COMMUNICATION

Facile synthesis and photoelectric properties of carbon dots with upconversion fluorescence using arc-synthesized carbon by-products

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1, Detailed experimental procedure

SWNT synthesis

The synthesis of SWNTs was performed in a DC arc discharge furnace. In a typical experiment, the anode was a sintered graphite rod (6 mm diameter, 100 mm length) with the catalyst Ni/Y, in which the mole ratio among C/Ni/Y was 94.8:4.2:1.0. The powders were mixed by ball milling at a speed of 300 rpm for 12 h. Then the mixture was extrusion molded to form graphite rods with coal tar as a binder. Finally, the graphite rods were annealed at 1000 ºC for 8 h under N_2 atmosphere. The cathode was a pure graphite rod with 8 mm diameter and 300 mm length. The SWNT samples were synthesized with a current of 90 A under He buffer gas (50 kPa). The arc gap between anode and cathode was kept at a constant value of 2~3 mm.

CD synthesis

Firstly, 2g SWNT products were adequately dispersed in 2000 ml SDS (1 wt%) solution under

ultrasonic vibrations, followed by centrifugation at 6000 rpm to remove large carbon particles and catalysts. The stable dispersions were further centrifuged at 9000 rpm, and the residual carbon particles were collected after SDS removal and freeze drying. For the synthesis of fluorescent graphitic CDs, 500 mg carbon particles were added into 250 ml concentrated H_2SO_4-HNO_3 mixtures (V/V=3/1) under magnetic stirring, followed by acid reflux at 120 ºC for different times. After reactions, the solution was diluted with distilled water (1500 ml), and the pH was adjusted to 7 with Na_2CO_3. The resulting suspension was dialyzed in a dialysis bag (MWCO: 2000 Da) for 3 days. Finally, the CD solution was obtained after rotary evaporation concentration.

$NaBH_4$ reduction process

10 ml of the CD solution (~10 μg/ml) was diluted with distilled water (30 ml) under ultrasonic irradiation. 0.5 g $NaBH_4$ was added slowly into the above solution and ultrasonically dispersed for 30 min. After the reduction reaction for 20 h at room temperature under magnetic stirring, the resulting solution was dialyzed in a dialysis bag (MWCO: 2000 Da) for 1 day.

PL tests

The PL tests have been performed at room temperature using spectrophotometer (HITACHI, F-4600) with different excitation wavelengths. The PL spectra of the as-synthesized CDs and reduced CDs were measured after the dispersion in aqueous solutions. The exiction wavelengths were changed from 300 to 380 nm. To measure the up-conversion properties of the as-synthesized CDs and reduced CDs, the excitation wavelengths were changed from 550 to 900 nm.

Prototype photodetector device

The as-synthesized CDs were firstly dispersed in deionized water (~10 μg/ml) under ultrasonic vibrations for 60 min. Then, a suspension of the CDs was dropped onto two Au electrodes on SiO_2 substrate aligned parallel to each other, and the electrode gap is 10 μm, followed by drying under infrared lamp. The dropping-drying processes were repeated for several times until the CDs connected with two electrodes. The photoelectric response of CD-based prototype device was measured with

Agilent 4156C under UV irradiations.

Quantum Yield (QY) measurements

Quinine sulphate in 0.1 M H_2SO_4 (QY = 0.54 at 350 nm) was chosen as a standard. The quantum yield of the as-synthesized CDs in water was calculated according to the following equation:

$$\varphi_x=\varphi_{st}(K_x/K_{st})(\eta_x/\eta_{st})^2$$

where φ is the quantum yield, K is the slope determined by the curves and η is the refractive index. The subscript "st" refers to the standards and "x" refers to the unknown samples. For these aqueous solutions, $\eta_x/\eta_{st}=1$.

2, Supporting characterizations

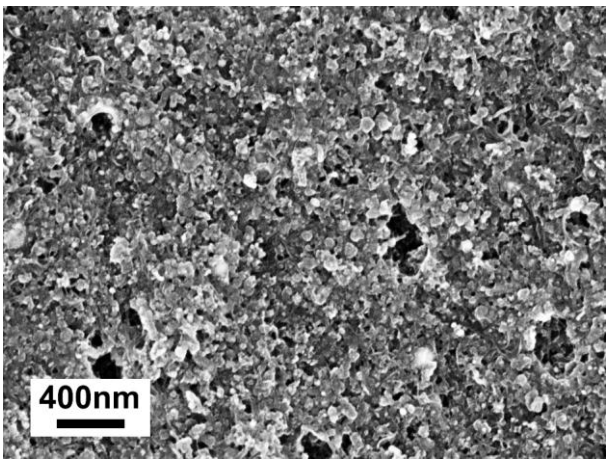

Fig S1 A typical SEM image of the carbon particles after centrifugation at 9000 rpm.

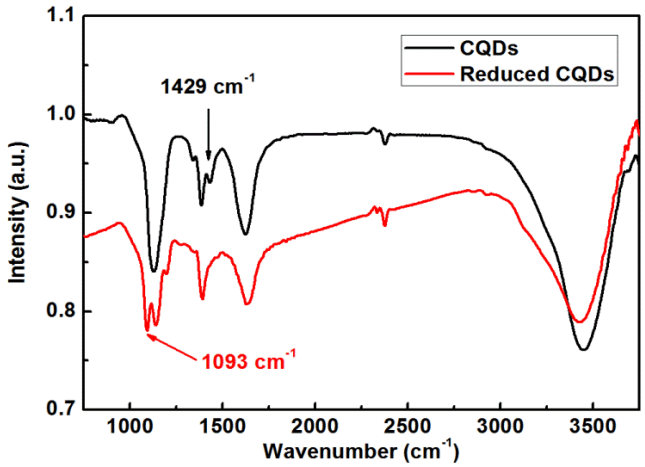

Fig. S2 FTIR spectra of the CDs before (black) and after (red) $NaBH_4$ reduction.