Electronic Supplementary Information

Light irradiation-assisted synthesis of ZnO-CdS/reduced graphene oxide heterostructured sheets for efficient photocatalytic H_2 evolution

Preparation of ZnO-CdS/Reduced Graphene Oxide (RGO) Sheets Graphene oxide used was prepared by a modified Hummer method.[1] The suspension of graphene oxide was added in a 100 mL aqueous solution containing 0.02 mol zinc acetate at room temperature. The mixed solution was irradiated by UV-visible light from a 300 W Xe lamp under stirring for 1 h. Then 50 mL aqueous solution containing 0.04 mol NaOH was dropwise added in the solution under the light irradiation for 30 min. After this step, 0.004 mol cadmium acetate was added in the solution under stirring and light irradiation for another 30 min. Finally, 50 mL aqueous solution containing 0.004 mol Na_2S was added dropwise under stirring for 1 h. The product collected from the reaction solution was washed with distilled water for several times and dried at 100 ^oC for 24 h.

Loading of Pt Cocatalyst The loading of Pt nanoparticles on ZnO-CdS/reduced graphene oxide sheets was conducted by a photodeposition method.

Characterization X-ray diffraction patterns were recorded on Rigaku diffractometer using Cu K_α irradiation. Scanning electron microscopy images and Energy Dispersive X-ray spectroscopy profiles were obtained on a Nova Nano SEM 430. Transmission electron microscope images and were obtained by a Tecnai F30. UV-visible absorption spectra were measured with a UV-visible spectrophotometer (JACSO-V550).

Computational Details Our first-principles calculations were performed within the framework of density functional theory as implemented in the Vienna ab initio simulation package code,[2] using the generalized approximation of Perdew-Burke-Ernzerhof.[3] The electron-ion interaction was described using the frozen-core projector augmented wave approach. [4, 5] We used a 400 eV cut-off energy for the plane-wave basis set expansion. The k-space sampling was restricted to the Γ-point due to large

supercell adopted in our calculations. A 7×4 supercell consisting of 6 Zn-O atomic layers (168 Zn atoms and 168 O atoms) with a large vacuum distance of 18 Å was constructed to model the ZnO with (110) surface exposed, the bottom 2 layers was fixed during the geometry relaxation. In order to avoid the issue of lattice mismatch between graphene (or RGO) with crystal ZnO, a large polyaromatic hydrocarbon (PAH) molecule consisting of 54 C atoms and 18 H atoms was used to represent the graphene. The RGO with hydroxyl group and epoxide group was modeled by adding a OH group and an O atom on the PAH surface, respectively, since the residual oxygen-containing functional groups on GRO are mainly hydroxyl and epoxide based on numerous experiments[6, 7] and theory calculations.[8]

Photocatalytic Hydrogen Generation Measurement Photocatalytic hydrogen generation reactions were carried out in a gas-closed circulation with vacuum. Typically, photocatalyst powder (100 mg) was dispersed in 300 mL of aqueous solution containing 0.1 M Na_2S and 0.1 M Na_2SO_3. The light source was a 300 W Xe lamp (PLX-300UV). The amount of hydrogen generation was determined using a gas chromatograph.

References

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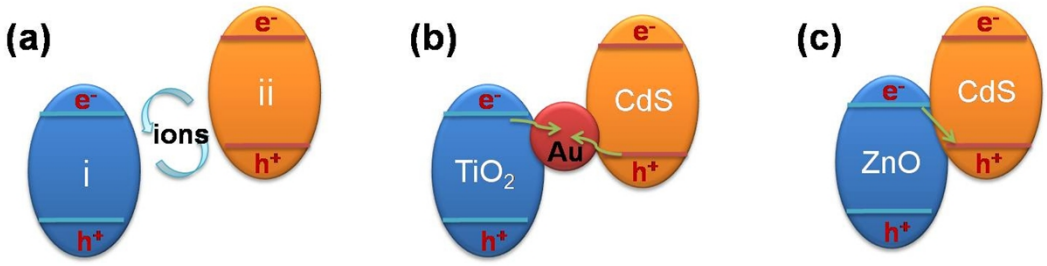

Fig. S1 Schematic of three kinds of typical heterostructures working on Z-scheme mechanism with different electron mediators: (a) shuttle redox pairs (i.e., Fe^{3+}/Fe^{2+}, IO_3^-/I^-), (b) Au and (c) no mediator.

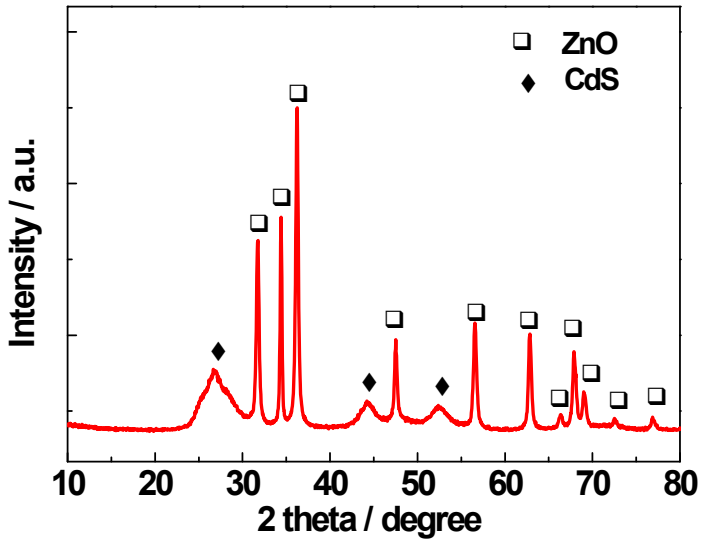

Fig. S2 XRD pattern of ZnO-CdS/2 wt% RGO.

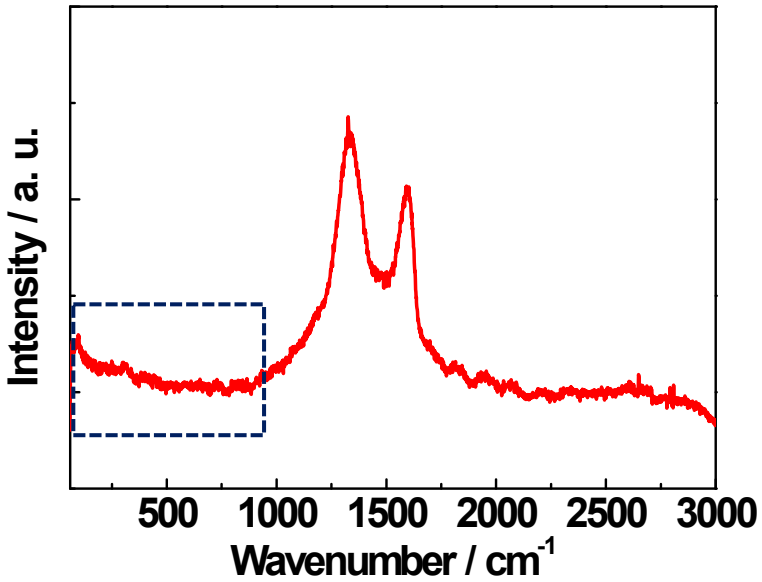

Fig. S3 Raman spectrum of ZnO-CdS/2 wt% RGO.

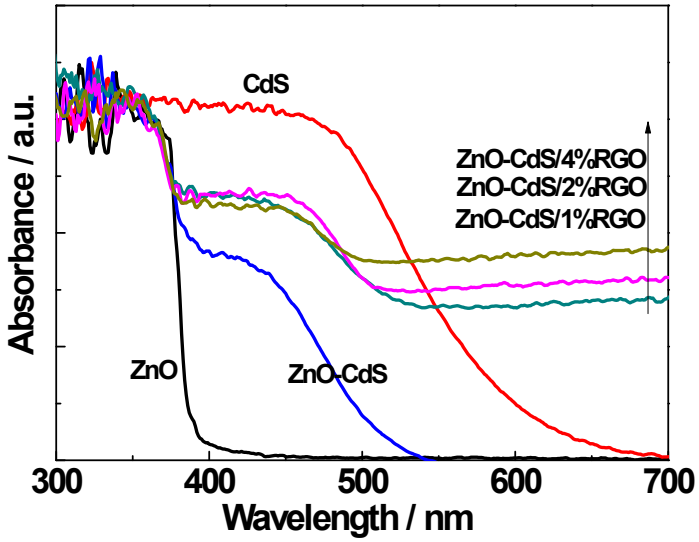

Fig. S4 UV-visible absorption spectra of ZnO, ZnO-CdS, CdS and ZnO-CdS/RGO with different contents (1 wt%, 2 wt%, 4 wt%) of RGO.

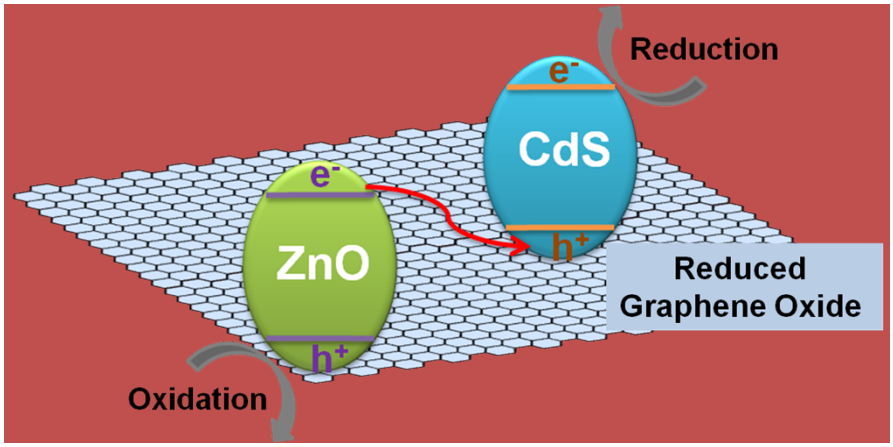

Fig. S5 Schematic illustration of a Z-scheme transport process of charge carriers in the heterostructured sheet of ZnO-CdS/RGO.