

Supplementary Information

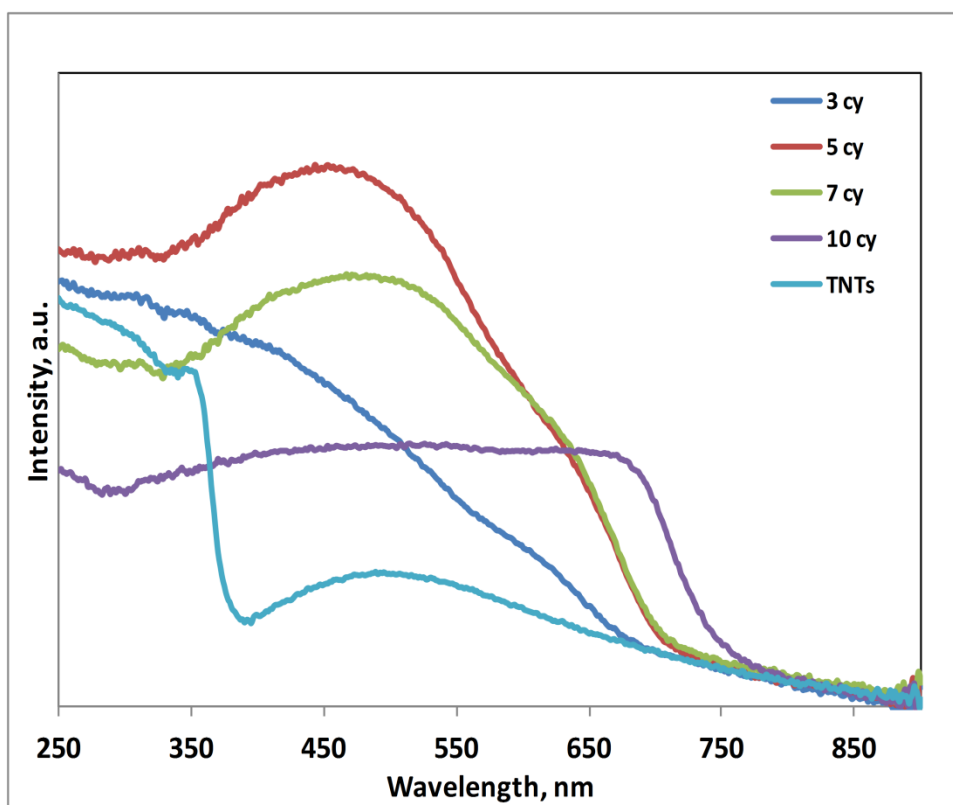


Fig S1. Absorption spectra of unsensitized and sensitized TiO₂ NTA film with different deposition cycles annealed at 300°C.

Electrode	Annealing Temperature	No. of deposition cycles		
		3 cycles	5 cycles	7 cycles
TiO ₂ NTA/Zn _x Cd _{1-x} Se				
	UA	2.77	5.23	4.74
	200°C	3.88	7.21	7.52
	300°C	7.62	11.48	12.71

T1. Table summarizing the photocurrent values from I-V analysis

Electrode	Annealing Temperature	No. of deposition cycles		
		3 cycles	5 cycles	7 cycles
TiO ₂ NTA/Zn _x Cd _{1-x} Se				
	UA	1.99	5.02	4.96
	200°C	3.49	6.52	7.84
	300°C	6.70	12.02	12.04

T1. Table summarizing the photocurrent values from I-t analysis

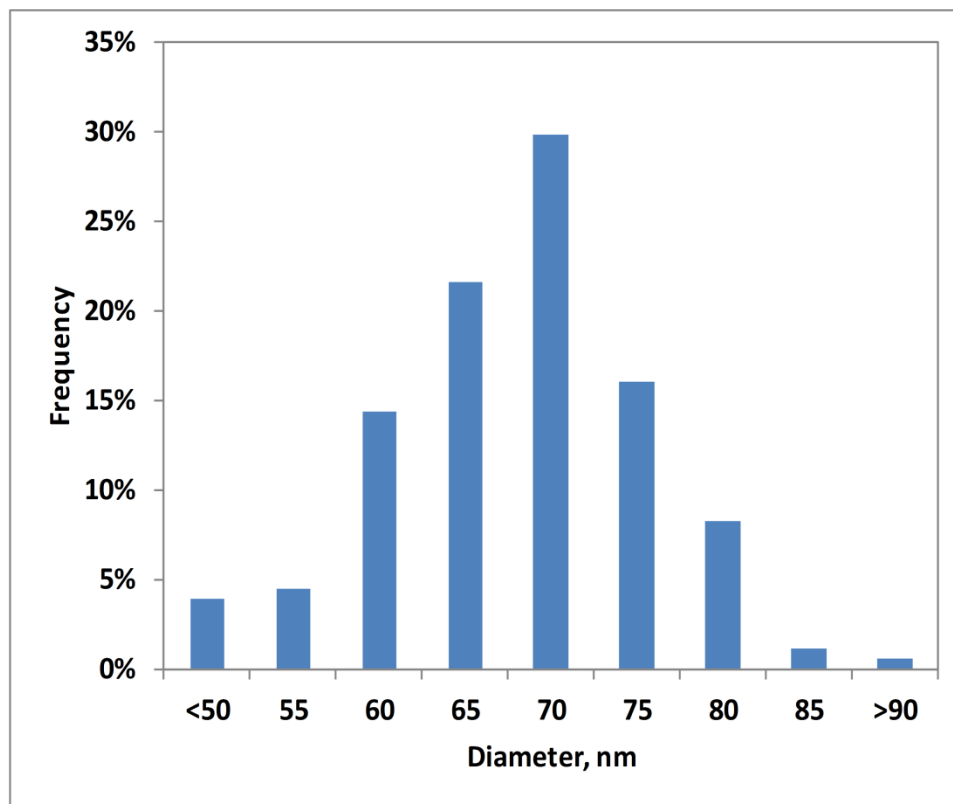


Fig S2. Histogram depicting diameter of nanotubes.

Raman Analysis

Raman spectra of TiO_2 NT/ $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ (7)-300°C is shown below (Fig. S3). The Raman features at 148, 414, 515 and 632 cm^{-1} correspond to TiO_2 nanotubes. An additional feature was observed at 206 cm^{-1} for the composite film. The peak in question can be attributed to CdSe with another dopant.¹ This data indicates the formation of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ alloy.

Further, as secondary confirmation, Raman features for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (at 390 cm^{-1})² and ZnO were (437 and 574 cm^{-1})³ were not observed. Since the starting material, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and the only other possibility, ZnO, were not found, the only explanation for Zn^{2+} seen in XPS is its presence in $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$.

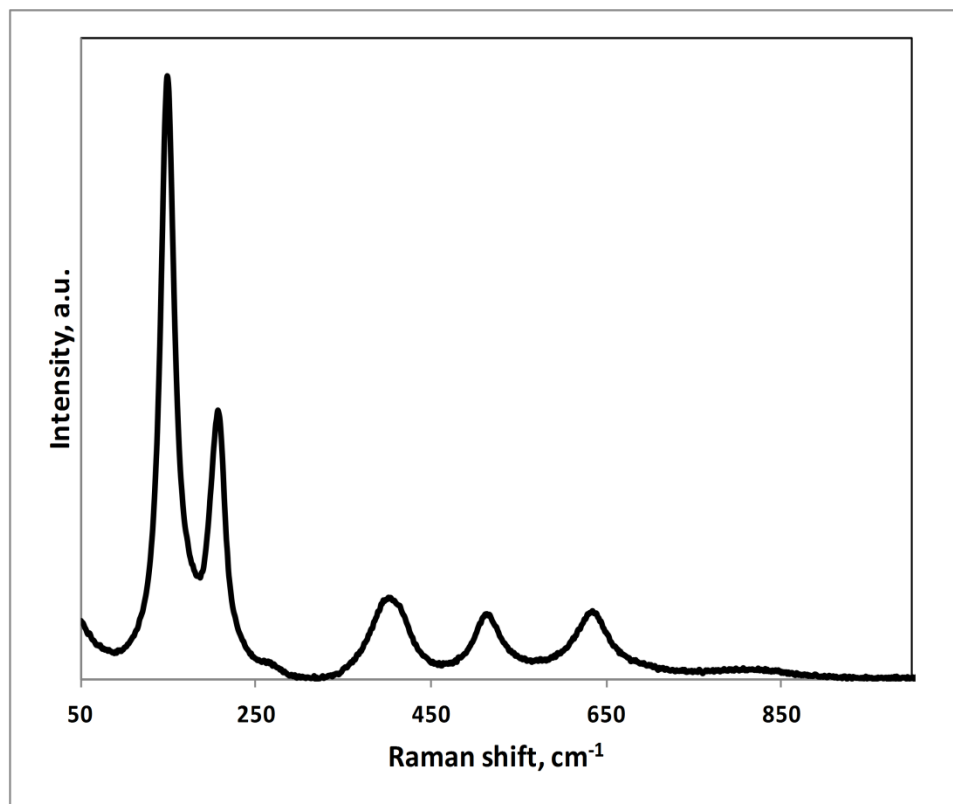


Fig S3. Raman spectra for the composite film TiO₂ NT/Zn_xCd_{1-x}Se(7)-300°C.

Stability Study

Long term I-t study showed that the photocurrent decreased by 53.88% after 2 hours and by 79.6% after about 24 hours (Fig. S4).

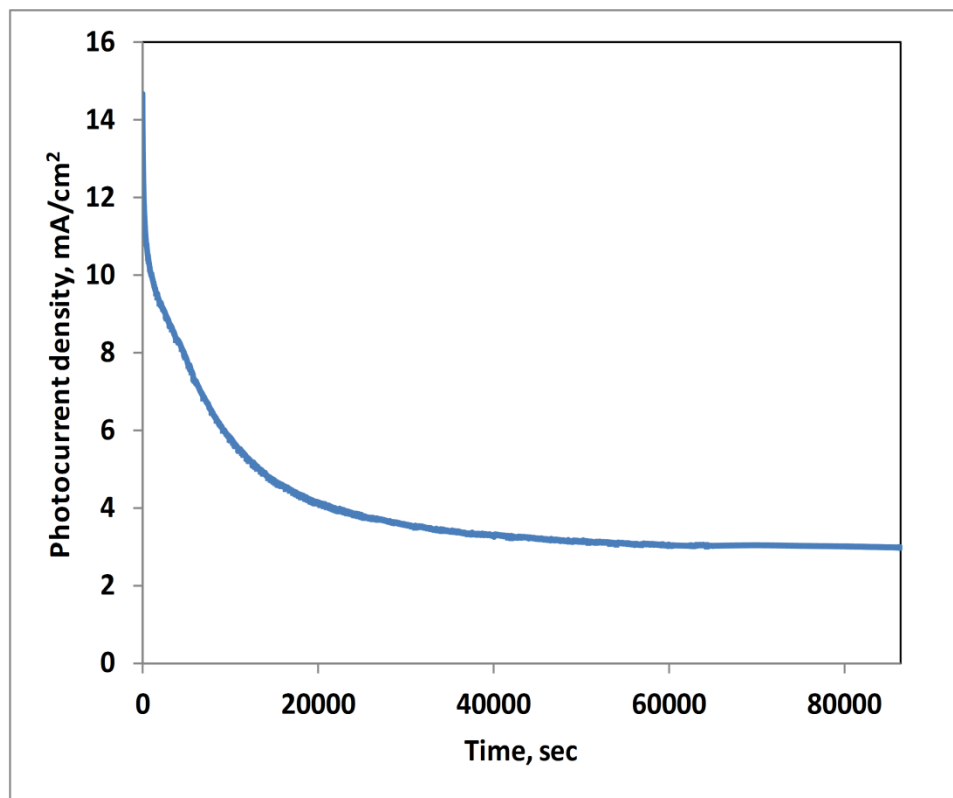
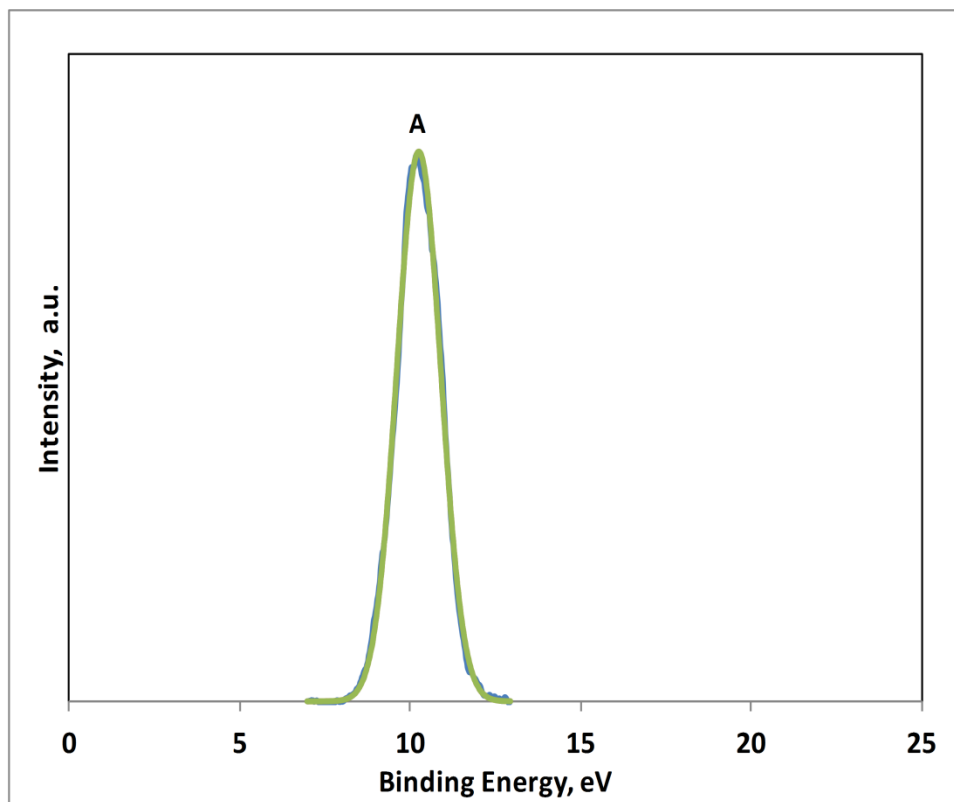


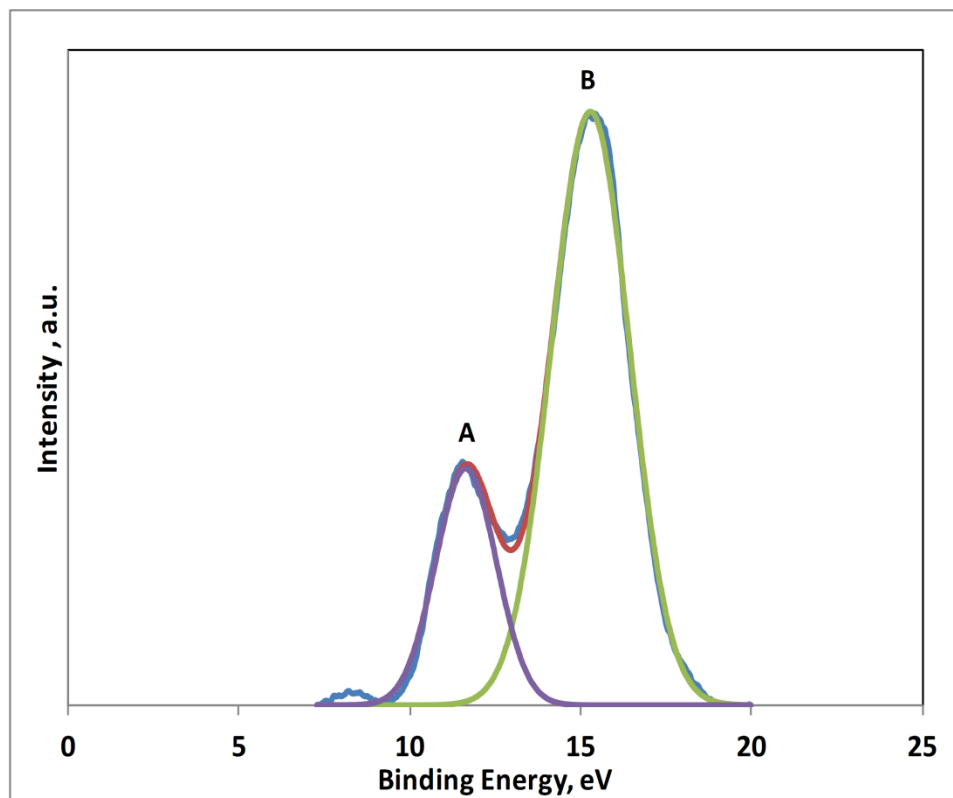
Fig S4. Long term I-t analysis curve obtained for TiO₂ NTA/ZnCdSe(7)-300°C film.

To confirm the chemical stability of the photoelectrode, XPS was used to analyze the surface of the film before and after I-t analysis. All the sensitized species (Zn, Cd and Se) were found to be intact on the surface of the film after stability test. To further confirm that Zn_xCd_{1-x}Se was not converted to Zn_xCd_{1-x}S, a core-level scan was carried out (Fig. S5) in the low binding energy region (10-20 eV) to confirm the absence of characteristic S 5s peak (~15eV) of CdS (Fig. S6). Though not optimal, only the 5s peak of the S could be used due to interference from Se/Cd at all other binding energy levels. Even at this level Cd 4 (~10eV) is close but does not directly interfere in analysis of S 5s peak. S 5s peak is absent in the sample proving that S did not replace Se. The presence of S 5s in CdS was demonstrated (as a control) by core-level spectrum of standard CdS (Fig. S6)



Peak label	Due to	BE (eV)	FWHM
A	Cd 4d	10.4	1.0

Fig. S5: XPS spectra of TiO₂ NTA/ZnCdSe(7)-300°C film after long term i-t analysis. The peak shown here is due to Cd 4d.



Peak label	Due to	BE (eV)	FWHM
A	Cd 4d	11.8	1.0
B	S 5s	15.5	1.1

Fig S6: XPS data for Standard CdS (peak at lower binding energy corresponds to Cd 4d). spectrum is not charge corrected.

References

1. V. M. Dzhagan, M. Y. Valakh, A. G. Milekhin, N. A. Yeryukov, D. R. T. Zahn, E. Cassette, T. Pons and B. Dubertret, *The Journal of Physical Chemistry C*, 2013, **117**, 18225-18233.
2. A. Wahab and S. Mahiuddin, *Journal of Chemical & Engineering Data*, 2004, **49**, 126-132.
3. Z. Zhaochun, H. Baibiao, Y. Yongqin and C. Deliang, *Materials Science and Engineering: B*, 2001, **86**, 109-112.