A facile and simple method for synthesis of graphene oxide quantum dots from black carbon

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1. Experimental section

1.1 Materials and reagents

Black carbon (BC) is produced by the incomplete combustion of wood (*Cunninghamia lanceolata*). H_2O_2 was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other regents of analytical grade were obtained from Beijing Chemical Company (Beijing, China) and were used as received without any further purification. Ultrapure water (18.2 MΩ cm^{-1}; Millpore., USA) was used throughout the experiments.

1.2 Apparatus

The UV-Vis spectra and the fluorescence spectra (FL) were obtained using a UV-2450 UV-Vis spectrophotometer (Shimadzu Co., Japan) and a QM40 fluorescence spectrophotometer (PTI Ltd, Canada), respectively. Transmission electron microscopy (TEM) images were collected from a JEOL-1230 transmission electronic microscope (JEOL, Japan). Fourier transform infrared spectra (FT-IR) in the 4000 to 400 cm^{-1} regions were recorded on a Nicolet Nexus 670 FT-IR spectroscope (Nicolet Instrument Co., USA). X-ray photoelectron spectroscopy (XPS) analysis was done on an Thermo Fisher Scientific K-Alpha 1063 X-ray photoelectron spectrometer (Thermo Fisher Scientific, Britain) using Al, K as the exciting source. X-ray diffraction (XRD) patterns were collected using a Rigaku 2500 (Japan) X-ray diffractometer. Atomic force microscope (AFM) image of GO-dots was obtained using a MIPicoLE Atomic Force Microscope (MI, USA).

1.3 Synthesis of GO-dots

In a typical synthesis, 0.02 g BC powder and 15 mL H_2O_2 (1%, wt%) were added to a 25 mL Teflon-lined autoclave and heated at 180 °C for 90 min. After cooling to room temperature, the GO-dots were obtained in the supernatant. As control experiments, replace 15 mL H_2O_2 (1%, wt%) with 15 mL HCl (1%, wt%) or 15 mL NaOH (1%, wt%) or 15 mL pure water, and other conditions are the same.

1.4 The procedure for the determination of the fluorescence quantum yields

Fluorescence (FL) quantum yields of the GO-dots were obtained by using the comparative method. The quantum yield of GO-dots, Φ_x, is calculated according to the following equation:

$$\Phi_x = \Phi_{std}\left(\frac{F_x}{F_{std}}\right)\left(\frac{A_{std}}{A_x}\right)\left(\frac{n_x}{n_{std}}\right)^2$$

Where Φ, F, A, and n are quantum yield of the standard sample, integrated FL intensity, absorbance, and refractive index, respectively. The subscript "*std*" refers to the standard fluorophore of known quantum yield, for an example, quinine sulfate used in present work (The quantum yield of quinine sulfate dissolved in 0.1 M H_2SO_4 is 0.54.). To minimize re-absorption effects, the absorbance of GO-dots and quinine sulfate solution in the 10 mm fluorescence cuvette were adjusted never exceed 0.05 at the excitation wavelength. The quinine sulfate was dissolved in 0.1 M H_2SO_4 (n_{std} was 1.33).

1.5 Cellular imaging and cytotoxity assays

The living HeLa cells were grown in DMEM (Dulbecco's Modified Eagle's Medium) supplemented with 10% FBS (fetal bovine serum) and incubated at 37 °C in 5% CO_2 atmosphere. The cells were then incubated with GO-dots (0.2 mg mL^{-1}) in medium (2 mL) for 1 h at 37 °C, and washing with phosphate buffered saline (PBS) three times to remove the extracellular GO-dots. After that, the cell fluorescence images were acquired using an oil dipping objective (100×) on a confocal laser scanning fluorescence microscope setup consisting of an Olympus IX81 inverted microscope with an Olympus FV1000 confocal scanning system. The cytotoxicity of GO-dots was examined by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. First, HeLa cells were seeded in 96-well plates. After incubating for 24 h, the medium was then replaced by the culture solution containing GO-dots with various concentrations (0, 0.05, 0.10, 0.15, 0.20 and 0.25 mg mL^{-1}), and the cells were continued to incubate for another 24 h. Next, the cells were washed three times with PBS, and then, freshly prepared MTT (0.5 mg mL^{-1}) solution was added to each well. Finally, the MTT medium solution was carefully removed after 4 h incubation, and DMSO was then added into each well. The plate was gently shaken for 10 min at room temperature to dissolve all precipitates, and the absorbance of MTT at 570 nm was monitored in a spectrophotometer.

1 Table S1 Methods for synthesizing GO-dots

Precursor	Synthetic process	Post-processing steps	Time	Reference
XC-72 carbon black	Acid refluxing, HNO_3, 24 h	Centrifugalization, vacuum filtration, vacuum freeze dry	> 24 h	[1]
Graphite nanoparticles	Step 1: ultrasonication H_2SO_4/HNO_3, Step 2: acid refluxing, H_2SO_4/HNO_3, 12 h	Centrifugalization, dialysis	> 2 d	[2]
Graphite nanoparticles	Step 1: oxidation by Hummers method, $H_2SO_4/KMnO_4/NaNO_3/H_2O_2$, > 2 h Step 2: ultrasonication, 3 h	Centrifugalization	> 5 h	[3]
Cellulose	Step 1: microwave treatment, H_2SO_4, 2 h Step 2: acid refluxing and ultrasonic treatment, HNO_3, 1 h	Filter, rotary evaporation, vacuum dry	> 1 week	[4-6]
Graphite powder	Step 1: oxidation by Hummers method, $H_2SO_4/KMnO_4/NaNO_3/H_2O_2$, > 1 d Step 2: hydrothermal method, N,N-dimethylformamide, 6 h	Dialysis, filter, rotary evaporation,	> 8 h	[7]
CX-72 carbon black	Step 1: ultrasonication, HNO_3, 2 h Step 2: acid refluxing, HNO_3, 24 h	Centrifugalization, evaporation, redispersion	> 24 h	[8]
Coal	Acid refluxing, HNO_3, 12 h	Centrifugalization, vacuum dry, redispersion, Centrifugalization	> 12 h	[9]
Graphite nanoparticles	Step 1: ultrasonication, H_2SO_4, HNO_3, 3 h Step 2: acid refluxing, H_2SO_4, HNO_3, 12 h	Centrifugalization, dialysis, further dialysis	> 3 d	[10]
Graphite	Step 1: oxidation by Hummers method, $H_2SO_4/KMnO_4/NaNO_3/H_2O_2$, > 1 d Step 2: acid refluxing, HNO_3, 8 h Step 3: ultrasonic, NaOH, 0.5 h	Centrifugalization, dialysis, filtration	> 1 week	[11]
Graphite	Step 1: oxidation by Hummers method, $H_2SO_4/KMnO_4/NaNO_3/H_2O_2$, > 1 d Step 2: acid oxidizing, HNO_3, 12 h Step 3: ultrasonication, 10 h Step 4: heated in oven, 12 h	Not mentioned	> 2.5 d	[12]
Graphene nanofibers	Step 1: acid oxidizing, $NaClO_3$, fuming HNO_3, 12 h Step 2: acid refluxing, $NaClO_3$, fuming HNO_3, HNO_3, 6 h Step 3: ultrasonication, HCl, 1 h	Dialysis, vacuum dry	> 1 week	[13]
Graphite	Step 1: oxidation by Hummers method, $H_2SO_4/KMnO_4/NaNO_3/H_2O_2$, > 1 d Step 2: further oxidation by Hummers method, $H_2SO_4/KMnO_4/NaNO_3/H_2O_2$, > 1 d	Centrifugalization, dialysis	> 2 d	[14]

Graphite	Step 1: oxidation by Hummers method, $H_2SO_4/K_2S_2O_8/P_2O_5$, > 1 d Step 2: acid refluxing, HNO_3/H_2SO_4, 24 h, Step 3: ultrasonication, NaOH, 0.5 h	Centrifugalization, dialysis, filtration	> 1 week	[15]
Graphite	Step 1: oxidation by Hummers method, $H_2SO_4/KMnO_4/NaNO_3/H_2O_2$, > 1 d Step 2: acid oxidizing and sonication, HNO_3, 10 h Step 2: acid refluxing, HNO_3, 10 h	Centrifugalization, filtration, freeze dry, centrifugalization,	> 2 d	[16]
Black carbon	Hydrothermal method, H_2O_2, 1.5 h	Not required	1.5 h	This work

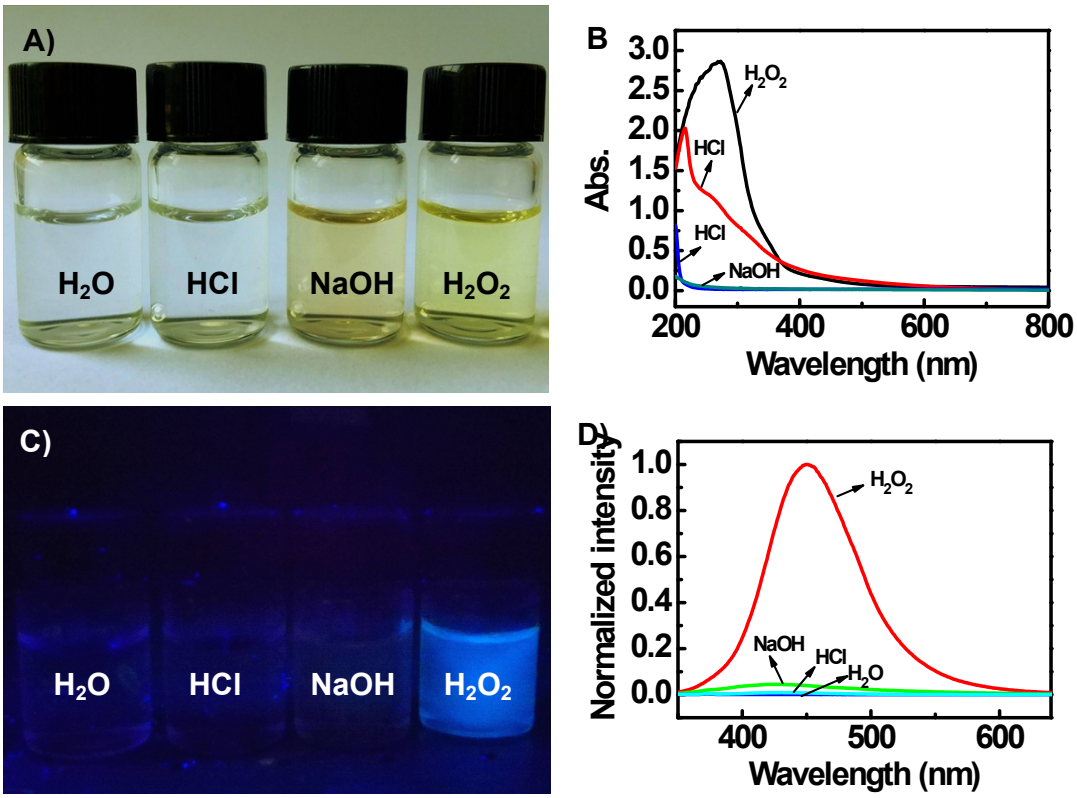

Fig. S1 The (A) day light and (C) 365 nm UV light irradiation photographs of synthesized products under different conditions, and corresponding (B) UV-vis and (D) FL spectra, respectively. (The aqueous solutions are without dilution or enrichment, the excitation wavelength of (D) is 331 nm.)

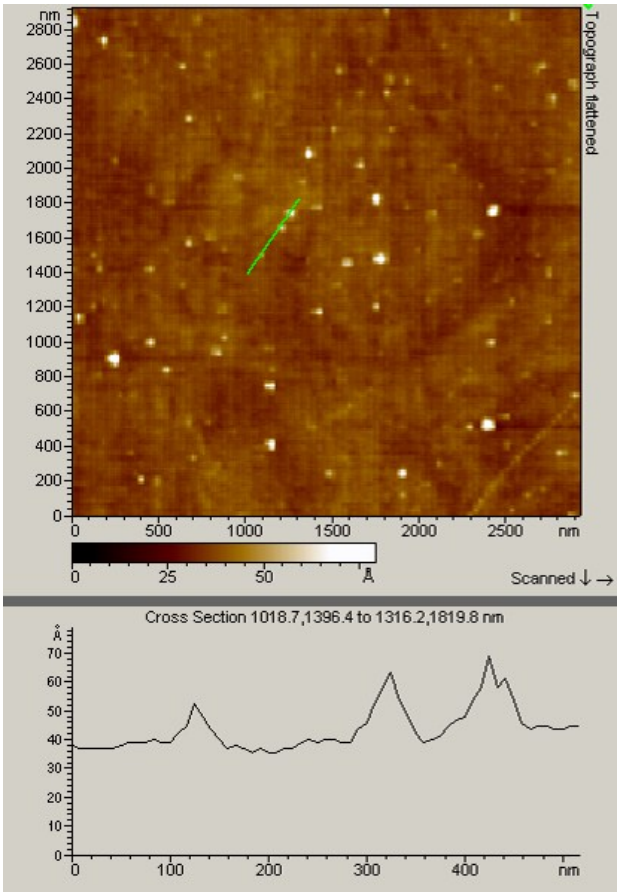

Fig. S2 AFM image of as-synthesized GO-dots.

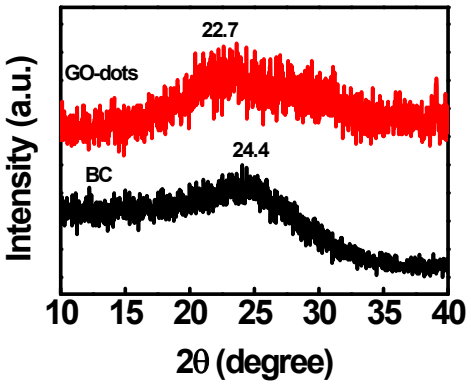

Fig. S3 XRD patterns of BC and GO-dots

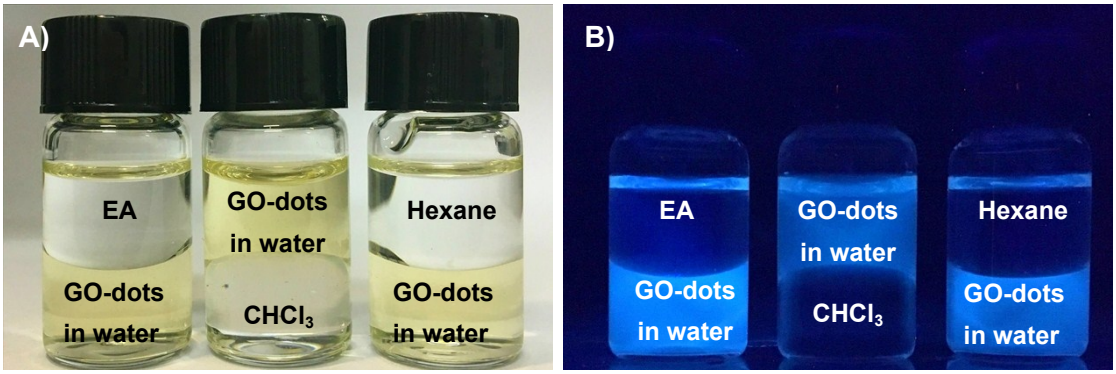

Fig. S4 The photographs of as-synthesized GO-dots in the mixture of water and EA, water and $CHCl_3$, water and hexane under (A) day light and (B) 365 nm UV light irradiation.

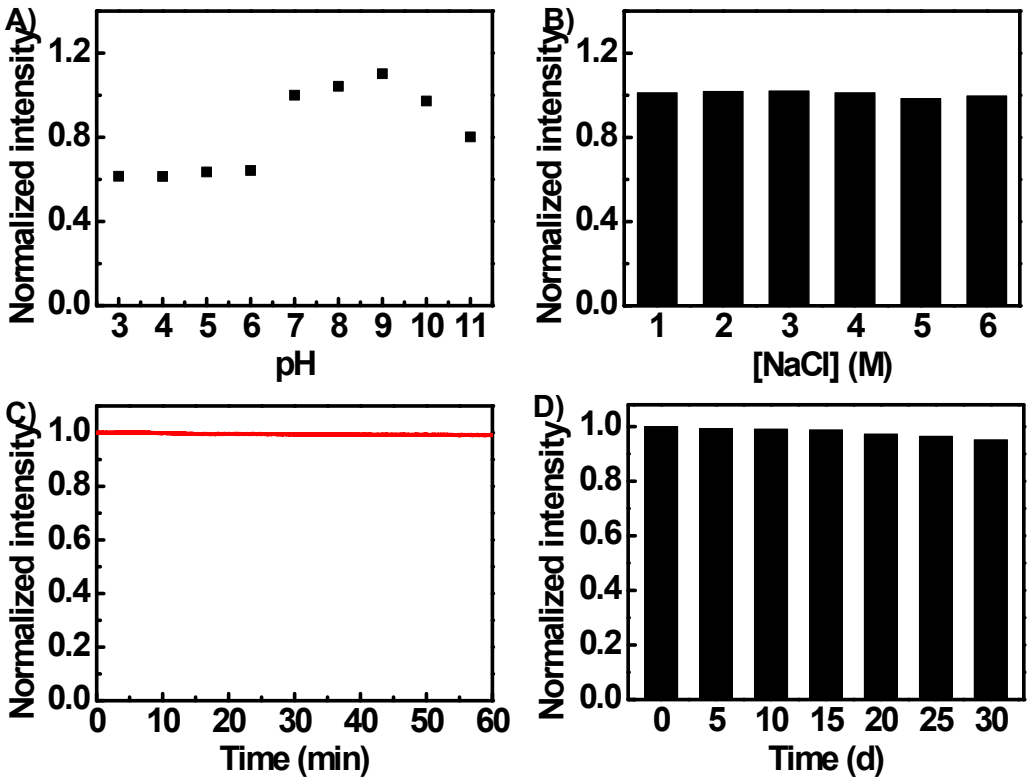

Fig. S5 Normalized FL intensity of GO-dots (A) at different pH, (B) in the presence of different concentration of NaCl, (C) continuous excitation with a 150 W Xe lamp for 60 min and (D) at room temperature for a month, respectively. (The excitation wavelength is 331 nm, the emission wavelength is 446 nm.)

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