Electronic supplementary information

Chemical Vapor Deposition of PbSe/CdS/Nitrogen doped TiO2 nanorod arrays photoelectrode and its band edge levels structure

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1 Infrared (IR) absorbance spectroscopy of electrodes

We have assembled PbSe and CdS nanoparticles co-sensitized Nitrogen doped TiO_2 nanorod arrays (PbSe/CdS/NT) photoelectrode by CVD. The PbSe NPs ensitized the CdS/NT electrode into IR region and made it to be a panchromatic harvesting photoelectrode. The IR absorbance spectroscropy of NT, CdS/T, PbSe/CdS/NT electrode was shown in Fig. S1 indicating the enhancement of absorbance in IR region. The absorption cutoff of PbSe NPs spans from about 1500 to 2500 nm, which is complementary to the light absorption of most sensitizers in solar energy spectrum.

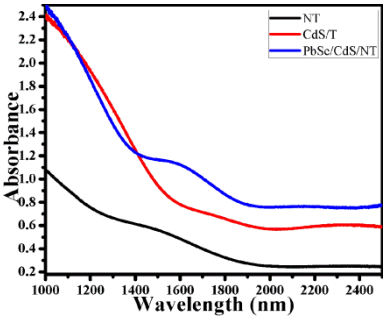

Fig. S1 Room temperature IR absorbance spectrum of 3 electrodes

2 Photocurrent decay measurements of PbSe/CdS/NT photoelectrode

The serious obstacle that hinders the practical application of PbSe/CdS/NT photoelectrode is the poor photocurrent stability during H_2 generation. Fig. S2 shows the time course for the photocurrent of PbSe/CdS/NT electrode at a fixed applied potential of -0.5 V vs. Ag/AgCl under continuous visible light irradiation. A nearly linear decrease is observed in the photocurrent which can be attributed to oxidative deactivation of PbSe surface by photogenerated holes. Noticeably, after visible light irradiation for 3h, about 76% of the initial stable state photocurrent is maintained for PbSe/CdS/NT photoelectrode. Actually, slow kinetics for water oxidation usually results in holes accumulation at the surface, and subsequent surface oxide of sensitizer occurs.[1] Dark for a time interval of several seconds and illuminating the photoelectrode again cannot recover the initial photocurrent, suggesting that the photocurrent decay is derived from the irreversible deleterious reactions to PbSe NPs during the PEC measurement.

After Photocurrent decay measurements, the chemical states of PbSe/CdS/NT photoelectrode were checked by XPS to investigate the oxidation of PbSe NPs (Fig. S3). Along with the typical Pb 4f (137.2 eV and 142.1 eV) and Se 3d (53.3 eV) peaks of PbSe, the peaks of Pb 4f with E_B = 138.5 and 143.5 eV could be assigned to PbO and the peak of Se 3d with E_B = 58.5 eV could be assigned to SeO_2. [2] This is the reason of the decay and irreversibility of photocurrent of PbSe/CdS/NT photoelectrode. During the course of stability measurement, bubbles were observed on the surface of counter electrode continuously, indicating the formation of H_2 upon light irradiation.

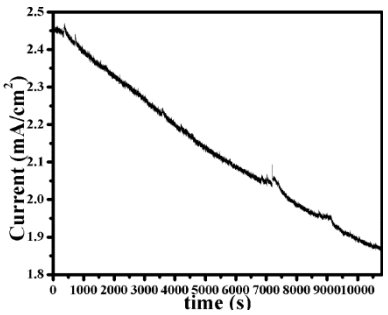

Fig. S2 Time course of photocurrent of PbSe/CdS/NT photoelectrode at -0.5 V (vs.Ag/AgCl) under simulated sun light illumination for 3 hours

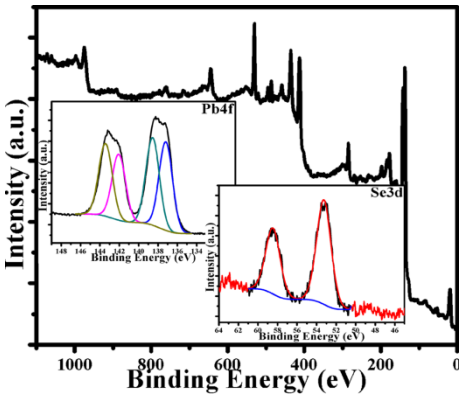

Fig. S3 XPS spectrum of PbSe NPs after illumination shows the photo corrosion of the electrode

References

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2. (a) R. Würz, M. Rusu, Th. Schedel-Niedrig, M. Ch. Lux-Steiner, H. Bluhm, M. Hävecker, E. Kleimenov, A. Knop-Gericke, R. Schlögl, *Surface Science*, 2005, 580, 80; (b) C. Park, M. Won, Y. Oh, Y. Son, *Applied Surface Science*, 2005, 252, 1988.