Metal ions doped carbon quantum dots: Synthesis, physicochemical properties, and their applications

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ABSTRACT

As an efficient method to improve the intrinsic properties of carbon quantum dots (CQDs), doping CQDs with heteroatoms including nonmetallic atoms and metal ions recently receive great attention. Since the summary about the achievements of CQDs doping with nonmetallic atoms has been carried out. In this minireview, we will overview the state-of-the-art knowledge of metal ions doped-CQDs (M-CQDs). The synthetic routes for M-CQDs, the novel physicochemical properties originating from their unique morphology and constitute, and their applications in environmental, biological and energy-related areas will be summarized and highlighted. The review aims to provide new insights into the exploitation of the methods in order to improve the functionality of M-CQDs, the relationship between newly novel physicochemical properties and metal ions doping, as well as their possible applications in future.

1. Introduction

Photoluminescent carbon quantum dots (CQDs), which usually can be classified into carbon dots (CDs) and graphene quantum dots (GQDs), have aroused much attention since they were accidentally discovered during the electrophoretic fractionation in 2004 [1]. In general, CQDs endow several favorable attributes including chemical inertness, resistance to photobleaching, tunable luminescence emission, ease of preparation, low cytotoxicity and excellent biocompatibility [2,3]. As a result, they show growing applications in energy conversion/storage, catalysis, biological imaging, drug delivery, environmental monitor and remediation [4–8].

Up to now, low quantum yields (QYs) and few functional surface groups for bioconjugation and further applications as two considerable problems for original CQDs have limited their applications based on their photoluminescent properties. The recent study on the photoluminescence mechanism of CQDs shows that surface functionalization and chemical heteroatoms doping are two efficient routes to improve the photoluminescence performance and expand the application scope of CQDs [9–11]. However, surface functionalization with polymers and small organic molecules involves complex synthesis and purification steps with low production yield and decrease some originally functional positions for specifically analytical and sensing applications [12,13].

Chemical heteroatoms doping, which is relatively convenient for large scale synthesis, aims to change the electronic structures related to the energy gap of CQDs endowing CQDs with different intrinsic properties through introducing non-metal atomic impurities and metal ions into CQDs. Some studies have demonstrated that CQDs possess electronic structures and exhibit $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ electronic transitions, which are in close relationship with their physicochemical properties, particularly optical properties (absorption and fluorescence) [9,14]. It is believed that the heteroatoms bonded to CQDs would affect the interaction between $\pi$- and n-states in CQDs by the extent of orbital overlap and electron withdrawing/donating abilities of heteroatoms. Previous reports show that most nonmetallic heteroatoms doped-CQDs can be easily obtained via facile synthetic methods from rich raw materials [15–18]. And the enhancement of QYs of CQDs and the expansion of their applications have realized due to the nonmetallic heteroatoms doping.

In comparison with most nonmetallic heteroatoms, there are more electrons easy to lose and unoccupied orbitals outside of most metal ions (especially for transition metal ions) and metal ions endow larger atomic radius than nonmetallic heteroatoms. Once metallic ions doping into CQDs, there will be more opportunity for
changing charge density and charge transition forms between the metal ions and graphene matrix via combining metal ions with the excellent electronic mobility of CQDs, which is poised to tune the physicochemical properties of CQDs to a greater extent. And the introduction of metal ions might induce new physicochemical properties of CQDs like catalytic property. On the one hand, the electrons and unoccupied orbitals outside of metal ions facilitate them chelating with amino and carboxyl groups on the surface of CQDs in the chemical reaction procedure. On the other hand, it has been widely demonstrated that the fluorescence of CQDs could be quenched via the coordination between metal ions and the surface groups of CQDs [5,6]. From this view, the surface functionalization with metal ions seems to be unacceptable. As research continues, Feng’s group proposed a new perspective that charge-exchangeable coordinating “functional knots” in the CQDs’ backbones could be formed by directly binding metal dopants to the sp² characterized heteroatoms other than surface functionalization with metal ions in 2015 [19]. From then on, metal ions doped-CQDs (M-CQDs) have been considered as an alternative option for CQDs doping and received more and more attention. So far, M-CQDs doped with different metal ions have been obtained, and they not only possess excellent optical properties but also endow new intrinsic properties due to the doping of metal ions.

This review will comprehensively retrospect the various synthetic routes adopted to prepare M-CQDs. Their specific physicochemical properties derived from the different kinds of dopants and applications will be covered and discussed. At last, based on the available work of M-CQDs, a perspective for M-CQDs will be given. This review will offer valuable insight for the investigation of M-CQDs and further inspire the exploration in a multitude of exciting areas.

2. Synthetic strategies for M-CQDs

The available synthetic methods for M-CQDs concentrate on the chemical reaction between the relative metallic compound and organic molecules under certain reaction conditions, which can be classified into two categories: one-step synthesis and multi-step synthesis. The one-step synthesis methods include hydrothermal method, solvothermal method, microwave method, pyrolysis, ultrasonic chemical method. In addition, M-CQDs can also be prepared through multi-step routes, which prepare M-CQDs by exfoliating the large metal ions doped carbonaceous materials obtained via extra metal ions doping step into the cleavage.

2.1. One-step synthesis routes

2.1.1. Hydrothermal method

Hydrothermal method is the most widely adopted synthetic route for the preparation of M-CQDs due to its convenient implementation, low-cost, high efficiency and eco-friendliness. This method usually refers to treat the mixture of small organic molecules such as citric acid (CA), ascorbic acid, polymers and metallic dopants at high temperature for several hours. Up to date, single cules such as citric acid (CA), ascorbic acid, polymers and metallic

2.1.2. Solvothermal method

The one-pot solvothermal method for the preparation of Zn-CQDs has been carried out by Cheng et al. [27]. In their work, CA, urea and ZnCl₂ were dissolved in toluene and heated at 200 °C for 12 h (Fig. 2), and then the supernatant was collected by removing large particles via centrifuging at 12,000 rpm for 20 min. After evaporating the solvent, the soluble Zn-CQDs were obtained. The synthesized Zn-CQDs emitted robust yellow fluorescence under a UV lamp. The products were uniform dispersion with particle diameters of 2–5 nm and land form height in the range from 2.5 to 4.5 nm. Later, in view of the coordination between Mn(II) ions and ethylene diamine tetracetic acid (EDTA) and triethylenetetramine derived Cd’s, Han et al. carbonized the mixture of EDTA, triethylenetetramine and MnCl₂ in ethylene glycol at 150 °C for 10 h to obtain Mn-CQDs [28]. The product could uniformly disperse with a diameter range of 4.6 ± 0.9 nm and an inter planar spacing of 0.22 nm close to the [100] facet of graphite. In 2017, Zhang et al. adopted solvothermal method to treat the mixture of 1-(2-pyrpyridylazo)-2-naphthol and CuCl₂ in ethanol at 180 °C for 4 h to obtain cobalt(II)-doped CDs (Co-CQDs) [29]. The products were re-dispersed in ethanol after a series of purification including drying to remove solvent, being re-dissolved with ethyl acetate and extracted with water, and dialyzed. The HRTEM images showed that the average diameter of Co-CQDs was 2.93 nm and there was lattice spacing of 0.213 nm referring to the [100] facet of graphitic structure on the surface of Co-CQDs. Compared with hydrothermal method, solvothermal method is more dangerous at high temperature due to the use of harmful organic solvent in this method, and the excess organic solvent needs special treatment after the synthesis.

2.1.3. Microwave method

Microwave method is an efficient method, which can be completed in several minutes. For example, Yang et al. dissolved the mixture of l-tartaric acid, urea, and FeCl₃·6H₂O in oleic acid, and heated it to 210 °C within 1 min by microwave and maintained for 10 min [30]. Followed by repeatedly extractions to remove the redundant oleic acid and purification via silica column chromatography, the product Fe, N-CQDs were finally re-dispersed in water. The HRTEM image showed that the Fe, N-CQDs distributed uniformly and there were lattice fringes of 0.22 nm on their surface, which agreed well with the [100] facet of graphitic carbon. Meanwhile, the peak around 710 eV in X-ray photoelectron spectroscopy (XPS) spectrum also confirmed the successful doping of iron element in the obtained products. In the other case, the mixture of sucrose, concentrated H₂SO₄, GdCl₃, and diethylene glycol was heated in domestic microwave oven for 50 s to obtain green luminescent gadolinium-doped CDs (Gd-CQDs) [31]. The obtained Gd-CQDs were well-separrated with the size of approximately 5 nm. There was also