

Carbon quantum dots: nanolights

Abstract

Carbon quantum dots are generally small carbon nanoparticles with the attractive properties of high stability, good conductivity, low toxicity, environmental friendly, simple synthetic routes as well as comparable optical properties to quantum dots. Various methods are developed to synthesize carbon quantum dots like laser ablation, arc discharge, electrochemical techniques, hydro thermal method, ultrasonic method, acid dehydration method, and pyrolysis method. Applications of Carbon quantum dots lie in the field of optronics, Bio-imaging, bio-sensing, drug delivery, materials for dye-sensitized solar cells, organic solar cells, super capacitor, and light emitting devices and catalysis. In this paper, recent hot researches on the synthesis, properties and applications of Carbon quantum dots are reviewed and some problems in the progress of Carbon quantum dots are also summarized.

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Introduction

Carbon is commonly a black material, and famous for its weak fluorescence. But baby member of carbon Nano-club carbon quantum dots caught wide attention because of their strong luminescence, for which they are referred to as carbon nanolights. Carbon quantum dots are generally small carbon nanoparticles (less than 10 nm in size) with the attractive properties of high stability, good conductivity, low toxicity, environmental friendly, simple synthetic routes as well as comparable optical properties to quantum dots. In 2004 Xu et al.¹ accidentally discover CQDs during the purification of single-walled carbon nanotubes. From that moment much progress has been achieved in the synthesis, properties and applications of carbon-based quantum dots. Because of their applications in bio imaging, biomedicine, drug delivery, optronics, photovoltaic's, catalysis, and sensing extensive investigations is carried out by researchers.

The fundamental mechanisms accountable for the fluorescence capability of CQDs are much debated. Some researchers comes up with the evidence of size-dependent fluorescence properties, suggesting that the emission arises from electronic transitions with the core of the dots, influenced by quantum confinement effects²⁻³ whereas other works have rather indorsed the fluorescence to recombination of surface-trapped charges,⁴ or proposed a form of coupling between core and surface electronic states.⁵ The excitation-dependent fluorescence, leading to tuneable emission characteristic, has been mostly linked to the in homogeneous distribution of their emission characteristics.⁵⁻⁹

Properties

Generally, CDs are nearly spherical nanocrystals with the diameter less than 10nm and comprising few molecules or atoms of nanoclusters.¹⁰⁻¹¹ There exist a large amount of -OH and -COOH and -NH₂ and other groups on CDs surfaces,⁹ which endow CDs with good water solubility and polymerization ability with various inorganic, organic, or biologically active substances. As far as properties concern carbon-based quantum dots are superior in terms of high (aqueous) solubility, robust chemical inertness, facile modification and high resistance to photo bleaching, low toxicity and good biocompatibility.

Optical properties of CDs

The excellent optical properties of CDs mainly include high fluorescence stability, non blinking, tuneable excitation, and emission

wavelengths.¹²⁻¹⁷ CDs have strong absorption in the ultraviolet region, which can also extend to visible region.¹² After modification of some passivating agents, the absorption spectral region may be red shift continuously.¹³ Even under the same excitation light it is found that the emission wavelengths of fluorescent CDs depend on the particle sizes. The emission wavelength is gradually red shift with the increasing of the particle size. CDs with blue,¹⁴ orange-yellow, and green fluorescence¹⁵ are also reported.

Bio compatibility and low toxicity of CDs

Since carbon element is the basic of all living body, full carbon nanomaterials have a lower toxicity compared with other nanomaterials; simultaneously, the particle size of CDs is smaller and then more convenient to enter the cell in vivo, which makes CDs have great potential application in the biological fields. In addition, the surface of CDs contains a lot of functional groups, so that the surface of CDs can be modified with organic, inorganic, polymer, and other substances endowing different functional properties.

Synthesis

Various methods are developed by Researchers to synthesize CDQs like laser ablation, arc discharge, electrochemical techniques, hydro thermal method, ultrasonic method, acid dehydration method, and pyrolysis method.¹⁶⁻³⁴ Among them, the most widely used are the hydrothermal method and microwave-assisted pyrolysis method and microwave synthetic routes. Different base material used as the carbon source for synthesis are C60, carbohydrate, burned eggshell into ashes, sucrose, chitosan, candle ash, graphite rods shock, citric acid^{14,25,27-30,35} whereas the few of the different solvent used are PEG200,²⁷ NaOH aqueous solution²⁸ phosphoric acid²⁹ aqueous solution, ionic liquid solvent.¹⁸ The methods also differ in reaction time such as reaction time for one of the method is just 3 minutes and 40 seconds²⁹ for others, microwave power radiation for 2~10min²⁷ microwave radiation for five minutes²⁸ laser radiation for 4h²⁰ With visible light (425-720nm) irradiation for five hours³⁵ and so on. With all this diversity synthetic methods for CQDs are roughly divided into two categories, "top-down" and "bottom-up" routes.

Modification of CQDs is also very important to get good surface properties which are essential for solubility and selected applications. This modification can be done during preparation or post-treatment. Early preparation approaches "Top-down"

synthetic route refers to breaking down larger carbon structures such as graphite, carbon nanotubes, and nanodiamonds into CDQs using laser ablation, arc discharge, and electrochemical techniques. For example, Zhou et al.⁸ first applied electrochemical method into synthesis of CQDs. They grew multi-walled carbon nanotubes on a carbon paper. The carbon paper then inserted into an electrochemical cell containing supporting electrolyte including degassed acetonitrile and 0.1 M tetrabutyl ammonium perchlorate. However, the fluorescence quantum yield of the CDs prepared in electrochemical methods is not high and needs further improvement. Sun et al. pioneered in synthesis of fluorescent CDs by means of laser ablation.¹⁹ Hu et al.²⁰ combined laser ablation and surface passivation merger in one-step reaction to obtained fluorescence CDs with particle size about 3.2nm, and the quantum yield is 12.2%, which significantly improved the fluorescence quantum yield of CDs.

“Bottom-up” synthetic route involves synthesizing CQDs from small precursors such as carbohydrates, citrate, and polymer-silica nanocomposites. This strategy includes hydro thermal method^{14,21–26} ultrasonic method³¹ acid dehydration method³² and pyrolysis method.^{33,34} For instance, Zhu et al.²⁶ described a simple method of preparing CQDs by heating a solution of poly (ethylene glycol) (PEG) and saccharide in 500W microwave oven for 2 to 10 min. In the past two years, a lot of reports are about the researches of preparing CDs through hydrothermal method using different carbon sources, and the fluorescence quantum yield of CDs has been greatly increased.

Recently, green synthetic approaches have also been employed for fabrication of CQDs. Wang et al.²⁸ created a “green,” “fast,” “economy” CDs synthesis method by means of microwave method. They first burn eggshell into ashes, then mixed the ashes with NaOH aqueous solution, and treated the solution via microwave radiation for five minutes to get CDs. This method is quite simple; the raw materials are cheap and available, and the consuming time is very short; the fluorescence quantum yield of CDs reaches to 14%. For particular applications and so size control of CDQs is also of great importance which can be done during preparing process or via post-treatment. A majority of the reports demonstrated the processes of purifying the as-synthesized CQDs fragments via post-treatment such as filtration, centrifugation, column chromatography and gel-electrophoresis.

In addition to post-treatment, controlling the size of CQDs during the preparing process is also widely used. For instance, Zhu reported hydrophilic CQDs through impregnation of citric acid precursor. After pyrolyzing CQDs at 300°C for 2 hours in air, then removing silica, followed by dialysis, they prepared CQDs with a uniform size of 1.5–2.5 nm which showed low toxicity, excellent luminescence, good photo stability, and up-conversion properties.

In order to survive the competition with conventional semiconductor quantum dots, a high quantum yield should be achieved. Although a good example of CQDs with ~80% quantum yield was synthesized, most of the quantum dots synthesized have a quantum yield below 10% so far. Surface-passivation and doping methods for modifications are usually applied for improving quantum yield. For instance, Gao and so forth²⁵ chose C60 as the carbon source and CTAB as passivator to prepared CDs with high fluorescence quantum yield up to 60%. Even more, the fluorescent CDs prepared in their method possess the distinctive property of aggregation induced enhanced emission, which is different from the common reports in the literatures. Surface passivation prevents surfaces of CQDs from being polluted by their environment.

In addition to surface passivation, doping is also a common method used to tune the properties of CQDs. various doping methods with elements such as N, S, and P have been demonstrated for tuning the properties of CQDs, among which N doping is the most common way due to its great ability in improving the photo luminescence emissions.

Applications

Applications of CQD lie in the field of optronics, bio imaging, bio sensing, drug delivery, materials for dye-sensitized solar cells, organic solar cells, super capacitor, and light emitting devices and catalysis. As reported CQDs can be used as photosensitizer in dye-sensitized solar cells and the photoelectric conversion efficiency is significantly enhanced. It is found that the composite of TiO₂ nanoparticles and carbon dots can effectively broaden the range of the optical response of the composite structure and increase the utilization of solar energy and transformation.

Guo et al.³⁵ synthesized a series of multicolor CDs by the thermolysis of epoxy group containing polystyrene microspheres. CDs produced under 200, 300, and 400°C could emit blue, orange, and white fluorescence with the excitation of single wavelength ultraviolet, respectively, and the fluorescent quantum yield is 47%. With the excellent properties, those CDs could be used as the above-mentioned three colour LED devices. As another application CQD incorporated hybrid silica based sol can be used as transparent Fluorescent paint.

Due to their fluorescence emissions and biocompatibility CQDs can be used for bio imaging. By injecting solvents containing CQDs into a living body, images in vitro can be obtained for detection or diagnosis purposes. One example the presence of H₂S could tune the blue emission of the organic dye-conjugated CQDs to green so the organic dye-conjugated CQDs could be used as an effective fluorescent probes for H₂S. By using a fluorescence microscope, the organic dye-conjugated CQDs were able to visualize changes in physiologically relevant levels of H₂S.

CQDs were also applied in biosensing as biosensor carriers for their flexibility in modification, high solubility in water, nontoxicity, good photo stability, and excellent biocompatibility. The biosensors based on CQD could be used for visual monitoring of cellular copper, glucose, pH and nucleic acid. A general example is about nucleic acid lateral flow assays. The discriminating tags on the amplicons are recognized by their respective antibodies and fluorescence signals provided by the attached CQDs. More generally, the fluorescence of CQDs efficiently responds to pH, local polarity, and to the presence of metal ions in solution, which further expands their potential for nanosensing applications, for instance in the analysis of pollutants.

Nontoxicity and biocompatibility of CQDs assist them with their applications in biomedicine as drug carriers, fluorescent tracers as well as controlling drug release. This is exemplified by the use of CQDs as photosensitizers in photodynamic therapy to destroy cancer cells.

The flexibility of functionalization with various groups CQDs makes them possible to absorb lights of different wavelengths, which offers good opportunities for applications in photo catalysis. CQDs-modified P25 TiO₂ composites exhibited improved photocatalytic H₂ evolution under irradiation with UV-Vis. The CQDs serve as a reservoir for electrons to improve the efficiency of separating of the electron-hole pairs of P25. Zhang et al. used CDs-TiO₂ composites as catalyst successfully to get H₂.

Conclusion

In this article, recent progress in the field of CQDs is described, focusing on their luminescent mechanism, modification strategies, synthetic methods, size control and applications. They have numerous excellent applications in a variety of fields involving chemical and biological sensing, biological imaging, drug delivery and photo catalysis, which are greatly promising for the future development. The application ranges should still be further improved and make sufficient use of surface rich functional groups on CDs, broadening their composite structural applications in various fields. On the part of synthesis, though several methods have been proposed towards the synthesis of CQDs, well-defined structure and precise sizes are hardly available yet. It is critical to synthesize CQDs in a simplistic and green manner with designed structure and size for selected applications.

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Conflict of interest

The author declares no conflict of interest.

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