Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Graphene Oxide/Carbon Dot Composite: A New Photoelectrode Material for Photocurrent Response Enhancement

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1. Experiment and Characterization

1.1 Materials synthesis

1.1.1 Preparation of the GO: GO was synthesized by a modified Hummer's method.[1] The GO suspension was first dialyzed to remove inorganic acids and metal ions. After gradient centrifugation (6000 rpm for 15 min and then 12000 rpm for 15 min) of the neutral GO suspension, heating the GO suspension at 50-70 ^{o}C for 5 hours in vacuum to remove all the water and finally get GO dry film.

1.1.2 Preparation of the NS-CD: The NS-CD was prepared by thermal polymerization method in the manner of heating organic molecular precursors.[2,3] In a typical procedure of NS-CD preparation, 1.0 g (4.76 mmol) L-cysteine was put into a 10 mL beaker and heated to 280 ^{o}C under mechanical stirring. About 40 minutes later, the raw NS-CD solid sample was collected and purified by column chromatography.

1.1.3 Preparation of GO/NS-CD suspension: 100 mL deionized (DI) water and 1570 mg NS-CD powder were added into one volumetric flask, and then GO solid powder

was added into the volumetric flask. After sonication for 30 min, the NS-CD and GO were well dispersed in water and formed GO/NS-CD suspension.

1.2 Material characterization

All chemicals were purchased from Sigma-Aldrich Co. Ltd., and were used as received without further purification. Indium tin oxide (ITO) glass was purchased from Shenzhen JMT GLASS CO., LTD. UV-vis absorption spectra were recorded with a T6 UV-vis Spectrometer. Photoluminescence (PL) measurements were performed using a LS55 Fluorescence Spectrometer (PE, USA). Atomic Force Microscopy (AFM) measurements were taken using an Agilent 5500 atomic force microscope. Scanning Electron Microscope (SEM) studies were performed using Hitachi S-4800. The Transmission Electron Microscopy (TEM) measurements were performed using a Hitachi S4800 and the samples were prepared by dropping solution onto copper grids and dried in air. Electrochemical impedance spectroscopy (EIS) Nyquist plots of prepared NS-CD, GO, and GO/NS-CD photoelectrodes in 0.2 M Na_2SO_4 aqueous solution with using platinum sheet count electrode and Ag/AgCl reference electrode.

1.3 Photoelectrode construction

To keep good contact of photoactive layer with ITO-coated glass, electrodeposition as a facile and fully scalable approach was applied in this work. The ITO glass was firstly pre-cleaned with detergent-cleaning under sonication for 30 min followed by distilled water washing. Then a home-built electro-deposition system including a glass container (25 mL) and two ITO-coated glass electrode (deposition area: 1.0 cm^2),

which are facing each other to simulate a parallel-plate-like geometry with a separation of 1.0 cm. The electrodeposition process was performed at 20 V constant voltage in NS-CD, GO and GO/NS-CD aqueous solutions, respectively. After electrodeposition process, the deposited ITO glass was washed with ethanol and left to dry at room temperature.

1.4 Performance measurement

1.4.1 Photoelectrochemical (PEC) cell: A PEC cell with three-electrode configuration was constructed in this work. The platinum wire and saturated calomel electrode (SCE) were respectively used as the counter electrode and the reference electrode. The PEC performance of the photoelectrode was measured in 0.05 M Na_2S aqueous electrolyte. A 300W Xe lamp was used as light source. The current response was recorded with a CHI 660B electrochemical workstation.

1.4.2 Solid state device: A single layer ITO/GO/NS-CD/Cu device was prepared for photocurrent response activity measurement. The top electrode (working electrode) was a 0.4×0.5 cm^2 copper foil, which was simply covered onto the active layer of GO/NS-CD by electrode holder fixing. The ITO as bottom electrode was used as both counter electrode and reference electrode. The photocurrent response activities of the prepared GO, NS-CD and GO/NS-CD films as active layers based devices subjected to light on/off cycles were measured.

2. Figures

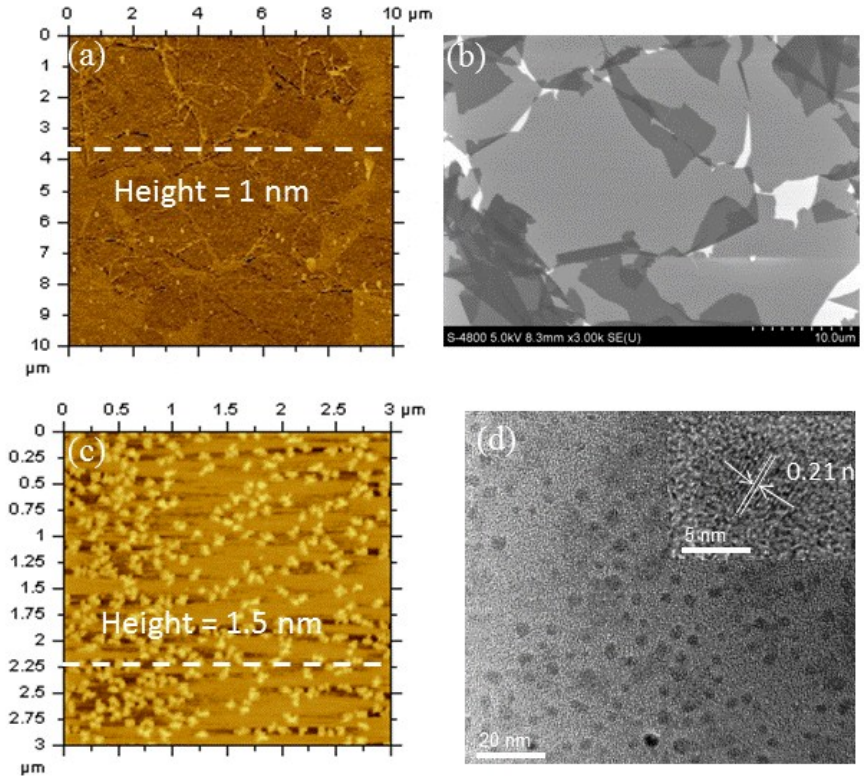

Figure S1. (a) AFM and (b) SEM images of the prepared GO. (c) AFM and (d) TEM images of the prepared NS-CD. Inset is the HRTEM of the NS-CD.

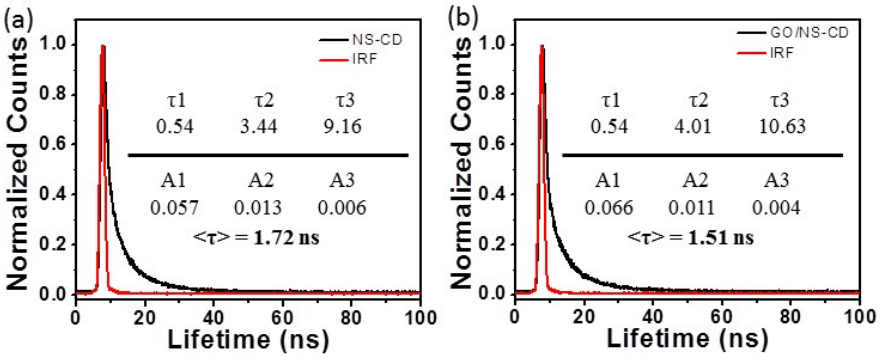

Figure S2. Time-resolved fluorescence spectra of pure NS-CD and GO/NS-CD blend aqueous solution. (Measured at λ_{ex} = 360 nm and λ_{em} = 433 nm)

The averaged lifetimes were estimated by using equation (S1), where τ_i and Ai are time constants and amplitudes, respectively.[4]

$$<\tau> = \frac{\sum_i Ai\tau i}{\sum_i Ai} = \frac{\tau 1 \times A1 + \tau 2 \times A2 + \tau 3 \times A3}{A1 + A2 + A3} \qquad \text{Equation (S1)}$$

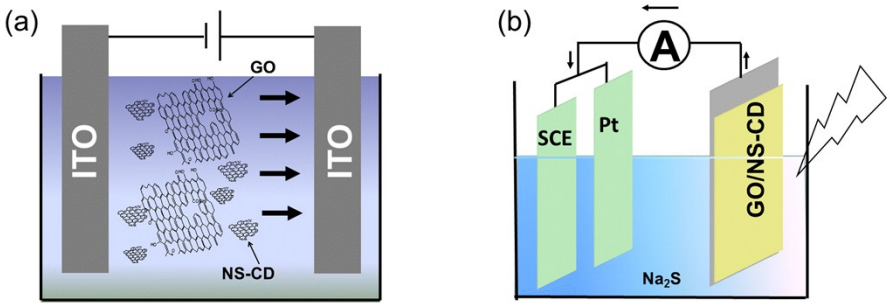

Figure S3. Schematic photocurrent response activity of GO/NS-CD photoelectrode based on electrophoretic deposition method preparation PEC cell measurement. (a) Illustration of the electrodeposition approach for preparing GO/NS-CD composite film on ITO substrate; (b) A PEC cell with three-electrode configuration was constructed in this work.

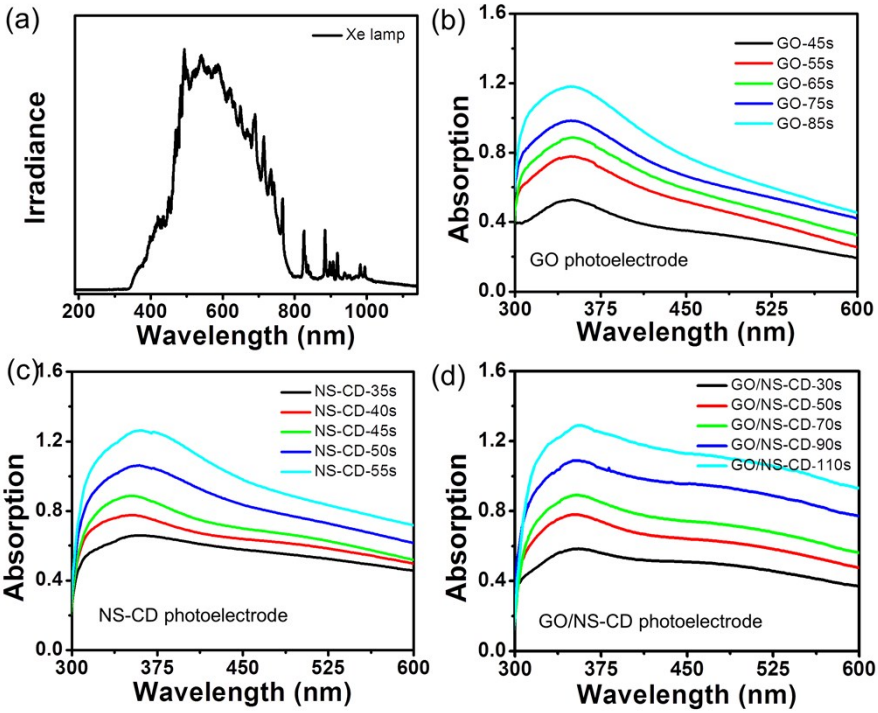

Figure S4. (a) The irradiation spectrum of the excitation light, which provided by a Xe lamp light source. (b-d) the UV-vis absorption spectra of the prepared (b) GO, (c) NS-CD and (d) GO/NS-CD photoelectrodes.

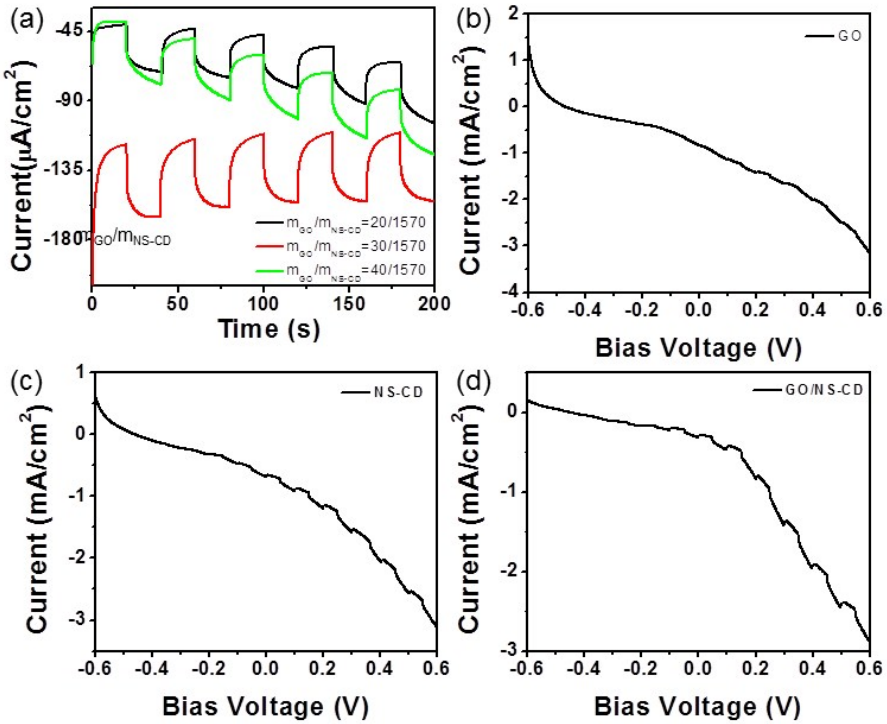

Figure S5. (a) The photocurrent response curves of the GO/NS-CD photoelectrode which prepared by electrodeposition in the GO/NS-CD mixing dispersion with three kinds of GO and NS-CD component content. (b-d) Periodic on/off photocurrent responses of the prepared (b) GO, (c) NS-CD and (d) GO/NS-CD photoelectrodes under -0.6 volt bias to 0.6 volt bias in the PEC cells.

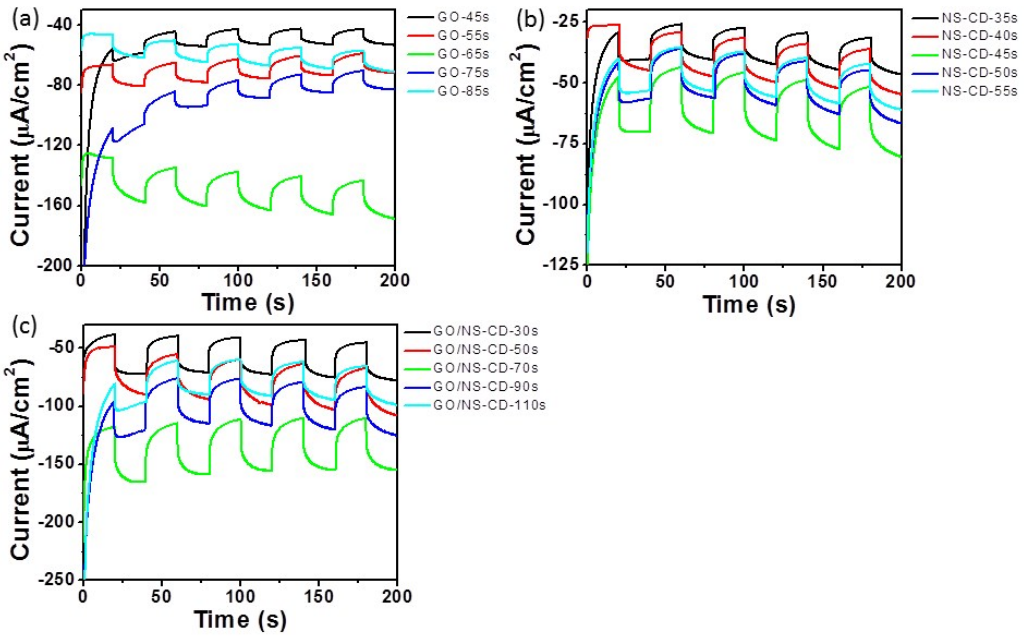

Figure S6. The photocurrent response curves of the prepared (a) GO, (b) NS-CD and (c) GO/NS-CD photoelectrodes in PEC cells.

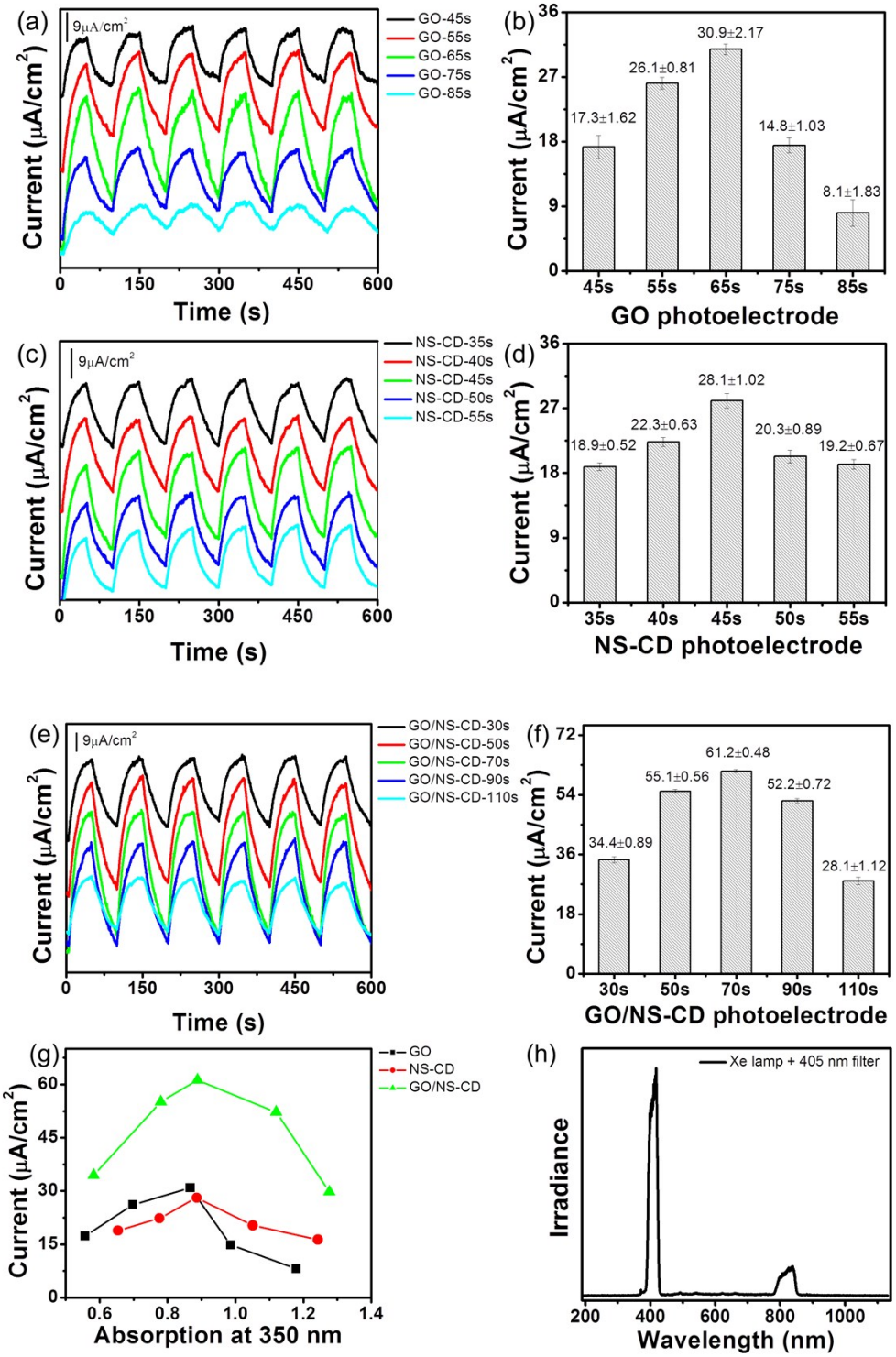

Figure S7. (a-f) The photocurrent response curves and performance statistics of the prepared GO (a-b), NS-CD (c-d) and GO/NS-CD (e-f) photoelectrodes in solid state devices. (g) The photocurrent response performance statistics of the GO, NS-CD and GO/NS-CD photoelectrodes in the solid state devices with corresponding films' optical absorption at 350 nm. (h) The irradiation spectrum of the excitation light, which provided by a 405 nm filter and a Xe light source.

3. References

1. W. S. H. Jr., R. E. Offeman, *J. Am. Chem. Soc.*, **1958**, 80, 1339.
2. H.-X. Wang, J. Xiao, Z. Yang, H. Tang, Z.-T. Zhu, M. Zhao, Y. Liu, C. Zhang, H.-L. Zhang, *J. Mater. Chem. A*, **2015**, 3, 11287.
3. C.-B. Ma, Z.-T. Zhu, H.-X. Wang, X. Huang, X. Zhang, X. Qi, H.-L. Zhang, Y. Zhu, X. Deng, Y. Peng, Y. Han, H. Zhang, *Nanoscale*, **2015**, 7, 10162.
4. B. Xu, Z. Chi, J. Zhang, X. Zhang, H. Li, X. Li, et al., *Chem Asian J.,* **2011**, 6, 1470.