

Electronic Supplementary Information

Promoted photoelectrocatalytic hydrogen evolution of a type II structure via Al₂O₃ recombination barrier layer deposited by atomic layer deposition

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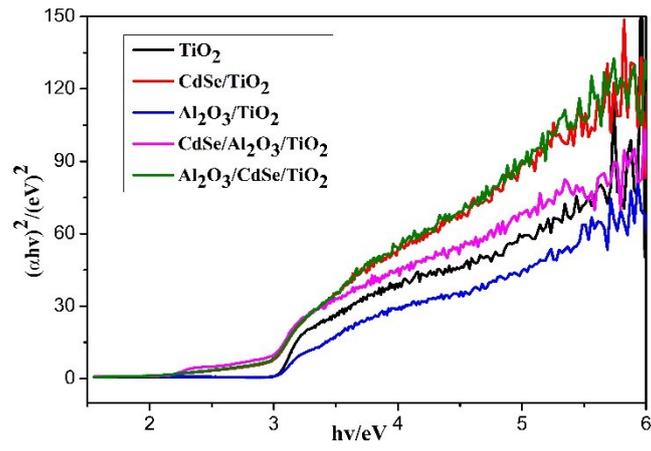


Fig. S1 a plot of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) of TiO_2 nanowire arrays and different configurations based on TiO_2 nanowire arrays

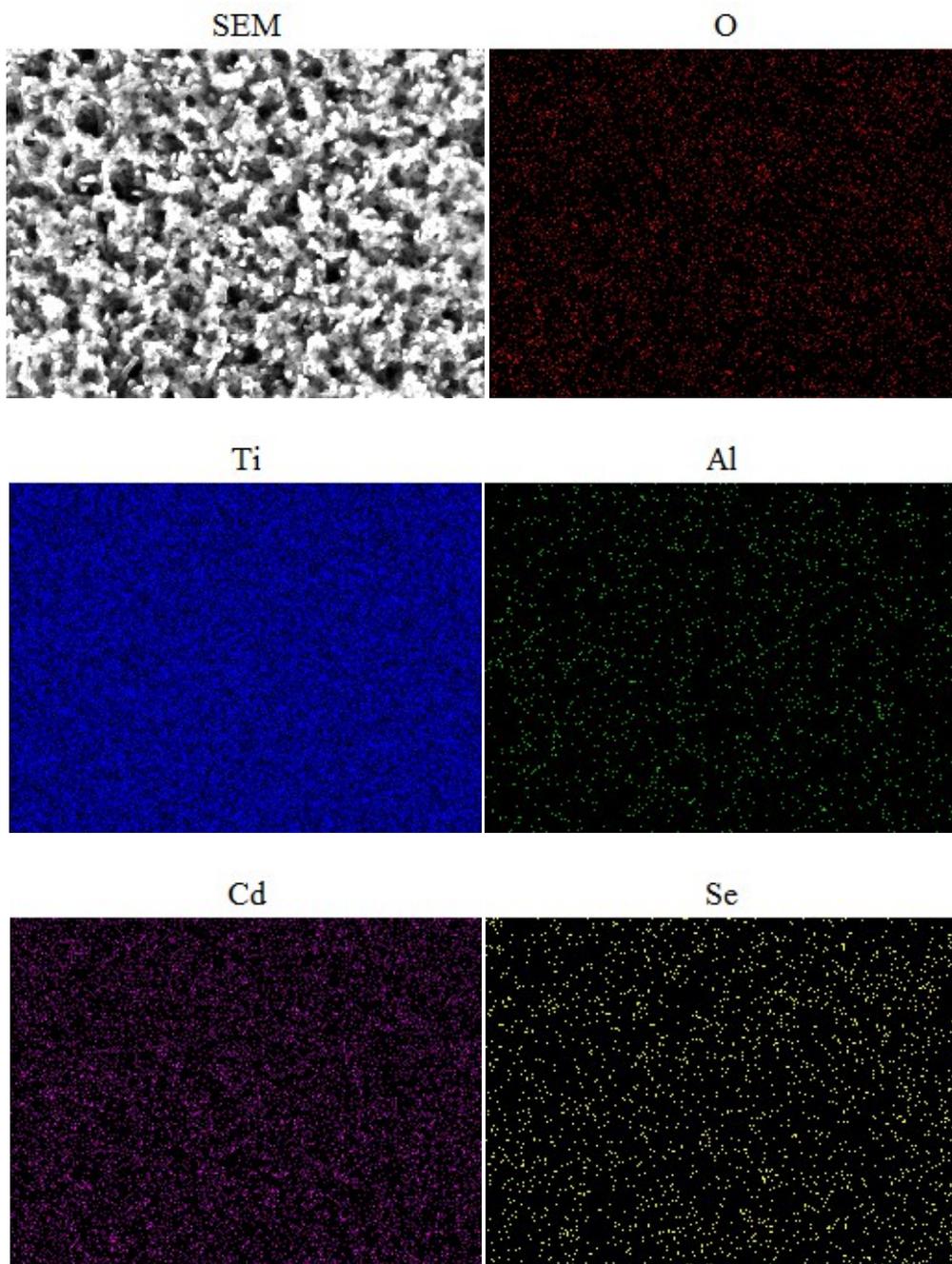


Fig. S2 SEM image and elemental mapping images of CdSe/Al₂O₃/TiO₂ nanowires

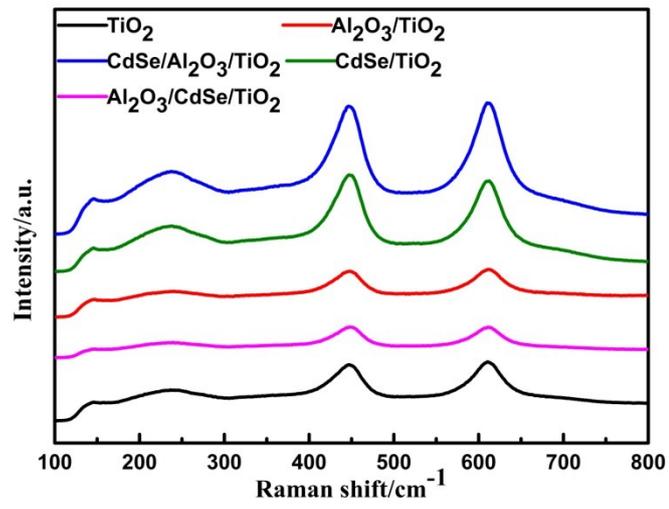


Fig. S3 Raman spectra of TiO_2 , $\text{Al}_2\text{O}_3/\text{TiO}_2$, CdSe/TiO_2 , $\text{CdSe}/\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{Al}_2\text{O}_3/\text{CdSe}/\text{TiO}_2$ nanowire arrays

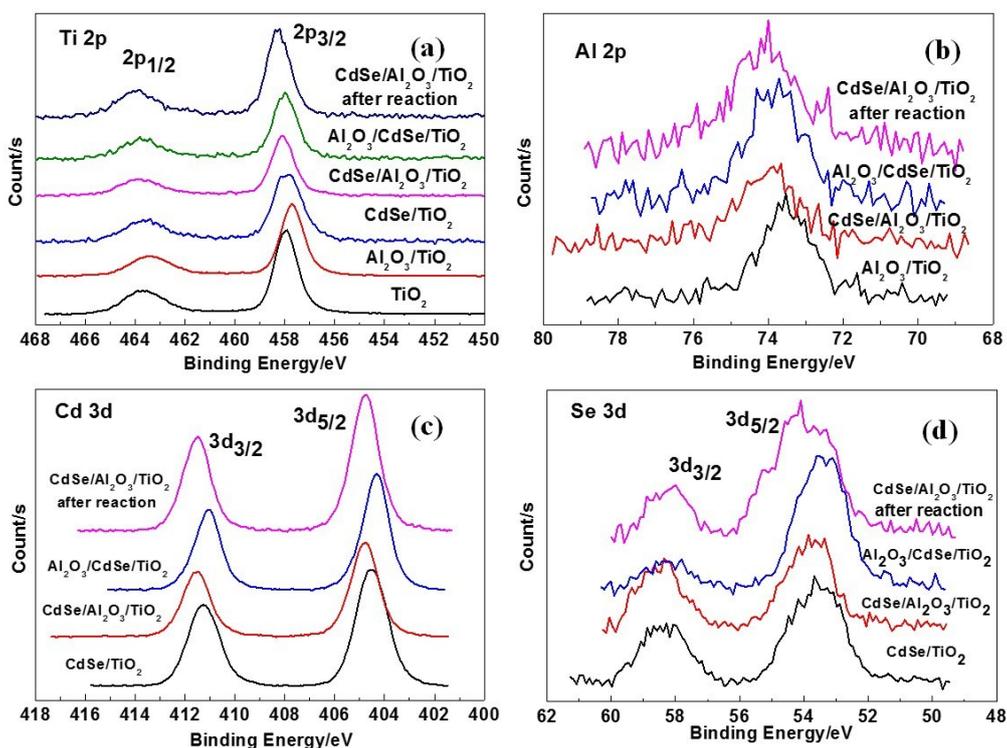


Fig. S4 XPS spectra of TiO_2 , $\text{Al}_2\text{O}_3/\text{TiO}_2$, CdSe/TiO_2 , $\text{CdSe}/\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{Al}_2\text{O}_3/\text{CdSe}/\text{TiO}_2$ nanowire arrays: (a) Ti 2p peaks, (b) Al 2p peaks, (c) Cd 3d peaks and (d) Se 3d peaks.

The XPS measurement was performed to investigate the chemical states of each element in the TiO_2 nanowire arrays and different configurations based on TiO_2 nanowire arrays. Fig. S4 shows the XPS magnified spectra of Ti 2p, Al 2p, Cd 3d and Se 3d. In the Ti 2p spectra, the peaks with binding energy of 457.9 and 463.7 eV are attributed to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, indicating that Ti is in the form of Ti^{4+} [1]. The Ti 2p peaks in the $\text{Al}_2\text{O}_3/\text{TiO}_2$, CdSe/TiO_2 , $\text{Al}_2\text{O}_3/\text{CdSe}/\text{TiO}_2$ and $\text{CdSe}/\text{Al}_2\text{O}_3/\text{TiO}_2$ all present a slight shift when compared to that of pure TiO_2 . This result indicates that the chemical environment of Ti has changed after CdSe and Al_2O_3 deposition and chemical interactions between the TiO_2 , CdSe and Al_2O_3 have formed. In the Al 2p spectra, the peak at 73.8 eV corresponds to the binding energy of Al 2p, which can be ascribed to the Al_2O_3 [2]. The Al 2p peaks in the $\text{Al}_2\text{O}_3/\text{CdSe}/\text{TiO}_2$ and $\text{CdSe}/\text{Al}_2\text{O}_3/\text{TiO}_2$ also present a slight shift when compared to that of pure $\text{Al}_2\text{O}_3/\text{TiO}_2$. In the Cd 3d spectra, two peaks located at 404.5 and 411.3 eV are related to the Cd 3d_{5/2} and Cd 3d_{3/2}, belonging to the Cd^{2+} [3]. The Se 3d

spectra shows two different peaks at 53.6 and 58.4 eV, corresponding to the Se $3d_{3/2}$ and Se $3d_{5/2}$ [3]. The Se 3d peaks in the $\text{Al}_2\text{O}_3/\text{CdSe}/\text{TiO}_2$ and $\text{CdSe}/\text{Al}_2\text{O}_3/\text{TiO}_2$ all present a slight shift when compared to that of CdSe/TiO_2 . These results all imply that there are chemical interactions between Al_2O_3 , CdSe and TiO_2 , which is beneficial to the charge separation and transfer.

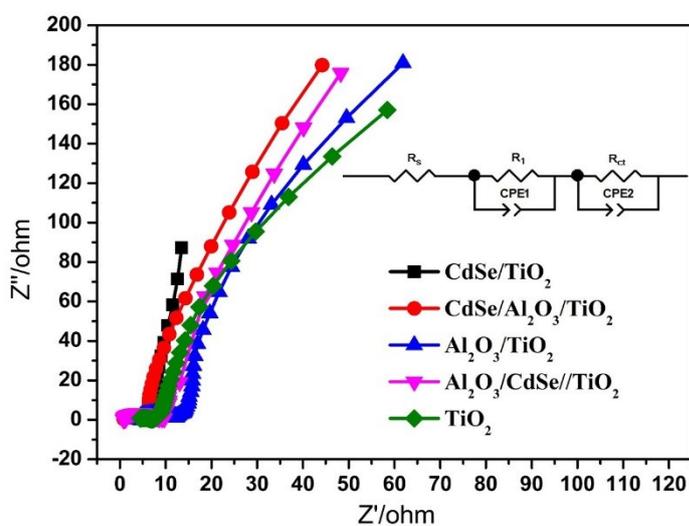


Fig. S5 EIS Nyquist plots of TiO_2 , $\text{Al}_2\text{O}_3/\text{TiO}_2$, CdSe/TiO_2 , $\text{CdSe}/\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{Al}_2\text{O}_3/\text{CdSe}/\text{TiO}_2$ nanowire arrays

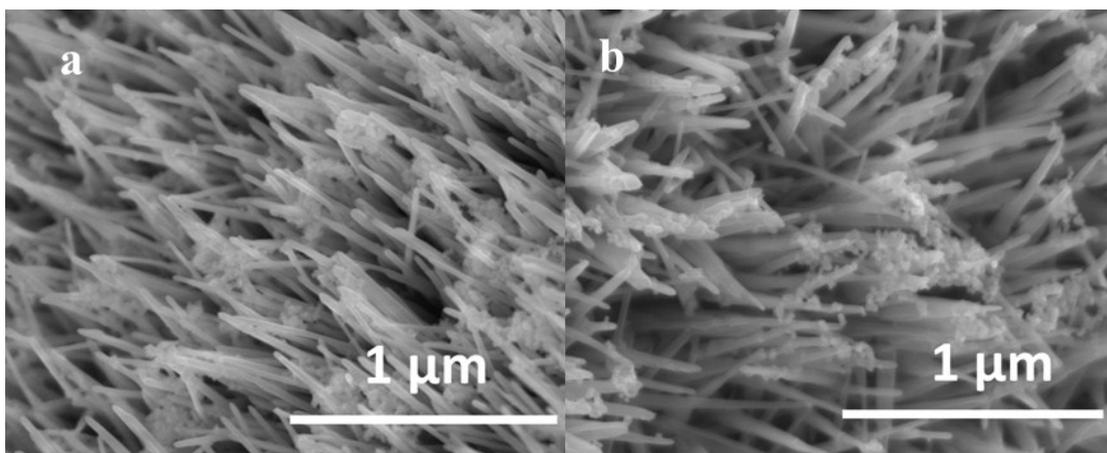


Fig S6 SEM images of CdSe/Al₂O₃/TiO₂ before (a) and after (b) PEC hydrogen evolution reaction

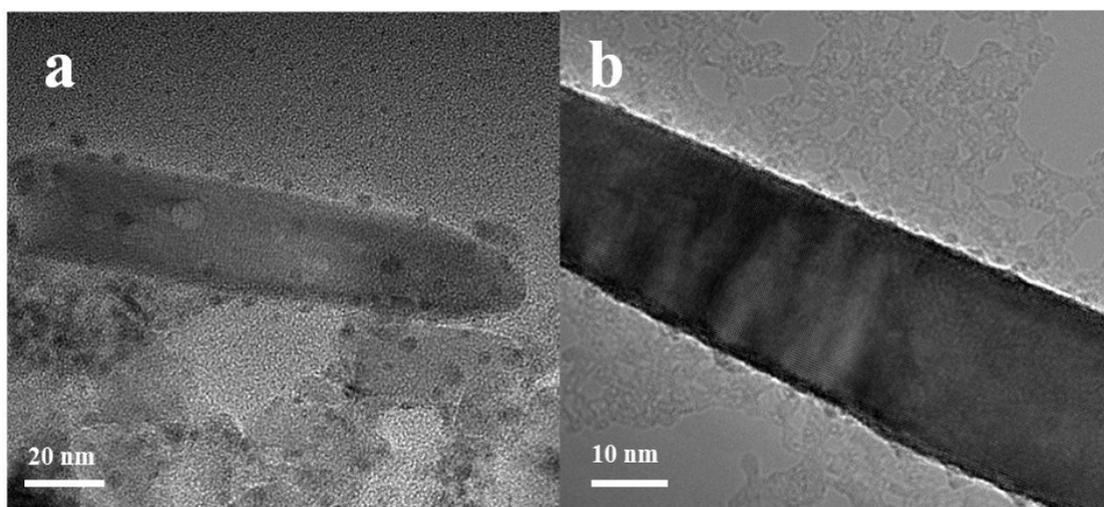


Fig S7 TEM images of CdSe/Al₂O₃/TiO₂ before (a) and after (b) PEC hydrogen evolution reaction

References

- [1] Surf. Coat. Tech., 2014, 242, 20-28.
- [2] J. Nanosci. Nanotechnol., 2016, 16, 4820-4824.
- [3] J. Mol. Catal. A: Chem., 2006, 247, 268-274.