

Journal of Electrochemistry

Volume 26
Issue 5 Memorial Special Issue for Professor
Chuansin Cha

2020-10-28

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Recommended Citation

Lei BAO, Dai-Wen PANG. Electrochemical Engineering of Carbon Nanodots[J]. *Journal of Electrochemistry*, 2020, 26(5): 639-647.

DOI: 10.13208/j.electrochem.200644

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol26/iss5/13>

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DOI: 10.13208/j.electrochem.200644

Article ID:1006-3471(2020)05-0639-09

Cite this: *J. Electrochem.* 2020, 26(5): 639-647

Http://electrochem.xmu.edu.cn

Electrochemical Engineering of Carbon Nanodots

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Abstract: Carbon nanodots (CNDs), as zero-dimensional carbonaceous fluorescent nanomaterials, are valuable add-ons to the current cohorts of fluorescent nanoparticles. The fine control over the size and the surface is the key to gain designated photophysical properties of CNDs as well as empowers CNDs in many applications. Herein, a series of electrochemical strategies to manipulate the size and the surface of CNDs and to identify the surface structures was presented. Accordingly, the understandings on the originals of photoluminescence as well as the pathways of electrochemiluminescence of CNDs were revealed. These studies demonstrated that electrochemical methods were easy to operate, cost-effective and efficient in altering thin layers of the surface on CNDs within a few nanometers. The key findings in the luminescence mechanism provided guidelines for the rational design of CNDs with suitable features, which could promote applications of CNDs in bioimaging, sensing and catalytic conversion.

Key words: carbon nanodot; electrochemical method; luminescence mechanism; surface structure; electrochemiluminescence

CLC Number: O646

Document Code: A

Carbon nanodots (CNDs), referring to zero-dimensional carbonaceous luminescent nanomaterials, have merits of tunable luminescence emission^[1] and high resistance to photobleaching^[2]. They also possess unique properties associated with their intrinsic nature of carbon, such as high electron mobility, good biocompatibility and low toxicity^[3]. Besides, the photophysical properties, such as size-independent and excitation-dependent photoluminescence (PL), have distinguished CNDs from conventional quantum dots (QDs). Since the first report in 2004^[4], these nanoscopic carbon-based fluorophores have promised various applications in the fields of bioimaging^[5-7], sensing^[8-10] and energy conversion^[11-13].

Structurally, CNDs are composed of carbonic backbones and functional groups or polymer-capped surfaces. Depending on preparation methods and starting materials, their carbonic backbones can be

either in graphite crystalline or in the form of amorphous carbon. In some cases^[14-19], the obtained backbones only contain single or few atomic layers of graphene sheets, so-called graphene quantum dots (GQDs). As to surfaces, surface oxides are the common species covering the carbonic cores, resulting in hydrophilic CNDs. Hydrophobic CNDs can also be obtained through carbonization of organic moelcues^[20]. Considering the rather small size of CNDs (less than 10 nm), there are significant amounts of surface moieties over the whole structures. The surface properties have played vital roles in determining optical properties, stabilities, solubility and functionalities^[21]. Controlling the surface without damage to the carbonic core structure is demanding but challenging in this research field.

Despite enormous reports on CNDs over the last decades, limited methods can provide precise control

Received: 2020-06-30, Revised: 2020-08-02. *Corresponding author, Tel: (86-27)68756759, E-mail: dwpang@whu.edu.cn (Permanent). This paper is dedicated to Prof. Chuan-Sin Cha. Dai-Wen Pang is grateful for the indelible mentorship from Prof. Chuan-Sin Cha and Prof. Zhongli Wang and acknowledges the support from the National Natural Science Foundation of China (Nos. 21535005, 20621502 and 20921062). Lei Bao acknowledges the support from the Australian Research Council (DE190101514).

of size as well as the surface in the synthesis. Moreover, how surface properties impact the photophysical properties of CNDs remains an open question. Many approaches such as wet oxidation, laser ablation, ultrasound and carbonization have been developed to obtain CNDs. The features of different synthesis methods have been covered by several comprehensive reviews^[22-26]. Among these methods, electrochemical exfoliation or etching is considered as a representative top-down approach to synthesize CNDs. Through controlling parameters (e.g. applied potentials, electrode materials or electrolytes), the size and the surface of CNDs can be modulated during the preparation. Additionally, combining with electrochemical voltammetry and electrochemiluminescence techniques, comprehensive information on the structures and luminescent mechanism of CNDs can be accessed.

In the past few years, several electrochemical strategies^[27-29] have been developed to control the size, to tune the surface, to identify the surface structures, and hence, to reveal PL essentials of CNDs. In this review, we highlight our research progress in this regard and provide perspectives on using electrochemical methods for the study of CNDs as well. This paper is organized as follows: Section 1 describes the electrochemical synthesis of CNDs in aqueous and non-aqueous electrolyte solutions. Section 2 covers how to identify surface groups by cyclic voltammetry and to tune the surface oxidation groups of CNDs electrochemically. In Section 3, electrochemiluminescence of CNDs is presented, followed by the summary and outlook in Section 4.

1 Electrochemical Synthesis of CNDs

In electrochemical methods, carbon-based electrodes (e.g. graphite rods^[30-31], multiwalled carbon nanotubes (MWCNTs)^[32], carbon fibers^[33], carbon paste electrodes^[34]) were electrochemically etched (Fig. 1A) in either aqueous media or nonaqueous media to form luminescent carbon nanoparticles. The resultant CNDs generally contain carbon cores and surfaces covered with oxygen-containing functional groups.

In NaH_2PO_4 aqueous solution, fluorescent CNDs

were successfully obtained by electro-oxidizing carbon electrodes at a high applied potential. When polarizing graphite rods at +3 V (vs. SCE) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaH_2PO_4 aqueous solution^[30], $1.9 \pm 0.3 \text{ nm}$ CNDs emitting blue PL as well as $3.2 \pm 0.5 \text{ nm}$ CNDs emitting yellow PL were gained (Fig. 1B). Notably, fluorescence peaks of the resultant CNDs did not shift as changing excitation wavelength (Fig. 1C). It is the first time that fluorescence-non-shifting CNDs were prepared. Also, these CNDs displayed pH-sensitive fluorescence and low cytotoxicity, which could be used for monitoring intracellular pH change (Fig. 1D). It was noticed that PL shifting and non-shifting CNDs could be controllably synthesized by varying the composition of carbon electrodes. Home-made carbon paste electrodes (CPEs) were electro-oxidized at +9 V (vs. SCE) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaH_2PO_4 aqueous solution^[34]. When employing 64% CPEs (64% mass fraction of conductive carbon black and 36% liquid olefin), the emissions of as-resulting blue CNDs (64% CNDs) shifted with the varied excitations. While 73% CNDs prepared by using 73% CPEs exhibited emission wavelength shifting along with excitations (Fig. 2A), despite the statistical diameters of 73% CNDs as the same as 64% CNDs. The measurement of charging currents has identified that the oxidation current passing through 64% CPEs was about four times higher than that through 73% CPEs (Fig. 2B). Consequently, 64% CNDs possessed higher oxidation degree on the surface than 73% CNDs. It is likely that the abundant oxides on the surface lead to multiple emissive sites, showing different emission wavelengths.

In the aqueous solution, when applying high positive potentials, anodic oxidation of water occurs ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, $E^0 = 1.23 - 0.059\text{pH}$), which is accompanied by generation of hydroxyl radicals ($\text{H}_2\text{O} \rightarrow \text{OH}^\cdot + \text{e}^- + \text{H}^+$) and oxygen radicals ($\text{OH}^\cdot + \text{H}_2\text{O} \rightarrow \text{O}_2^{\cdot-} + 3\text{H}^+ + 2\text{e}^-$). The electrochemically generated oxidative radicals (OH^\cdot and $\text{O}_2^{\cdot-}$) cleave bulk carbon-based electrodes into small fragments effectively, attributed to the formation of CNDs. Because the oxidation through radicals is non-selective, the obtained CNDs are of polydispersity. Thus, post-separation is

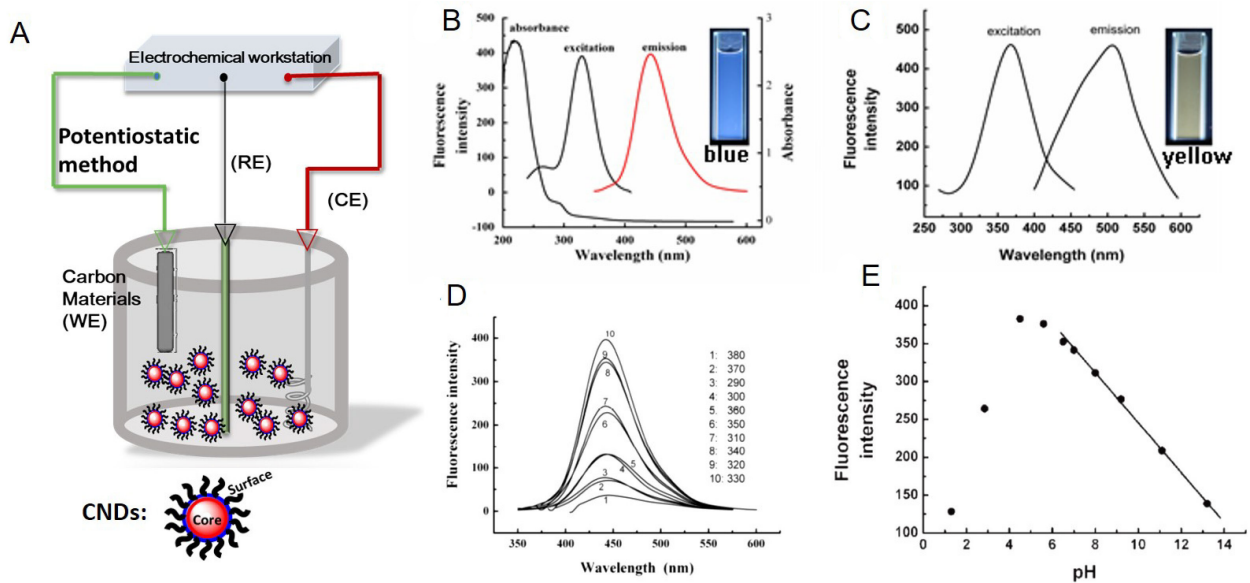


Fig. 1 (A) The schematic illustration of electrochemical set-up to prepare CNDs. (B) UV-vis absorption and fluorescence spectra of blue CNDs (< 5 kD) (left) and (C) yellow CNDs (5 ~ 10 kD) (right) in aqueous solution. (D) Emission spectra of blue CNDs under different excitation wavelengths as indicated. (E) The correlation of fluorescence intensity of CNDs with environmental pH. Reproduced with permission from Ref 30. Copyright 2008 Royal Society of Chemistry.

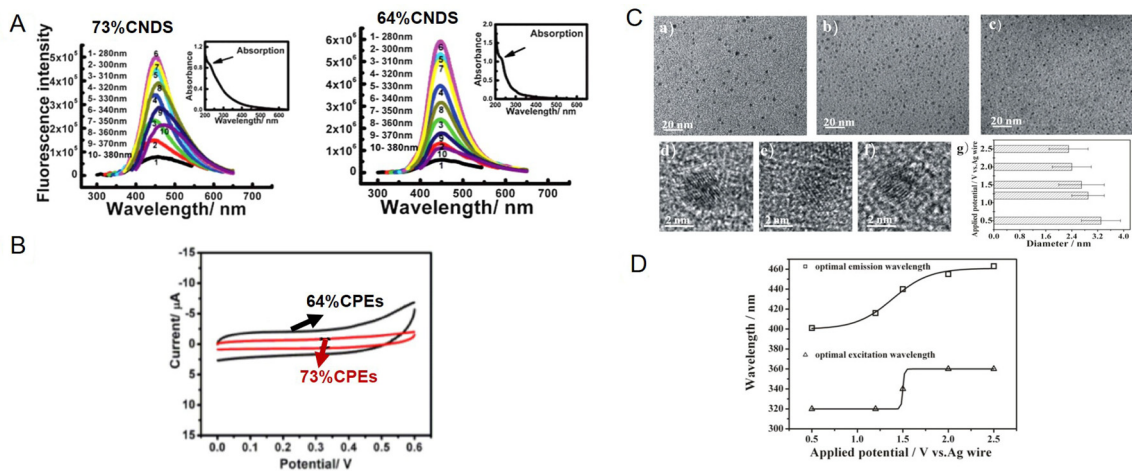


Fig. 2 (A) The emission spectra of as-prepared 73%CNDs (left) and 64%CNDs (right) under corresponding excitations as indicated. (B) CVs of 64% and 73% carbon paste electrode in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ NaH}_2\text{PO}_4$ aqueous solution. Reproduced with permission from Ref 34. Copyright 2012 Royal Society of Chemistry. (C) TEM images of obtained CNDs and a summary of their size under indicated applied potentials. (D) The optimal emission and excitation wavelengths of as-prepared CNDs prepared under different potentials. Reproduced with permission from Ref 33. Copyright 2011 Wiley.

generally required to narrow down the size distribution and to remove non-fluorescent carbon particles. Nevertheless, the aqueous-based electro-oxidation process has the merit of large-scale production due to high oxidation efficiency. Another advantage is that luminescent CNDs with long-emission wavelength

tend to be yielded in this process.

While in a non-aqueous solution, as applied potentials locate in the potential window of a non-aqueous electrolyte solution, the polarization of carbon-based electrodes predominates over the polarization of electrolyte. Oxidation and break of carbon

bonds in carbon-based electrodes have been initiated by the applied potentials. Meanwhile, the intercalation of electrolyte cations or anions into graphite layer structures may also be driven, which further facilitates fragmentation. CNDs are expected to be generated under the synergetic effect of the above reactions. Considering the reaction rate is controlled by applied potential and current, the CNDs yielded in this process primarily possess blue luminescence with narrow size distribution.

More precise size-control has been done for the first time by tuning the oxidation potentials applied onto carbon fibers in 0.1 mol · L⁻¹ tetrabutylammonium perchlorate (TBAP) acetonitrile solution in our group^[33]. The CNDs in the sizes of 3.3 ± 0.6 nm, 2.9 ± 0.5 nm, 2.7 ± 0.7 nm, 2.4 ± 0.6 nm and 2.2 ± 0.6 nm were gained under the applied potentials at +0.5 V, +1.2 V, +1.5 V and +2.5 V (vs. Ag wire), respectively (Fig. 2C). It has shown that monodisperse fluorescent CNDs could be directly obtained without further separation. The size of the as-prepared CNDs was dependent on the applied potential. The higher applied potential facilitated the formation of smaller sized CNDs, implying that increased applied potential was more efficient to ‘cut’ bulk materials into small pieces. The emission spectra of these CNDs were excitation-dependent. It is also interesting to see that large-sized CNDs have short emission wavelengths (Fig. 2D). This feature is contrary to the size-dependent behavior of conventional quantum dots, in which large-sized particles typically have long emission wavelengths. This research has indicated that not only size but also the surface of CNDs has a significant impact on their PL properties.

2 Electrochemical Modulation of the Surfaces

Considering the high surface-to-volume ratio, the surface properties of CNDs have largely influenced the physical and chemical properties, such as solubility, stability, photo-physics and catalytic ability. Oxygen moieties (e.g. -OH, -CO, -COOH), which facilitate water-solubility and subsequent functionalization of CNDs, are common species largely existing

on the surface of CNDs. Some of the groups are redox-active. Hence, cyclic voltammetry (CV) can be used to identify specific group units on the surface. For instance, CV was utilized to verify surface structures of 2.7 nm GQDs^[35]. The CVs of GQDs solutions presented a pair of symmetrical redox peaks at glassy carbon electrodes (Fig. 3A). The formal potential at 0.29 V with the separation of the peak potential 36 mV implies a two-electron quasi-reversible electrochemical reaction. The formal potential linearly depends on pH (from 7.2 to 11.0) with a slope of -56 mV · pH⁻¹, indicating a two-proton-coupled electron transfer process. These two-proton and two-electron redox reactions match with typical electro-reactions of quinone-diol derivatives in aqueous media. Among the derivatives, quinones were preferred structures as the oxidation peak disappeared while the reduction peak enhanced after the first cycle of CVs. Specifically, ortho-quinone structures were assigned in this case because the formal potential of the reversible peaks was close to that of catechol (21 mV) rather than hydroquinone under the same experimental conditions. Given the existence of ortho-quinone structures, it is achievable to modulate the PL emissions of GQDs by attaching 1,2-diamine compounds. The increase in the overall conjugation structures of GQDs resulted in the red-shift of PL emission, indicating that conjugation system can affect bandgap.

Moreover, surface oxygen species on CNDs could introduce surface disorder structures, generate surface states and influence the luminescent properties of CNDs consequently. Therefore, tuning the surface-oxidation degree is a considerable scenario to explore the new features and PL mechanism of CNDs. Our research has demonstrated that the extent of oxidation on the surface of CNDs can be electrochemically adjusted without changing the size of CNDs. In 0.1 mol · L⁻¹ TBAP acetonitrile solution, the prepared CNDs were further oxidized on a working electrode of platinum (Pt) at an applied potential of +2.5 V (vs. Ag wire) for two hours^[33]. The further oxidized CNDs displayed red-shifted emissions compared to the original CNDs (Fig. 3B). The images of

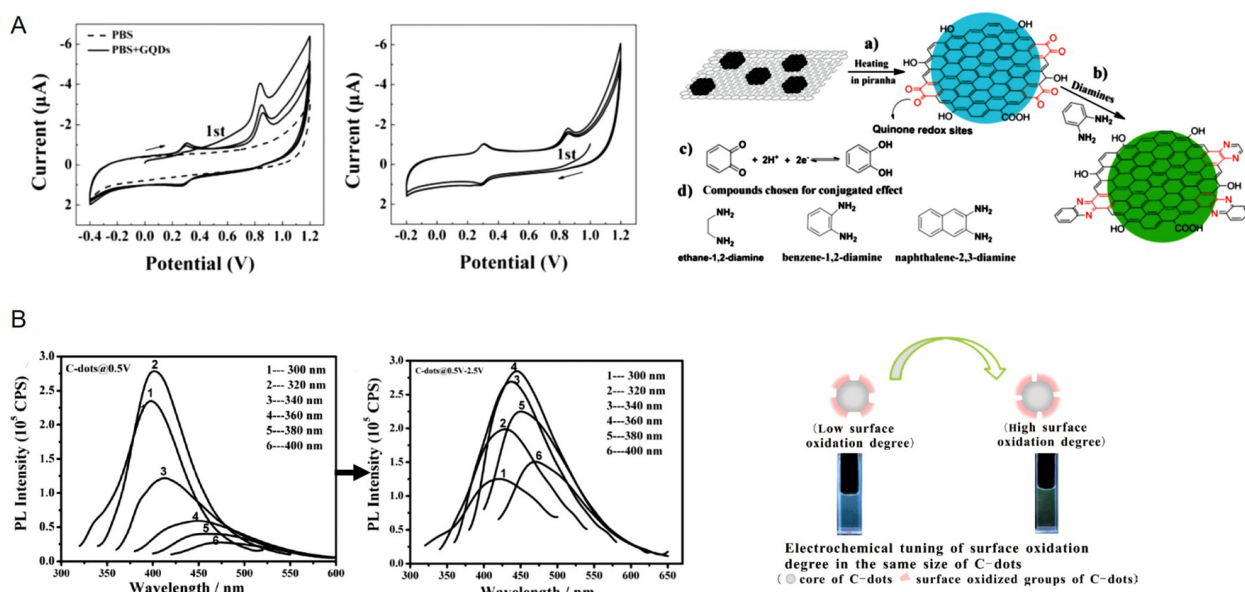


Fig. 3 (A) CVs of a glassy carbon electrode in $0.2 \text{ mol} \cdot \text{L}^{-1}$ pH 7.2 phosphate buffer solution containing (solid line) $0.15 \text{ mg} \cdot \text{mL}^{-1}$ GQDs: scan direction starting towards positive potentials (left panel) and towards negative potentials (middle panel). Illustrative surface modification of GQDs with indicated molecules (right panel). Reproduced with permission from Ref 35. Copyright 2015 Royal Society of Chemistry. (B) The emission spectra of CNDs before (left panel) and after (middle panel) further electro-oxidation. Demonstration of CND-luminescence varied with surface oxidation. Reproduced with permission from Ref 33. Copyright 2011 Wiley.

transmission electron microscopy (TEM) indicated that the size of CNDs remained the same. While the spectra of X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FT-IR) verified that the content of oxygen on the surface of CNDs increased after further electrochemical oxidation. Specifically, the percentage of C-OH and C=O groups on CNDs raised significantly. Analogously, the CNDs, electro-oxidized on Pt wire in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaH_2PO_4 solution at +1.5 V (vs. Ag/AgCl) for 1.5 h, exhibited improved surface oxidation degree evident by XPS and FT-IR spectra^[34]. Compared to the original CNDs with nonshifting PL, the as-oxidized CNDs had unchanged size but their PL spectra started to shift along with excitation wavelength changing. These observations clearly implicated surface oxidation-related luminescence of CNDs. It is asserted that the higher the surface-oxidation degree, the more surface defects created on the surface, which are accountable for the red-shifted emission as well as for the multi-emissive sites induced shifting PL. There-

fore, the present electrochemical method is an effective manner to modulate the fluorescent characteristics of CNDs via tuning the surface oxidation degree.

3 Electrochemiluminescence (ECL) of CNDs

Besides photoluminescence, the light from CNDs can be generated by electrochemical reactions. That is to say when applying certain potentials, cation radicals ($\text{CNDs}^{+\bullet}$) and anion radicals ($\text{CNDs}^{-\bullet}$) are formed simultaneously. The collisions between cation and anion radicals produce excited state CNDs^* , which relax back to the ground states to give off ion-annihilation ECL. In the case of $\text{CNDs}^{+\bullet}$ or $\text{CNDs}^{-\bullet}$ alone produced in the system, co-reactants, such as $\text{S}_2\text{O}_8^{2-}$ or L-cysteine, are employed to facilitate the formation of CNDs^* for anodic or cathodic ECL. The results of ECL are informative because the redox potential, corresponding current and light intensity are captured at the same time. The explication of the ECL process is imperative to get insights into electron transfer pathways and energy levels in nanoparti-

cles, as well as to develop nanomaterial-based catalysts and biosensors^[36].

As aforementioned, surface oxides are accountable for forming surface states, and trapping electrons and holes in CNDs. Considering that electrons transfer between electrodes and nanoparticles will pass through their surface in ECL, it is possible to decode the particular oxygen-containing units on the surface of CNDs through understanding the ELC process. By introducing CNDs into classic Ru(bpy)₃²⁺-ECL system, our group have revealed that benzylic alcohol units on the surface of CNDs enabled these fluorescent carbon nanomaterials as co-reactants in the anodic ECL of Ru(bpy)₃²⁺^[37](Fig. 4A). During the potential scan from +0.20 to +1.40 V (vs. Ag/AgCl), Ru(bpy)₃²⁺ were electro-oxidized into Ru(bpy)₃³⁺ at 1.15 V. Meanwhile, benzyl alcohol units on CNDs were oxidized to form strong reductive intermediates, α-hydroxybenzylic radicals[C₆H₅CHOH][•], which then deprotonated to C₆H₅CHO upon oxidation. The standard potential

$E^0([C_6H_5CHOH]^•/C_6H_5CHO)$ was estimated to be -1.25 V (vs. NHE), which is sufficient enough to reduce Ru(bpy)₃³⁺ into Ru(bpy)₃^{2+*} with $E^0(Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+*})$ of -0.86 V (vs. NHE). This newly established Ru(bpy)₃³⁺-CNDs ELC system with excellent reproducibility, stability and eco-friendly features also promised the quantitative detection of dopamine in the range of 0.5 ~ 20 μmol · L⁻¹ with the detection limit down to 0.3 μmol · L⁻¹.

With the uncovering of CNDs being co-reactants, so-called ‘self-co-reactant’ ELC pathway was recognized for the first time to rationalize that CNDs can emit anodic ECL without additional co-reactants^[38]. An H-shaped electrolytic cell was employed in the study to separate a Pt disc working electrode with a Pt coil counter electrode and hence to exclude interferences. The main findings are as follows: i) when applying positive potentials from 0 to +1.5 V (vs. Ag/AgCl), CNDs^{•+} were created electrochemically and the surface units, benzylic alcohols, were transited

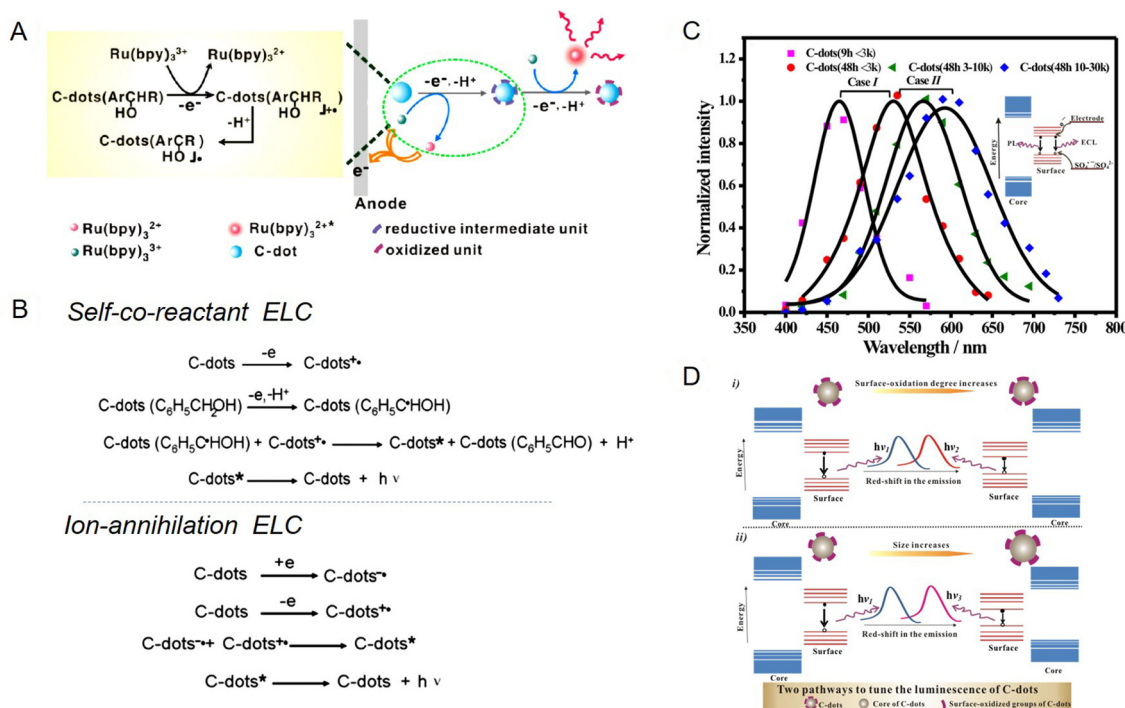


Fig.4 (A) Scheme of CNDs as co-reactants in the anodic ECL of Ru (bpy)₃²⁺. Reproduced with permission from Ref 37. Copyright 2014 American Chemical Society. (B) Two types of the mechanism of CND-ECL. Reproduced with permission from Ref 38. Copyright 2018 Elsevier. (C) ECL spectra of CNDs either with different sizes or with different surface oxidation degrees. (D) Illustration showing the impacts of the surface and the size on CND-luminescence. Reproduced with permission from Ref 39. Copyright 2015 Wiley.

into $[\text{C}_6\text{H}_5\text{CHOH}]^*$. The subsequent recombination from the exciton pair of $(\text{CNDs}^{+\bullet} - [\text{C}_6\text{H}_5\text{CHOH}]^*)$ resulted in the observed anodic ECL (Fig. 4B top). ii) When pulsing or cycling potentials between negative and positive regions, the observed ECL signals were ascribed to both self-co-reactants ECL and ion-annihilation ECL (Fig. 4B bottom).

Furthermore, as ECL is susceptible to the surface of nanoparticles, the comparison of ELC spectra with PL spectra can provide insights into the emission origins. Our group measured ECL spectra of different sized CNDs, which were synthesized via chemical oxidation of carbon fibers^[39]. Each ECL spectrum matched with its corresponding PL spectrum, implying that both PL and ECL emitters came from the surface (Fig. 4C). The red-shifted ECL spectrum along with the increased size or surface-oxidation of CNDs disclosed that the energy levels of the surface emissive sites are attributed to both the π -electron system and the surface chemistry^[40] (Fig. 4D). These understandings have provided insights into the rational design of CNDs, facilitating to expand full potentials of CNDs in many applications.

4 Summary and Outlooks

In this review, the effects towards the rational design of CNDs via electrochemical methods were described. Both the size and the surface composition of CNDs can be modulated through designated electrochemical reactions. The established electrochemical strategies can easily tune the surface of CNDs with a size of several nanometres without changing the core size, which is hard to be realized by other methods. The subsequent alternation of photo-properties associated with the surface suggested the surface-related luminescence of CNDs. Moreover, the redox potentials shown in the electrochemical reactions not only can be treated as fingerprints to identify exact surface structures of CNDs, but also can be used to determine energy levels of CNDs. These electrochemical strategies can also be adapted into the study of other novel nanomaterials such as Ag clusters and ultrasmall Ag_2Se QDs.

Although electrochemical methods have shown

as effective ways to manipulate CNDs, there are still more efforts required on precise control of specific surface groups. One way is to combine with additional chemical modification, which has selectivity towards certain surface groups^[40]. With improved selectivity, electrochemical methods can be powerful in modifying and probing specific surface structures of nanomaterials. As for CNDs, besides their applications in bioimaging and biosensing, considering enriched surface states existing on CNDs, there will be considerable potentials for CNDs as catalysis or redox species in electrochemical reactions, which is worth further efforts.

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电化学方法调控荧光碳点的研究

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摘要: 作为零维碳基发光纳米材料, 碳点是对现有发光纳米材料的重要补充. 精准控制粒径及表面结构对实现碳点的性质调控及其应用至关重要. 本文介绍了本课题组在利用电化学方法研究荧光碳点方面的进展. 重点展示了利用电化学方法实现对碳点粒径的控制, 对表面氧化程度的调节以及对其发光机理的研究. 电化学方法可对只有几纳米厚度的材料表面进行有效的控制, 可操作性强且经济环保. 通过对碳点的粒径及表面的调控, 作者也进一步揭示了碳点的发光与表面结构的相关性. 这些工作为碳点的合成及其性质调控提供了可循的规律, 有利于推动碳点在生物医生成像、传感检测、催化及能源转化等领域的应用.

关键词: 碳点; 电化学合成; 发光机理; 表面结构; 电致化学发光