

Electronic Supplementary Information

Vertically aligned ZnO-Au@CdS core-shell nanorod arrays as an all-solid-state vectorial Z-scheme system for photocatalytic application

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Fig. S15 TEM images of (A) fresh and (B) used ZnO-Au@CdS-2.

References

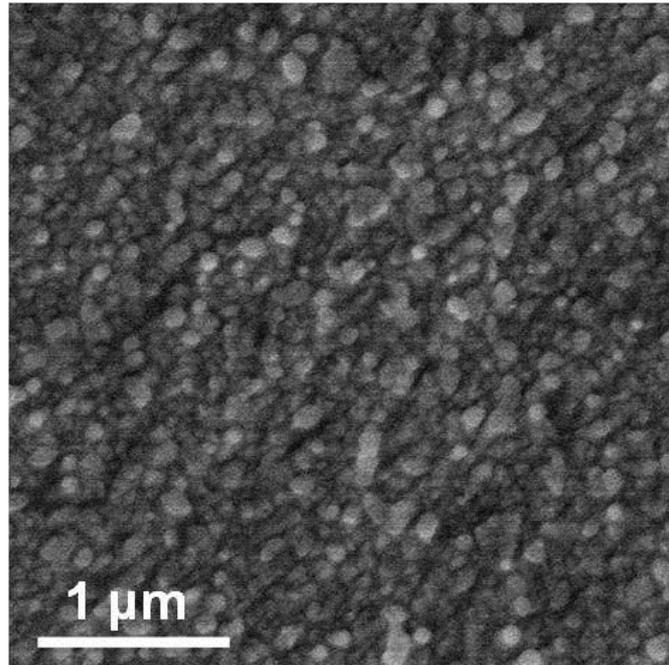


Fig. S1 FESEM image of ZnO seeds on FTO substrate.

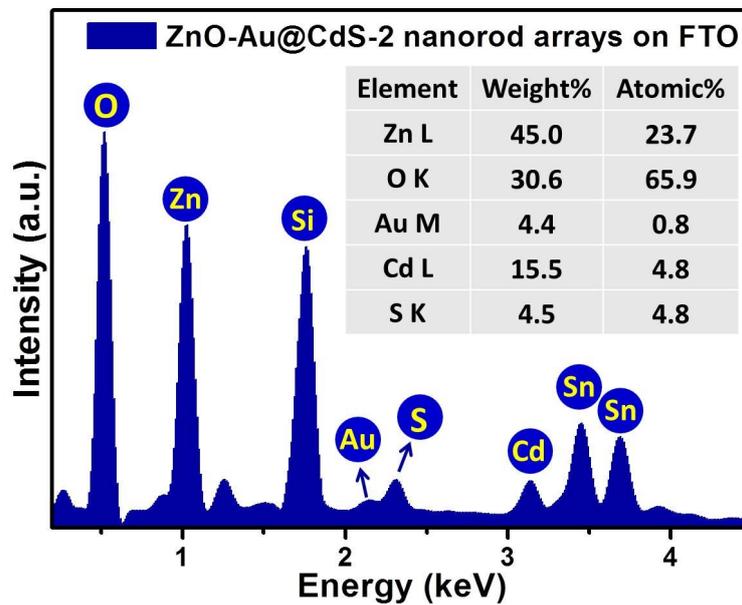


Fig. S2 EDX spectrum for ZnO-Au@CdS-2 composite (the inset is the quantification results according to the EDX result).

Note: Fig. S2 shows the energy-dispersive X-ray (EDX) spectrum of ZnO-Au@CdS-2 nanorod arrays on FTO substrate. The results demonstrate that the ZnO-Au@CdS-2 composite contains O, Zn, Au, Cd and S elements. The signals of Si and Sn and the relatively high intensity of O signal can be ascribed to the presence of FTO substrate.

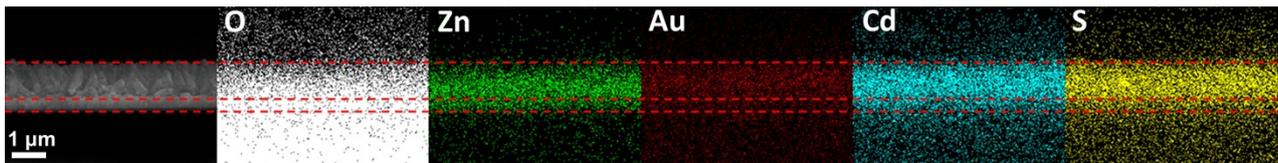


Fig. S3 Cross-sectional FESEM image and the corresponding elemental mapping results of ZnO-Au@CdS-2 nanorod arrays on FTO substrate.

Note: As revealed by the cross-sectional elemental mapping results in **Fig. S3**, the elements of O, Zn, Au, Cd and S are evenly distributed in the arrays formed on the surface of FTO substrate and well consistent with the cross-section view FESEM image of ZnO-Au@CdS-2 nanorod arrays, as indicated by the dash lines.

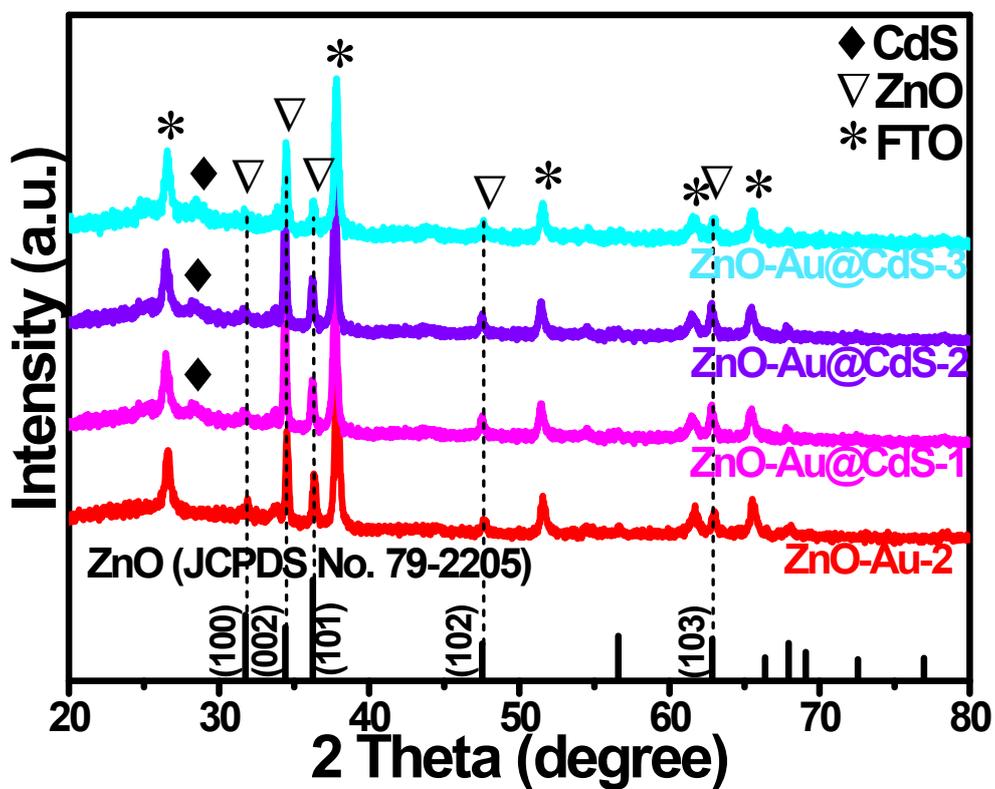


Fig. S4 XRD patterns of the ZnO-Au-2 and ZnO-Au@CdS composites with different contents of Au nanoparticles.

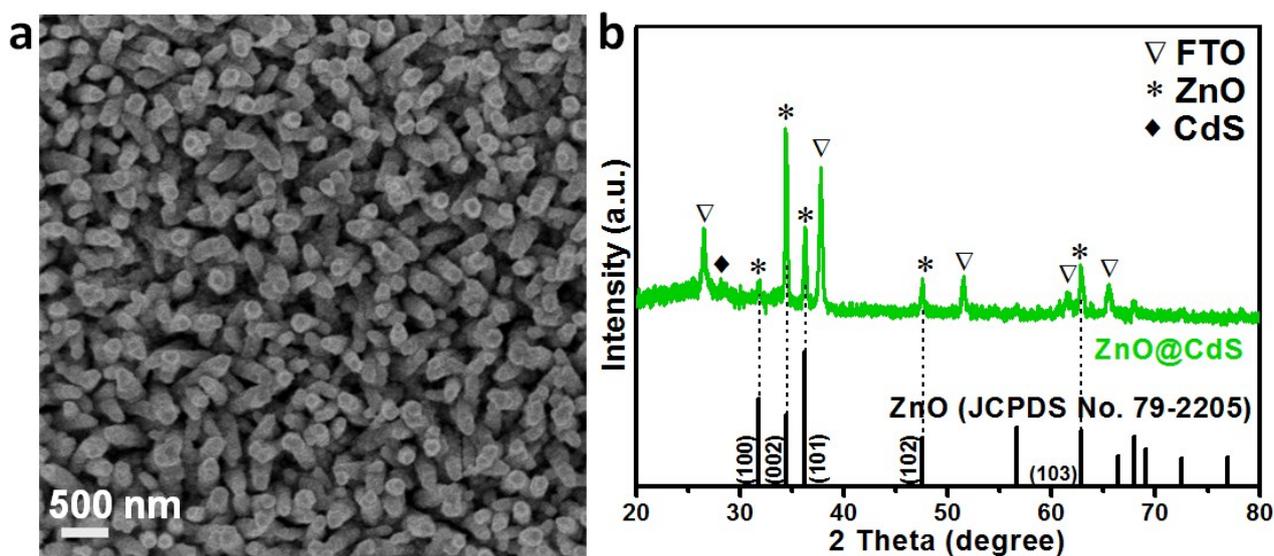


Fig. S5 (a) FESEM image and (b) XRD pattern of ZnO@CdS composite.

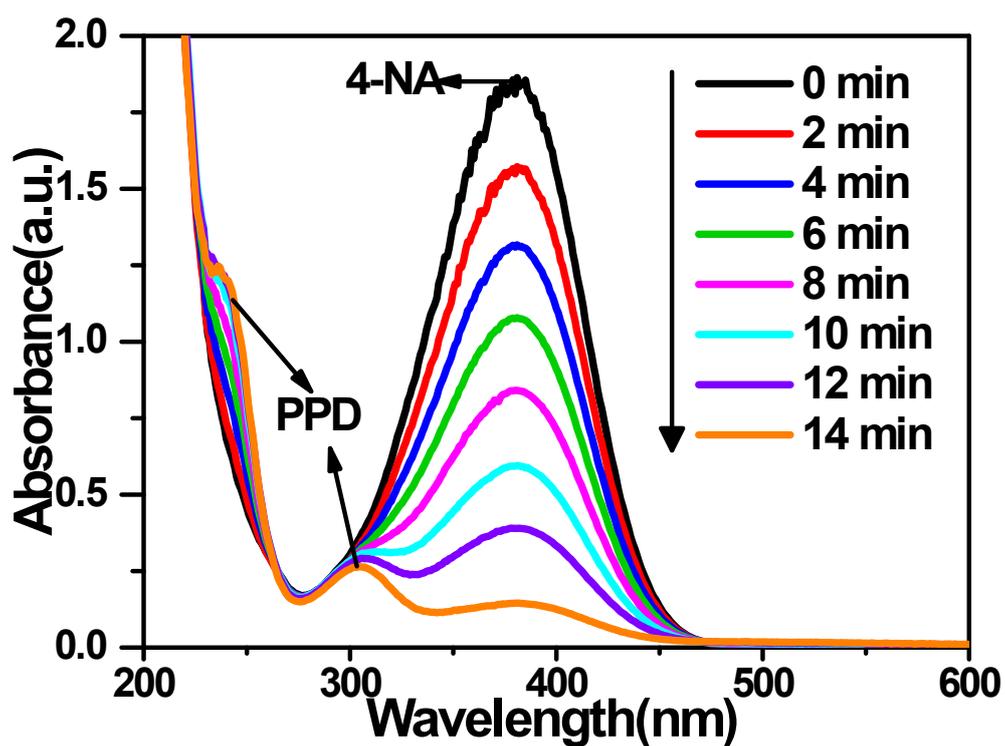
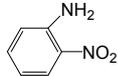
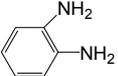
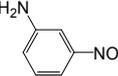
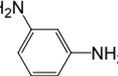
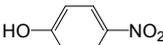
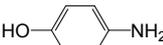
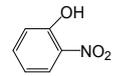
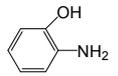
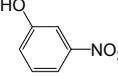
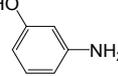
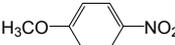
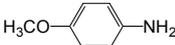


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Table S1. Photocatalytic performance of ZnO-Au@CdS-2 composite for selective reduction of substituted aromatic nitro compounds in water under simulated sunlight irradiation with the addition of ammonium formate as holes scavenger and N₂ purge.

Entry	Substrate	Product	Time/min	Conversion/% ^a	Selectivity/%
1			14	97	92
2			14	92	93
3			14	64	96
4			14	52	95
5			14	63	95
6			14	87	97

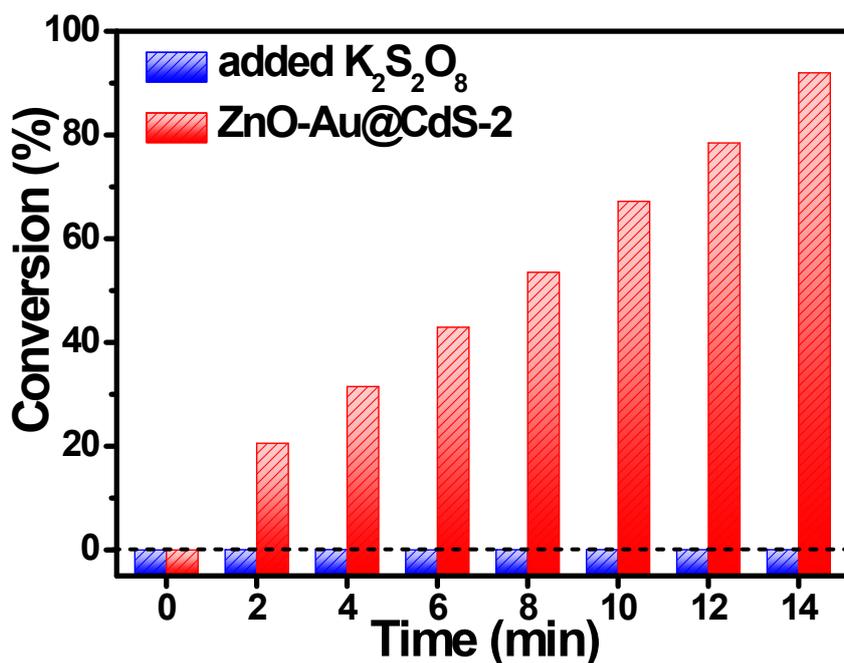


Fig. S7 Controlled experiments for 4-NA reduction over ZnO-Au@CdS-2 nanorod arrays composite using K₂S₂O₈ as scavenger for photogenerated electrons under simulated solar light irradiation with the addition of ammonium formate as holes scavenger and N₂ purge in water.

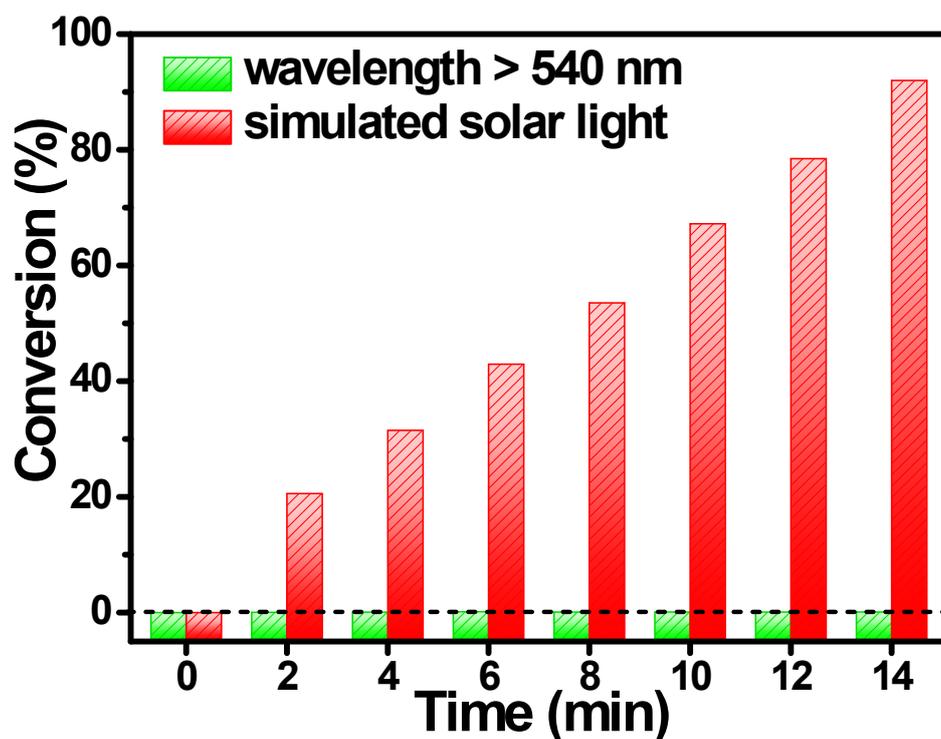


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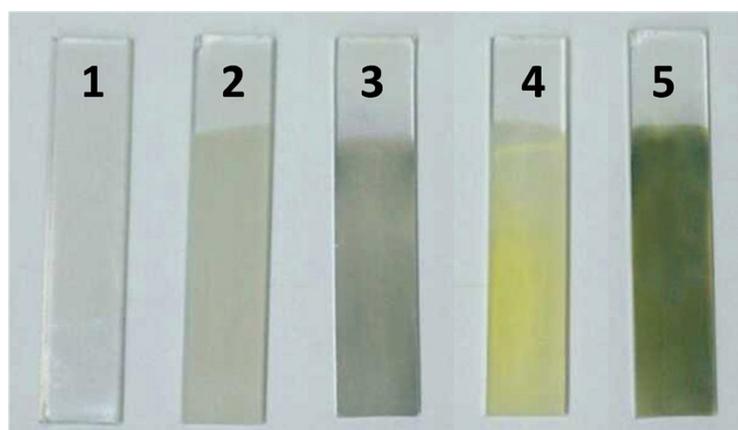


Fig. S9 Photographs of (1) bare FTO substrate, (2) ZnO nanorod arrays, (3) ZnO-Au-2 nanorod arrays, (4) ZnO@CdS nanorod arrays, and (5) ZnO-Au@CdS-2 nanorod arrays on FTO.

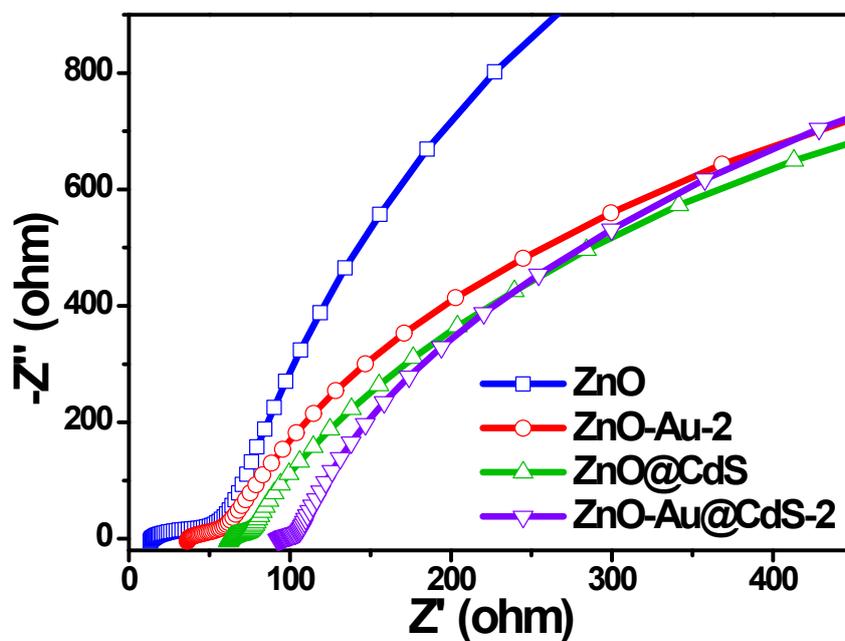


Fig. S10 Electrochemical impedance spectroscopy (EIS) Nyquist plots of ZnO, ZnO-Au-2, ZnO@CdS and ZnO-Au@CdS-2 nanorod arrays electrodes in the electrolyte of Na_2SO_4 (0.2 M).

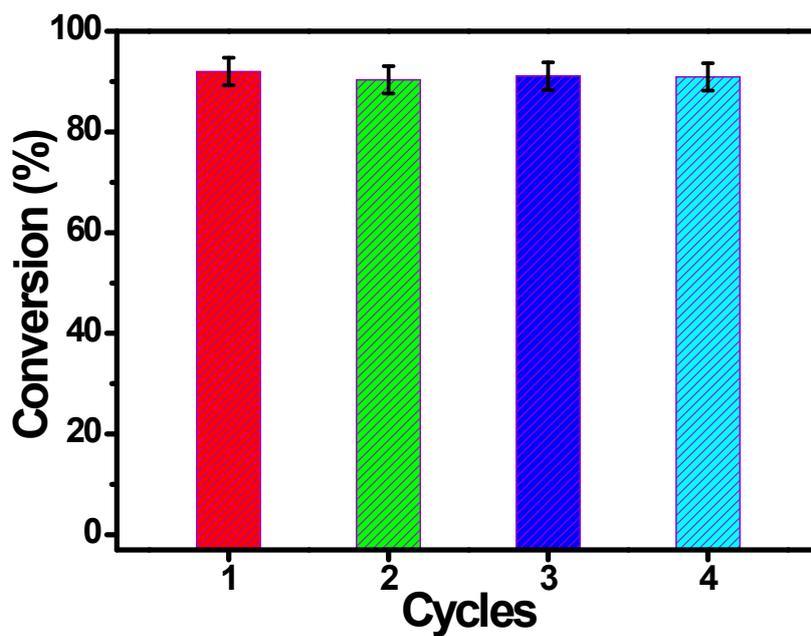


Fig. S11 Recycling photocatalytic reduction of 4-NA over ZnO-Au@CdS-2 nanorod arrays composite under simulated solar light irradiation with the addition of ammonium formate as holes scavenger and N_2 purge in water; the irradiation time for each run is 14 min.

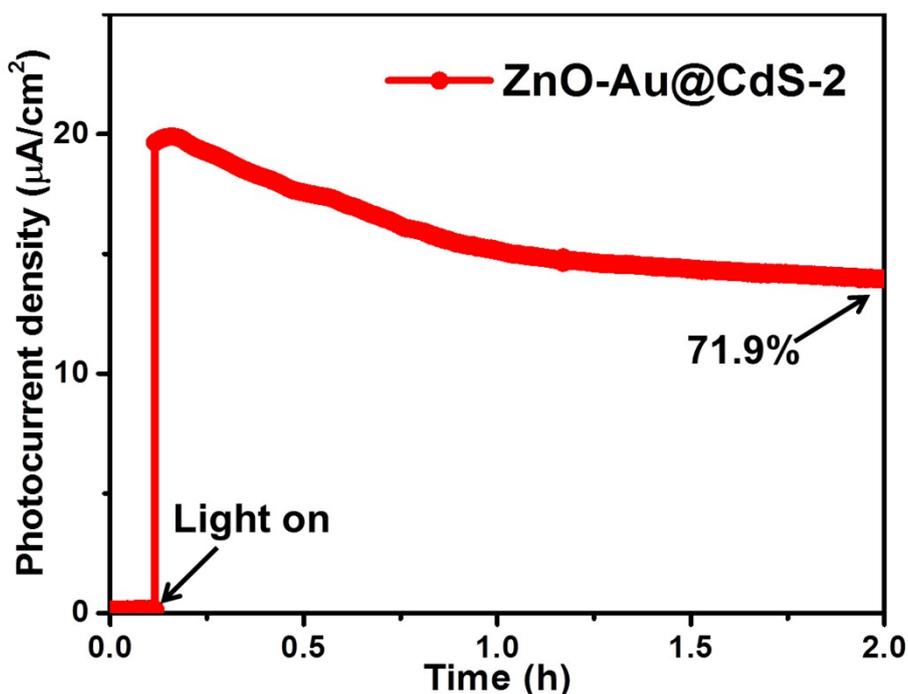


Fig. S12 Chronoamperometry result of ZnO-Au@CdS-2 on the FTO glass without bias in the electrolyte of 0.2 M Na_2SO_4 with the addition of ammonium formate as holes scavenger under simulated sunlight irradiation.

Note: It can be seen from the chronoamperometry result in **Fig. S12** that with the simulated sunlight irradiation for nearly 2 h, the ZnO-Au@CdS-2 electrode is able to keep about 71.9% photocurrent density of the initial value, indicating its relatively good stability.^{S1, S2}

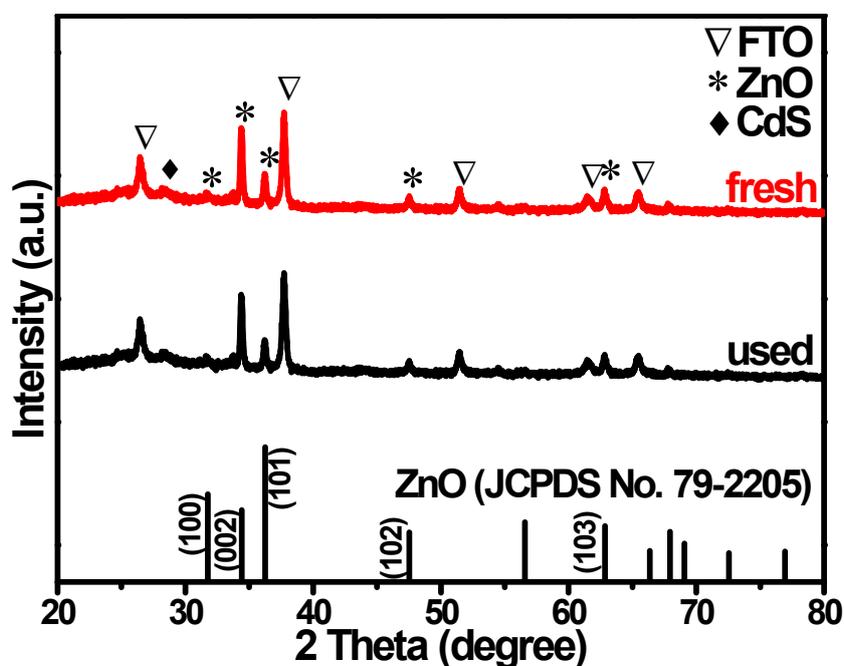


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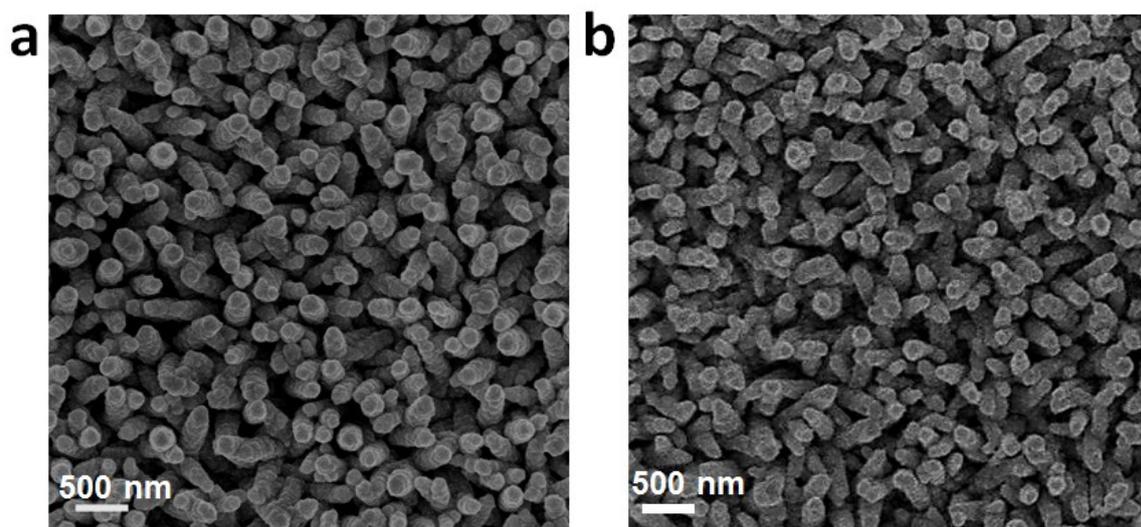


Fig. S14 SEM images of (A) fresh and (B) used ZnO-Au@CdS-2.

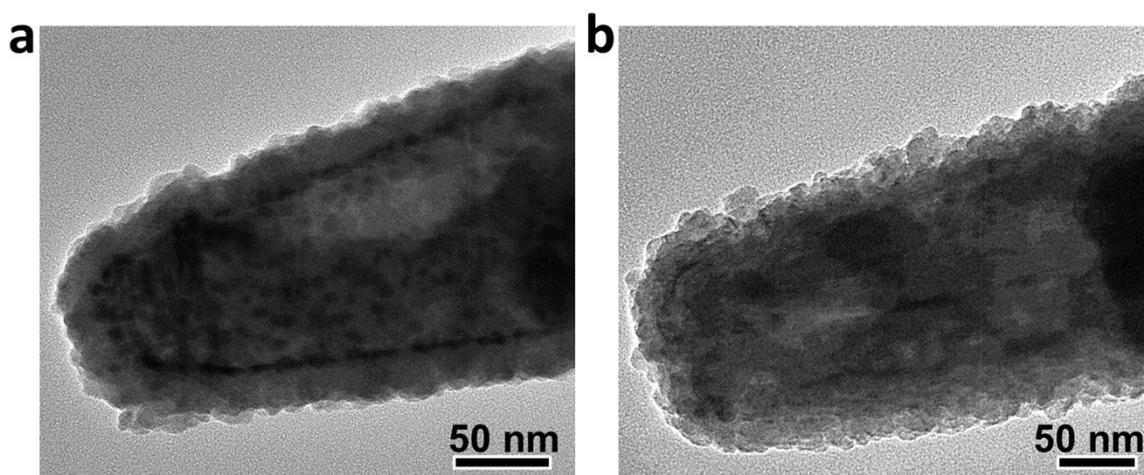


Fig. S15 TEM images of (A) fresh and (B) used ZnO-Au@CdS-2.

References

- S1. A. U. Pawar, C. W. Kim, M. J. Kang and Y. S. Kang, *Nano Energy*, 2016, **20**, 156-167.
- S2. J. Y. Zheng, S. I. Son, T. K. Van and Y. S. Kang, *RSC Adv.*, 2015, **5**, 36307-36314.