Cascaded photo-potential in carbon dot-hematite system driving

the overall water splitting under visible light

(Supplementary Information)

EXPERIMENTAL SECTION

Synthesis of CDs. CDs were obtained by a common electrolytic procedure using two graphite rods as carbon sources, which was reported by our group before.¹ In detail, two 99.99 % pure graphite rods with diameter of 6.15 mm and length of 15 cm (from Alfa Aesar Co. Ltd.) were cleaned by ultrasonic agitation in deionized water for 15 min. After 3 times of washing process, the cleaned rods were applied both as anode and cathode respectively in ultrapure water (18.2 M Ω ·cm⁻¹, 1000 mL). The two electrodes were set apart of each other with a distance of 7.5 cm, and bulged 5 cm out the electrolyte level. Then, 30 V was applied across the electrodes using a direct current (DC) power supply as the electric source. The electrolytic process was kept for two weeks under magnetic stirring. The originally transparent electrolyte changed into a dark solution gradually during the long process due to the electro-corrosion of the graphite rods. The resultant solution was then filtered with a slow-speed quantitative filter paper, following with centrifuging at 8000 rpm for 15 minutes to remove the precipitated graphite oxide and bigger graphite particles. After that, the CDs aqueous solution was dried by cryodesiccation, which was used in the following procedure.

Synthesis of Fe₂O₃ particles. The Fe₂O₃ particles were synthesized by a facile heat treatment in the tubular furnace. In detail, 0.3 g of commercial Fe₂O₃ powder (purchased from Alfa Aesar Co. Ltd.) was added into a porcelain boat. Then the porcelain boat was put into a tubular furnace with the ramping temperature rate of 0.5 °C/min under the vacuum atmosphere, and kept at 300 °C for 2 h. After cooling down

to room temperature, a red powder of product was obtained. Then, the product was washed by ethanol and deionized water respectively for several times. After that, the samples were dried at 80 °C in a vacuum drying oven over night. Finally, the powder of Fe_2O_3 particles was obtained.

Synthesis of CDs-Fe₂O₃ composites. The synthesis of CDs-Fe₂O₃ nanocomposite was similar to the synthetic process of Fe₂O₃ particles in the following procedure: 0.3 g of Fe₂O₃ powder and 0.015 g of CDs powder were ground for 15 min to get a homogeneous mixture. After that, the heat treatment and washing process were the same as that of the Fe₂O₃ particles. Finally, we got the catalyst denoting as CDs-Fe₂O₃. For the next step, we changed the annealing temperature (100, 200, 400 and 500 °C) for obtaining different CDs-Fe₂O₃ catalysts. In the following procedures, we also added different quantities of CDs (0.003, 0.01, 0.03 and 0.18 g) into the composites.

Structural characterization. All the regents are purchased from Sigma and Alfa Aesar without further purification. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were measured by using a FEI-Tecnai F20 transmission electron microscope with an accelerating voltage of 200 kV. The scanning electron microscope (SEM) and electric force microscope (EFM, Cypher S) were applied to characterize the surface morphology and electrical information of the samples. UV/VIS/NIR spectrophotometer (Lambda 750, Perkinelmer) was employed to acquire the UV-vis absorption spectra. Powder X-ray diffraction (XRD) was carried out to characterize the crystal structure of the as-

prepared products by using a powder X-ray diffraction (XRD) by using an X'PertProMPD (Holand) D/max- γ AX-ray diffractometer with Cu K α radiation (λ = 0.154178 nm). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a KRATOS Axis ultra-DLD X-ray photo-electron spectroscope with a monochromatic Mg K α X-ray source (hv = 1283.3 eV). Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with He I (21.22 eV) as the monochromatic light source and a total instrumental energy resolution of 100 meV. Surface photovoltage (SPV) was measured using a lock-in based SPV measurement system, which was consist of a source of monochromatic light (Omni-5007,Zolix), a lock-in amplifier (SR830-DSP, Stanford) with a light chopper (SR540, Stanford), a photovoltaic cell, and a computer. A low chopping frequency of 23 Hz was used in the conventional testing. All the electrochemical measurements were conducted on a CHI 920C workstation (CH Instruments, Shanghai, China), using a standard threeelectrode system, in which an Ag/AgCl (saturated KCl) as the reference electrode, a platinum wire as the counter electrode and a glass carbon (GC) electrode as the working electrode. Electrochemical impedance spectra (EIS) measurements were carried out at the open circuit potential with a frequency ranging from 1 MHz to 0.01 Hz and an AC voltage amplitude of 5 mV in ultrapure water. The thermogravimetric analyses (TGA) were conducted on a Mettler-Toledo TGA/DSC in N₂.

Measurement of the relative content of hydroxyls and carboxylic groups on CDs. A DDS-11A conductance titrator was used to conduct the conductometric titration

experiment. 100 mg of dried CDs powder, 40 mL of solvent (pyridine/acetone = 1/4),

1 mL of deionized water and 1 mL of ethanol were added into a 50 mL triangular flask with thoroughly stirring at 300 rpm for 15 min. After that, we used 0.005 mol/L KOH-isopropyl alcohol standard solution as the titrant (C). Figure S2 (for CDs) shows the conductivity changing with the titration volumes, which were recorded by the conductance titrator. Here, A and B represent the equivalence points for carboxyl and hydroxyl groups, respectively. The contents of carboxyl and hydroxyl groups were estimated by: n (carboxyl) = V_A C and n (hydroxyl) = (V_B-V_A) C. Hence, COOH / OH = n (carboxyl) / n (hydroxyl) = V_A C / (V_B-V_A) C = V_A / (V_B-V_A). The content ratios of carboxyl/hydroxyl of different CDs, are listed in Table S1.

Electric Force Microscopy (EFM) test. EFM is one of the testing modes in AFM techniques; the technique oscillates the tip at its resonance frequency above the surface while a direct current (DC) bias is applied between the tip and the sample. The electric field between the tip and the sample creates a force gradient between the two that causes a shift in the resonance frequency of the cantilever. Assuming the cantilever as a harmonic oscillator, this shift in resonance in turn causes a shift in the phase lag between the drive and response of the cantilever, which can be expressed by the following equation :^{2,3}

$$\Phi(x) = -\frac{Q}{2k}C''(h)(V_{tip} - V_s)^2$$

where Q is the cantilever quality factor, k is the spring constant, C"(h) is the second derivative of the tip-sample capacitance as a function of h and V_s is the local electrostatic potential on the sample surface. By monitoring the phase shift, we can find areas under the tip that perturb the electric field between the tip and the sample.

The phase indicates whether the shift is attractive or repulsive. Attractive forces show a shift in the phase to higher than free air value. Repulsive forces shift the phase below the free air value.

Water splitting test. The photocatalytic property of the synthetic samples was evaluated using (300 W Xe-lamp, PLS-SXE 300, Beijing Trusttech Co. Ltd, China), a bandpass filter was used to get visible light ($\lambda \ge 420$ nm). No sacrificial or cocatalysts were added into the reaction system. In a detailed procedure, 30 mg of the catalysts was added into 25 mL ultrapure water, and ultrasonic dispersion was carried out to get a homogenous solution. Then the homogenous solution was transferred into a glass photoreactor (equipped with a quartz window at the bottom for illumination), which was sealed with a rubber plug. The reacting system was degassed for 15 min with nitrogen to completely remove dissolved O₂ from the air. Then we put the photoreator into a multichannel photochemical reaction system. To detect the gas production, a gas chromatograph (GC-7900) set up with a 5 Å molecular sieves column and a thermal conductivity detector (TCD) was utilized. During the measurement, the temperature parameters of oven, injection and detector were set as 50, 130, and 130 $^{\circ}$ C, respectively. Nitrogen (N₂) was used as the carrier gas with the flow rate of 30 $mL \cdot min^{-1}$.

Determination of electron transfer number. Rotating disk-ring electrodes (RRDE) testing system (RRDE-3A, ALS Co., Ltd) was used to measure the electron transfer number, which were performed in ultrapure water (N_2 saturated for 15 min) with a scan rate of 10 mV·s⁻¹ and different rotating speed under visible light irradiating. The

disk potential was set at the open circuit potential to avoid electrochemical water oxidation. The Pt ring potential was set at 0.9 V vs. SCE. The photogenerated H_2O_2 on the disk can be oxidized to O_2 at this potential. All the data were collected by a CHI 920C electrochemical workstation (CH Instruments, Shanghai, China).

The electron transfer number (n) was obtained according to the following equation:⁴

$$n = \frac{4I_d}{I_d + I_r/N}$$

Where I_d and I_r represent the disk and ring current, respectively. N is the RRDE collection efficiency determined to be 0.24.

Supplementary tables.

Table S1 - Quantification of hydroxyls and carboxylic groups on CDs surface.

	Carboxylic acid	Hydroxyl	Ratio
	(mol/100 mg)	(mol/100 mg)	(COOH/OH)
CDs	0.590×10 ⁻⁴	1.186×10 ⁻⁴	1:2.01

Supplementary figures.



Figure S1. (a) XPS full scan spectra of CDs. (b) High-resolution C 1s XPS spectra of CDs.



Figure S2. The conductivity-titrant amount curve of CDs. (A and B are the equivalence points which represent carboxyl and hydroxyl groups, respectively). The relative ratio of carboxylic acid and hydroxyls for CDs are about 1:2.01.



Figure S3. Schematic process of the EFM test. During the test, there is a direct

current bias of +3 V applying on the tip.



Figure S4. (a) Height. (b) Height profile along the red line CD shown in (a). (c) Height. (d) Height profile along the red line CD shown in (c), respectively. (c-d) are obtained under the illumination of blue light (λ =405 nm). These height data show that CDs have the height of about 10 nm.



Figure S5. (a) and (b) are SEM the images of commercial Fe_2O_3 particles, (c) and (d) are the TEM and HRTEM of commercial Fe_2O_3 , respectively.



Figure S6. Deconvoluted O 1s core level spectrum acquired from (a) Pure Fe₂O₃ and

(b) CDs, respectively.



Figure S7. XPS spectra of CDs-Fe₂O₃ composites (0.05 $g_{CDs}/g_{catalyst}$). (a) The full spectrum; (b) Fe 2p core level spectrum; (c) C 1s core level spectrum, respectively.



Figure S8. XRD patterns of CDs-Fe₂O₃ composites treating with different annealing

temperature. (black line represents 100 °C, red line is 200 °C, blue line is 300 °C, pink line is 400 °C and green line is 500 °C, respectively). The concentration of CDs for CDs-Fe₂O₃ samples measured is 0.05 $g_{CDs}/g_{catalyst}$.



Figure S9. The RRDE collection experiment for CDs-Fe₂O₃ with different rotating speeds (400, 800, 1200, 1600 and 2000 rpm). Here, the concentration of CDs for CDs-Fe₂O₃ samples measured is 0.05 $g_{CDs}/g_{catalyst}$.

References

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