Electronic Supplementary Information

Hydrogen Evolution from Water Using Semiconductor Nanoparticle/Graphene Composite Photocatalysts Without Noble Metals

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Contents:

S6. Photoluminescence (P. L.) spectra of (1) CdS, (2) CdS-mG and (3) mG solution. Excitation wavelength: 355 nm.

S7. The on-off photocurrent under visible light (λ > 400 nm) illumination (I-t) without bias in a two-electrode configuration for the (a) (1) CdS, (2) CdS-mG and (3) CdS-Pt. (b) (1) P25, (2) P25-G and (3) P25-Pt as photoanodes in 0.1 M KNO_3 solution.

S8. References of Supplementary Information.

Supplementary Experimental Section

Materials

Graphite powder (99.95%, 325 mesh) was purchased from Alfa Aesar. TiO_2 (P25, 20% rutile and 80% anatase) was purchased from Degussa. Analytical pure $CdCl_2$, Na_2S and Na_2SO_3 were obtained commercially from the Beijing Chemical Reagent Plant (Beijing, China) and used as received without further purification. Ultrapure water (resistivity ≥ 18 MΩ cm) was used during the experimental process.

Preparation of graphene oxide (GO)

Graphene oxide (GO) was obtained by chemical reduction of exfoliated graphite oxide.[1] Graphite (3.0 g) was put into a mixture of concentrated H_2SO_4 (12 mL), $K_2S_2O_8$ (2.5 g) and P_2O_5 (2.5 g). The solution was heated to 80 °C and kept stirring for 5 h in an oil bath. Then the mixture was diluted with 500 mL of deionized water, and the product was obtained by filtering using 0.2 μm Nylon film and dried under ambient condition. Thereafter, the product was reoxidized to produce the graphite oxide. After the exfoliation by sonicating 0.1 mg/mL of graphite oxide dispersion for 1 h, the graphene oxide was recovered by filtration and vacuum drying.

Sulfonation of graphene

The sulfonation of graphene was carried out using the aryl diazonium salt of sulfanilic acid in an ice bath.[2] Briefly, A sodium borohydride solution (1 M, 1000 mL) was added into the dispersion of graphene oxide (0.1 g) after its pH was adjusted to 9-10 with 5 wt% sodium carbonate solution. The mixture was then kept at 80 °C for 1 h under constant stirring. After centrifuging and rinsing with water several times, the partially reduced graphene oxide can be redispersed in 1000 mL water via mild sonication. The aryl diazonium salt used for sulfonation was prepared from the reaction of 23 mg sulfanilic acid and 9 mg sodium nitrite in 1000 mL water and 0.3 g 1N HCl solution in an ice bath. The diazonium salt solution was added to the dispersion of partially reduced graphene oxide in an ice bath under stirring, and was kept in ice bath for 2 h. After centrifuging and rinsing with water several times, sulfonated graphene oxide is re-dispersed in 1000 mL water. In the post-reduction step, 1.0 g hydrazine in 5.0 g water is added into the dispersion and the reaction mixture was kept at 100 °C for 24 h under constant stirring. A few drops of 5 wt% sodium carbonate solution were then added into the mixture in order to precipitate the lightly sulfonated graphene. After rinsing with water thoroughly, the graphene prepared can be readily dispersed in water via a few minutes sonication.

Photocurrent response

Photocurrent response spectra were measured in a two-electrode configuration, where the CdS-mG or P25-G photoanodes served as the working electrode with an active area about 1 cm2 and a platinum wire was used as the counter electrode. The generated photocurrent signals were collected by using a lock-in amplifier (Stanford instrument SR830 DSP) synchronized with a light chopper (Stanford instrument SR540). A 500-W Xe lamp with a monochromator and a cutoff filter was used as the light source. The electrolyte was 0.1 M KNO_3 aqueous solution.

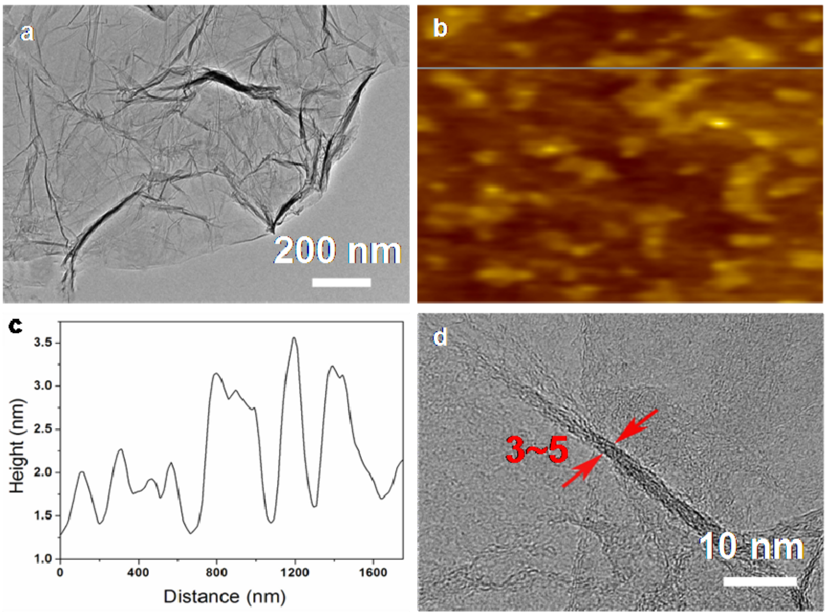

Figure S1. (a) Transmission electron microscopy (TEM) image of graphene oxide. (b) Atomic force microscopy (AFM) image of graphene oxide. (c) Height and (d) High resolution transmission electron microscopy (HRTEM) of graphene oxide.

Figure S1a shows the typical TEM image of graphene oxide. The prepared graphene oxide showed the two dimensional sheet structures with some wrinkles of micrometers long. AFM characterization (Figure S1b and c) showed that the thickness of graphene oxide was ca. 1.0–2.2 nm. HRTEM revealed that the graphene oxide is about 3-5 sheets thick (Figure S1d).

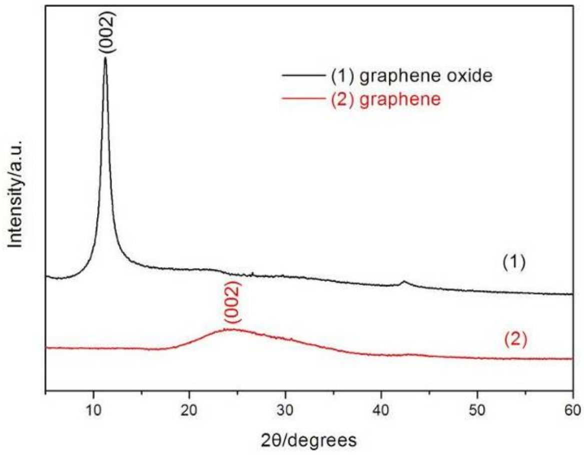

Figure S2. X-ray diffraction (XRD) patterns of GO and graphene.

The XRD patterns of GO and graphene are displayed in Figure S2. GO exhibits a peak centered at 2θ = 10.4°, corresponding to the (002) interplanar spacing of ca. 9 Å. Graphene sheets were obtained by hydrothermal reduction of GO and their structure was verified by the characteristic peak at about 24.7°.[3]

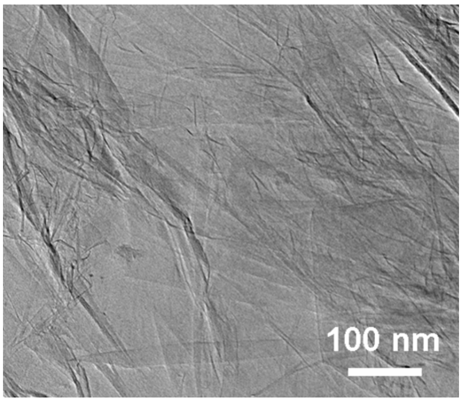

Figure S3. TEM image of a partially folded water-soluble graphene sheet.

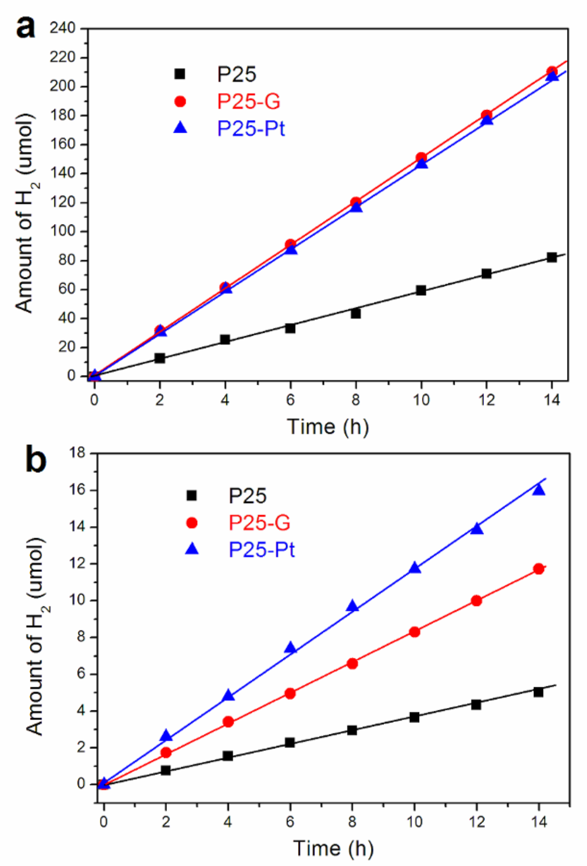

Figure S4. Hydrogen production based on P25 and its composite photocatalysts in 20 mL Na_2S (0.05M) and Na_2SO_3 (0.07 M) aqueous solution upon irradiation with **(a)** UV-vis and **(b)** visible light irradiation ($\lambda > 380$ nm).

In 20 mL Na_2S (0.05M) and Na_2SO_3 (0.07 M) aqueous solution, the graphene co-catalyst also enhances hydrogen evolution from P25-G composite photocatalysts under UV-vis irradiation. The amount of H_2 generation is as much as that of P25-Pt, about twice that of P25 alone under UV-vis irradiation (Figure S4a). Under irradiation with visible light (Figure S4b), the fastest rate of hydrogen evolution was obtained from P25-Pt, which is attributed to the broader absorption of P25-Pt in visible range compared with P25-G.

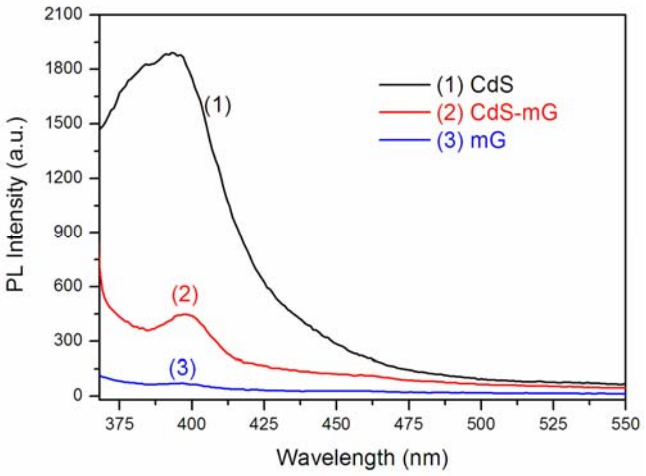

Figure S5. Photoluminescence (P. L.) spectra of (1) CdS, (2) CdS-mG and (3) mG solution. Excitation wavelength: 355 nm.

Photoluminescence (P. L.) spectra demonstrate that significant fluorescence quenching of CdS in CdS-mG as shown in Figure S5, which indicates that efficient electron transfer from QDs to modified graphene. The results are consistent with our previous published paper that PB-graphene had fluorescence quenching of CdS QDs.[4] Importantly, modified graphene didn't show obvious photoluminescence at 355 nm excitation wavelength light (line 3, blue, Figure S5).

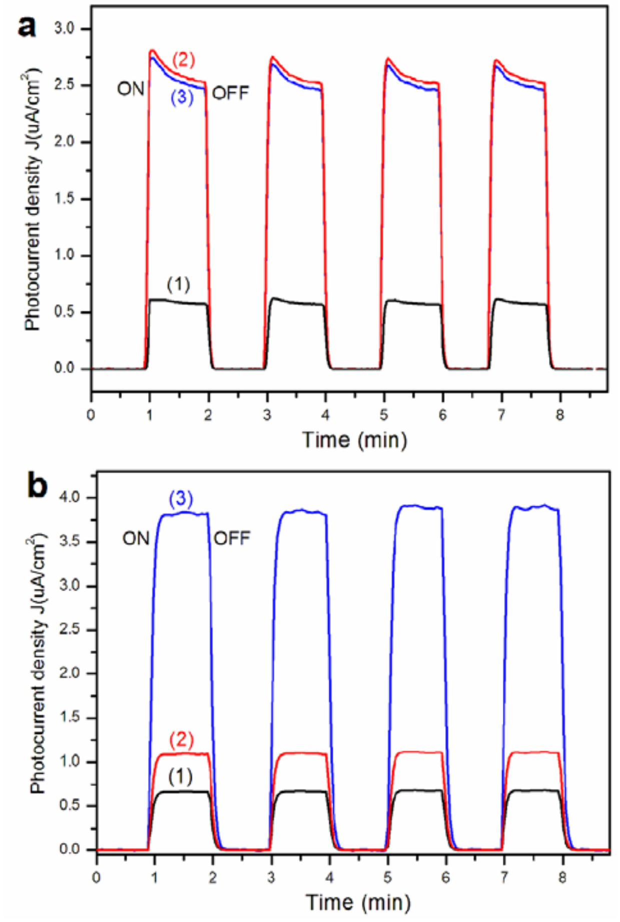

Figure S6. The on-off photocurrent under visible light ($\lambda > 400$ nm) illumination (I-t) without bias in a two-electrode configuration for the (a) (1) CdS, (2) CdS-mG and (3) CdS-Pt. (b) (1) P25, (2) P25-G and (3) P25-Pt as photoanodes in 0.1 M KNO_3 solution.

Photocurrents generated responses of CdS, CdS-mG and CdS-Pt on fluorine-doped SnO_2 glass substrate (FTO) electrode were measured without bias upon the on/off illumination with visible light irradiation. As demonstrated in Figure S5a, the transient photocurrent responses show CdS-mG and CdS-Pt electrodes have the significant photocurrents compared with that of CdS with visible light irradiation, which are in good agreement with the investigated results of their photocatalytic hydrogen evolution in the systems mentioned above. Figure S5b demonstrates the photocurrent generated responses of P25 and its composite photocatalyst electrodes follow the order P25-Pt > P25-G > P25 with visible light irradiation. The results indicate that graphene served as an acceptor of the generated electrons of CdS or P25 and effectively suppressed the charge recombination. On the other hand, graphene has unexpectedly excellent conductivity due to its two-dimensional planar structure, which remained the steady for the photoexcited current.

References

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