

Supporting Information

Bioelectrochemical Synthesis of High-quality Carbon Dots with Strengthened Electricity Output and Excellent Catalytic Performance

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Experimental details

Chemicals

Graphite rods (>99.9 %, $\Phi = 0.8$ mm) and porous carbon felt were purchased from Sinopharm Chemical Reagent Co., Ltd. Proton exchange membrane (PEM) was bought from Dupont company. The anode medium was consistent to the former work. 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) and rhodamine B (RhB) were gained from Aladdin Reagent Company. All chemicals were used without further purification. All glasswares were cleaned with aqua regia (volume ratio HCl: HNO₃ = 3:1) and thoroughly rinsed with Wahaha water (Hangzhou wahaha group Co. Ltd. China). Wahaha water was used in the whole experiments.

Characterization of as-prepared CDs

The photoluminescence spectrophotometer (PL, Hitachi FL-4500), UV-vis spectrophotometer (UV2300 II, Japan) and UV-vis diffuse reflectance spectra (DRS) (JASCO, UV-550, Japan) were used to inspect the optical properties of CDs solution. The morphology and crystalline were measured by the high resolution transmission electron microscopy (HRTEM) analyses (FEI Tecnai F30 electron microscope, using a 200 kV accelerating voltage). Besides, X-ray diffraction (XRD) using a diffractometer with Cu $K\alpha$ radiation (D/max-2400, Japan, source light at the wavelength (λ) of 0.1541 nm) was also analyzed the crystalline structure. The

chemical compositions of as-prepared CDs solution was investigated by an X-ray Photoelectron Spectroscopy (XPS) (Thermo ESCALAB 250XI, USA). The zeta potential was measured by Nano ZS90 size analyzer (ZEN3690, English). The FT-IR spectroscopy (VERTEX 70-FT-IR, Bruker, Germany) was used to ascertain the presence of oxygen group functionalized CDs. The low temperature electron paramagnetic resonance (EPR) signals of the radicals trapped were detected on a Bruker A200- 9.5/12 by using DMPO spin-trapping agent. The output of MFC voltage was collected using a 16 channel data acquisition device (MPS-010602, China). The PEC performances of CDs were measured using a three-electrode electrochemical workstation (CHI 760C, Shanghai Chenhua, China). The ns-level time-resolved PL (TRPL) decay spectrophotometer (FL sp920, Edinburgh Analytical Instrument, UK) was used to survey the lifetime of charge carrier at room temperature. H₂ production was analyzed by Shimadzu LC-6AD gas chromatography (GC).

In order to investigate other semiconductors coupled with MFC synthesized CDs, in this work, choosing the traditional TiO₂ nanotubes (NTs) as supported electrode, the CDs@TiO₂ electrode was used to explain its synergistic effect. Firstly, the TiO₂ NTs was prepared by the anodization method, then the CDs was deposited on TiO₂ by the impregnation method. The coupled CDs@TiO₂ material was further inspected by electrochemical characterization and photoelectrocatalytic performance.

In **Figure S8**, the photocurrent response measurement indicated the CDs decorated TiO₂ electrode obviously enhanced photocurrent conversion, 2.12 times higher than that of TiO₂ electrode. Also, the as-prepared CDs itself showed obviously photocurrent response. More importantly, the composited material presented steady current, implying that CDs could accelerate the stable of the composite system. These results demonstrated the surface hybrid heterostructure formed between CDs and TiO₂ can enhance the catalytic activity of CDs/TiO₂ electrode.

The electrochemical impedance spectrum (EIS) was carried out to study the charge transfer and reaction resistance over CDs/TiO₂ electrode. The EIS plots of TiO₂ and CDs/TiO₂ electrodes (**Figure S9**) were measured in 0.05 M Na₂SO₄ electrolyte with 10⁻²–10⁵ Hz frequency under dark and simulated sunlight irradiation, respectively. It was found that the curve radius of CDs/TiO₂ NTs was apparently smaller than that of TiO₂ NTs either in dark or under sunlight. Meanwhile, the intersection of the X axis implied that the addition of CDs diminished the resistance and improved their

conductivity, suggesting that a fast interfacial charge transfer over the decorated electrode.

The photoelectrocatalytic performance of this composite was investigated by the degradation of antibiotics levofloxacin (LEV) pollutant. In **Figure S10**, the LEV degradation under dark, self-photolysis and photoelectrocatalytic (TiO_2 and CDs/TiO_2 electrodes), it presented that the CDs/TiO_2 material showed excellent photoelectrocatalytic activity for LEV removal, reaching to approximately 80% removal rate in 3 h. The **Figure S10(c)** indicated that this composite enhanced the catalytic performance of TiO_2 , 1.33 times higher than that of un-decorated TiO_2 . The introduction of CDs largely enhanced the catalytic performance of the original TiO_2 electrode, and the possible catalytic mechanism could be proposed in **Figure S10(d)**. Under simulated sunlight irradiation, the VB of CDs and TiO_2 would be excited, the generated photoelectrons could be transferred to the corresponding CB. Subsequently, the generated electrons of TiO_2 CB would be transferred to the CB of TiO_2 . Due to the up-converted effect of as-prepared CDs, the decorated CDs could absorb long-wavelength visible light and then relax by emitting short-wavelength UV photons, thereby inducing TiO_2 photo-excitation. The electron/hole pairs generated then liberated active oxygen radicals ($\cdot\text{O}_2^-$, $\cdot\text{OH}$) resulting in the degradation of LEV. So, the investigation of CDs based materials would open up a new platform for designing of optoelectronic and photo response devices.

Table S1. Photogenerated charge carrier lifetimes (τ_1 and τ_2) and relative intensities (Int.) of the graphite rod and different synthesized time carbon dots.

Samples	τ_1 (ns)/Int. (%)	τ_2 (ns)/Int. (%)	χ^2
Graphite rod	0.40/100	-	1.066
2 h-carbon dots	0.98/25.04	4.46/74.96	1.093
4 h-carbon dots	1.42/29.21	5.74/70.69	1.057
6 h-carbon dots	1.14/20.85	5.91/79.15	1.109

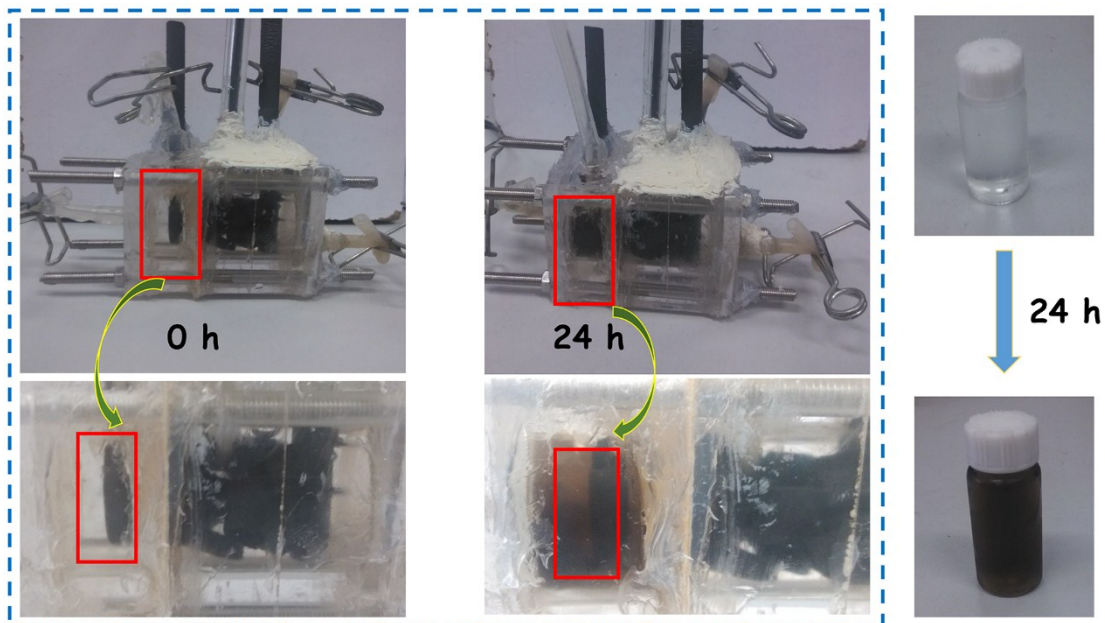


Figure S1. The photographs of the CDs synthesis route from MFC.

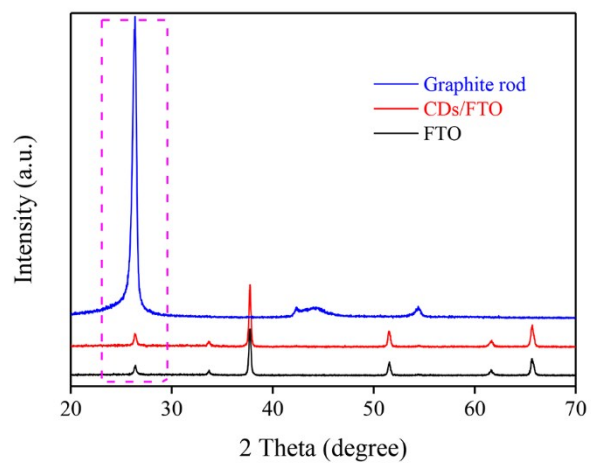


Figure S2. XRD patterns of the bio-synthesized carbon dots.

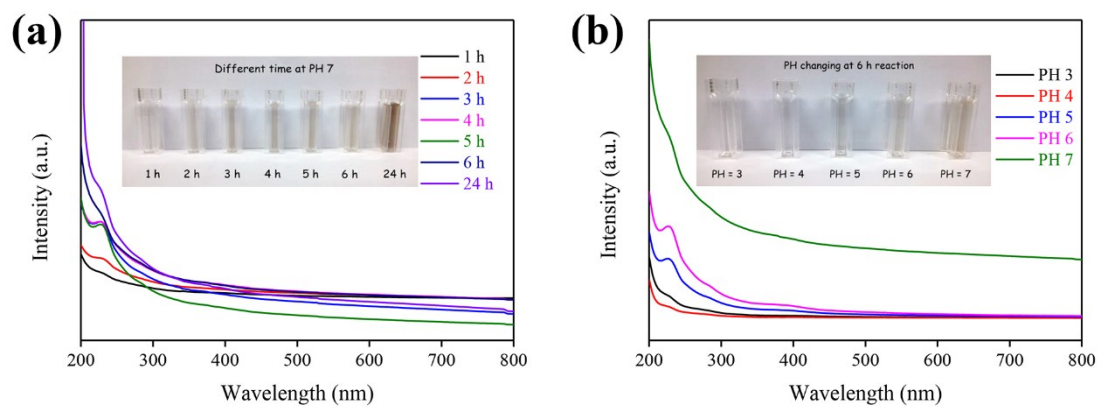


Figure S3. UV-vis absorption spectrum of the MFC synthesized CDs at different time at pH = 7 (a) and (b) at different pH in 6 h.

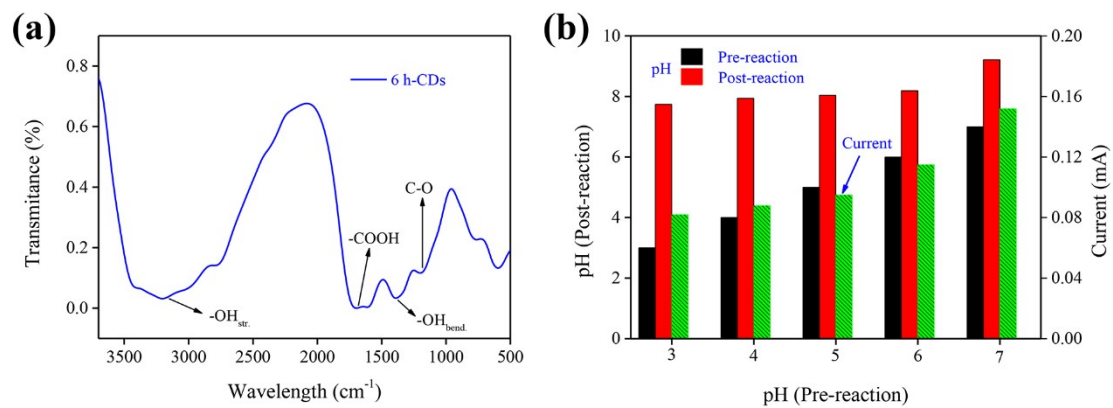


Figure S4. (a) FTIR spectra of 6 h as-prepared CDs; (b) the output current and pH values vary of the cathode effluent recorded at the condition of different pH values.

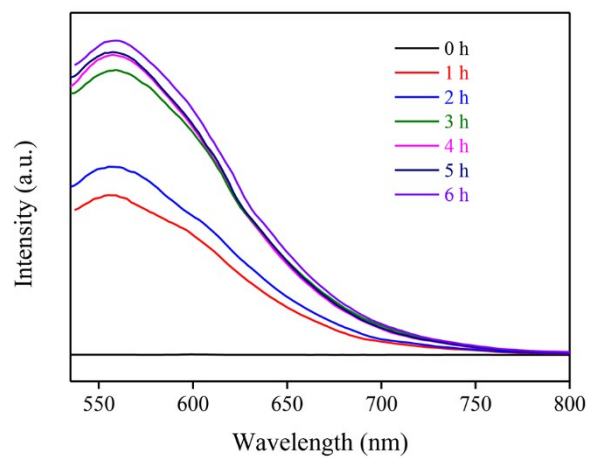


Figure S5. Photoluminescence spectra of biosynthesis carbon dots at different time (Recorded at an excitation wavelength of 500 nm).

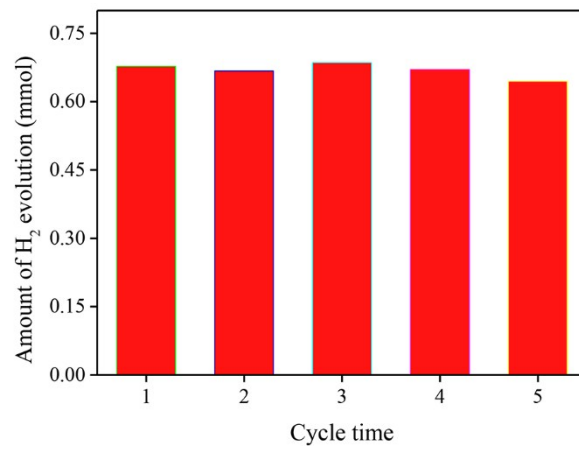


Figure S6. Five-cycle experiments of H₂ generation in the SCMFC system under 0.5 V bias vs SCE (During 2.5 h).

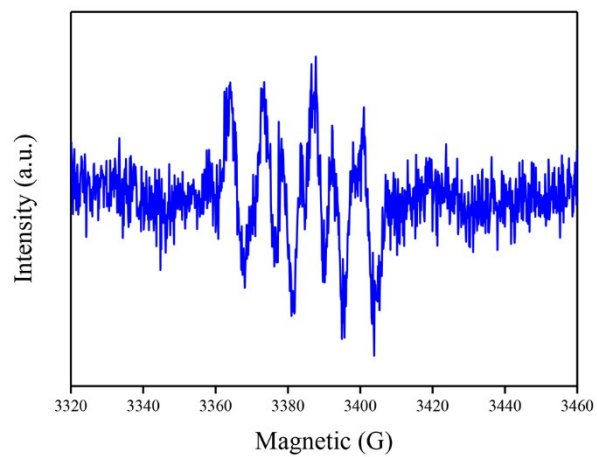


Figure S7. ESR spectra of radical adducts trapped by DMPO-O_2^- for as-obtained CDs under simulated light irradiation ($I_0 = 35 \text{ mW cm}^{-2}$).

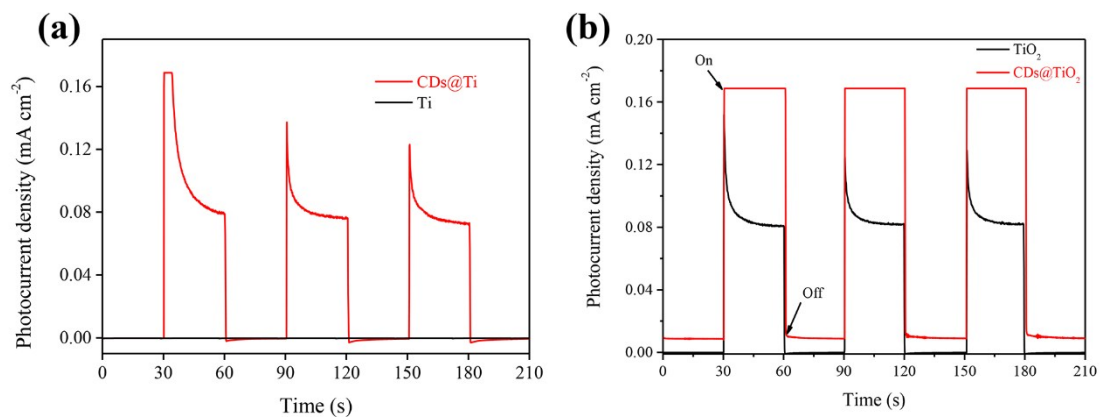


Figure S8. Transient photocurrent density vs. time of (a) CDs@Ti, Ti and (b) TiO₂, CDs@TiO₂ under simulated sunlight ($\lambda > 400$ nm, $I_0=35$ mW cm⁻², the applied potential is 0.3 V)

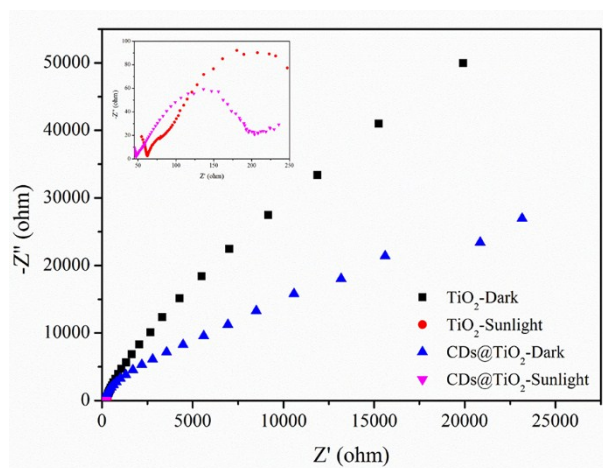


Figure S9. EIS Nyquist plots of the TiO₂ and CDs@TiO₂ in dark and under simulated sunlight ($\lambda > 400$ nm, $I_0 = 35$ mW cm⁻², applied potential is 0.3 V)

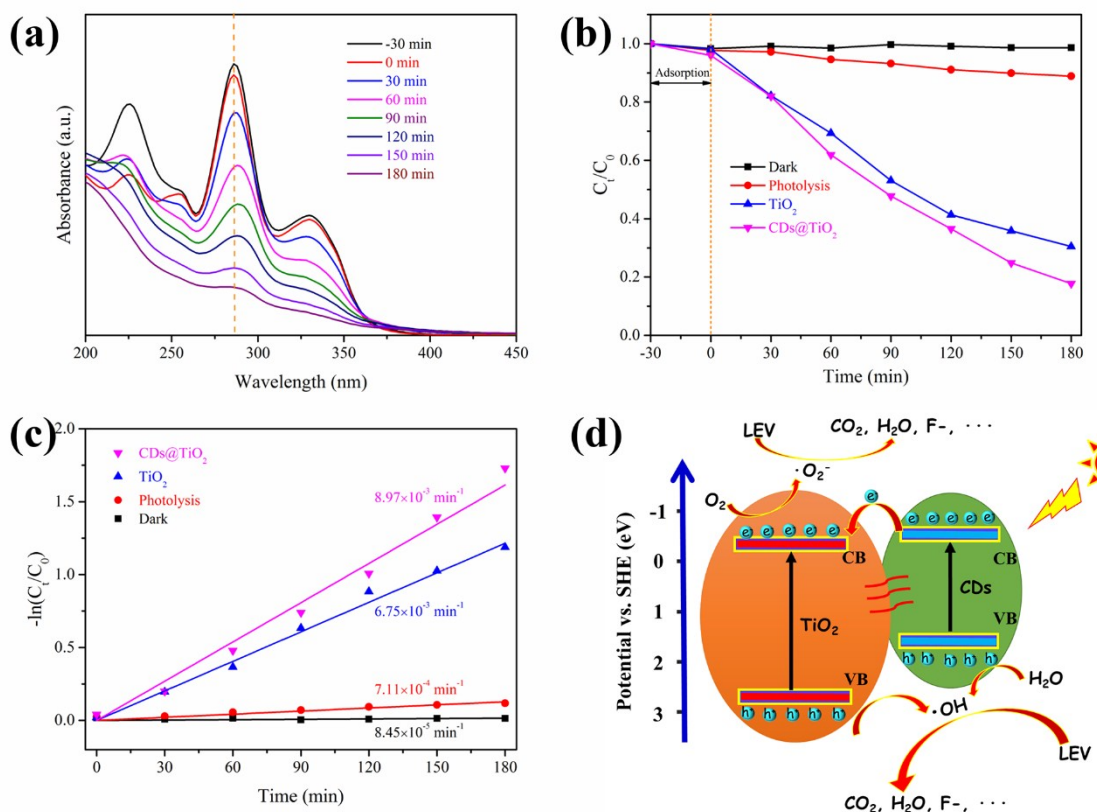


Figure S10. (a) UV-vis spectra of LEV during photocatalytic degradation process by the CDs@TiO₂ catalyst under simulated sun light irradiation; (b) degradation curves and (c) kinetic regression curves of LEV under different conditions; (d) the proposed mechanism of the electron-hole pairs transfer and separation process for CDs@TiO₂ composite electrode under simulated sunlight irradiation.