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Bifunctional fluorescent carbon nanodots: green synthesis *via* soy milk and application as metal-free electrocatalysts for oxygen reduction†Chengzhou Zhu,^{ab} Junfeng Zhai^a and Shaojun Dong^{*ab}

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We demonstrated a facile and green approach to synthesize bifunctional fluorescent carbon nanodots *via* soy milk, which not only showed favorable photoluminescent properties, but also exhibited good electrocatalytic activity towards oxygen reduction reaction.

Carbon nanomaterials, which include carbon nanotubes, fullerenes, and graphene, have generated much excitement for a wide variety of promising applications in nanotechnology, biosensing, and drug delivery.¹ Recently, fluorescent carbon nanodots (FCNs), a new class of carbon nanomaterials, have been actively pursued and well applied in bioimaging and biosensing. In striking contrast to semiconductor quantum dots, carbon nanodots are superior fluorescent nanomaterials with low toxicity, high chemical stability, and low environmental hazard.² To date, considerable approaches such as arc-discharge,³ laser-ablation,⁴ electrochemical synthesis,⁵ microwave synthesis⁶ and combustion/thermal⁷ routes were used to synthesize FCNs. Among them, the thermal route was regarded as a direct and efficient way and considerable effort was made to produce FCNs.⁸ However, it should be noted that their purification and functionalization are complex and time-consuming.⁹ Moreover, most reported FCNs have been prepared for bioimaging,^{2b,10} which limits the application of FCNs in other fields. In this context, it has become urgent to develop effective routes to synthesize functional FCNs as well as expand their applications.^{8b,11}

On the other hand, Nature provides a nearly limitless resource for material scientists to get bioinspiration for preparing materials with novel structures and properties.¹² Several successful demonstrations were given to prepare nanomaterials using natural biomass, which exhibited potential applications in various fields, such as energy nanomaterials,¹³ analytical sensing,^{11b} and other functionalized materials.¹⁴ As we all know, soybean abounds with carbon, nitrogen and oxygen elements owing to the existence of sugar, proteins and lipids.

In this regard, it is expected that this natural source could provide an alternative precursor to synthesize advantageous nanomaterials. Herein, we developed a simple, low cost, and green preparative strategy toward water-soluble, nitrogen-doped FCNs by hydrothermal treatment of soy milk. The carbonization, surface functionalization and doping will occur simultaneously during the hydrothermal treatment, which leads to the formation of the nitrogen-doped FCNs. Moreover, electrochemical oxygen reduction on these nitrogen-doped FCNs was investigated, further expanding the potential application of carbon nanodots.

Soy milk can be made at home with a soy milk machine. The one-step hydrothermal treatment of soy milk at 180 °C leads to a yellow FCNs dispersion with excellent water solubility (Fig. 1A). The photograph of the dispersion under UV light (365 nm) exhibits a blue color, further revealing that the resultant FCNs exhibit blue fluorescence. The absorption and emission spectra of the as prepared FCNs were first investigated. The absorption spectrum shows a narrow peak at 275 nm which is ascribed to the p-p* transition of nano-carbon (Fig. 1B).^{6b,7b} When these FCNs were excited at the

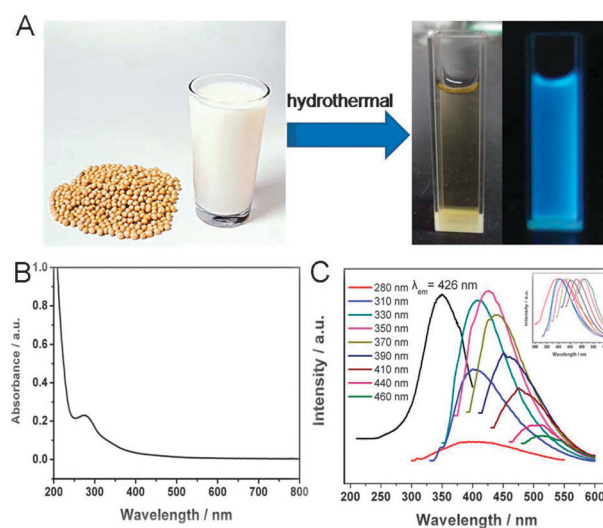


Fig. 1 (A) A schematic illustration of the preparation procedure of FCNs by hydrothermal treatment of soy milk (photograph of the samples excited by daylight and a 365 UV lamp). UV-vis absorption spectra (B) and photoluminescent spectra (C) of FCNs at different excitation wavelengths as indicated.

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excitation edge of 350 nm, a maximum emission peak at 426 nm was observed (Fig. 1C). In addition, a characteristic feature of the obtained FCNs is that the photoluminescent (PL) emission peaks shifted to longer wavelengths with increasing excitation wavelength (Fig. 1B). This excitation-dependent emission from carbon nanodots has also been reported previously.^{2a,9,10} The PL quantum yield measured using quinine sulfate as a reference is 2.6%, comparable with those of the reported luminescent carbon nanodots.^{7a,10b,15} Interestingly, the as-synthesized FCNs were shown to possess the upconversion PL properties, as shown in Fig. S1 (ESI†). It is clear that the PL spectrum of FCNs excited by an 800 nm laser with the maximum upconverted emission located at about 475 nm. It is noticed that excitation-dependent emission was also observed under infrared, likely due to the anti-Stokes photoluminescence.¹⁶ Just because the strong PL interference excited under wavelengths ranged from the visible to the near-infrared region, we cannot obtain the corresponding Raman spectrum.

Fig. 2A shows the typical transmission electron microscopy (TEM) image of the as-prepared FCNs. It is found that their diameters are mainly distributed in the range of 13–40 nm (25 nm average diameter) (Fig. 2B). In comparison with the FCNs reported previously, the diameter of the as-prepared FCNs was larger.^{2a} According to TEM characterization, we can conclude that the diameter is not the key parameter to evaluate the PL properties of the FCNs. However, the high resolution TEM (HRTEM) image of the FCNs did not reveal any clear lattice fringes, indicating the amorphous nature of the FCNs. At the same time, the XRD pattern of the FCNs showed a broader peak at $2\theta = 23^\circ$ (Fig. S2, ESI†), revealing an amorphous carbon phase, which agrees well with the HRTEM analysis.

The structure and component of the FCNs were characterized by Fourier transformed infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) (Fig. 3A). The obtained FCNs exhibited characteristic absorption bands of O–H and N–H stretching vibrations of amine groups at 3285 cm^{-1} , C–H stretching vibrations at 2937 and 2875 cm^{-1} , N–H bending vibrations at 1651 and 1539 cm^{-1} and C–H bending vibrations at 1130 – 1064 cm^{-1} .^{7b,10a} Obviously, these functional groups can be ascribed to the degradation of the involved sugar, proteins and lipids through hydrothermal treatment. XPS was further performed to analyze the surface state of the FCNs and the results revealed that it contained mainly carbon, oxygen and nitrogen as well as a limited

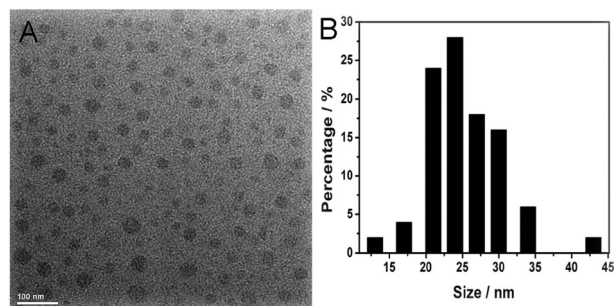


Fig. 2 TEM image (A) and size distribution (B) of the as-synthesized FCNs.

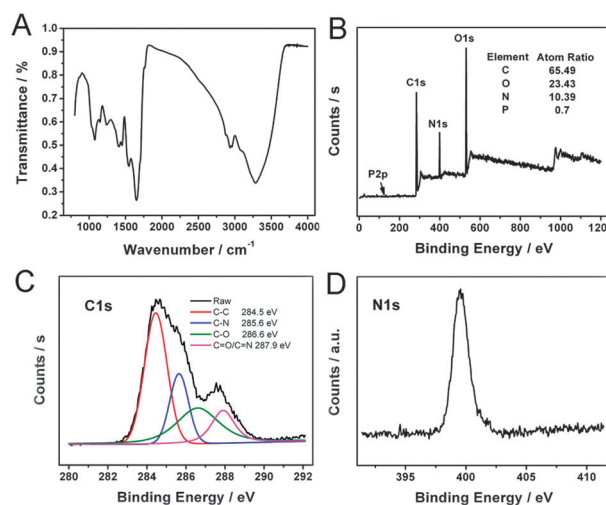


Fig. 3 (A) Fourier transformed infrared spectrum and (B) XPS, (C) C1s and (D) N1s spectra of the products thus obtained.

amount of P element, which may come from the phospholipid in the soy milk. The content of each element is displayed in Fig. 3B. In detail, the C1s spectrum (Fig. 3C) shows four peaks at 284.5, 285.6, 286.6, and 287.9 eV, which are attributed to C–C, C–N, C–O, and C=N/C=O, respectively.^{11b} Furthermore, the nitrogen content can reach 10.39%, which was higher than that of nitrogen-doped carbon nanomaterials reported previously.^{11b,17} It was postulated that the attachment of nitrogen-containing functional groups formed during hydrothermal treatment can be used for the surface passivation of FCNs, imparting them with PL properties. Thus, this method based on hydrothermal treatment of soy milk provides a green and effective way to prepare nitrogen-doped FCNs.

On the other hand, considerable research efforts have been focused on the preparation of nitrogen-doped carbon nanomaterials and their applications in various fields.¹⁸ Thus, these newly-synthesized FCNs could be not only used as bioimaging nanomaterials based on their PL properties, but also applied as novel electrocatalysts. Specifically, considerable contribution was made to synthesize nitrogen-doped carbon nanomaterials and investigate their electrocatalytic activity towards oxygen reduction reaction (ORR), and it was proved that the doped nitrogen plays a key role in enhancing their electrocatalytic activity.^{17a,19} To the best of our knowledge, there are no reports on the investigation of the electrocatalytic activity of the nitrogen-doped FCNs obtained from natural biomass. The electrocatalytic activity of the as-prepared FCNs towards ORR in basic medium was evaluated. Cyclic voltammograms (CVs) at FCN electrodes in N_2 and O_2 -saturated 0.1 M KOH solution were recorded, respectively (Fig. 4A). It is clear that FCNs showed a substantial reduction process in the presence of oxygen with the cathodic reduction peak at around -0.35 V , whereas no obvious response was observed under nitrogen. However, compared with E-TEK Pt/C, the ORR process on FCNs exhibited negative onset potential (E-TEK Pt/C, 0.06 V; FCN, -0.15 V) with low limiting current (Fig. 4B). The introduction of nitrogen was favorable for the ORR process. As we all know, the bonding state of the N atom was found to have a significant effect on the selectivity and catalytic

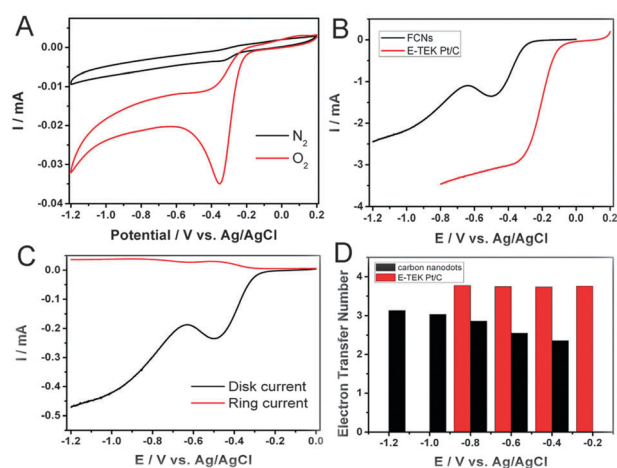


Fig. 4 (A) CVs of oxygen reduction at the FCN electrodes in N_2 - and O_2 -saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} . (B) Linear sweep voltammograms (LSVs) for ORR on the FCNs and E-TEK Pt/C electrodes in an O_2 -saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1} and a rotation rate of 1600 rpm. (C) ORR on the RRDE of FCN electrodes in an O_2 -saturated 0.1 M KOH solution. (D) The electron transfer number of FCNs at various potentials based on the corresponding RRDE data.

activity for ORR. Taking the synthesis process into consideration, active center structure of nitrogen-doped FCNs could not be effectively formed likely due to the low reaction temperature. In such a case, the catalytic activity was inevitably inhibited. In addition, the electrochemical performances of the FCNs were then investigated with an electrochemical active probe, $Fe(CN)_6^{4-/3-}$ and compared against that of a bare electrode. As we can see from Fig. S3 (ESI †), no obvious redox peaks were observed at FCNs, suggesting that the $Fe(CN)_6^{4-/3-}$ redox couple has a very slow electron transfer kinetics, due to the presence of negatively charged oxygen containing moieties of FCNs (zeta potential: -10 mV), similar to that of graphene oxide modified electrodes we reported previously.²⁰ A rotation ring-disk electrode (RRDE) was used to evaluate the ORR performance of the as-prepared FCNs. Fig. 4C shows the disk and ring currents at the FCNs, respectively. The number of electrons involved in the overall ORR was calculated to be 3.15 at -1.20 V ,²¹ indicating that a four-electron pathway and a two-electron transfer pathway occurred simultaneously. This value was smaller than that of E-TEK Pt/C (3.75) in the range of potentials investigated (Fig. 4D). Significantly, continuous ORR on the FCNs caused only a slight loss (9%) of current density before leveling off, indicating that the FCNs possessed good stability (Fig. S4, ESI †). Exploring the catalytic mechanism and further elevating the catalytic activity towards ORR were still underway. Based on the discussion mentioned above, these results showed that the newly-prepared FCNs derived from soy milk had a promising application as metal free electrocatalysts and provided a new method to synthesize nitrogen-doped FCNs via a natural source, achieving the bifunctionalization of the final product in different application fields.

In summary, we succeeded in synthesizing the bifunctional nitrogen-doped FCNs via hydrothermal treatment of soy milk for the first time. These FCNs not only showed

favorable PL properties, but also exhibited good electrocatalytic towards ORR. Along with this green and cost-effective protocol of synthesis, we expect that these novel carbon nanodots have potential applications in bioimaging and electrocatalysis.

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