Cu–N Dopants Boost Electron Transfer and Photooxidation Reactions of Carbon Dots**

Wenting Wu, Liying Zhan, Weiyu Fan, Jizhong Song, Xiaoming Li, Zhongtao Li, Ruiqin Wang, Jinqiang Zhang, Jingtang Zheng, Mingbo Wu,* and Haibo Zeng*

Abstract: The broadband light-absorption ability of carbon dots (CDs) has inspired their application in photocatalysis, however this has been impeded by poor electron transfer inside the CDs. Herein, we report the preparation of Cu–N-doped CDs (Cu-CDs) and investigate both the doping-promoted electron transfer and the performance of the CDs in photo-oxidation reactions. The Cu–N doping was achieved through a one-step pyrolytic synthesis of CDs with Na₂[Cu(EDTA)] as precursor. As confirmed by ESR, FTIR, and X-ray photoelectron spectroscopies, the Cu species chelates with the carbon matrix through Cu–N complexes. As a result of the Cu–N doping, the electron-accepting and -donating abilities were enhanced 2.5 and 1.5 times, and the electric conductivity was also increased to 171.8 as cm⁻¹. As a result of these enhanced properties, the photocatalytic efficiency of CDs in the photo-oxidation reaction of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate is improved 3.5-fold after CD doping.

Increasing interest in photocatalysis has been fueled by the ecological and economical advantages of using visible light as an abundant source of energy. For the efficient conversion of light energy into chemical energy and in related areas, photocatalytically active nanomaterials have been employed as photocatalysts to study electron-transfer processes and in charge separation.[1] The challenge in this area is to develop more low-cost photocatalysts to replace the known limited photocatalysts based on noble-metal nanoparticles, such as Ru nanoparticles.[10] Fortunately, carbon dots (CDs) shows unique electron transfer and broadband light-absorbing abilities, a large specific surface area, and are abundant, inexpensive, and nontoxic.[2–13] These excellent properties are beneficial to intermolecular electron transfer, which plays a key role in many photooxidation reactions. However, most of the recent research has focused mainly on the emission properties of CDs.[5,6,10–12] There have been few recent efforts devoted to the fabrication of composites based on CDs to enhance their photocatalytic ability.[3,4,14–16] For example, Kang et al. prepared Au/CD composites as photocatalysts for the oxidation of cyclohexane in the presence of H₂O₂.[14] CD/TiO₂ nanotube composites were prepared for the degradation of rhodamine B.[17,18] However, CDs alone as photocatalysts show great potential. There have been relatively few examples of unfunctionalized CDs employed as photocatalysts which were designed to have enhanced electron-transfer properties, such as an electron-accepting ability, electron-donating ability, and conductivity.[4,19]

The selection of functionalized precursors with a fixed structure is a powerful approach to the design of novel CDs. Ethylenediaminetetraacetic acid (EDTA), with a flexible structure, is a common starting material for CDs. Interestingly, a saturated Schiff-base-like structure could be formed after EDTA chelated with metal ions such as Cu[17,18] (Na₂[Cu(EDTA)]). Using Cu[11] complexes, which prefer square-planar geometries,[20] a flaky graphite conductive structure could be easily formed. Cu complexes themselves used as commercial photocatalysts play important roles in electron-transfer processes for the conversion of solar energy.[20–23] For example, incorporating Cu complexes with the Schiff base ligand into zeolite significantly enhanced the photocatalytic ability.[24] Therefore, Na₂[Cu(EDTA)] is a new source with a saturated Schiff-base-like planar structure to fabricate novel CDs.

Herein, Cu–N-doped CDs (Cu-CDs) were prepared by a facile one-step pyrolytic synthesis from Na₂[Cu(EDTA)] precursors. During pyrolysis, this saturated Schiff-base-like structure transforms into a Cu coordination complex chelated with graphene matrixes, which is confirmed by ESR, TEM, XRD, FTIR, Raman, and X-ray photoelectron (XPS) spectroscopies. Under an atmosphere of air instead of pure oxygen, Cu-CDs were used as the photocatalyst for the photooxidation reaction of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (1,4-DHP), which is the key component in a variety of bioactive compounds, such as anti-hypertensives and calcium-channel blockers.[25] This Cu-CD material, unlike previous CD-based composite photocatalysts, show outstanding electron-transfer properties. The conversion of 1,4-DHP
catalyzed by Cu-CDs is 3.5 times higher than that of CDs without Cu–N doping.

Cu-CDs were prepared through thermolysis of Na₂[Cu(EDTA)] at 250°C, 300°C, and 350°C, as shown in Figure 1a. When the temperature is lower than 250°C, it is hard to carbonize Na₂[Cu(EDTA)] to form CDs. On the other hand, when the temperature is higher than 350°C, the carbonization degree is too high to form CDs in the nanoscale, resulting instead in the formation of powders on the microscale. An atomic absorption spectrum verified that the Cu content in CDs decreased with increasing temperature (see Figure S1 in the Supporting Information). For Cu-CDs prepared at 250°C, denoted Cu-CDs(250), the Cu content is 2.1%. However, as temperatures were increased to 300°C and 350°C, the Cu content decreased to 1.0% and 0.59%, respectively. This may be as a result of the easier reduction of Cu²⁺ by carbon at higher temperature, which is confirmed by the XRD results. The XRD pattern of the precipitate after centrifugation of the mixture containing Cu-CDs(250) shows prominent peaks at 2θ = 26°, 43°, and 50°(Cu²⁺) (Figure S2a). However, the precipitate prepared at 350°C (Figure S2b) shows a weaker peak attributable to graphite at 2θ = 26°. These results indicate that Cu²⁺ was easily reduced into Cu⁰ by carbon, and the higher thermolysis temperature causes the decrease of Cu²⁺ content in Cu-CDs. In this work, Cu-CDs were prepared at 250°C.

The TEM image of Cu-CDs clearly displays the uniformity of Cu-CDs with an average diameter of about 2.3 nm, as shown in Figure 1b and Figure S3. The high-resolution TEM (HRTEM) image demonstrates the good crystallinity of Cu-CDs with a lattice spacing of 0.36 nm corresponding to the lattice fringes of the (002) planes of graphite. The XRD and Raman spectroscopic results were consistent with these results (Figure S4), supporting the formation of a graphite-like structure, which should be beneficial for enhancing conductivity in the electron-transfer process.

Significantly, the visible-light-harvesting ability of CDs was greatly enhanced after doping, as shown in Figure 1c. Na₂[Cu(EDTA)] absorbs strongly only in the UV region of the electromagnetic spectrum. However, Cu-CDs show a broadband absorption from λ = 300 nm to 600 nm. Meanwhile, the absorption intensity of Cu-CDs is higher than that of pure CDs, which could be attributed to the existence of Cu–N dopants, producing Cu-to-graphite charge-transfer (CT) absorption. The color of the Cu-CD solution is brown, as shown in the inset of Figure 1c. The solution of Cu-CDs gives blue emission upon excitation by UV light at λ = 365 nm. After irradiation for 160 min, there is no obvious photo-bleaching for Cu-CDs, indicating that Cu-CDs are stable (Figure S5), which will be beneficial for their application in photocatalysis.

The valence states of the Cu species in Cu-CDs were further investigated, as shown in Figure 2 and Figure S7. The high-resolution Cu 2p XPS spectra (Figure S7) shows the presence of Cu in Cu-CDs (932.5 eV, 934.2 eV, 952.5 eV). Therefore, it demonstrates the existence of Cu⁰ in Cu-CDs prepared by the one-step pyrolytic synthesis. To further analyze the valence state of copper, Cu-CDs were measured by ESR spectroscopy at room temperature, as shown in Figure 2a. If the g tensor parameter (g) is less than 2.3, the species can be assigned to being in a covalent environment, otherwise it is in an ionic environment. The g value of Cu-CDs is 2.16, which is less than 2.3, indicating the covalent character of the Cu–ligand bond inside CDs.[30,31] The FTIR spectra of Cu-CDs from 900 to 1100 cm⁻¹ were amplified to further characterize the chemical bond between the Cu and the matrix, as shown in Figure 2b and Figure S8. Compared with pure CDs, Cu-CDs show new bands at 1050 cm⁻¹ and 1020 cm⁻¹, which can be assigned to a N-Cu-N stretching vibration, further confirming the formation of Cu coordination complexes in Cu-CDs.[32]

To compare the photocatalytic abilities of Cu-CDs with pure CDs, the photooxidation of 1,4-DHP was carried out as shown in Figure 3a and Figure S9. 1,4-DHP was irradiated under an atmosphere of air instead of an atmosphere of pure oxygen. Upon irradiation of the mixed solution of Cu-CDs and 1,4-DHP with a xenon lamp (λex > 385 nm; Figure 3b), the absorption of 1,4-DHP at λ = 374 nm decreased and the absorption of the product (pyridine derivatives, 1b in Figure 3a) at λ = 280 nm increased. The formation of the
incorporated Cu–N dopants have enhanced the photocatalytic reaction. The mechanism, involving electron catalyzed by Cu-CDs, is proposed in Figure 4a, wherein the role of Cu-CDs changes from being an electron acceptor to an electron donor. First, Cu-CDs were photoexcited into the excited state (Cu-CDs*) and subsequent electron transfer from 1,4-DHP (electron donor) to Cu-CDs* (electron acceptor) produced the Cu-CD radical (Cu-CD*). Secondly, O2 reacts with Cu-CD* to produce O2•−, which leads to the recovery of the photocatalyst, producing concomitantly the superoxide anion radical (O2•−). Finally, O2•− reacts with H+ to produce H2O2. As a result of the presence of CDs, H2O2 is subsequently decomposed into O2 and H2O, meeting the demands of green chemistry by producing environmentally friendly side products.[16,37]

To confirm the electron-transfer mechanism, ESR spectroscopy was employed to monitor the trapping of O2•− intermediates with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), which acts as a scavenger for O2•− as shown in Figure S12. 1,4-DHP, Cu-CDs, and DMPO were mixed in an aerated aqueous solution. A strong signal for the DMPO–O2•− adduct was detected. In the absence of any of the three reagents, no signal was detected. Compared with that of pure CDs, Cu-CDs show a stronger signal for the DMPO–O2•− adduct, indicating that Cu–N dopants have improved the efficiency of electron transfer from the substrate to the Cu-CDs, as well as from the Cu-CDs to O2.

For an efficient electron-transfer process, excellent electron accepting and donating abilities and strong conductivity are key. Herein, these three factors are examined for Cu-CDs. First, the quenching effect of emission intensity by the known electron acceptor 2,4-dinitrotoluene (DNT) upon excitation at 350 nm in H2O was studied by plotting the ln(A/A0)–t curves, as shown in Figure S9 and Table S1. The slope (kobs) of the photooxidation with Cu-CDs(250) is 46 × 10−3 min−1, which is higher than those of Cu-CDs prepared at 300°C (Cu-CDs(300); 43 × 10−3 min−1) and at 350°C (Cu-CDs(350); 26 × 10−3 min−1). These results indicate that the actual photocatalysts are Cu-CDs, but not Na2[Cu(EDTA)], and that the incorporated Cu–N dopants have enhanced the photocatalytic activity of the CDs.

Electron transfer is a crucial underlying process for the photooxidation reaction. The mechanism, involving electron transfer for the photooxidative aromatization of 1,4-DHP catalyzed by Cu-CDs, is proposed in Figure 4a, wherein the role of Cu-CDs changes from being an electron acceptor to an electron donor. First, Cu-CDs were photoexcited into the excited state (Cu-CDs*) and subsequent electron transfer from 1,4-DHP (electron donor) to Cu-CDs* (electron acceptor) produced the Cu-CD radical (Cu-CD*) and the 1,4-DHP radical cation (1,4-DHP+). Highly reactive 1,4-DHP+ is preferable to release H+ (1,4-DHPH+), and electron transfer process from 1,4-DHP to O2 results in the production of the final aromatization product 1b and the reactive oxygen radical O2•−. Subsequently, O2•− gains an electron from Cu-CDs− (electron donor), which leads to the recovery of the photocatalyst, producing concomitantly the superoxide anion radical (O2•−). Finally, O2•− reacts with H+ to produce H2O2. As a result of the presence of CDs, H2O2 is subsequently decomposed into O2 and H2O, meeting the demands of green chemistry by producing environmentally friendly side products.[16,37]

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Volmer quenching constants ($K_V$) for Cu-CDs(250), Cu-CDs(300), Cu-CDs(350), and CDs are 24.78 m$^{-1}$, 19.8 m$^{-1}$, 16.77 m$^{-1}$, and 9.54 m$^{-1}$, respectively (Figure 4b). With increasing Cu content, the electron-accepting abilities of Cu-CDs were enhanced. Cu-CDs also acted as a strong electron donor, allowing highly efficient emission quenching by 2,4-dinitrothiophene (Figure S14). The $K_V$ value of Cu-CDs incorporating Cu--N dopants is about 95 m$^{-1}$, which is higher than that of CDs (65.7 m$^{-1}$; Figure 4c). The above results confirmed that introducing Cu--N into CDs could enhance the electron donating and accepting abilities, which are beneficial to their application in photooxidation reactions.

Furthermore, the conductivities of the Cu-CDs were measured using a DDS-307 A electric conductivity meter. The electric conductivity of the Cu-CDs(250), Cu-CDs(300), and Cu-CDs(350) are 171.8 $\mu$S cm$^{-1}$, 113.9 $\mu$S cm$^{-1}$, and 104.4 $\mu$S cm$^{-1}$, respectively (Table S1). Additionally, Nyquist diagrams for electrochemical impedance spectroscopy (EIS) measurements of Cu-CDs, Na$_2$[Cu(EDTA)], and pure CDs were studied (Figure 4d). The diameter of the semicircle of these complexes in the Nyquist plots close to zero suggests an ultra-small interface electron resistance ($R_e = 0$). At the same time, the slope of the Nyquist plots of Cu-CDs is higher than others, indicating that Cu-CDs have higher electron diffusion ability. Therefore, it is clear that Cu--N dopants have enhanced the conductivity of CDs, which would also benefit the efficiency of electron transfer in the photooxidation reaction.

In conclusion, Cu--N-doped CDs were successfully synthesized by a facile one-step pyrolysis from Na$_2$[Cu(EDTA)], wherein Cu-CDs prepared at 250°C shows the highest Cu content of 2.1%. Under an atmosphere of air, Cu-CDs were used as photocatalysts for the photooxidation of 1,4-DHP in aqueous solution. In this reaction, the yield of the product is 60.80%, which is 3.5 times higher than that measured when pure CDs were employed. Based on the emission quenching and conductivity measurements, Cu-doped CDs were found to enhance the electron-accepting and electron-donating abilities as well as the conductivity of CDs. These improved properties ultimately benefit the entire electron-transfer process and further improve the photocatalytic ability.

**Experimental Section**

Synthesis and purification of Cu-CDs and CDs: A quartz boat filled with Na$_2$[Cu(EDTA)] (analytical reagent, 1.6 g) was placed in the center of a quartz tube and calcined in a tube furnace at 250°C, 300°C, or 350°C for 2 h at a heating rate of 5°C min$^{-1}$ under a N$_2$ atmosphere (Figure 1a). The product was ground and dissolved in water (100 mL), and the suspension was ultrasonically treated (300 W, 40 kHz) for 15 min at room temperature, and then centrifuged at a high speed (10000 rpm) for 20 min. The upper brown solution was filtered using a slow-speed quantitative millipore filter (0.25 μm) to remove the nonfluorescent deposited Na salts. After the filtration process, the solution was dialyzed with a MD34 (3500 Da) dialysis tube for 48 h to remove the remaining salts and small fragments. Pure luminescent Cu-CDs powder was obtained by drying the concentrated solution at 60°C for 24 h. The powder is soluble in water and some organic polar solvents.

**Keywords:** carbon dots · doping · electron transfer · luminescence · photooxidation

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