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Turning waste into wealth: facile and green synthesis of carbon nanodots from pollutants and applications to bioimaging†

Weifeng Chen,^{‡a} Jialu Shen,^{‡a} Zuo Wang,^{‡b} Xiang Liu,^{ID *a} Yanyi Xu,^b Haiyu Zhao^{ID *b} and Didier Astruc^{ID *c}

In an effort to turn waste into wealth, Reactive Red 2 (RR2), a common and refractory organic pollutant in industrial wastewater, has been employed for the first time as a precursor to synthesize carbon nanodots (CNDs) by a facile, green and low-cost route, without utilization of any strong acids or other oxidizers. The detailed characterizations have confirmed that the synthesized CNDs exhibit good water dispersibility, with a mean particle size of 2.43 nm and thickness of 1–3 layers. Importantly, the excellent fluorescence properties and much reduced biotoxicity of the CNDs confer its potential applications in further biological imaging, which has been successfully verified in both *in vitro* (cell culture) and *in vivo* (zebrafish) model systems. Thus, it is demonstrated that the synthesized CNDs exhibit nice biocompatibility and fluorescence properties for bioimaging. This work not only provides a novel economical and environmentally friendly approach in recycling a chemical pollutant, but also greatly promotes the potential application of CNDs in biological imaging.

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1. Introduction

Carbon nanodots (CNDs) have gained tremendous research attention worldwide due to their preeminent water solubility, highly tunable band gaps, superior photo and chemical stability, low cytotoxicity, excellent biocompatibility, easy functionalization, brilliant catalytic properties and high photoluminescence (PL) intensity.¹ These nanomaterials that usually possess heavily functionalized graphene-like structures² have been extensively applied in many areas including biomedical optical imaging, catalysis, heterojunction solar cells, drug delivery, environmental monitoring, supercapacitors and bio-sensing.³ The synthesis of CNDs has been typically classified into top-down and bottom-up strategies. The top-down strategies involve the synthesis of CNDs from graphite, graphene

nanosheets, carbon nanotubes, candle soot, coal and graphite rods by physical or chemical cutting treatment;⁴ on the other hand, the bottom-up strategies target the fabrication of CNDs from conventional organic molecules or biomass by plasma treatment, ultrasonic/microwave irradiation, hydrothermal treatment or thermal decomposition.⁵ However, many of these methods are associated with some demerits, such as high cost, low yields, time-consuming processes, or the utilization of strong acids.⁶ Therefore, it is still a considerable challenge to develop more facile and green approaches for the synthesis of CNDs from abundant and low-cost precursors.

The rapidly increasing usage of organic dyes (*e.g.*, reactive red 2) in industrial manufacture, such as textile, papermaking, plastics, pigments and paint, has rendered them among the most globally hazardous pollutants of water.⁷ Approximately 10% of organic dyes containing aromatic groups and azo groups (–N=N–) have been discharged into natural water.⁸ The mass discharge of these azo dyes represents a great threat for aquatic organisms and ecological environments since most of azo dyes are highly toxic, carcinogenic and teratogenic.⁹ A large number of methods, such as ozonation, biological treatment, ionic exchange, photocatalysis, oxidative process and adsorption have been developed for the removal of organic dyes from water.¹⁰ However, these efforts are always associated with high chemical and energy consumption, as well as costly equipment investment. Therefore, developing more eco-friendly and efficient tactics for the removal of the organic dyes and turning these chemical pollutants into wealth is still a very meaningful and challenging research.¹¹

^aCollege of Materials and Chemical Engineering, Engineering Research Center of Eco-environment in Three Gorges Reservoir Region, Ministry of Education, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang, Hubei 443002, P. R. China. E-mail: xiang.liu@ctgu.edu.cn

^bGansu Key Laboratory of Biomonitoring and Bioremediation for Environmental Pollution, School of Life Sciences, Lanzhou University, Lanzhou, Gansu, 730000, P. R. China. E-mail: zhaohy@lzu.edu.cn

^cISM, UMR CNRS No. 5255, Univ. Bordeaux, 351 Cours de la Libération, 33405 Talence Cedex, France. E-mail: didier.astruc@u-bordeaux.fr

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‡ These authors have equally contributed to this work and should be considered as co-first authors.

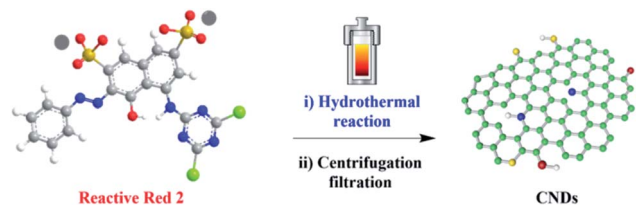


Fig. 1 The synthesis of CNDs from reactive red 2.

For this purpose, our laboratories have a long-term interest in the synthesis of carbon nanodots from abundant and low-cost biomass and their applications in catalysis, sensor and bioimaging.¹² Herein, we report a facile, green and turning wastes into wealth route to synthesize the typical material carbon nanodots (CNDs) by using chemical pollutant reactive red 2 (RR2) as the precursor for the first time, *via* simple hydrothermal treatment (Fig. 1). Thereafter, the morphology structure, fluorescence properties and chemical composition of the as-synthesized CNDs have been comprehensively investigated. Importantly, this work provides some insights into the biotoxicity of the synthesized CNDs in comparison with the RR2 precursor, at the cellular and organismal level. Our results verified that the biotoxicity was dramatically reduced when the pollutant was fully converted into CNDs. In addition, the synthesized CNDs with excellent fluorescent properties have been successfully applied in the bioimaging of both living cell and the popular zebrafish model system, demonstrating practically biological applications in the future.

2. Results and discussion

2.1 Structural characterization of the CNDs

First, the CNDs were synthesized from only RR2 and water under green hydrothermal conditions. Indeed, RR2 was successfully fully converted into CNDs, because the adsorption peak at approximately 500 nm and the characteristic peaks of RR2 completely disappeared in the UV-vis spectra (Fig. 2). Meanwhile, the peaks at 234 nm, 269 nm and 358 nm (the characteristic peaks of CNDs) appeared in the UV-vis spectra.



Fig. 2 UV-vis spectra of RR2 and CNDs; inset image: CNDs solution exhibits intense blue fluorescence under 365 nm ultraviolet lamp.



Fig. 3 (a) TEM image, (b) HRTEM image, (c) AFM image, and (d) height profile of CNDs.

Among them, the peaks at 234 nm and 269 nm are assigned to π - π^* transitions of C=C/C-C bonds in the sp^2 hybridization region, while the peak of 358 nm is due to the n - π^* transition.¹³ The CNDs solution exhibited an intense blue fluorescence under 365 nm ultraviolet lamp (Fig. 2). The transmission electron microscope (TEM) image shows that the CNDs are well dispersed with an average diameter of 2.43 nm (Fig. 3a). Besides, the interplanar spacings of 0.240 nm and 0.256 nm were observed by high resolution TEM (HRTEM, Fig. 3b), and assigned to the (1120) and (020) plane of graphitic carbon, respectively (JCPDS 26-1076).¹⁴ The atomic force microscope (AFM) image of CNDs (Fig. 3c) indicates that the height is less than 1.5 nm (Fig. 3d), suggesting that the thickness of CNDs is 1–3 layers.¹⁵ Then, X-ray photoelectron spectroscopy (XPS) was utilized to study the valence states of the different atoms of CNDs, *i.e.*, C, N, O, and S (Fig. 4). The spectrum of C 1s (Fig. 4a) shows the typical peaks at 284.8 eV, 286.27 eV and 288.84 eV corresponding to C=C/C-C, C-O-C and O-C=O, respectively.¹⁶



Fig. 4 The C 1s, N 1s, O 1s, and S 2p XPS of CNDs.



Moreover, the XPS of N 1s (Fig. 4b) exhibited two peaks at 399.83 eV and 401.90 eV belonging to the pyrrolic N and pyridinic N, respectively. As shown in Fig. 4c, two characteristic peaks at 531.68 eV and 532.82 eV are assigned to C–O and C=O, respectively. Besides, the XPS spectrum of S 2p (Fig. 4d) shows that the S 2p spectra is decomposed into two peaks, C–SO₂–C at 168.07 eV and C–O–SO₂–O at 169.15 eV, respectively.

The structure of the produced CNDs was further investigated by Raman spectroscopy (Fig. 5a), revealing that the peaks of the D-band, G-band and 2D-band of the CNDs are located at 1300 cm^{−1}, 1584 cm^{−1} and 2778 cm^{−1}, respectively. The D-band and 2D-band are due to the disordered carbon, while the G-band is assigned to the graphite carbon. The value of I_D/I_G is 1.7, indicating the CNDs have some defects in the crystal lattices.¹⁷ Fourier transform infrared spectroscopy (FT-IR) was also been used to investigate the chemical groups of CNDs, as shown in Fig. 5b. The peak at 3418 cm^{−1} is corresponding to the stretching vibration of O–H/N–H, whereas the characteristic peaks of 3166 cm^{−1}, 1660 cm^{−1}, 1405 cm^{−1}, 1055 cm^{−1} and 1624 cm^{−1} are attributed to the stretching vibrations of C–H, C=O, C–N and C–O, and bending vibration of N–H, respectively. Fig. 5c also exhibits a typical profile with a broad peak at approximately 24°, the characteristic peak of (002) graphene appears in the X-ray diffraction (XRD) spectrum (JCPDS card no. 75-0444). In addition, it indicates that the synthesized CNDs solution shows excitation-dependent PL property, as shown in Fig. 5d. When the excitation wavelength is set from 300 nm to 580 nm, the emission wavelength is improved from 423 nm to 619 nm. The maximum emission is at the position of 428 nm when being excited by 360 nm. In this work, rhodamine B in ethanol (QY = 69.0%) was used as a standard for CNDs. The quantum yield (QY) of CNDs was calculated to be 15.7%.¹⁸ The fluorescence of CNDs is mainly attributed to emission from oxygen-rich surface defects.¹⁹ To sum up, these results confirmed that the graphene-like structure containing sp²



Fig. 6 Proposed mechanism of CNDs formation from RR2.

hybridization of these fluorescent CNDs has been formed from RR2 by hydrothermal reaction.

The formation mechanism of CNDs from RR2 involves two steps (Fig. 6); first RR2 was decomposed into small carbon substances under hydrothermal conditions. Then the small carbon substances were polymerized, grown and oxidized into these fluorescent CNDs with abundant surface O, N and S-containing functional groups. Finally, the fluorescence of CNDs is mainly attributed to these highly functional surface groups.^{19,20}

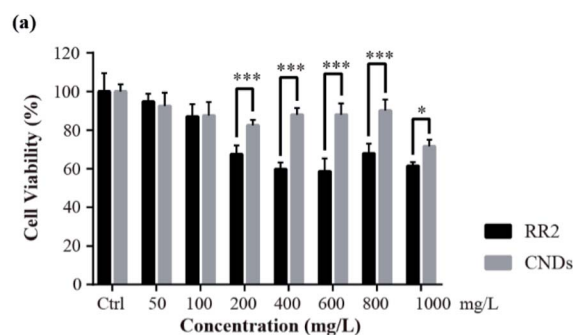


Fig. 7 Cytotoxicity assessment and fluorescence imaging. (a) Effect of the same amount of RR2 and CNDs on HeLa cell viability. MTT cell viability assay was performed in HeLa cells after RR2 and CNDs exposure (0–1000 mg L^{−1}) for 24 hours. Concentrations are plotted on the X axes, cell viability (%) ± SEM (n = 6) with respect to untreated cells (Ctrl) is plotted on the Y axes. Significant differences are indicated by asterisks (***p < 0.001, **p < 0.01, *p < 0.05). (b–g) Confocal fluorescence images of HeLa cells (bright field images, b and e) stained with CNDs (100 mg L^{−1}, 24 hours) at the excitation of 405 (c and f) and 488 nm (d and g) laser beams respectively.

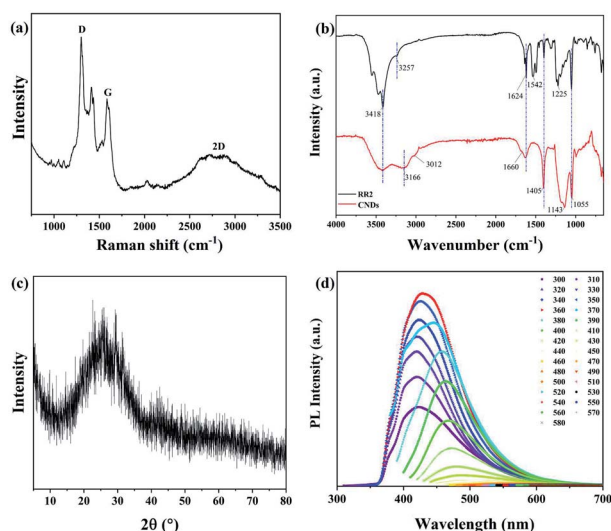
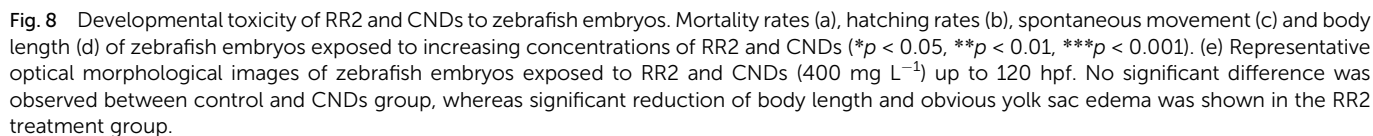


Fig. 5 (a) Raman spectrum, (b) FT-IR spectra, (c) XRD and (d) corresponding PL spectra at different excitation wavelengths from 300 nm to 580 nm for CNDs.

2.3 Living cells fluorescence imaging

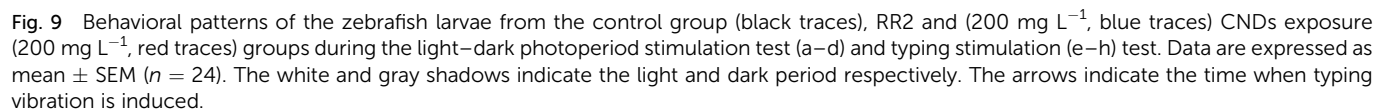
Living cell fluorescence imaging was performed to demonstrate their practicability in biological applications.²¹ The zeta potential value of CNDs is -24.1 mV (Fig. S2†), suggesting that the as-synthesized CNDs are relatively stable.²² After incubating the HeLa cells with CNDs (100 mg L^{-1}) for 24 h at 37 °C, a significant fluorescence in the HeLa cells was observed (Fig. 7b–i). The CNDs were mostly localized at the cytoplasm of HeLa cells, since the cytoplasmic area exhibited a strong photoluminescence. Importantly, no photobleaching was observed within one hour for the cell imaging, suggesting that they are suitable for long-term cellular imaging. In addition, distinctive colors were available for the observation of the cells incubated with CNDs when they were excited with 405 nm and 488 nm laser beams, respectively. This intrinsic excitation separation property is particularly ideal for multichannel imaging, suggesting that CNDs are an excellent counterstain in cooperation



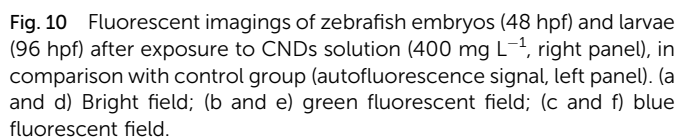
significantly reduced, and the yolk sac edema was obvious (Fig. 8e). All these notable morphological differences implied that in comparison with the RR2, the biotoxicity of CNDs was significantly reduced, and the CNDs (up to 400 mg L⁻¹) had no potential toxicity hazard to zebrafish development. CNDs have been reported to be unable to infiltrate the cell nucleus, which suggested that they did not disrupt the genetic structure of the organisms and caused cellular toxicity. This supports the hypotoxicity of our CNDs and its bio-compatibility for further utilization.

2.5 Neurobehavioral alteration induced by RR2 and CNDs

To further evaluate the developmental toxicity of RR2 and our synthesized CNDs, the neurobehavior of the zebrafish larvae exposed chronically was tested.²⁵ Specifically, we detected their locomotor activity as well as the response to environmental signals, for example light and vibration stimulations. The swimming speed, distance moved, cumulative mobility as well as maximum acceleration of zebrafish larvae was quantified in different assays. In our results, the developmental exposure to RR2 (200 mg L⁻¹) caused behavioral impairment including hypoactivity in locomotor activity as well as reduced reactivity to light-dark cycles. The swimming behaviors was significantly repressed by RR2 exposure especially during the dark period (Fig. 9a–d, black and blue traces, $p < 0.05$). Similarly, in the experiment testing the zebrafish response to vibration stimulations, a significant hypoactivity in swimming activity was observed in the RR2 exposure group during the whole process (Fig. 8e–h, black and blue traces, $p < 0.05$). However, in contrast to the RR2 that dramatically decreased the activity as well as the



Toxicological criteria	Timepoints	Exposure concentrations (mg L ⁻¹)	Results
Survival rates (mortality)	4 hpf to 5 dpf	0, 50, 100, 200, 300, 400	Fig. 8a
Hatching rates	2 dpf to 5 dpf	0, 50, 100, 200, 300, 400	Fig. 8b
Spontaneous movement	24 hpf	0, 50, 100, 200, 300, 400	Fig. 8c
Body length	96 hpf	0, 50, 100, 200, 300, 400	Fig. 8d
Morphological feature	6 hpf to 120 hpf	400	Fig. 8e
Behavioral test	24 hpf, 6 dpf	0, 50, 100, 200, 300, 400	Fig. 9



2.6 Fluorescence imaging of CNDs in zebrafish model

3. Conclusions

precursor, in which azo groups are the main cause of cytotoxicity.²⁷ The fluorescence properties and low cytotoxicity of the synthesized CNDs confer its very favorable potential applications in biological imaging, as verified in the *in vitro* (cell culture) and *in vivo* (zebrafish embryo) model systems. In an effort to turn waste into wealth, the discovery of CNDs from RR2 provides new economically and environmentally friendly opportunities in both bioimaging and waste-water remediation.

All zebrafish husbandry and experimental procedures were performed in accordance with the Guiding Principles for the Care and Use of Laboratory Animals and were reviewed and approved by the Animal Care Committee of Lanzhou University (ethic approval ID no. EAF2020007).

All data, models, or code generated or used during the study are available from the corresponding author by request.

X. L., D. A. and H. Z. conceived this project; W. C., J. S., Z. W. and Y. X. performed the experiments; X. L., D. A. and H. Z. analyzed the data and wrote the paper. All authors provided scientific input, edited, and approved the final manuscript.

There are no conflicts to declare.

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