

Electric Supplement Information

Electrophoretic Fabrication of Highly Robust, Efficient, and Benign Heterojunction Photoelectrocatalysts Based on Graphene-Quantum-Dot Sensitized TiO₂ Nanotube Arrays

Dengyu Pan*, Chen Xi, Zhen Li, Liang Wang, Zhiwen Chen, Bo Lu, and Minghong Wu*

Preparation of GQDs. GQDs were prepared by a modified hydrothermal cutting method.¹¹ Graphene oxide (GO) sheets were obtained from graphite powder by the Hummers method. Graphene sheets (GS) were acquired by thermal deoxidization of the GO sheets in a tube furnace at 200 °C for 2 h with a heating rate of 10 °C min⁻¹. GSs (2 g) were oxidized in concentrated H₂SO₄ (30 mL) and HNO₃ (90 mL) for 10 h ultrasonication (500 W, 100 kHz). The mixture was then diluted with deionized (DI) water (1000 mL) and filtered through a 0.22 μm microporous membrane to remove the acids. Purified oxidized GSs (2 g) were re-dispersed in DI water (400 mL) and the pH was tuned to 8 with NH₃•H₂O. The suspension was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (100 mL) and heated at 200 °C for 10 h. After cooling to room temperature, the resulting black suspension was filtered through a 25 nm microporous membrane (Millipore Corporation), and a brown filter solution containing GQDs was separated for subsequent assembly and characterization.

Preparation of TNAs. TNAs were prepared by anodic oxidation.^{34b} Briefly, titanium foils (20 mm×20 mm) were soaked in a mixture of hydrofluoric acid and nitric acid for 1min (HF/HNO₃/H₂O = 1:4:5 in volume), rinsed with deionized water for 10 min, and then dried in air at room temperature to polish the foils. The polished foils were anodized in a conventional electrode cell using a solution of 0.3 wt% NH₄F, 0.6 wt% HF, 2 wt% deionized water, and 97.1% ethylene glycol as t electrolyte, platinum as counter electrode. Constant voltage was held at 60 V for 6 h. Subsequently, the samples were washed with ethylene, methanol and ethylene for about 15 min sequentially. The as-prepared TNAs were annealed at 500 °C in a fine quartz tube with a heating rate of 1.5 °C.

Fabrication of GQD-TNA heterojunction films. Vacuum-assisted and electrophoretic filling methods were used to prepare the heterojunction films. For the vacuum assisted filling method, the TNAs were immersed into GQD aqueous solution for 5 min under vacuum conditions in a vacuum oven at room temperature. The arrays were then rinsed with deionized water and dried at 60 °C. The process was repeated for 10 times. The electrophoretic assembly was performed in a three-electrode cell using the GQD aqueous solution (tuned to pH of 8 using 1M NaOH solution) as an electrolyte, TNA films as a working electrode, platinum electrode as a counter electrode, and saturated calomel electrode as a reference electrode. A +6V bias potential was applied to the TNA film for 2 h. As-prepared GQD-TNA films were rinsed with DI.

Material Characterization. AFM images were taken using a SPM-9600 atomic force microscope. TEM observations were performed on a JEOL JEM-2010F electron microscope operating at 200 kV. SEM images were taken with JEOL FESEM-6700F under voltage of 15 KV. X-ray powder diffraction (XRD) patterns were obtained with a Rigaku D/max-2500 using Cu K_α radiation. UV-vis Absorption and diffuse reflectance spectra were recorded at room temperature on a Hitachi 3100 spectrophotometer. Fluorescence spectra were recorded using a Hitachi 7000 fluorescence spectrophotometer. Raman spectra were recorded on a Renishaw in plus laser Raman spectrometer with λ_{exc} = 633 nm. Fourier transform infrared spectroscopy (FTIR) spectra were performed on Thermo Nicolet Avatar 370 FT-IR. The CV measurement was performed on GQDs

using a standard three-electrode system consisting of a platinum sheet coated with GQDs as the working electrode, a platinum wire as the counter electrode, Ag/AgCl as the reference electrode, and acetonitrile containing 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆, Aldrich) as the supporting electrolyte. The GQD electrode was prepared by drop-casting of GQDs/DCB solution onto the platinum electrode.

Photoelectrocatalytic (PEC) Measurement. PEC degradation experiments were conducted on methylene blue (MB) (30 ml, 10 mg L⁻¹, PH = 7) in a square quartz glass reactor, using GQD-TNA films as working electrode (1.5×1.5 cm²), 0.1 M Na₂SO₄ solution as supporting electrolyte, platinum sheet as counter electrode, and saturated calomel electrode (SCE) as reference electrode. A bias potential of 0.8 V was applied to the working electrode. Before the reaction, the MB solution was stirred in the dark for 1 h to reach adsorption-desorption equilibrium. A 300 W tungsten-halogen lamp was used as a simulated solarlight source, with a distance of 25 cm away from the working electrode (light intensity of 1.5 mW cm⁻²). The degradation rate of MB was measured by recording variations of the absorbance band of MB (664 nm) at given time intervals using a UV-visible spectrophotometer.

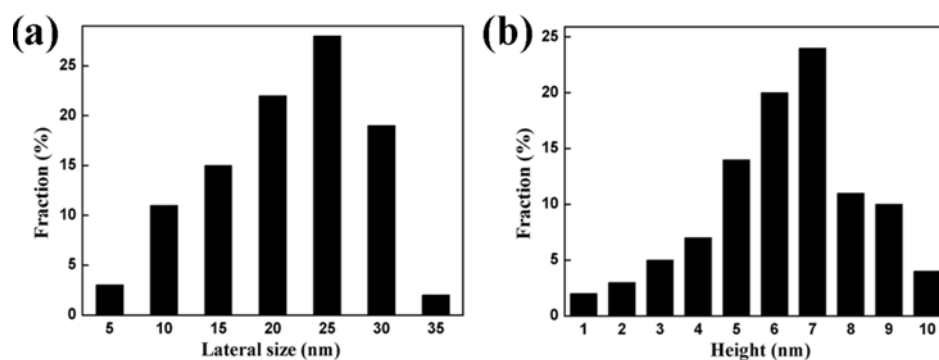


Fig. S1. Lateral size and height distributions of GQDs.

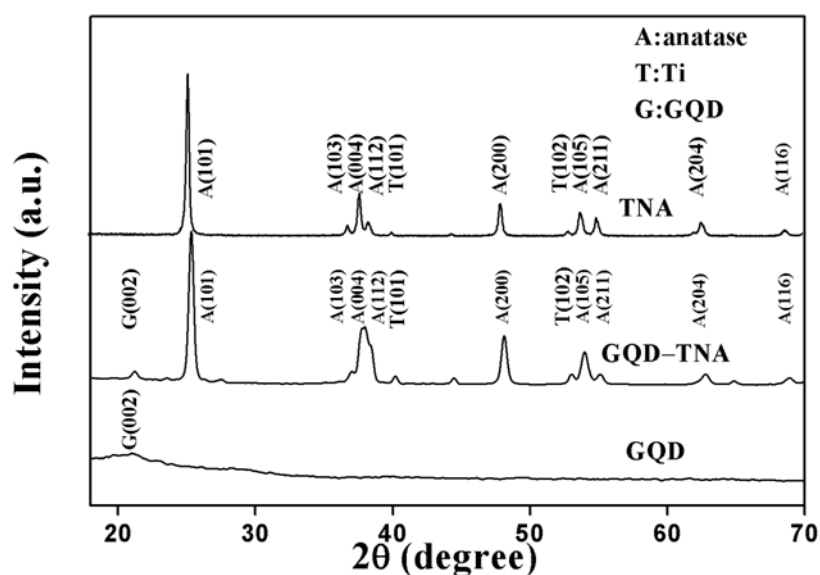


Fig. S2. XRD patterns of GQDs, TNA, and GQD-TNA. The d (002) of GQDs is 3.64 Å.

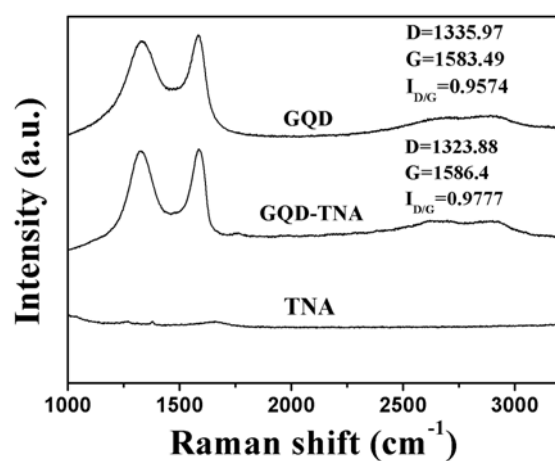


Fig. S3. Raman spectra of GQDs, TNA, and GQD-TNA.

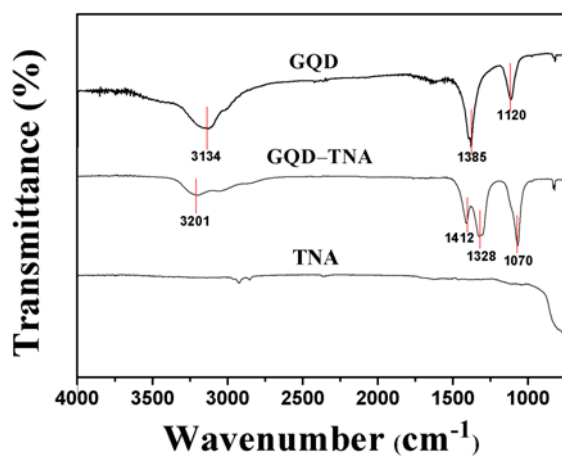


Fig. S4. FTIR spectra of GQDs, TNA, and GQD-TNA.

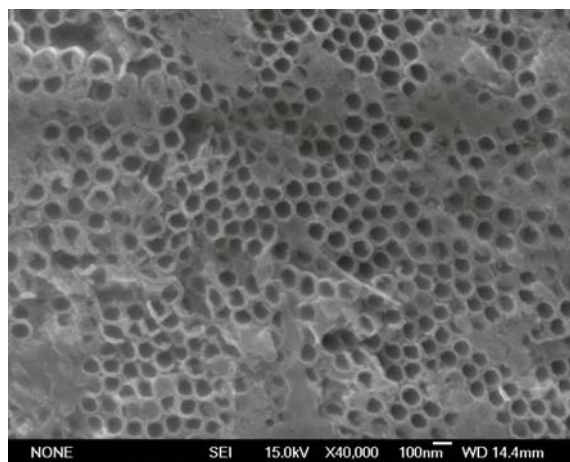


Fig. S5. SEM image of GQD-TNA film prepared by the vacuum assisted filling method.

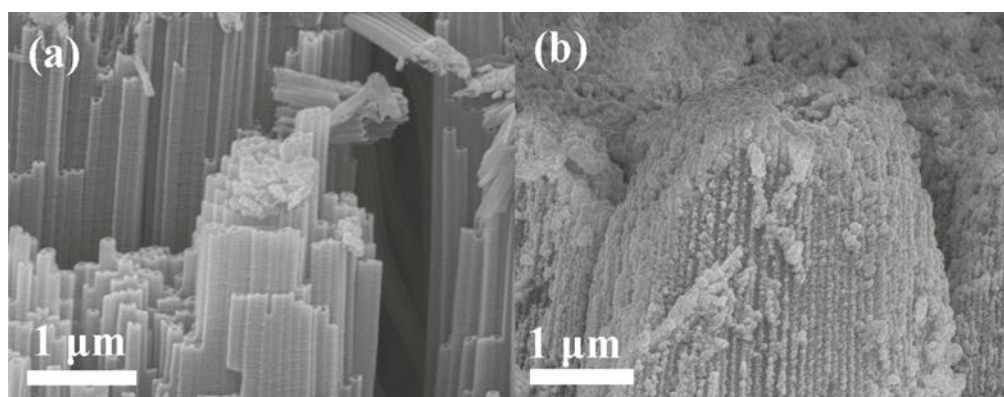


Fig. S6. Lateral SEM images of TNA (a) and GQD-TNA (b)

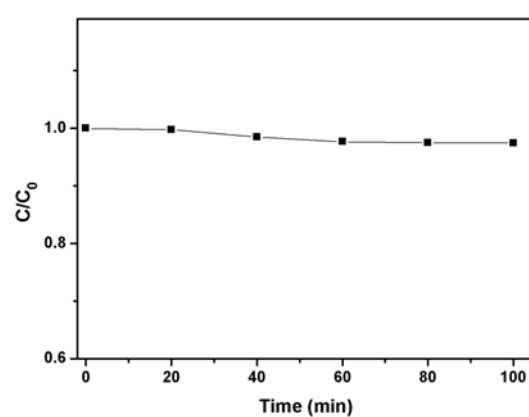


Fig. S7. PEC degradation of GQDs in aqueous solution using unfilled TNA as photoelectrocatalyst under UV irradiation (A 300 W high-pressure mercury lamp with main wave at 365 nm was used as the UV light source).

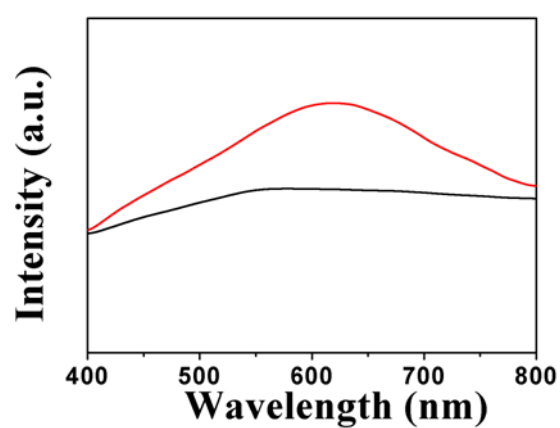


Fig. S8. Diffuse reflectance spectra of the GQD-TNA films: as-prepared by the vacuum assisted filling method (red) and soaked in water for 6h without light irradiation (black).

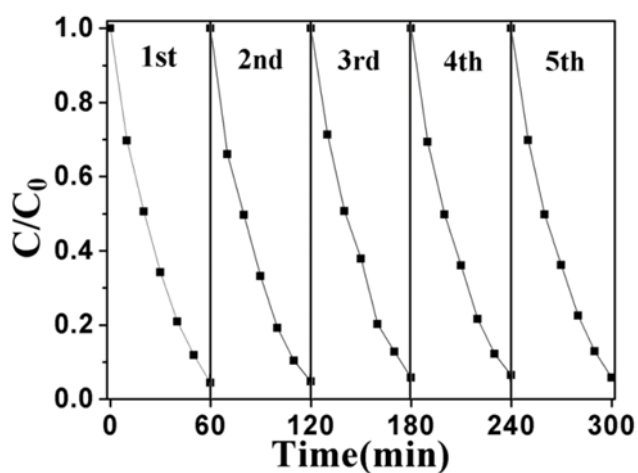


Fig. S9. PEC degradation of MB using GQD-TNA films as photoelectrocatalyst under UV irradiation for five cycles.

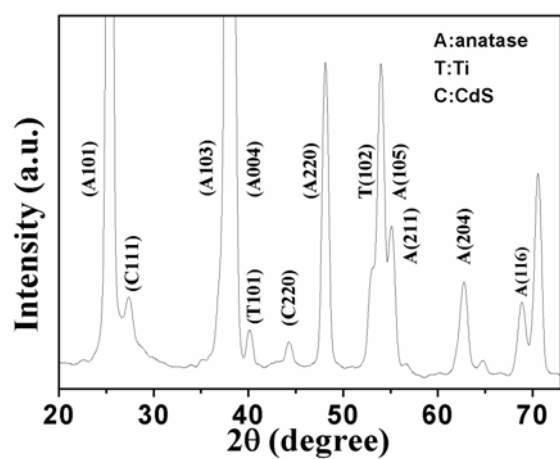


Fig. S10. XRD pattern of TNA filled with CdS quantum dots by a sequential chemical bath deposition method.

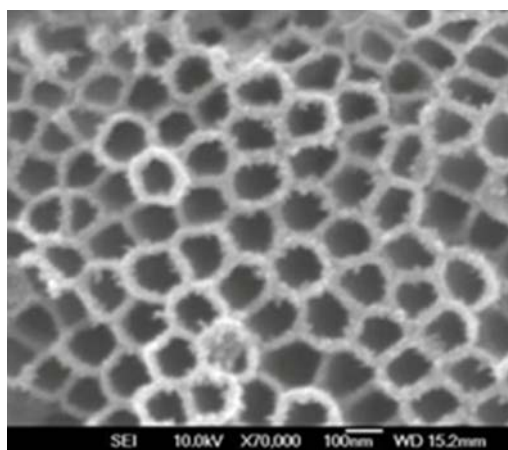


Fig. S11. SEM image of TNA filled with CdS quantum dots.

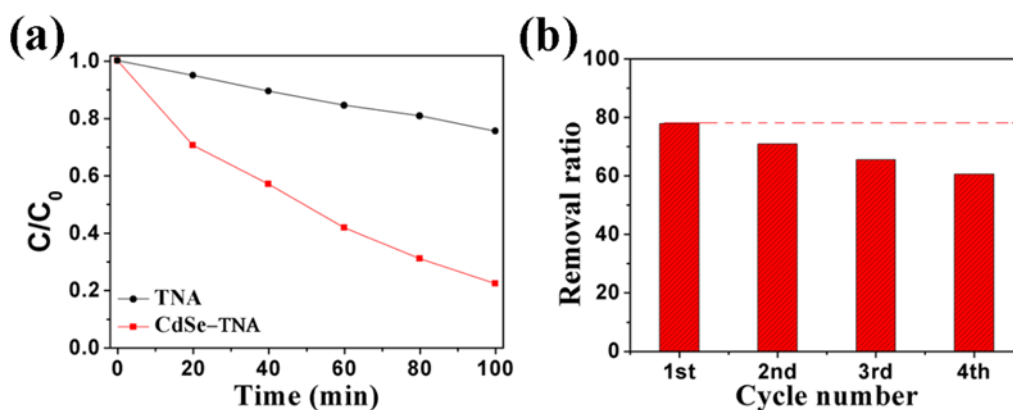


Fig. S12. PEC degradation rate curve (a) and cycling stability experiment (b) of MB using CdSe quantum dots electrodeposited in TNAs as photoelectrocatalyst under visible light. The preparation method was used according to the literature (Yang etc, J. Phys. Chem. C 2010, 114, 4783–4789).

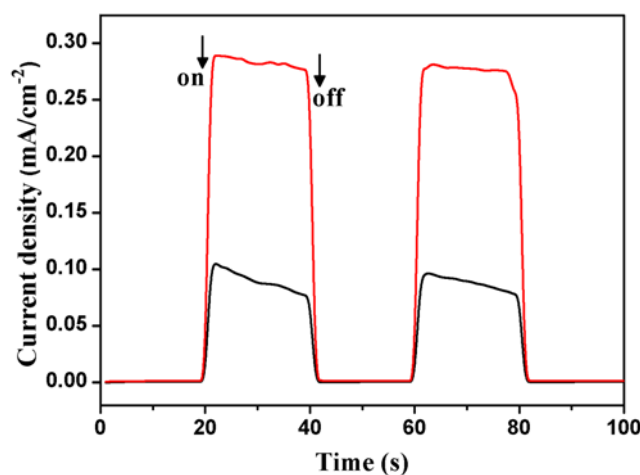


Fig. S13. Photocurrent curves of TNA and GQD-TNA films under simulated solar light irradiation at a light intensity of 1.5 mW cm⁻².

Table 1. Photoelectrocatalytic Degradation Rate Constants of MB Using TNA Photoanodes Sensitized by Different Species Based on $\ln(C_0/C) = kt$ as the Fitting Equation.

Samples	K (min ⁻¹)	R^2
TNA	0.00274	0.99838
GQD-TNA by vacuum assisted filling	0.01564	0.99637
GQD-TNA by electrophoretic assembly	0.02347	0.99698
CdS-TNA	0.00716	0.99832
CdSe-TNA	0.01475	0.99634