Adv.*, **2012**, 2(2), 411-413.

- [75] Li, H.; He, X.; Kang, Z.; Huang, H.; Liu, Y.; Liu, J.; Lian, S.; Tsang, C.H.A.; Yang, X.; Lee, S.T. Water-soluble fluorescent carbon quantum dots and photocatalyst design. *Angew. Chem. Int. Ed.*, **2010**, *49*(26), 4430-4434.
- [76] Cao, L.; Sahu, S.; Anilkumar, P.; Bunker, C.E.; Xu, J.; Fernando, K.A.S.; Wang, P.; Gulians, E.A.; Tackett, K.N.; Sun, Y.P. Carbon nanoparticles as visible-light photocatalysts for efficient CO₂ conversion and beyond. *J. Am. Chem. Soc.*, **2011**, *133*(13), 4754-4757.
- [77] Li, Q.; Zhang, S.; Dai, L.; Li, L.S. Nitrogen-doped colloidal graphene quantum dots and their size-dependent electrocatalytic activity for the oxygen reduction reaction. *J. Am. Chem. Soc.*, **2012**, *134*(46), 18932-18935.
- [78] Han, Y.; Huang, H.; Zhang, H.; Liu, Y.; Han, X.; Liu, R.; Li, H.; Kang, Z. Carbon quantum dots with photoenhanced hydrogen-bond catalytic activity in aldol condensations. *ACS Catal.*, **2014**, *4*(3), 781-787.
- [79] Gupta, V.; Chaudhary, N.; Srivastava, R.; Sharma, G.D.; Bhardwaj, R.; Chand, S. Luminescent graphene quantum dots for organic photovoltaic devices. *J. Am. Chem. Soc.*, **2011**, *133*(26), 9960-9963.
- [80] Zhao, H.X.; Liu, L.Q.; Liu, Z.D.; Wang, Y.; Zhao, X.J.; Huang, C.Z. Highly selective detection of phosphate in very complicated matrixes with an off-on fluorescent probe of europium- adjusted carbon dots. *Chem. Commun.*, **2011**, *47*(9), 2604-2606.
- [81] Dong, Y.; Wang, R.; Li, G.; Chen, C.; Chi, Y.; Chen, G. Polyamine-functionalized carbon quantum dots as fluorescent probes for selective and sensitive detection of copper ions. *Anal. Chem.*, **2012**, *84*(14), 6220-6224.
- [82] Yu, C.; Li, X.; Zeng, F.; Zheng, F.; Wu, S. Carbon-dot- based ratiometric fluorescent sensor for detecting hydrogen sulfide in aqueous media and inside live cells. *Chem. Commun.*, **2013**, *49*(4), 403-405.
- [83] Dong, Y.; Wang, R.; Tian, W.; Chi, Y.; Chen, G. "Turn- on" fluorescent detection of cyanide based on polyamine- functionalized carbon quantum dots. *RSC Adv.*, **2014**, *4*(8), 3701-3705.
- [84] Zhang, R.; Chen, W. Nitrogen-doped carbon quantum dots: Facile synthesis and application as a "turn-off" fluorescent probe for detection of Hg²⁺ ions. *Biosens. Bioelectron.*, **2014**, *55*, 83-90.
- [85] Zhao, A.; Zhao, C.; Li, M.; Ren, J.; Qu, X. Ionic liquids as precursors for highly luminescent, surface-different nitrogen-doped carbon dots used for label-free detection of Cu²⁺/Fe³⁺ and cell imaging. *Anal. Chim. Acta*, **2014**, *809*, 128-133.
- [86] Ahmed, G.H.G.; Laino, R.B.; Calzon, J.A.G.; Garcia, M.E.D. Highly fluorescent carbon dots as nanoprobe for sensitive and selective determination of 4-nitrophenol in surface waters. *Microchim. Acta*, **2015**, *182*(1-2), 51-59.
- [87] Wang, R.; Xu, Y.; Zhang, T.; Jiang, Y. Rapid and sensitive detection of Salmonella typhimurium using aptamer- conjugated carbon dots as fluorescence probe. *Anal. Methods*, **2015**, *7*(5), 1701-1706.
- [88] Guo, X.; Wang, C.F.; Yu, Z.Y.; Chen, L.; Chen, S. Facile access to versatile fluorescent carbon dots toward light- emitting diodes. *Chem. Commun.*, **2012**, *48*(21), 2692-2694.
- [89] Zhang, X.; Zhang, Y.; Wang, Y.; Kalytchuk, S.; Kershaw, S.V.; Wang, Y.; Wang, P.; Zhang, T.; Zhao, Y.; Zhang, H.; Cui, T.; Wang, Y.; Zhao, J.; Yu, W.W.; Rogach, A.L. Color-switchable electroluminescence of carbon dot light-emitting diodes. *ACS Nano*, **2013**, *7*(12), 11234-11241.
- [90] Veca, L.M.; Diac, A.; Mihalache, I.; Wang, P.; LeCroy, G.E.; Pavelescu, E.M.; Gavrilă, R.; Vasile, E.; Terec, A.; Sun, Y.P. Electroluminescence of carbon 'quantum' dots - From materials to devices. *Chem. Phys. Lett.*, **2014**, *613*, 40-44.
- [91] Wang, Y.; Kalytchuk, S.; Wang, L.; Zhovtiuk, O.; Cepe, K.; Zboril, R.; Rogach, A.L. Carbon dot hybrids with oligomeric silsesquioxane: Solid-state luminophores with high photoluminescence quantum yield and applicability in white light emitting devices. *Chem. Commun.*, **2015**, *51*(14), 2950-2953.
- [92] Chandra, S.; Patra, P.; Pathan, S.H.; Roy, S.; Mitra, S.; Layek, A.; Bhar, R.; Pramanik, P.; Goswami, A. Luminescent S- doped carbon dots: An emergent architecture for multimodal applications. *J. Mater. Chem. B*, **2013**, *1*(18), 2375-2382.
- [93] Lou, Q.; Qu, S.; Jing, P.; Ji, W.; Li, D.; Cao, J.; Zhang, H.; Liu, L.; Zhao, J.; Shen, D. Water-triggered luminescent "Nano-bombs" based on supra-(carbon nanodots). *Adv. Mater.*, **2015**, *27*(8), 1389-1394.
- [94] Suzuki, K.; Malfatti, L.; Carboni, D.; Loche, D.; Casula, M.; Moretto, A.; Maggini, M.; Takahashi, M.; Innocenzi, P. Energy transfer induced by carbon quantum dots in porous zinc oxide nanocomposite films. *J. Phys. Chem. C*, **2015**, *119*(5), 2837-2843.
- [95] Cao, L.; Wang, X.; Mezziani, M.J.; Lu, F.; Wang, H.; Luo, P.G.; Lin, Y.; Harruff, B.A.; Veca, L.M.; Murray, D.; Xie, S.Y.; Sun, Y.P. Carbon dots for multiphoton bioimaging. *J. Am. Chem. Soc.*, **2007**, *129*(37), 11318-11319.
- [96] Yang, S.T.; Cao, L.; Luo, P.G.; Lu, F.; Wang, X.; Wang, H.; Mezziani, M.J.; Liu, Y.; Qi, G.; Sun, Y.P. Carbon dots for optical imaging *in vivo*. *J. Am. Chem. Soc.*, **2009**, *131*(32), 11308-11309.
- [97] Yang, S.T.; Wang, X.; Wang, H.; Lu, F.; Luo, P.G.; Cao, L.; Mezziani, M.J.; Liu, J.H.; Liu, Y.; Chen, M.; Huang, Y.; Sun, Y.P. Carbon dots as nontoxic and high-performance fluorescence imaging agents. *J. Phys. Chem. C*, **2009**, *113*(42), 18110-18114.
- [98] Li, Q.; Ohulchanskyy, T.Y.; Liu, R.; Koynov, K.; Wu, D.; Best, A.; Kumar, R.; Bonoio, A.; Prasad, P.N. Photoluminescent carbon dots as biocompatible nanoprobe for targeting cancer cells *in vitro*. *J. Phys. Chem. C*, **2010**, *114*(28), 12062-12068.
- [99] Esteves da Silva, J.C.G.; Gonçalves, H.M.R. Analytical and bioanalytical applications of carbon dots. *TrAC Trend. Anal. Chem.*, **2011**, *30*(8), 1327-1336.
- [100] Wang, Y.; Anilkumar, P.; Cao, L.; Liu, J.H.; Luo, P.G.; Tackett, K.N.; Sahu, S.; Wang, P.; Wang, X.; Sun, Y.P. Carbon dots of different composition and surface functionalization: Cytotoxicity issues relevant to fluorescence cell imaging. *Exp. Biol. Med.*, **2011**, *236*(11), 1231-1238.
- [101] Goh, E.J.; Kim, K.S.; Kim, Y.R.; Jung, H.S.; Beack, S.; Kong, W.H.; Scarcelli, G.; Yun, S.H.; Hahn, S.K. Bioimaging of hyaluronic acid derivatives using nanosized carbon dots. *Biomacromolecules*, **2012**, *13*(8), 2554-2561.
- [102] Han, B.; Wang, W.; Wu, H.; Fang, F.; Wang, N.; Zhang, X.; Xu, S. Polyethyleneimine modified fluorescent carbon dots and their application in cell labeling. *Colloids Surf., B*, **2012**, *100*, 209-214.
- [103] Liu, J.H.; Yang, S.T.; Chen, X.X.; Wang, H. Fluorescent carbon dots and nanodiamonds for biological imaging: Preparation, application, pharmacokinetics and toxicity. *Curr. Drug Metab.*, **2012**, *13*(8), 1046-1056.
- [104] Zhang, M.; Bai, L.; Shang, W.; Xie, W.; Ma, H.; Fu, Y.; Fang, D.; Sun, H.; Fan, L.; Han, M.; Liu, C.; Yang, S. Facile synthesis of water-soluble, highly fluorescent graphene quantum dots as a robust biological label for stem cells. *J. Mater. Chem.*, **2012**, *22*(15), 7461-7467.
- [105] Ding, H.; Cheng, L.W.; Ma, Y.Y.; Kong, J.L.; Xiong, H.M. Luminescent carbon quantum dots and their application in cell imaging. *New J. Chem.*, **2013**, *37*(8), 2515-2520.
- [106] Liu, Q.; Guo, B.; Rao, Z.; Zhang, B.; Gong, J.R. Strong two-photon-induced fluorescence from photostable, biocompatible nitrogen-doped graphene quantum dots for cellular and deep-tissue imaging. *Nano Lett.*, **2013**, *13*(6), 2436-2441.
- [107] Nurumabi, M.; Khatun, Z.; Huh, K.M.; Park, S.Y.; Lee, D.Y.; Cho, K.J.; Lee, Y.K. *In vivo* biodistribution and toxicology of carboxylated graphene quantum dots. *ACS Nano*, **2013**, *7*(8), 6858-6867.
- [108] Parvin, M.; Mandal, T.K.; Roy, P. Polyelectrolyte carbon quantum-dots: New player as a noninvasive imaging probe in drosophila. *J. Nanosci. Nanotechnol.*, **2013**, *13*(10), 6499-6505.
- [109] Sachdev, A.; Matai, I.; Kumar, S.U.; Bhushan, B.; Dubey, P.; Gopinath, P. A novel one-step synthesis of PEG passivated multicolour fluorescent carbon dots for potential biolabeling application. *RSC Adv.*, **2013**, *3*(38), 16958-16961.
- [110] Xu, Y.; Wu, M.; Liu, Y.; Feng, X.Z.; Yin, X.B.; He, X.W.; Zhang, Y.K. Nitrogen-doped carbon dots: A facile and general preparation method, photoluminescence investigation, and imaging applications. *Chem. Eur. J.*, **2013**, *19*(7), 2276-2283.
- [111] Chen, M.; Yin, M. Design and development of fluorescent nanostructures for bioimaging. *Prog. Polym. Sci.*, **2014**, *39*(2), 365-395.
- [112] Cheng, L.; Li, Y.; Zhai, X.; Xu, B.; Cao, Z.; Liu, W. Polycation-b-polyzwitterion copolymer grafted luminescent carbon dots as a multifunctional platform for serum-resistant gene delivery and bioimaging. *ACS Appl. Mater. Interfaces*, **2014**, *6*(22), 20487-20497.
- [113] Datta, K.K.R.; Kozak, O.; Ranc, V.; Havrdova, M.; Bourlinos, A.B.; Saifaraova, K.; Hala, K.; Tomankova, K.; Zoppellaro, G.; Otyepka, M.; Zboril, R. Quaternized carbon dot- modified graphene oxide for selective cell labeling - controlled nucleus and cytoplasm imaging. *Chem. Commun.*, **2014**, *50*(74), 10782-10785.
- [114] Huang, Y.F.; Zhou, X.; Zhou, R.; Zhang, H.; Kang, K.B.; Zhao, M.; Peng, Y.; Wang, Q.; Zhang, H.L.; Qiu, W.Y. One- pot synthesis of highly luminescent carbon quantum dots and their nontoxic ingestion by zebrafish for *in vivo* imaging. *Chem. Eur. J.*, **2014**, *20*(19), 5640-5648.
- [115] Sachdev, A.; Matai, I.; Gopinath, P. Implications of surface passivation on physicochemical and bioimaging properties of carbon dots. *RSC Adv.*, **2014**, *4*(40), 20915-20921.
- [116] Wang, L.; Yin, Y.; Jain, A.; Zhou, H.S. Aqueous phase synthesis of highly luminescent, nitrogen-doped carbon dots and their application as bioimaging agents. *Langmuir*, **2014**, *30*(47), 14270-14275.
- [117] Wen, T.; Yang, B.; Guo, Y.; Sun, J.; Zhao, C.; Zhang, S.; Zhang, M.; Wang, Y. Organosilane-functionalized graphene quantum dots and their encapsulation into bi-layer hollow silica spheres for bioimaging applications. *Phys. Chem. Chem. Phys.*, **2014**, *16*(42), 23188-23195.
- [118] Du, F.; Li, J.; Hua, Y.; Zhang, M.; Zhou, Z.; Yuan, J.; Wang, J.; Peng, W.; Zhang, L.; Xia, S.; Wang, D.; Yang, S.; Xu, W.; Gong, A.; Shao, Q. Multi-color nitrogen-doped carbon dots for live cell imaging. *J. Biomed. Nanotechnol.*, **2015**, *11*(5), 780-788.
- [119] Huang, P.; Lin, J.; Wang, X.; Wang, Z.; Zhang, C.; He, M.; Wang, K.; Chen, F.; Li, Z.; Shen, G.; Cui, D.; Chen, X. Light- triggered theranostics based on photosensitizer-conjugated carbon dots for simultaneous enhanced-fluorescence imaging and photodynamic therapy. *Adv. Mater.*, **2012**, *24*(37), 5104-5110.
- [120] Liu, C.; Zhang, P.; Zhai, X.; Tian, F.; Li, W.; Yang, J.; Liu, Y.; Wang, H.; Wang, W.; Liu, W. Nano-carrier for gene delivery and bioimaging based on carbon dots with PEI-passivation enhanced fluorescence. *Biomaterials*, **2012**, *33*(13), 3604-3613.
- [121] Hu, L.; Sun, Y.; Li, S.; Wang, X.; Hu, K.; Wang, L.; Liang, X.J.; Wu, Y. Multifunctional carbon dots with high quantum yield for imaging and gene delivery. *Carbon*, **2014**, *67*, 508-513.
- [122] Kumar, V.; Toffoli, G.; Rizzolio, F. Fluorescent carbon nanoparticles in medicine for cancer therapy. *ACS Med. Chem. Lett.*, **2013**, *4*(11), 1012-1013.
- [123] Zhou, L.; Li, Z.; Liu, Z.; Ren, J.; Qu, X. Luminescent carbon dot-gated nanovehicles for pH-triggered intracellular controlled release and imaging. *Langmuir*, **2013**, *29*(21), 6396-6403.

- [124] Yang, X.D.; Xiang, H.J.; An, L.; Yang, S.P.; Liu, J.G. Targeted delivery of photoactive diazido Pt^{IV} complexes conjugated with fluorescent carbon dots. *New J. Chem.*, **2015**, 39(2), 800-804.
- [125] Huang, W.; Fernando, S.; Allard, L.F.; Sun, Y.P. Solubilization of single-walled carbon nanotubes with diamine-terminated oligomeric poly(ethylene glycol) in different functionalization reactions. *Nano Lett.*, **2003**, 3(4), 565-568.
- [126] Sun, Y.P.; Wang, X.; Lu, F.; Cao, L.; Meziari, M.J.; Luo, P.G.; Gu, L.; Veca, L.M. Doped carbon nanoparticles as a new platform for highly photoluminescent dots. *J. Phys. Chem. C*, **2008**, 112(47), 18295-18298.
- [127] Qiao, Z.A.; Wang, Y.; Gao, Y.; Li, H.; Dai, T.; Liu, Y.; Huo, Q. Commercially activated carbon as the source for producing multicolor photoluminescent carbon dots by chemical oxidation. *Chem. Commun.*, **2010**, 46(46), 8812-8814.
- [128] Wang, X.; Cao, L.; Yang, S.T.; Lu, F.; Meziari, M.J.; Tian, L.; Sun, K.W.; Bloodgood, M.A.; Sun, Y.P. Bandgap-like strong fluorescence in functionalized carbon nanoparticles. *Angew. Chem.*, **2010**, 122(31), 5438-5442.
- [129] Anilkumar, P.; Wang, X.; Cao, L.; Sahu, S.; Liu, J.H.; Wang, P.; Korch, K.; Li, K.N.T.; Parenzan, A.; Sun, Y.P. Toward quantitatively fluorescent carbon-based "quantum" dots. *Nanoscale*, **2011**, 3(5), 2023-2027.
- [130] Wang, F.; Pang, S.; Wang, L.; Li, Q.; Kreiter, M.; Liu, C.Y. One-step synthesis of highly luminescent carbon dots in noncoordinating solvents. *Chem. Mater.*, **2010**, 22(16), 4528-4530.
- [131] Kwon, W.; Lim, J.; Lee, J.; Park, T.; Rhee, S.W. Sulfur-incorporated carbon quantum dots with a strong long-wavelength absorption band. *J. Mater. Chem. C*, **2013**, 1(10), 2002-2008.
- [132] Liu, Y.; Liu, C.Y.; Zhang, Z.Y. Synthesis and surface photochemistry of graphitized carbon quantum dots. *J. Colloid Interface Sci.*, **2011**, 356(2), 416-421.
- [133] Liu, J.; Liu, X.; Luo, H.; Gao, Y. One-step preparation of nitrogen-doped and surface-passivated carbon quantum dots with high quantum yield and excellent optical properties. *RSC Adv.*, **2014**, 4(15), 7648-7654.
- [134] Pan, D.; Zhang, J.; Li, Z.; Wu, C.; Yan, X.; Wu, M. Observation of pH-, solvent-, spin-, and excitation-dependent blue photoluminescence from carbon nanoparticles. *Chem. Commun.*, **2010**, 46(21), 3681-3683.
- [135] Bourlinos, A.B.; Zboril, R.; Petr, J.; Bakandritsos, A.; Krysmann, M.; Giannelis, E.P. Luminescent surface quaternized carbon dots. *Chem. Mater.*, **2012**, 24(1), 6-8.
- [136] Qu, S.; Wang, X.; Lu, Q.; Liu, X.; Wang, L. A biocompatible fluorescent ink based on water-soluble luminescent carbon nanodots. *Angew. Chem. Int. Ed.*, **2012**, 51(49), 12215-12218.
- [137] Chen, X.; Zhang, W.; Wang, Q.; Fan, J. C8-structured carbon quantum dots: Synthesis, blue and green double luminescence, and origins of surface defects. *Carbon*, **2014**, 79, 165-173.
- [138] Hao, Y.; Gan, Z.; Xu, J.; Wu, X.; Chu, P.K. Poly(ethylene glycol)/carbon quantum dot composite solid films exhibiting intense and tunable blue-red emission. *Appl. Surf. Sci.*, **2014**, 311, 490-497.
- [139] Bourlinos, A.B.; Karakassides, M.A.; Kouloumpis, A.; Gournis, D.; Bakandritsos, A.; Papagiannouli, I.; Aloukos, P.; Couris, S.; Hola, K.; Zboril, R.; Krysmann, M.; Giannelis, E.P. Synthesis, characterization and non-linear optical response of organophilic carbon dots. *Carbon*, **2013**, 61, 640-643.
- [140] Hola, K.; Bourlinos, A.B.; Kozak, O.; Berka, K.; Siskova, K.M.; Havrdova, M.; Tucek, J.; Safarova, K.; Otyepka, M.; Giannelis, E.P.; Zboril, R. Photoluminescence effects of graphitic core size and surface functional groups in carbon dots: COO- induced red-shift emission. *Carbon*, **2014**, 70, 279-286.
- [141] Zhang, W.; Dai, D.; Chen, X.; Guo, X.; Fan, J. Red shift in the photoluminescence of colloidal carbon quantum dots induced by photon reabsorption. *Appl. Phys. Lett.*, **2014**, 104(9), 091902(1-5).
- [142] Qu, S.; Wang, X.; Lu, Q.; Liu, X.; Wang, L. A biocompatible fluorescent ink based on water-soluble luminescent carbon nanodots. *Angew. Chem. Int. Ed.*, **2015**, 51(49), 12215-12218.
- [143] Anilkumar, P.; Cao, L.; Yu, J.J.; Tackett, K.N.; Wang, P.; Meziari, M.J.; Sun, Y.P. Crosslinked carbon dots as ultra-bright fluorescence probes. *Small*, **2013**, 9(4), 545-551.
- [144] Wang, X.; Wang, D.; Guo, Y.; Yang, C.; Iqbal, A.; Liu, W.; Qin, W.; Yan, D.; Guo, H. Imidazole derivative-functionalized carbon dots: Using as a fluorescent probe for detecting water and imaging of live cells. *Dalton Trans.*, **2015**, 44(12), 5547-5554.
- [145] Gonçalves, H.; Esteves da Silva, J.C.G. Fluorescent carbon dots capped with peg200 and mercaptosuccinic acid. *J. Fluorescence*, **2010**, 20(5), 1023-1028.
- [146] Krishna, A.S.; Radhakumary, C.; Antony, M.; Sreenivasan, K. Functionalized carbon dots enable simultaneous bone crack detection and drug deposition. *J. Mater. Chem. B*, **2015**, 2(48), 8626-8632.
- [147] Yang, L.; Jiang, W.; Qiu, L.; Jiang, X.; Zuo, D.; Wang, D.; Yang, L. One pot synthesis of highly luminescent polyethylene glycol anchored carbon dots functionalized with a nuclear localization signal peptide for cell nucleus imaging. *Nanoscale*, **2015**, 7(14), 6104-6113.
- [148] Wang, F.; Xie, Z.; Zhang, H.; Liu, C.Y.; Zhang, Y.G. Highly luminescent organosilane-functionalized carbon dots. *Adv. Funct. Mater.*, **2011**, 21(6), 1027-1031.
- [149] Wang, W.; Kim, T.; Yan, Z.; Zhu, G.; Cole, I.; Nguyen, N.T.; Li, Q. Carbon dots functionalized by organosilane with double-sided anchoring for nanomolar Hg²⁺ detection. *J. Colloid Interface Sci.*, **2015**, 437, 28-34.
- [150] Dong, Y.; Pang, H.; Yang, H.B.; Guo, C.; Shao, J.; Chi, Y.; Li, C.M.; Yu, T. Carbon-based dots co-doped with nitrogen and sulfur for high quantum yield and excitation-independent emission. *Angew. Chem. Int. Ed.*, **2013**, 52(30), 7800-7804.
- [151] Kozak, O.; Datta, K.K.R.; Greplova, M.; Ranc, V.; Kaslik, J.; Zboril, R. Surfactant-derived amphiphilic carbon dots with tunable photoluminescence. *J. Phys. Chem. C*, **2013**, 117(47), 24991-24996.
- [152] Jahan, S.; Mansoor, F.; Naz, S.; Lei, J.; Kanwal, S. Oxidative synthesis of highly fluorescent boron/nitrogen co-doped carbon nanodots enabling detection of photosensitizer and carcinogenic dye. *Anal. Chem.*, **2013**, 85(21), 10232-10239.
- [153] Barman, M.K.; Jana, B.; Bhattacharyya, S.; Patra, A. Photophysical properties of doped carbon dots (N, P, and B) and their influence on electron/hole transfer in carbon dots-nickel (II) phthalocyanine conjugates. *J. Phys. Chem. C*, **2014**, 118(34), 20034-20041.
- [154] Qu, D.; Zheng, M.; Zhang, L.; Zhao, H.; Xie, Z.; Jing, X.; Haddad, R.E.; Fan, H.; Sun, Z. Formation mechanism and optimization of highly luminescent N-doped graphene quantum dots. *Sci. Rep.*, **2014**, 4, 5294(1-9).
- [155] Chen, H.; Xie, Y.; Kirillov, A.M.; Liu, L.; Yu, M.; Liu, W.; Tang, Y. A ratiometric fluorescent nanoprobe based on terbium functionalized carbon dots for highly sensitive detection of an anthrax biomarker. *Chem. Commun.*, **2015**, 51(24), 5036-5039.
- [156] Hou, J.; Dong, J.; Zhu, H.; Teng, X.; Ai, S.; Mang, M. A simple and sensitive fluorescent sensor for methyl parathion based on l-tyrosine methyl ester functionalized carbon dots. *Biosens. Bioelectron.*, **2015**, 68, 20-26.
- [157] Liu, Q.; Xu, S.; Niu, C.; Li, M.; He, D.; Lu, Z.; Ma, L.; Na, N.; Huang, F.; Jiang, H.; Ouyang, J. Distinguish cancer cells based on targeting turn-on fluorescence imaging by folate functionalized green emitting carbon dots. *Biosens. Bioelectron.*, **2015**, 64, 119-125.
- [158] Liu, S.; Zhao, N.; Cheng, Z.; Liu, H. Amino-functionalized green fluorescent carbon dots as surface energy transfer biosensors for hyaluronidase. *Nanoscale*, **2015**, 7(15), 6836-6842.
- [159] Shan, X.; Chai, L.; Ma, J.; Qian, Z.; Chen, J.; Feng, H. B-doped carbon quantum dots as a sensitive fluorescence probe for hydrogen peroxide and glucose detection. *Analyst*, **2014**, 139(10), 2322-2325.
- [160] Zheng, H.; Wang, Q.; Long, Y.; Zhang, H.; Huang, X.; Zhu, R. Enhancing the luminescence of carbon dots with a reduction pathway. *Chem. Commun.*, **2011**, 47(38), 10650-10652.
- [161] Hu, S.; Zhao, Q.; Dong, Y.; Yang, J.; Liu, J.; Chang, Q. Carbon-dot-loaded alginate gels as recoverable probes: Fabrication and mechanism of fluorescent detection. *Langmuir*, **2013**, 29(40), 12615-12621.
- [162] Linehan, K.; Doyle, H. Efficient one-pot synthesis of highly monodisperse carbon quantum dots. *RSC Adv.*, **2014**, 4(1), 18-21.
- [163] Linehan, K.; Doyle, H. Solution reduction synthesis of amine terminated carbon quantum dots. *RSC Adv.*, **2014**, 4(24), 12094-12097.
- [164] Li, Y.; Zhao, Y.; Cheng, H.; Hu, Y.; Shi, G.; Dai, L.; Qu, L. Nitrogen-doped graphene quantum dots with oxygen-rich functional groups. *J. Am. Chem. Soc.*, **2012**, 134(1), 15-18.
- [165] Liu, S.; Tian, J.; Wang, L.; Luo, Y.; Zhai, J.; Sun, X. Preparation of photoluminescent carbon nitride dots from CCl₄ and 1,2-ethylenediamine: A heat-treatment-based strategy. *J. Mater. Chem.*, **2011**, 21(32), 11726-11729.
- [166] Liu, S.; Wang, L.; Tian, J.; Zhai, J.; Luo, Y.; Lu, W.; Sun, X. Acid-driven, microwave-assisted production of photoluminescent carbon nitride dots from N,N-dimethylformamide. *RSC Adv.*, **2011**, 1(6), 951-953.
- [167] Zhang, Y.Q.; Ma, D.K.; Zhuang, Y.; Zhang, X.; Chen, W.; Hong, L.L.; Yan, Q.X.; Yu, K.; Huang, S.M. One-pot synthesis of N-doped carbon dots with tunable luminescence properties. *J. Mater. Chem.*, **2012**, 22(33), 16714-16718.
- [168] Mazzier, D.; Favaro, M.; Agnoli, S.; Silvestrini, S.; Granozzi, G.; Maggini, M.; Moretto, A. Synthesis of luminescent 3D microstructures formed by carbon quantum dots and their self-assembly properties. *Chem. Commun.*, **2014**, 50(50), 6592-6595.
- [169] Dey, S.; Govindaraj, A.; Biswas, K.; Rao, C.N.R. Luminescence properties of boron and nitrogen doped graphene quantum dots prepared from arc-discharge-generated doped graphene samples. *Chern. Phys. Lett.*, **2014**, 595-596, 203-208.
- [170] Fan, Z.; Li, Y.; Li, X.; Fan, L.; Zhou, S.; Fang, D.; Yang, S. Surmounting media sensitive photoluminescence of boron-doped graphene quantum dots for highly fluorescent dyed crystals, chemical sensing and bioimaging. *Carbon*, **2014**, 70, 149-156.
- [171] Hou, Y.; Lu, Q.; Deng, J.; Li, H.; Zhang, Y. One-pot electrochemical synthesis of functionalized fluorescent carbon dots and their selective sensing for mercury ion. *Anal. Chim. Acta*, **2015**, 866, 69-74.