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Nitrogen-doped carbon-based dots prepared by dehydrating EDTA with hot sulfuric acid and its electrocatalysis for oxygen reduction reaction

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Nitrogen-doped carbon-based dots (N-CDs) with fine electrocatatylic activity for oxygen reduction reaction has been prepared by dehydrating thylenediaminetetraacetic acid with hot and concentrated sulfuric acid. The as-prepared N-CDs are graphite-based nanosheets with an average lateral size of ~7 nm and a mean thickness of ~1.7 nm. The N-CDs possess abundant oxygen-containing groups and emit blue fluorescence under 365 nm UV light. Furthermore, the as-prepared N-CDs can be well deposited on graphene through a hydrothermal treatment, and show outstanding electrocatatylic activity for the oxygen reduction reaction.

Introduction

Carbon-based dots (CDs) mainly include carbon nanoparticles with a particle size less than 10 nm (also called carbon quantum dots, carbon dots or carbon nanocrystals) and graphene nanosheets with dimensions no more than 100 nm (so-called graphene quantum dots).[1,2] Like conventional semiconductor-based quantum dots (QDs), CDs are capable of showing unique optical and electronic properties.[3-5] Furthermore, CDs possess many additional advantages over QDs, such as low toxicity, good biocompatibility and robust chemical inertness. Accordingly, considerable attention has been paid to CDs, including their preparation and potential applications.[4,6] Up to date, many methods have been developed to prepare CDs, and the obtained CDs have been applied in various fields such as bio-imaging,[7] sensing,[8,9] photovoltaic devices and catalysis.[5,10-11] Recently, more and more attention has been paid to the doping of CDs, aiming to tune the optical and electronic properties of the hosts.[10,12] The N atom has a comparable atomic size and three unpaired electrons to bond with carbon atoms, and is facile to be chemically doped in various carbon-based nanomaterials (like activated carbon,[13] carbon nanotubes,[14] graphene,[15] hollow spheres,[16] and mesoporous graphitic arrays,[17] etc.). In addition, the N-doping usually grants the carbon-based nanomaterials some new properties, especially the catalytic activity.[13,14] Accordingly, the N-doped CDs (N-CDs) also attract increasing attention. There have been "top-down" and "bottom-up" methods developed to prepare N-CDs. The "top-down" methods include electrochemically treating graphene oxide (GO) film in acetontrile using N-containing tetrabutylammonium perchlorate as the electrolyte,[10] hydrothermally treating GO in the presence of ammonia,[18] and hydrothermally cutting N-doped graphene,[19] However, these methods usually suffer from disadvantages such as complex processes and low yield. Contrarily, the developed "bottom-up" methods by the carbonization of some special organics seem much more efficient in preparing N-CDs.[20-23] Herein, we would like to present a facile method to prepare N-CDs from a common N-containing organic precursor, thylenediaminetetraacetic acid (EDTA). The optical properties and electrocatalysis activity for the oxygen reduction reaction (ORR) of the obtained N-CDs were also studied.

Experimental

Chemicals

Ethylenediaminetetraacetic acid (99.995%) and citric acid (99.9%) were purchased from Sigma-Aldrich and used as received. All chemicals were of analytical grade and were used without further purification. Deionized water was used throughout the experiment.

Preparation of N-CDs

N-CDs were prepared from EDTA using hot and concentrated H_2SO_4. In brief, 10 mL concentrated H_2SO_4 was put into a 100 mL beaker, and heated to 200 ºC using a heating mantle. Put 10 g EDTA into the H_2SO_4 under vigorous stirring. The EDTA was soon dissolved in the hot concentrated H_2SO_4 to form a colourless solution. The colour of the solution rapidly turned to brown, and finally became black after 10 min. Then the heating was stopped, and the resultant black solution was diluted slowly with 90 mL H_2O. The diluted solution was neutralized with NaOH, and cooled to room temperature. After that, the solution was dialyzed against H_2O through a dialysis membrane (MWCO of 1 kDa) to remove the inorganic salt. Subsequently, the solution was ultra-filtered through a centrifugal filter device with a 30 kDa molecular weight cut off membrane (Amicon Ultra-4, Millipore) to remove big structures (> 30 kDa). The fraction of 1-30 kDa was finally collected and dried under vacuum-drying, yielding pure N-CDs (ca. 0.476 g)

Preparation of N-free CDs

N-free CDs were synthesized with the same method mentioned above using 10 g citric acid as the precursor.

Preparation of N-CDs/graphene and N-free CDs/graphene

15 mL of the as-prepared N-CDs or N-free CDs (2 mg/mL) was mixed with 15 mL graphene oxide (GO, 2 mg/mL) to form a homogeneous dispersion by slight ultrasonication. The aqueous solution was then sealed in a 50 mL Teflon-lined autoclave and maintained at 200 ºC for 12 h. The hydrothermal treatment can on only reduce the GO into high conductive graphene, but also combine CDs with graphene.[10]

Instrumentation

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a HRTEM JEOL 2100 system operating at 200 kV. The specimens were prepared by drop-casting the sample solution onto a carbon-coated copper grid, followed by being dried under room temperature. The height distribution of the obtained CDs was characterized by an atomic force microscope (AFM) (Nanoman, Veeco, Santa Barbara, CA) with tapping mode. X-Ray photoelectron spectroscopy (XPS) data for the CD solutions deposited on glass substrates were measured by a Kratos AXIS Ultra spectrometer with a monochromatized Al Kα X-ray source (1486.71 eV) for determining the composition and chemical bonding configurations. The crystal structure of the CDs was characterized by X-ray diffraction (XRD) by a Bruker AXS diffractometer (λ = 0.15418 nm). Fourier transform infrared spectra (FTIR) were obtained on a FTIR spectrophotometer (Thermo Nicolet 360). Raman spectra were measured using a Renishaw 1000 microspectrometer (with excitation wavelength of 514.5 nm). UV/vis spectra were obtained by a UV/Vis spectrophotometer (UV 2450). All fluorescence spectra were obtained by a spectrofluorometer (Fluoromax-4).

Electrochemical measurements

Cyclic voltammetric (CV) measurements were performed using a computer-controlled potentiostat (CHI 760D, CH Instrument, USA) with a three-electrode system, including a glassy carbon (GC) working electrode (3 mm in diameter), a Pt wire (0.5 mm in diameter) counter electrode and an Ag/AgCl reference electrode. Measurements on rotating disk electrode (GC, 5 mm in diameter) were carried out on a MSRX electrode rotator (Pine Instrument) and the CHI 760D potentiostat at a scan rate of 10 mV/s. Before use, the GC electrodes were successively polished using 0.3 μm alumina powder followed by being rinsed and sonicated in distilled water, and dried with N_2 gas. For all electrochemical measurements, an aqueous solution of 1 M KOH was used as the electrolyte. The O_2-free and O_2-saturated electrolyte solutions were obtained by bubbling the solutions with pure N_2 and O_2, respectively.

Preparation of electrode

3.6 μL (10 μL for the rotating disk electrode) of homogeneous catalyst ink (2 mg catalyst dispersed in 1 mL alcohol under ultrasonication) was dropped on the surface of the pretreated GC electrode. After being dried in air, the electrode surface was fully covered by the catalyst. Subsequently, 2 μL (for GC electrode) or 5 μL (for the rotating disk electrode) Nafion (1%) solution was dropped on the surface of the electrode to fix the catalyst.

results and discussion

Characterization of N-CDs

Transmission electron microscopy (TEM) image (Fig. 1a) indicates that the width of the obtained N-CDs ranges from 5 to 9 nm, with a mean value of ~7 nm. High resolution TEM (HRTEM) observation (Fig. 1b) reveals the good crystallinity of the N-CDs. Two kinds of well-defined lattice fringes with spacing of 0.21 and 0.32 nm can be observed, corresponding to the (100) facet and (002) facet of graphite, respectively.[3,23,24] The X-ray diffraction (XRD) pattern of N-CDs shows a broader (002) diffraction peak at ca. 23.5 º (Fig. S1). The Raman spectra show obvious G band and D band at 1350 and 1570 cm^{-1}, respectively (Fig. S2). All the characterization results are quite similar to those of N-free CDs (Fig. S1-S3), demonstrating the graphitic carbon property of the obtained N-CDs. The corresponding atomic force microscopy (AFM) images indicate that the height of the obtained N-CDs distributed in a range of 0.4-3.0 nm with an average value of 1.7 nm, which is much smaller than the scale of the width. Therefore, the obtained N-CDs should be mainly graphite-based nanosheets.

X-ray photoelectron spectroscopy (XPS) results illustrate that the N-CDs are mainly composed of carbon, oxygen and nitrogen

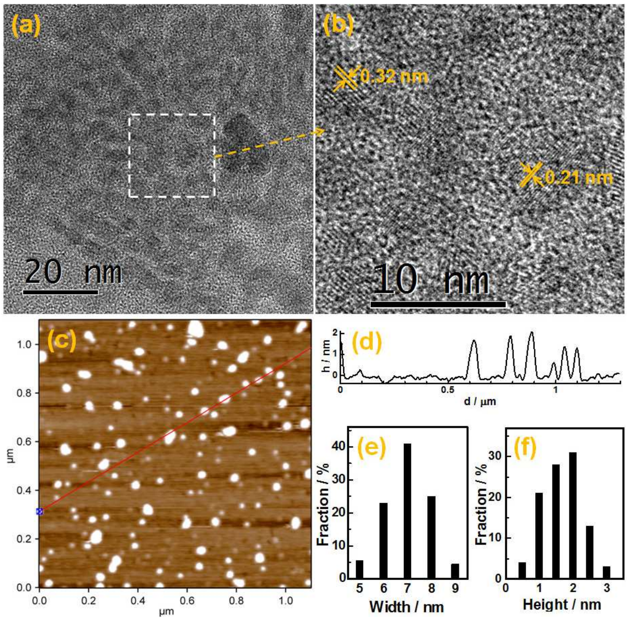

Fig. 1 (a) and (b) are TEM and HRTEM images of the N-CDs. (c) AFM image of the N-CDs. (d) Height profile along the line in (c). (e) and (f) show the width and height distributions of the N-CDs.

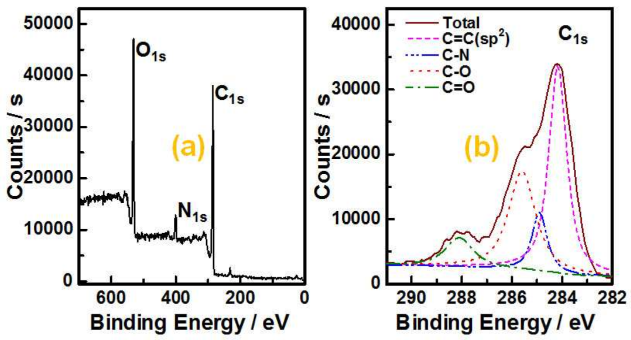

Fig. 2 (a) XPS spectra and (b) high-resolution C1s spectra of the N-CDs.

elements, while the N-free CDs are mainly composed of carbon, oxygen (Fig. S). The O/C atomic ratio is ca. 46.80%, which is higher than the N-free CDs (ca. 30.10%). The N/C atomic ratio is calculated to be ca. 8.95%, which is much higher than those of most other reported N-CDs.[10,19-22] The high resolution C 1s spectra of the N-CDs reveal not only the presence of the C=C (284.2 eV), C-N (285.0 eV) structures, but also the presence of oxygen-containing groups, such as C-O (285.6 eV), C=O (288.1 eV). Contrarily, the high resolution C 1s spectra of the N-free CDs show only the binding energy peaks for C=C, C-O and C=O. The FTIR spectra (Fig. S4) further confirms the results from XPS spectrum, showing the absorption peaks of C=C ($\nu_{C=C}$ at 1615 cm^{-1}), C-N (ν_{C-N} at 1110 cm^{-1}, ν_{N-H} at 3180 cm^{-1}), C-O (ν_{C-O} at 1230 cm^{-1}, ν_{O-H} at 3405 cm^{-1}), C=O ($\nu_{C=O}$ at 1720 cm^{-1}).

Optical properties of N-CDs

Due to the abundant oxygen-containing groups, the prepared N-CDs can be well-dispersed in the aqueous solution. As shown in Fig. 3, the yellow solution of N-CDs shows a broad UV-vis absorption below 600 nm with a shoulder peak at around 280 nm. The N-CD solution shows excitation-dependent photoluminescence (PL) emission, and emits blue luminescence when excited with 365 nm UV light. The main PL spectra of the N-CDs red-shits slightly when compared with those of the N-free CDs (Fig. S7). The PL quantum yield (PLQY) of the N-CD solution at 365 nm was calculated to be ~ 1.5%, which is close to that of N-free CDs (~1.6%). Furthermore, the N-CD solution exhibits robust stability, homogeneous phase without any noticeable precipitation at room temperature for 3 months observation, which is further confirmed by the results of TEM and PL (Fig. S5, S6).

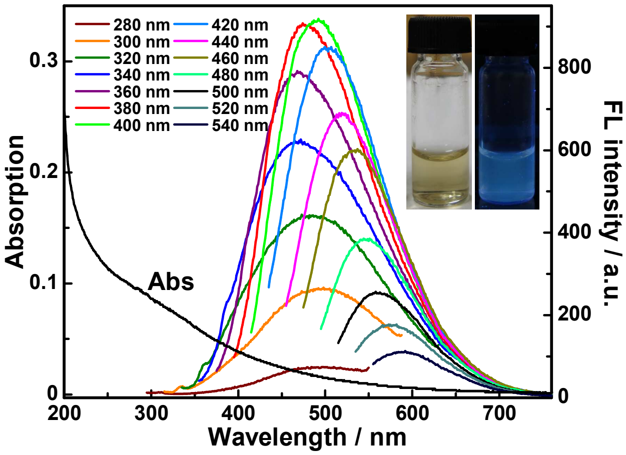

Fig. 3 UV-Vis absorption and PL spectra (recorded for progressively longer excitation wavelengths in 20 nm increments) of the obtained N-CDs. Inset: Photograph of the obtained N-CDs under illumination of white light (left) and UV (365 nm) light (right).

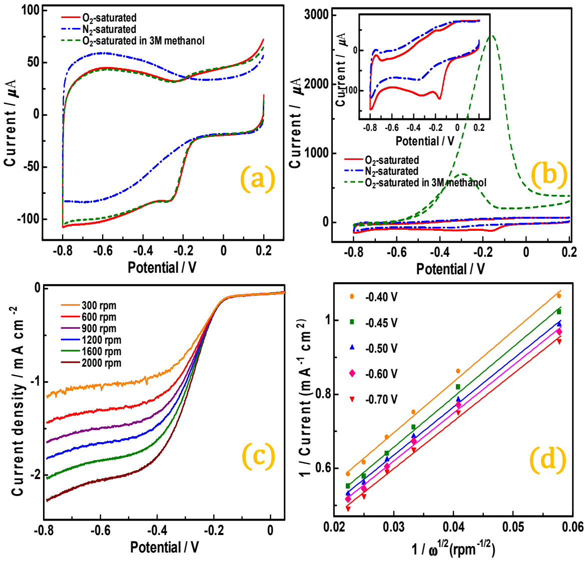

Fig. 4 (a, b) CVs of N-CD/graphene and commercial Pt/C on a GC electrode in O_2-saturated 1 M KOH, N_2-saturated 1 M KOH and O_2-saturated 1 M KOH containing 3 M CH_3OH at a scan rate of 50 mV/s.. The inset in (b) show amplified CVs of commercial Pt/C in O_2-saturated 1 M KOH, N_2-saturated 1 M KOH. (c) Rotating disk electrode (RDE) curves for N-CD/graphene in O_2-saturated 1 M KOH with with various rotation rates at a scan rate of 10 mV/s. (d) The Koutecky–Levich plots derived from the RDE measurements.

Electrocatalytic activity of N-CDs for the ORR

Although the obtained N-CDs have not obvious advantages in optical properties over other N-free CDs, they may exhibit attractive electrocatalytic activity for the ORR in alkaline solutions due to the high N-doping content.[13-17] However, the as-prepared N-CDs remain difficult to be used directly for the ORR because the abundant oxygen-containing groups and the tiny size make the obtained N-CDs poor conductive and difficult to be fixed on the electrode surface. Therefore, the obtained N-CDs were combined with large-area and electrically conductive graphene through a hydrothermal treatment, which was reported to be a mild method of forming N-CD/graphene assemblies without acutely changing the intrinsically chemical nature of N-CDs (Fig. S8).[10]

Fig. 4a shows CV curves of the ORR on N-CD/graphene-modified GC electrode. When the potential was cycled in the range from 0.2 to -0.8 V, the featureless voltammetric current was observed in the nitrogen-saturated solution whereas a well-defined cathodic peak can be observed in the oxygen-saturated solution, suggesting the pronounced electro-catalytic activity of the N-CD/graphene for oxygen reduction. As a control, the ORR on the N-free CD/graphene and graphene modified GC electrodes were also studied, showing no obvious electro-catalytic activity (Fig. S9). Therefore, the observed electro-catalytic activity of the N-CD/graphene should be attributed to the N-CDs. The peak potential of ORR under the catalysis of N-

CD/graphene is about -0.26 V, which is close to that in the presence of the Pt/C catalyst (Fig. 4b), and is comparable to those catalyzed by other N-doped carbon-based nanomaterials.[10,17,24] Moreover, the presence of 3 M methanol (a common fuel molecule) has no obvious effect on the electro-catalytic activity of N-CD/graphene for ORR. In contrast, the electro-catalytic activity of the Pt/C catalyst for ORR is inhibited greatly (Fig. 4b), i.e. the cathodic peak for the oxygen reduction disappears while a big oxidation current of the methanol appears. Apparently, N-CDs/graphene exhibits high selectivity for ORR with a remarkably good ability to avoid crossover effects and outperformed the Pt/C. Furthermore, the electro-catalytic activity of N-CD/graphene shows excellent stability. Both the peak potential and current density for ORR have no obvious change after 5000 cycles' continuous cycling in an O_2-saturated 1 M KOH solution (Fig. S10). All the results imply that the as-prepared N-CD/graphene has promising applications in direct methanol and alkaline fuel cells.

The reaction kinetics was studied by rotating-disk voltammetry. The voltammetric profiles in the O_2-saturated 1 M KOH as electrolyte show that the current density typically increases with the rotation rate from 300 to 2000 rpm (Fig. 4c). The corresponding Koutecky–Levich plots (J^{-1} *vs* $\omega^{-1/2}$) at various electrode potentials show good linearity (Fig. 4d), suggesting a first-order reaction kinetics with respect to dissolved oxygen.[17] The number of electrons transferred was derived to be 3.53-3.78 over the potential range from -0.4 to -0.7 V (Fig. 4d). This result suggests that N-CD/graphene leads to a four-electron transfer in oxygen reduction.

Summary

A simple and effective bottom-up method of dehydroting EDTA with hot H_2SO_4 has been developed to prepare N-CDs. The obtained N-CDs are mainly graphite-based nanosheets with an average lateral size of 7 nm and an average thickness of 1.7 nm. The obtained N-CDs show similar optical properties to most of reported CDs. In particular, N-CDs supported by graphene exhibit outstanding electrocatatylic activity for ORR, and have a great application potential in direct methanol and alkaline fuel cells.

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Notes and references

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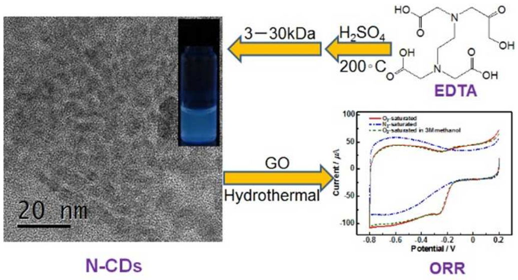
Table of Contents Graphic



Nitrogen doped carbon-based dots were synthesized by dehydrating thylenediaminetetraacetic acid, and were used for electro-catalyzing oxygen reduction.