Electronic Supplementary Information

Epitaxial Hetero-structure of CdSe/TiO_2 Nanotube Arrays with PEDOT as hole transfer layer for photoelectrochemical hydrogen evolution

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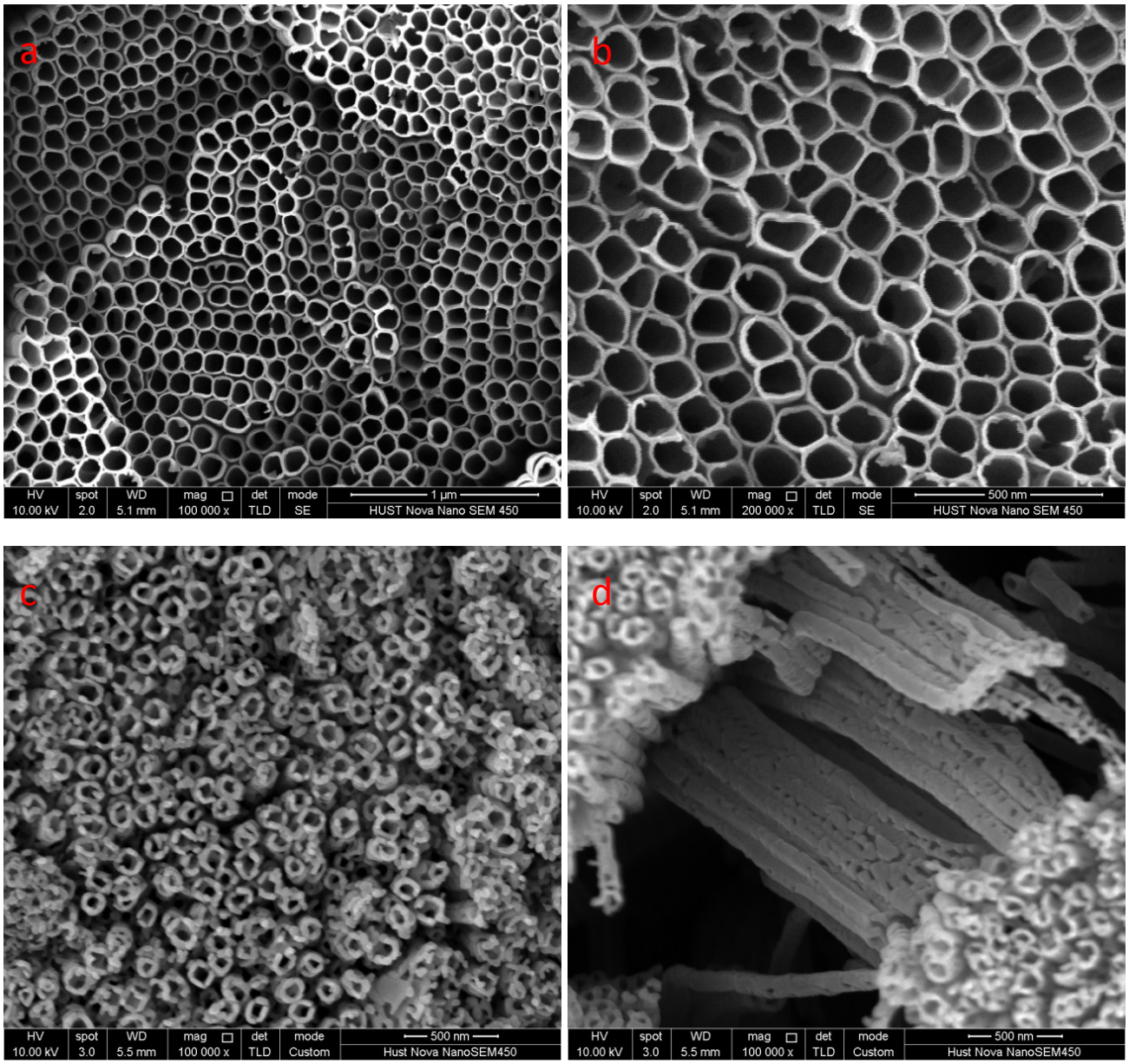

Figure S1. FESEM images of top-surface: (a, b) TiO_2 NTAs(300˚C); (c, d) TiO_2 NTAs(700˚C).

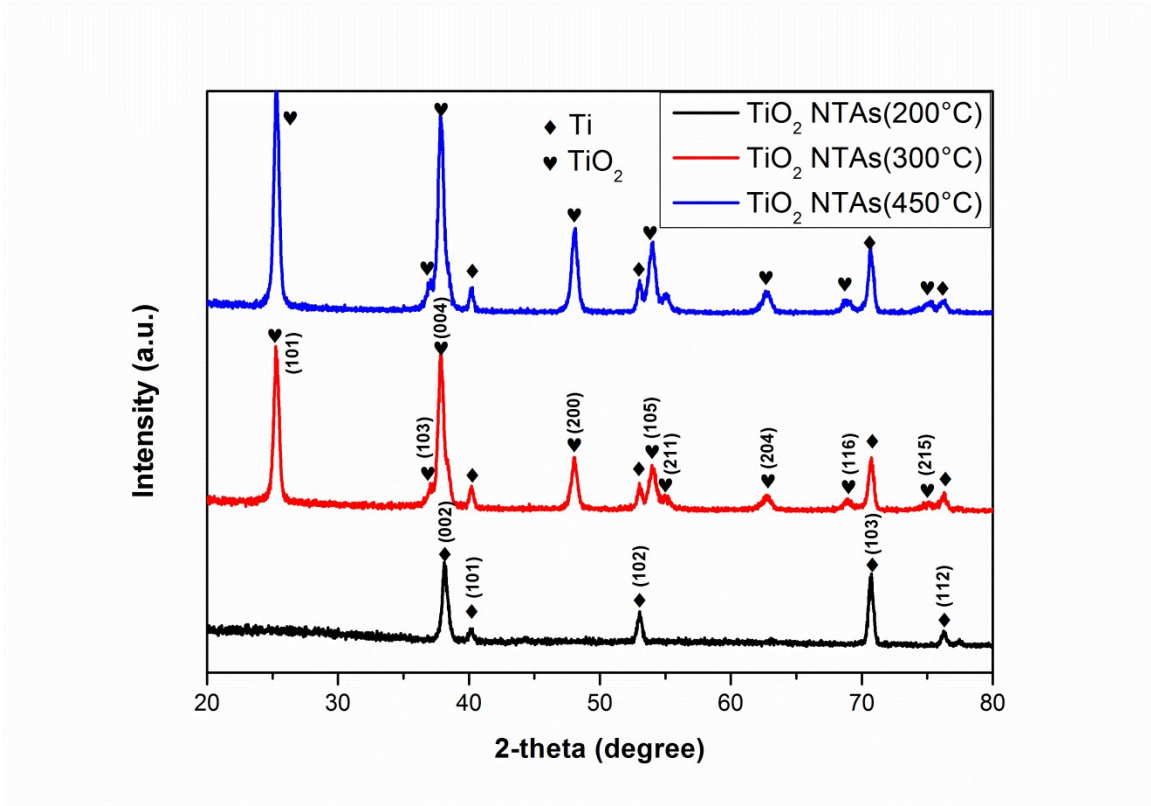

Figure S2. XRD diffractograms of samples: (black line) TiO_2 NTAs(200˚C); (red line) TiO_2 NTAs(300˚C); (blue line) TiO_2 NTAs(450˚C)

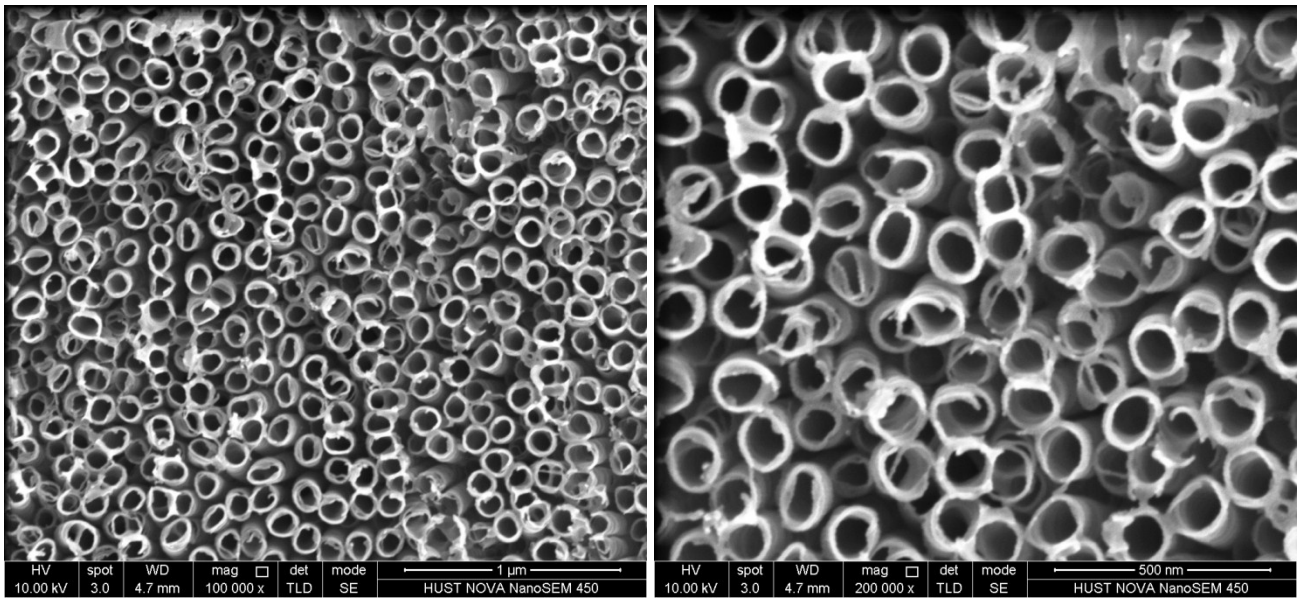

Figure S3. FESEM images of CdSe/TiO_2 NTAs(300°C).

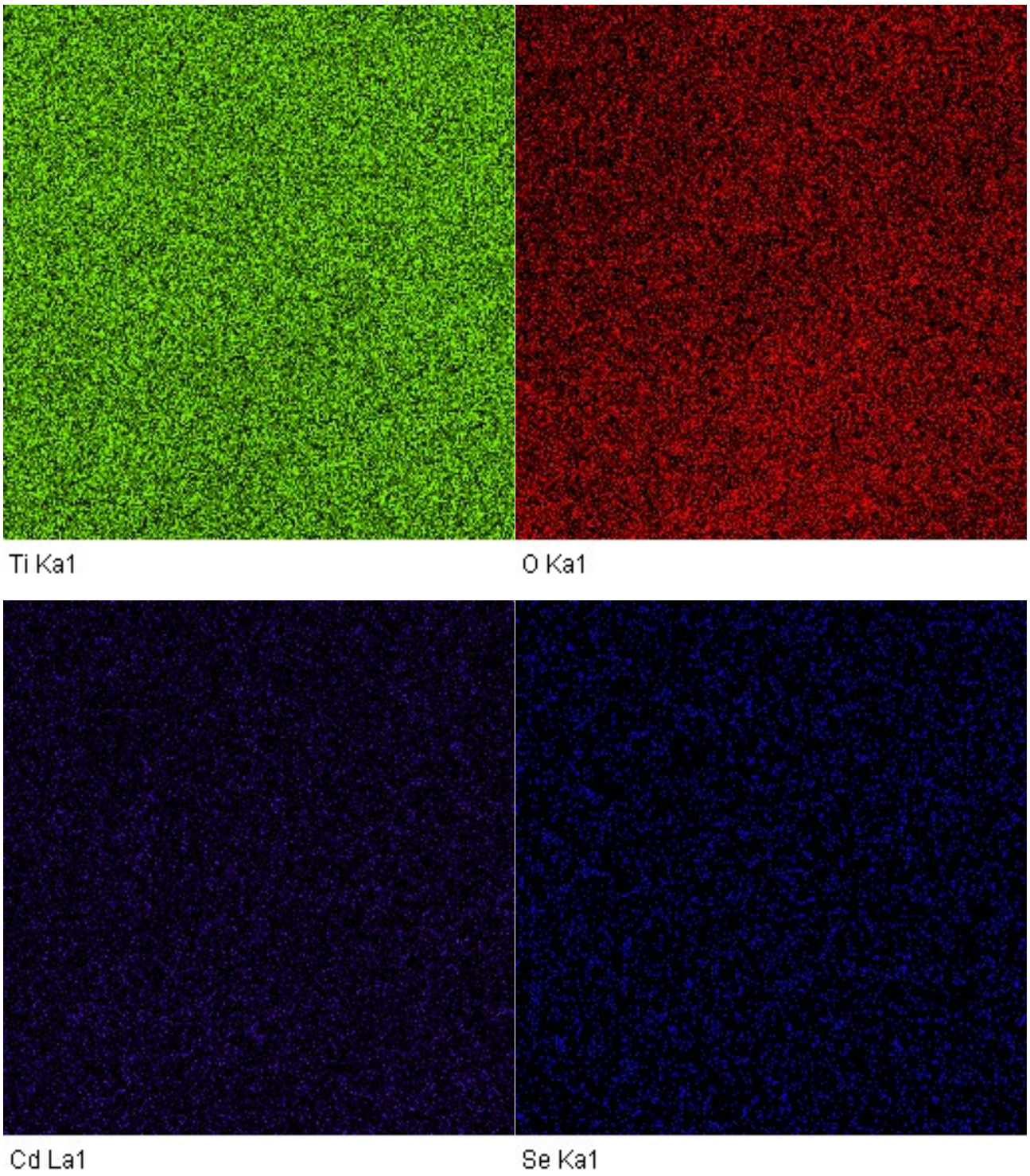

Figure S4. EDX elemental mapping images of sample CdSe/TiO_2 NTAs(300˚C).

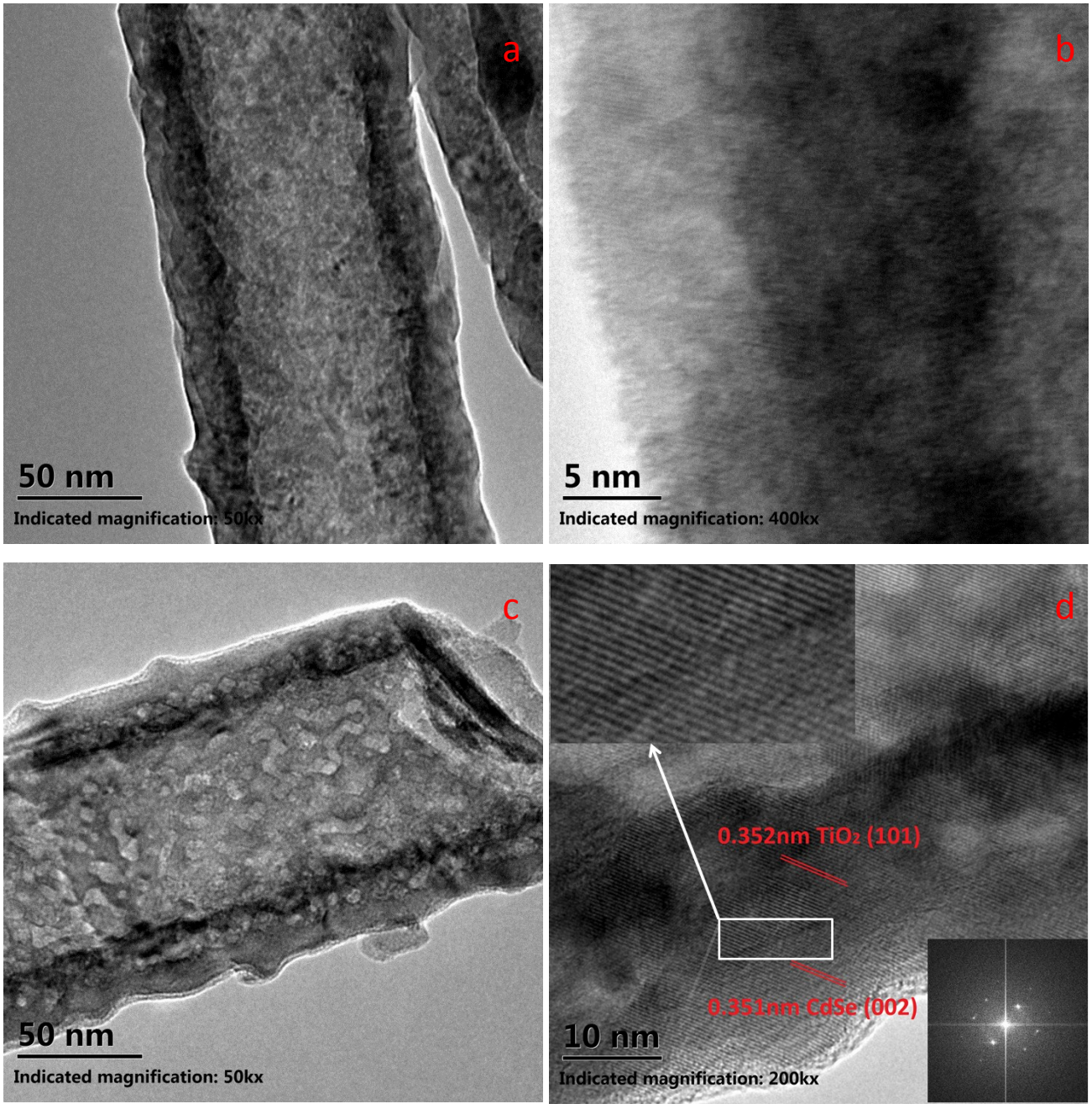

Figure S5. TEM and HRTEM images of samples. (a, b) TiO_2 NTAs(200°C); (c, d) CdSe/TiO_2 NTAs(200°C) Insets in d are the selected area enlarged picture and FFT pattern.

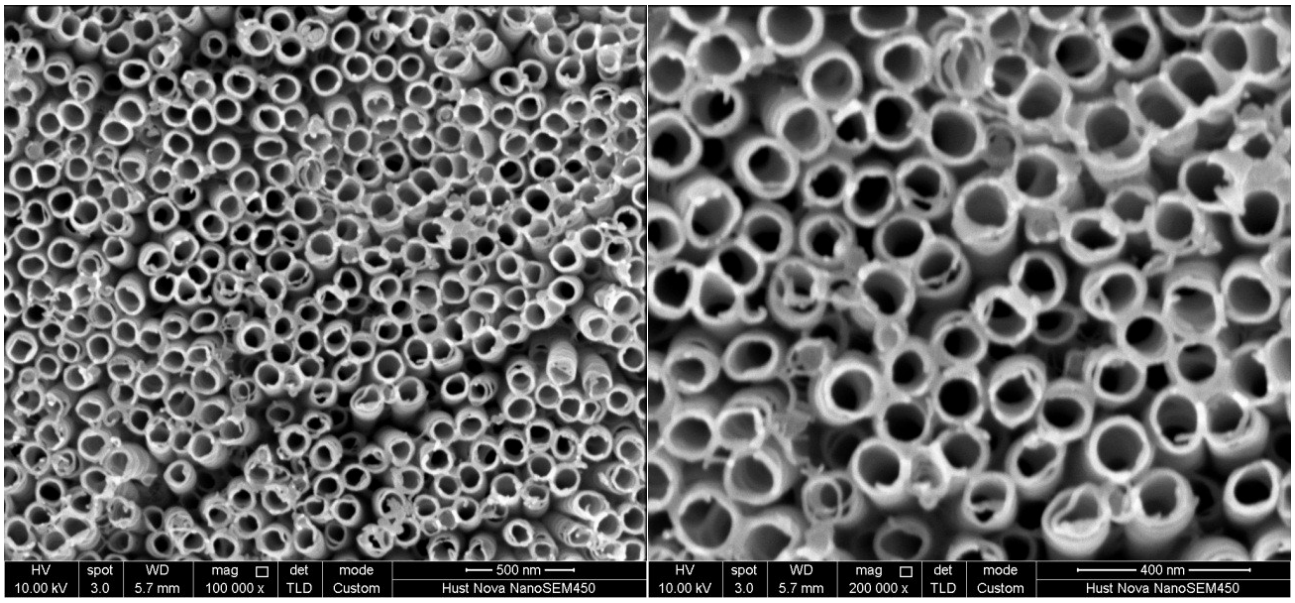

Figure S6. FESEM images of PEDOT/CdSe/TiO_2 NTAs(300°C).

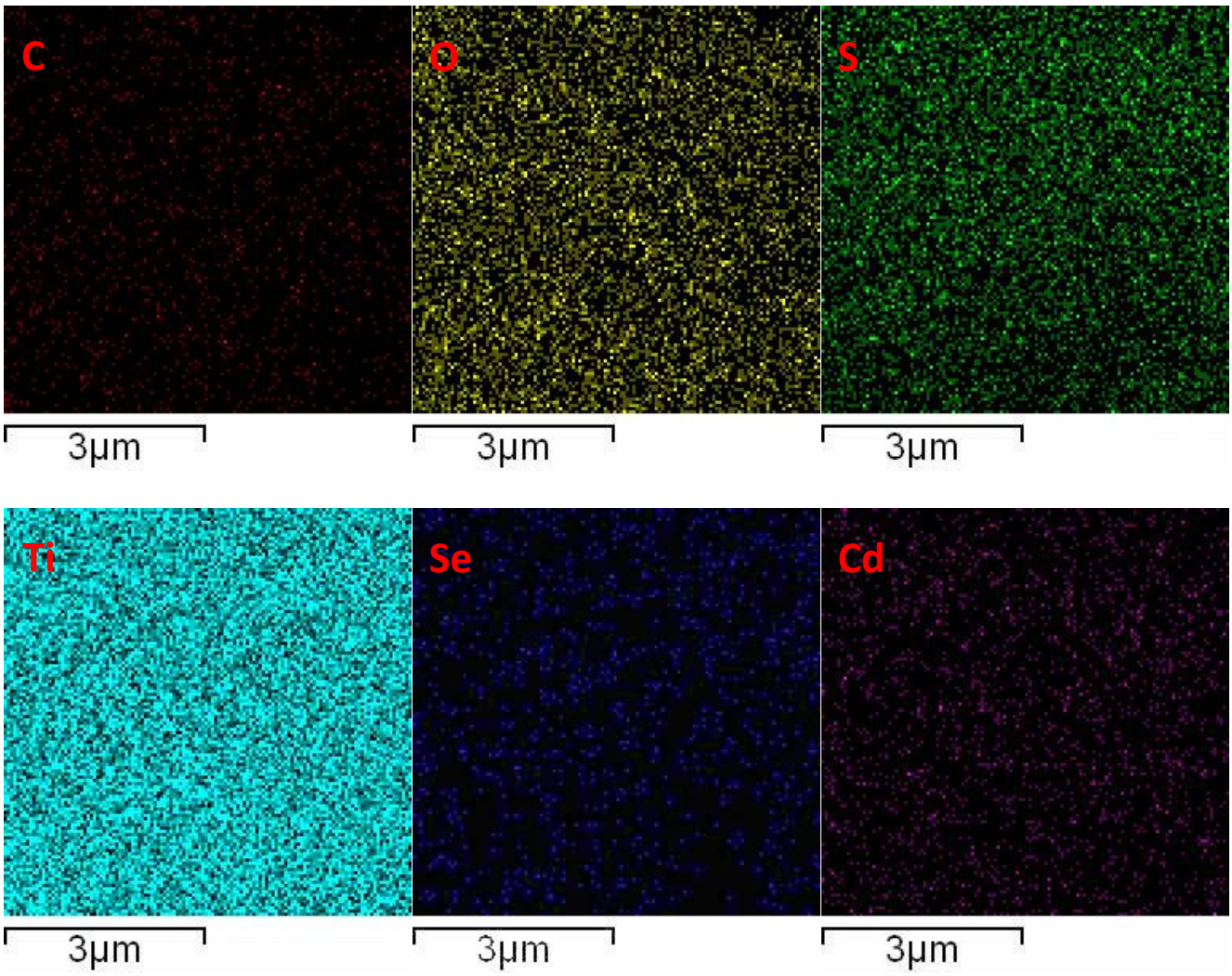

Figure S7. EDX elemental mapping images of sample PEDOT/CdSe/TiO_2 NTAs(300˚C).

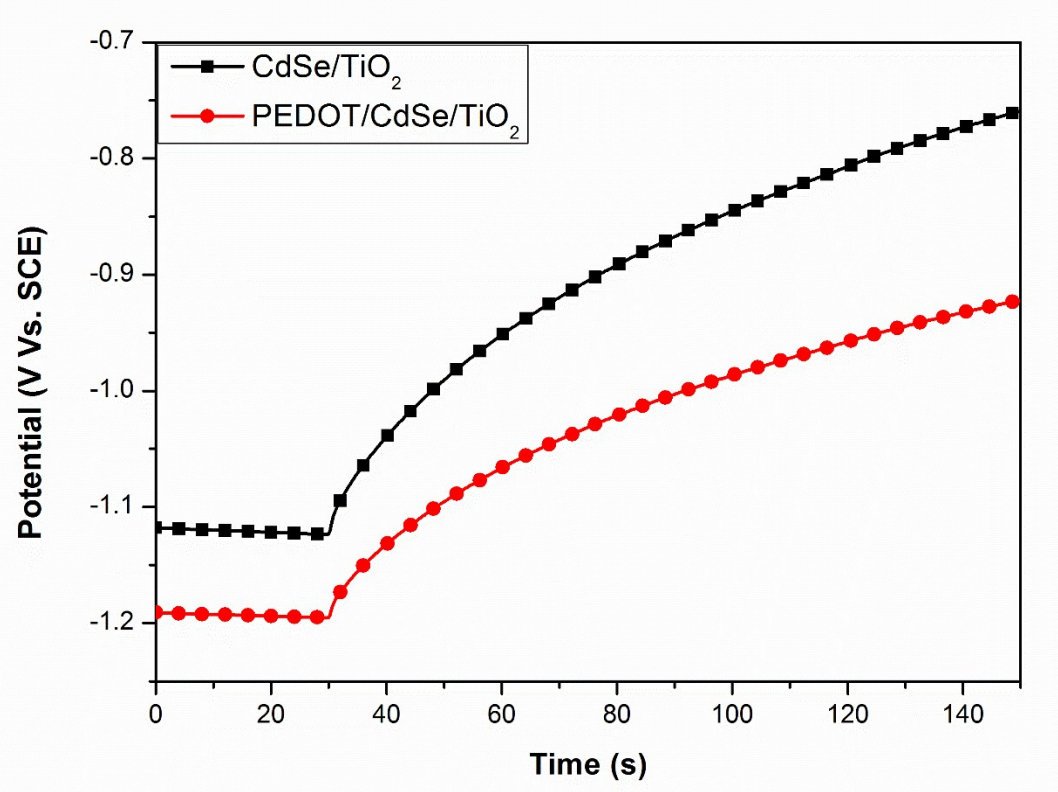

Figure S8. Profile of the potential decay of $CdSe/TiO_2$ and $PEDOT/CdSe/TiO_2$ electrodes.

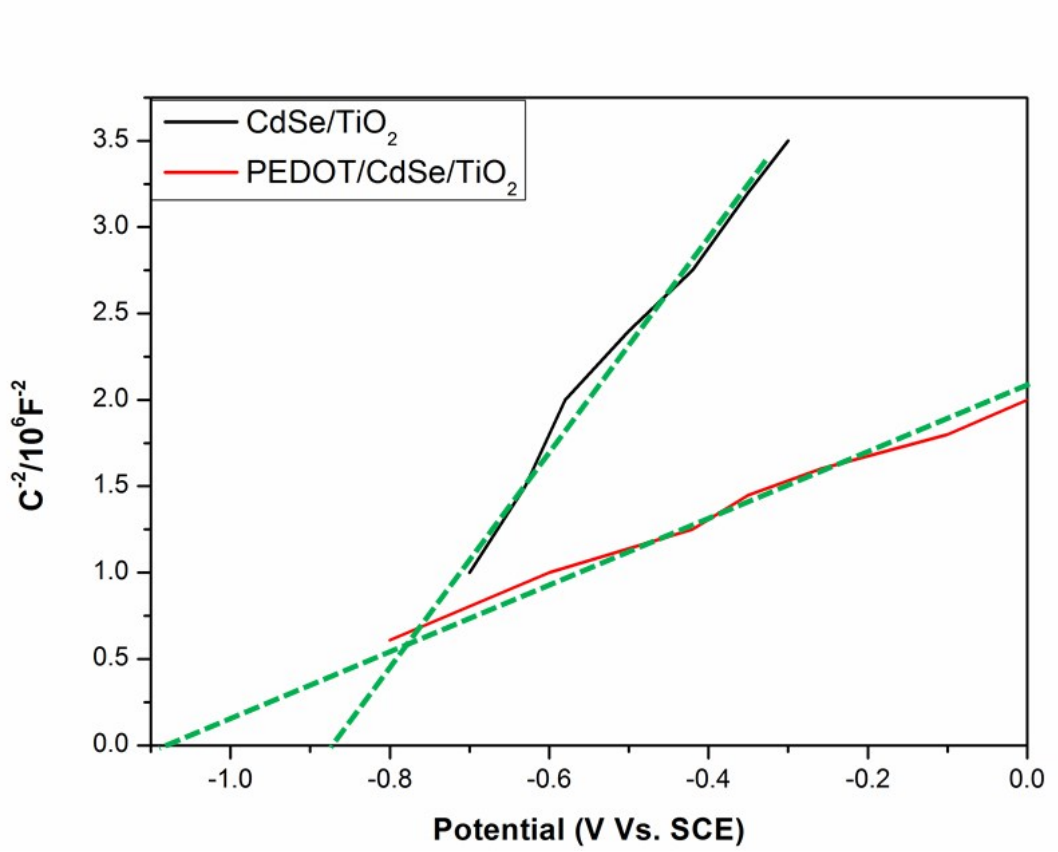

Figure S9. Mott-Schottky plots of $CdSe/TiO_2$ and $PEDOT/CdSe/TiO_2$ electrodes.

Table S1. The flatband, conduction and valence band potentials of CdSe and PEDOT.

Sample	**$CdSe/TiO_2$ (V)**	**$PEDOT/CdSe/TiO_2$ (V)**
V_{fb} vs. SCE	-0.88	-1.09
V_{fb} vs. NHE	-0.64	-0.85
V_{CB} vs. NHE	-0.74	-0.95
V_{VB} vs. NHE	0.86	0.55

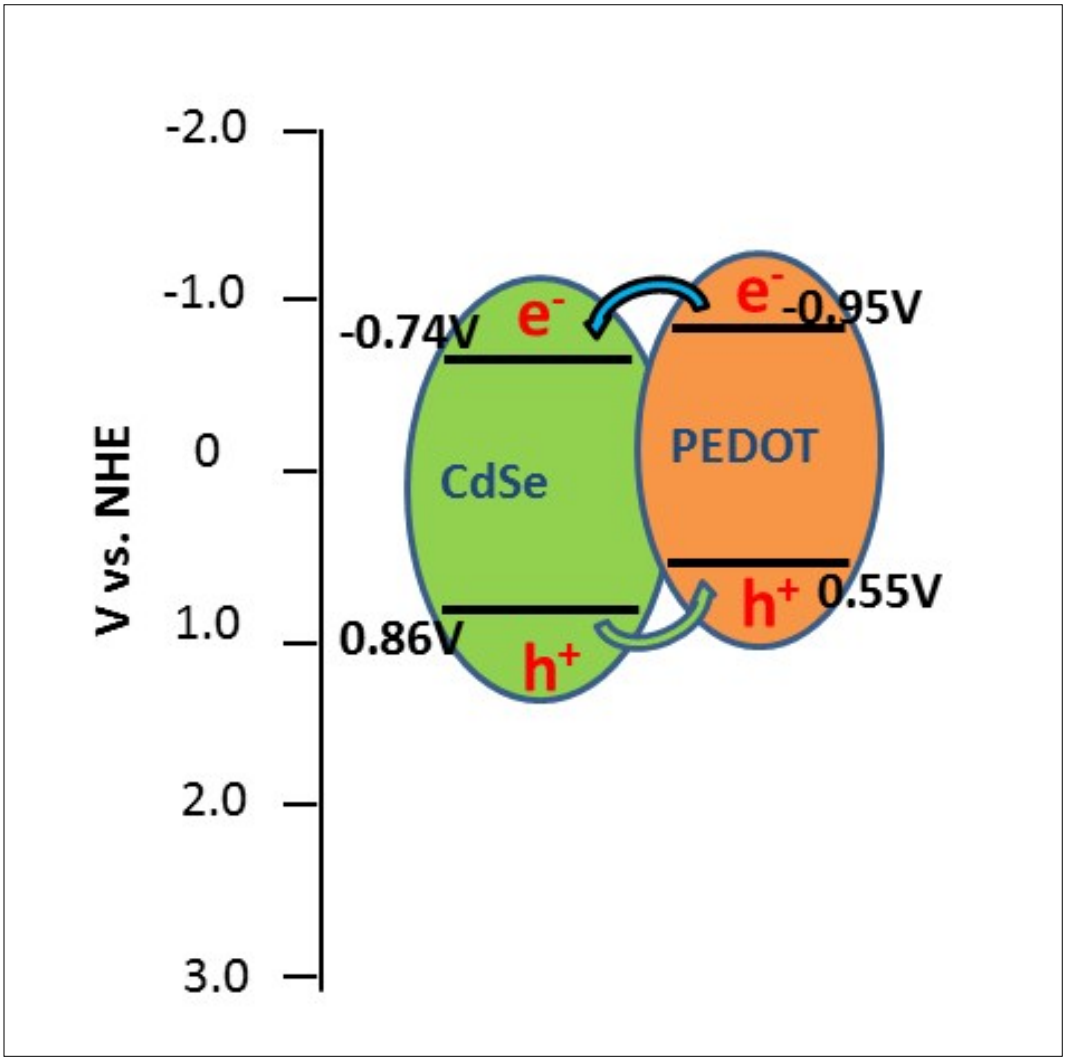

Figure S10. Illustrations of the energy band positions of CdSe and PEDOT and the photo-generated electron-hole transfer process in PEDOT-CdSe.

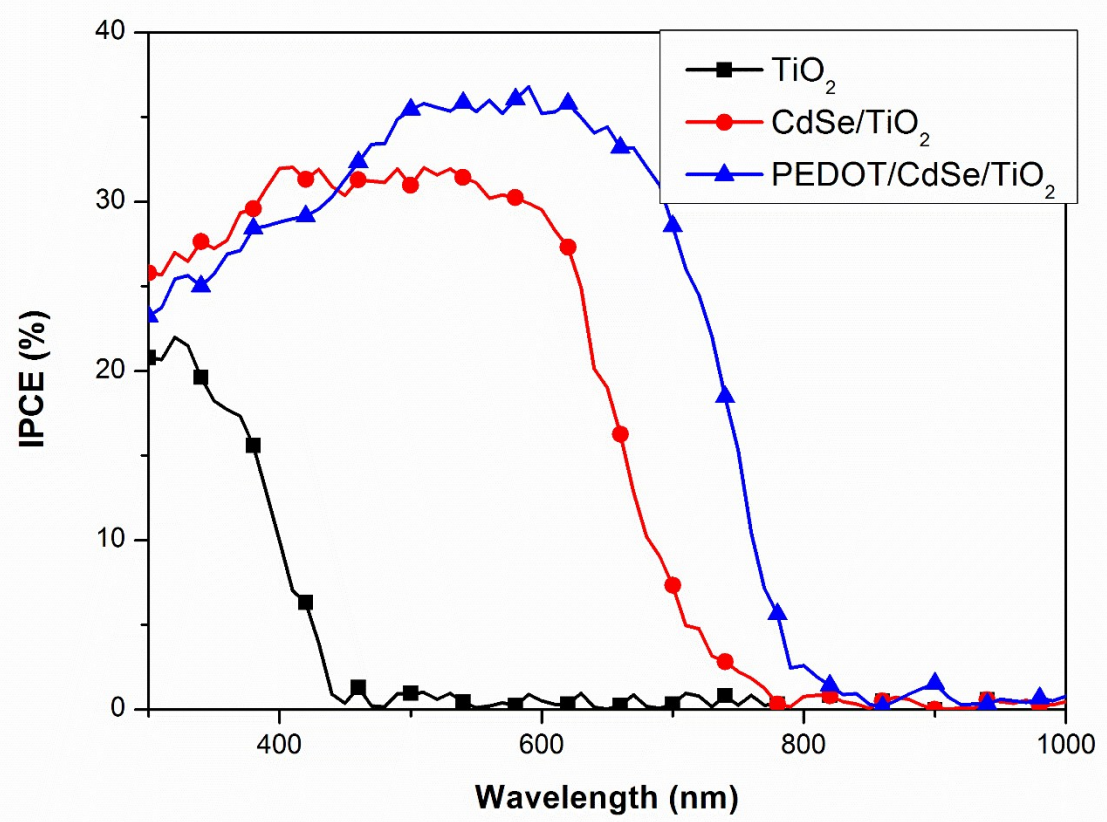

Figure S11. IPCE image of TiO_2 (black line); $CdSe/TiO_2$ (red line); $PEDOT/CdSe/TiO_2$ (blue line).

Table S2. Photoelectrochemical cell stability of different system

System	Electrolyte	Photocurrent Density	Stability	Reference
CdS/TiO_2 nanotubes	0.35 M Na_2SO_3 and 0.24 M Na_2S	1.9 mA /cm^2 at -0.9V(vs Ag/AgCl)	remaining 83% after 1h	[1]
CdSe/TiO_2 nanotubes	0.1 M Na_2S	3.84 mA/cm^2 at 0 V(vs Ag/AgCl)	Remaining 92% after 400s	[2]
CdSe/ZnO nanotubes	0.35 M Na_2S and 0.25 M K_2SO_3	5.1 mA /cm^2 at 0.35 V (vs. SCE)	remaining 86% after 600s	[3]
CdSe/ZnO nanorods	0.2 M Na_2S	14.9 mA /cm^2 at 0.8 V (vs. RHE)	remaining 86.2% after 1h	[4]
CdTe/CdS/TiO_2 nanotubes	0.35 M Na_2SO_3 and 0.24 M Na_2S	9.17 mA /cm^2 at -1.0V(vs Ag/AgCl)	remaining 75% after 1h	[1]

References:

1. **P. Sheng, W. Li, J. Cai, X. Wang, X. Tong, Q. Cai and C. A. Grimes, *Journal of Materials Chemistry A*, 2013, 1, 7806-7815.**
2. **B. Mukherjee, S. Sarker, E. Crone, P. Pathak and V. R. Subramanian, *ACS Applied Materials & Interfaces*, 2016, 8, 33280-33288.**
3. **N. Chouhan, C. L. Yeh, S.-F. Hu, R.-S. Liu, W.-S. Chang and K.-H. Chen, *Chemical Communications*, 2011, 47, 3493-3495.**
4. **J. Miao, H. B. Yang, S. Y. Khoo and B. Liu, *Nanoscale*, 2013, 5, 11118-11124.**