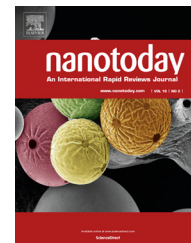




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NEWS AND OPINIONS

Beyond bottom-up carbon nanodots: Citric-acid derived organic molecules

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Summary In the past decade, a new exciting class of metal-free and carbon-rich fluorescent nanomaterials has been developed. By far, the most example is carbon nanodots (CNDs). CNDs are usually prepared by two main procedures: top-down cutting route from different carbon resources and bottom-up carbonization method from different molecules or polymers. CNDs prepared from the former route possess good carbon lattice with relative low quantum yield (QY), while the latter route is the reverse. However, CNDs prepared from bottom-up carbonization of citric acid based molecules usually contain small fluorophore molecules with high photoluminescence (PL). As a result, researchers should be aware of this significant component in CNDs, and figure out the relationship between chemical structures and PL centers.

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Introduction

In the evolution of fluorescent materials, considerable efforts have been devoted to the development of heavy-metal-free and low-toxicity photoluminescence (PL) nanoprobes. Carbon nanodots (CNDs), one class of these nanoprobes, have drawn much attention during recent years [1,2]. CNDs possess high photo-stability, tunable

emission, chemical inertness, good biocompatibility, low toxicity, photoelectric/optical properties, convenient surface modification, as well as low-cost production. Therefore, CNDs could find use in the fields of biomedical applications, optoelectronic devices, sensors and nanocomposites, etc. However, due to the diverse synthesis processes of CNDs, there are huge differences among the chemical structures and PL mechanisms [3,4].

Bottom-up methods were efficient routes to produce fluorescent CNDs in large scale. For example, small molecules and polymers may undergo dehydration and further carbonization to form CNDs. Citric acid (CA) is the most common reagent to synthesize CNDs through bottom-up

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methods. Many groups have synthesized CNDs from CA and amine-containing compounds as co-reagent via heating, hydrothermal or microwave assisted methods (as shown in Table S1). However, CNDs from bottom-up carbonization of CA and amine have not only the carbon core, but also some unknown substances with high PL quantum yield (QY), which is inconsistent with the typical CNDs [5–17]. As a result, it is very important to carefully characterize the chemical composition in the CA-derived CNDs.

Classification of the CNDs and the CA derived CNDs

The structure of CNDs consists of sp^2/sp^3 carbons with some connected functional groups. In fact, carbon dots also encompass graphene quantum dots (GQDs) and polymer dots (PDs) in addition to CNDs [18]. GQDs possess single or few layers graphene with anisotropic dimension [19–24]. PDs are aggregated or cross-linked polymer nanoparticles derived from linear polymer or monomers [25–27]. CNDs are always spherical, containing both the carbon nanoparticles without crystal lattices and carbon quantum dots with obvious crystal lattices [28–36]. Consequently, different CNDs have different PL centers, depending on the detailed structures of the CNDs. In this opinion, we will limit our discussion to CA-based CNDs.

Products in one-pot CA derived CNDs

During the synthesis of CA-based CNDs, small fluorophore molecules are first formed at low reaction temperatures. As the reaction temperature increases, carbon cores and polymer clusters are then formed by dehydration of the initial molecules or consumption of the fluorophores (Fig. 1a). For these CNDs, the PL center related to the molecular state possesses strongly PL emission with high QYs, while the PL center related to the carbon core state possesses weak PL behavior with high photo-stability. Giannelis et al. first investigated the formation mechanism of CNDs with both the molecular state and the carbon core state [7].

Yang's group reported a type of CNDs from CA and ethylenediamine (EDA) with ultrahigh QY [37,38]. They prepared CNDs at four different temperatures and found that QY decreases with temperature while photo-stability and excitation-dependent PL behavior increase (Fig. 1a).

Different components in one-pot synthesized CNDs have synergistic effects; the carbon core and polymer cluster can improve the solubility and PL emission of the molecule by stabilizing and increasing absorbance [39]. Therefore, although separation of the two phases is necessary to investigate the relationship of chemical structures and PL mechanism, such mixture in these CNDs may be sufficiently efficient for practical applications [40].

Separation of the CA derived CNDs

Many groups improved the synthetic and purification processes of these CNDs, as shown in Table S1. Sun's group

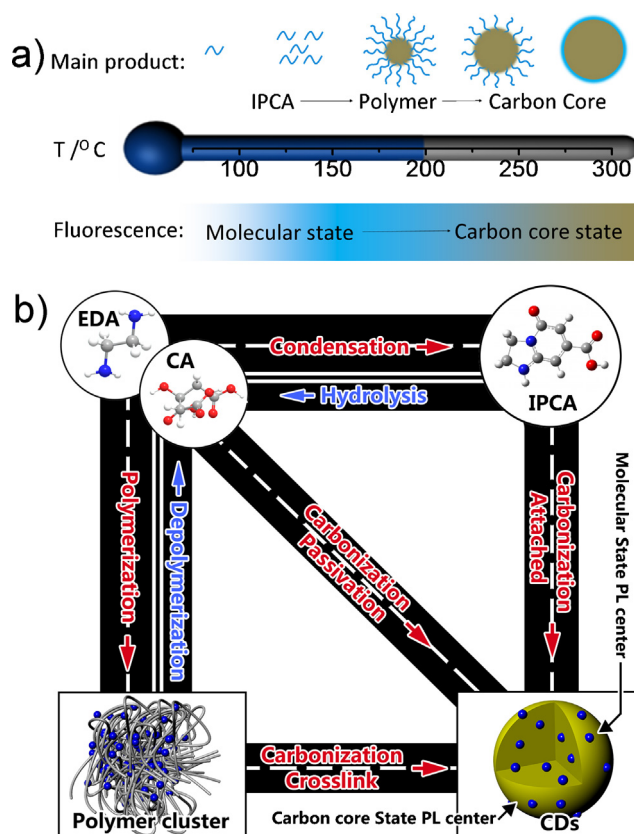


Figure 1 (a) The scheme of CNDs obtained from different temperatures in the one-pot hydrothermal system of CA and EDA. (b) The scheme of relationship between different products. The formed IPCA can be further connected in the inner or surface of the polymer clusters or carbon core. Reprinted with permission from Ref. [39], copyright 2015 Royal Society of Chemistry.

applied the “hydrophilicity gradient ultracentrifugation” to separate CNDs prepared from CA and EDA [41]. They found that separated CNDs of different sizes possessed similar PL, indicating that the PL of such CNDs arises primarily from the molecular state rather than size differences. Furthermore, the separated polymer-like nanoparticles possessed higher QY compared with the carbogenic ones. They also separated CNDs by high-performance liquid chromatography [42].

In the further work of Yang's group [39], a kind of fluorophore (imidazo[1,2-*a*]pyridine-7-carboxylic acid, 1,2,3,5-tetrahydro-5-oxo-, IPCA) with high QYs was purified by column chromatography on silica. Meanwhile, polymer clusters and carbon nanoparticles were also detected, so there is some reaction competition among IPCA, polymer clusters and carbon nanoparticles (Fig. 1b). Elevated reaction temperature will produce more polymer cluster or carbon core (the reaction equilibrium changes based on the reaction temperature). The researchers believed that the IPCA is an independent fluorescent molecule or possibly connected to the surface/inside of the carbon core by covalent bonds (Fig. 2). The amount of IPCA appeared to be dependent on the reaction.

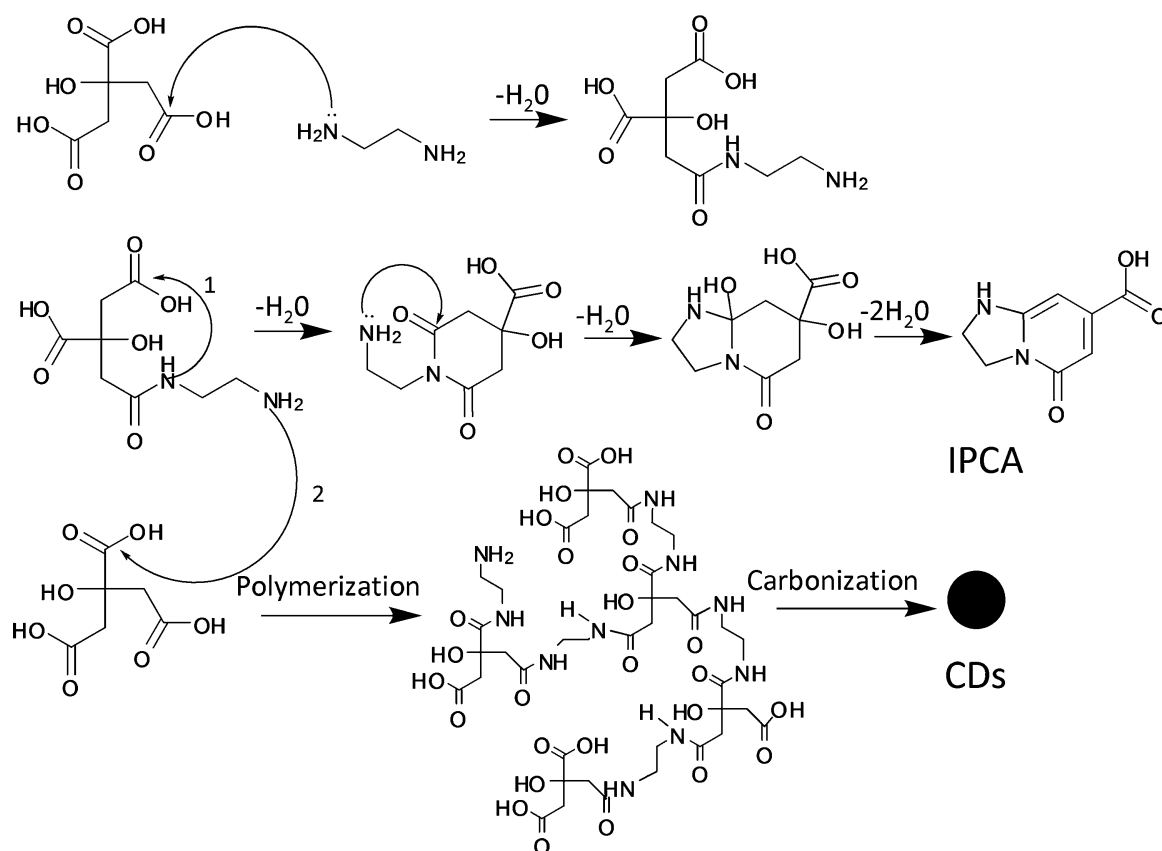


Figure 2 The assumed process of forming the IPCA, polymer cluster and carbon core from CA and EDA. Reprinted with permission from Ref. [39], copyright 2015 Royal Society of Chemistry.

Possible fluorophore molecules in CA derived CNDs

CA-derived CNDs produced via the above-mentioned separation routes, definitely contain fluorophore molecules (they are always detected in the solution out of the dialysis bag during purification of CNDs). Sell et al. first found that CA was able to form fluorescent citrazinic acid by condensation with ammonia [43].

CA is able to react with specific α , β or α , γ bi-amines to produce five or six ring fused 2-pyridone based fluorophores. Kasprzyk's group and Yang's group reported a series of novel fluorescent compounds from condensation mixtures of CA and specific amines with very high QYs (Fig. 3) [39,44,45]. The formation mechanism of those fluorescent compounds is assumed to be as follows (the 1st route of Fig. 2). First, the amide bond between CA and amine is formed with a few intramolecular condensation processes. Then, the intermediate product undergoes further dehydration, forming

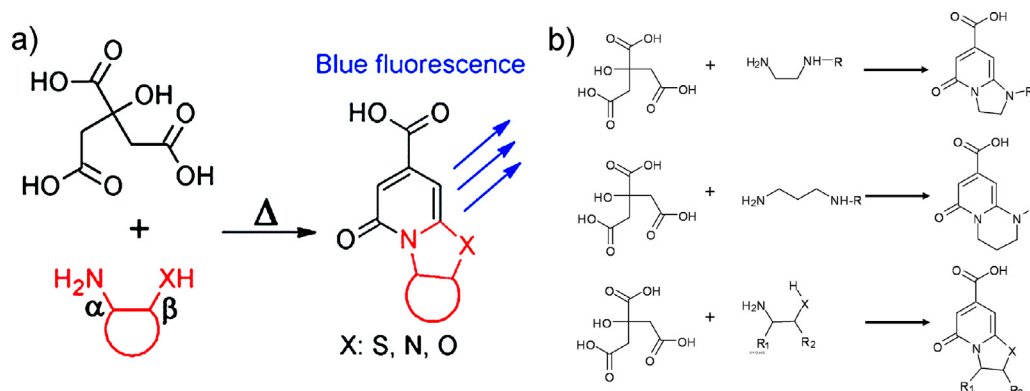


Figure 3 (a) Formation of fluorescent 2-pyridones from CA and amines. Reprinted with permission from Ref. [45], copyright 2015 Royal Society of Chemistry. (b) The potential fluorophore in CA-based CNDs, the R can be small molecular groups or polymer chains. Reprinted with permission from Ref. [39], copyright 2015 Royal Society of Chemistry.

a five-membered ring fused 2-pyridone by condensation of amino group with pyridone oxygen [46,47]. Due to the high reactivity, it is also easy to obtain different fluorescent compounds from CA and other nucleophiles (β -amino alcohols).

Outlook

The citric-acid derived organic molecules in CNDs are discussed in this perspective, and great progresses have been made on the chemical structures and PL mechanism of CNDs. However, this area is still in its infancy and faces several key challenges. First, an important PL center of CA derived CNDs is molecular state, which is very different with previous carbon core state and surface state. We should confirm if there are molecular fluorophores in other non-CA CNDs through bottom-up methods. Second, although the molecular fluorophore is confirmed in the CA derived CNDs, researcher should be conscious of the CNDs with functional molecular state only when the molecular fluorophores are covalently bonded onto the carbon cores. As a result, we should exclude the case that molecule fluorophores are physically absorbed on the carbon cores, which dominate the PL. Third, because the molecular state of CNDs is highly fluorescent, more synthetic approaches should be developed to fabricate these nanodots with high stability and emission in the visible region.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.nantod.2015.09.002>.

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