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Electronic Supplementary Information

# 1D conical nanotubular $TiO_2$ / CdS heterostructure for superior photon-to-electron conversion

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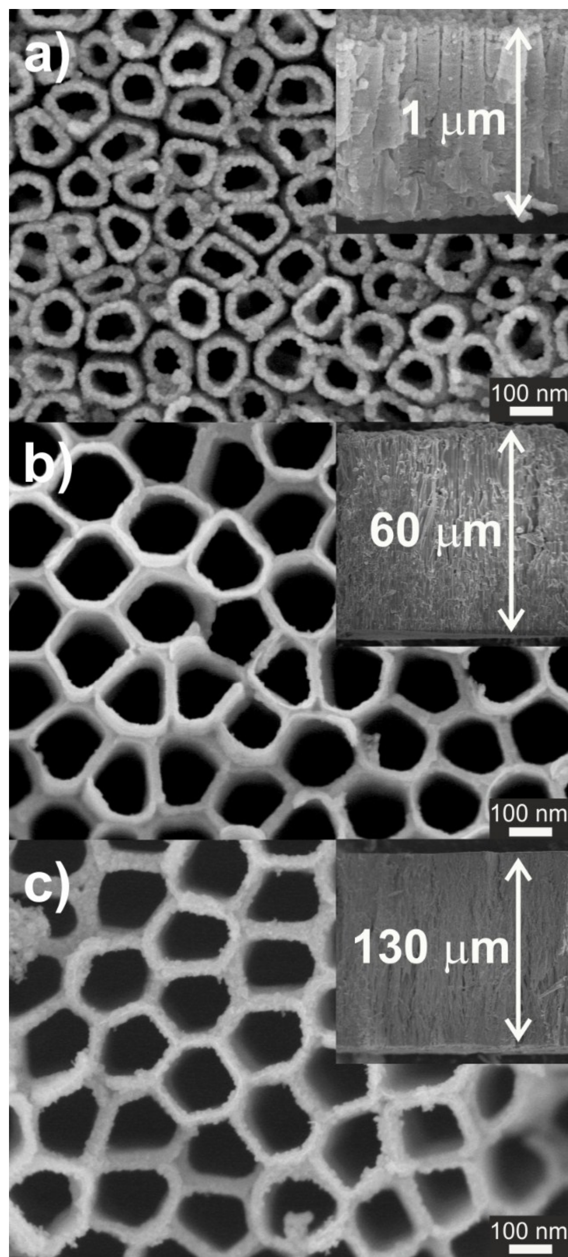


**Fig. S1.** SEM top view images of the CdS coated (5 nm) $TiO_2$ nanotube layers of different thickness: 1 μm (a, b) 60 μm (c, d) and 130 μm (e, f). Insets: cross-sectional SEM images of the corresponding $TiO_2$ nanotube layers.

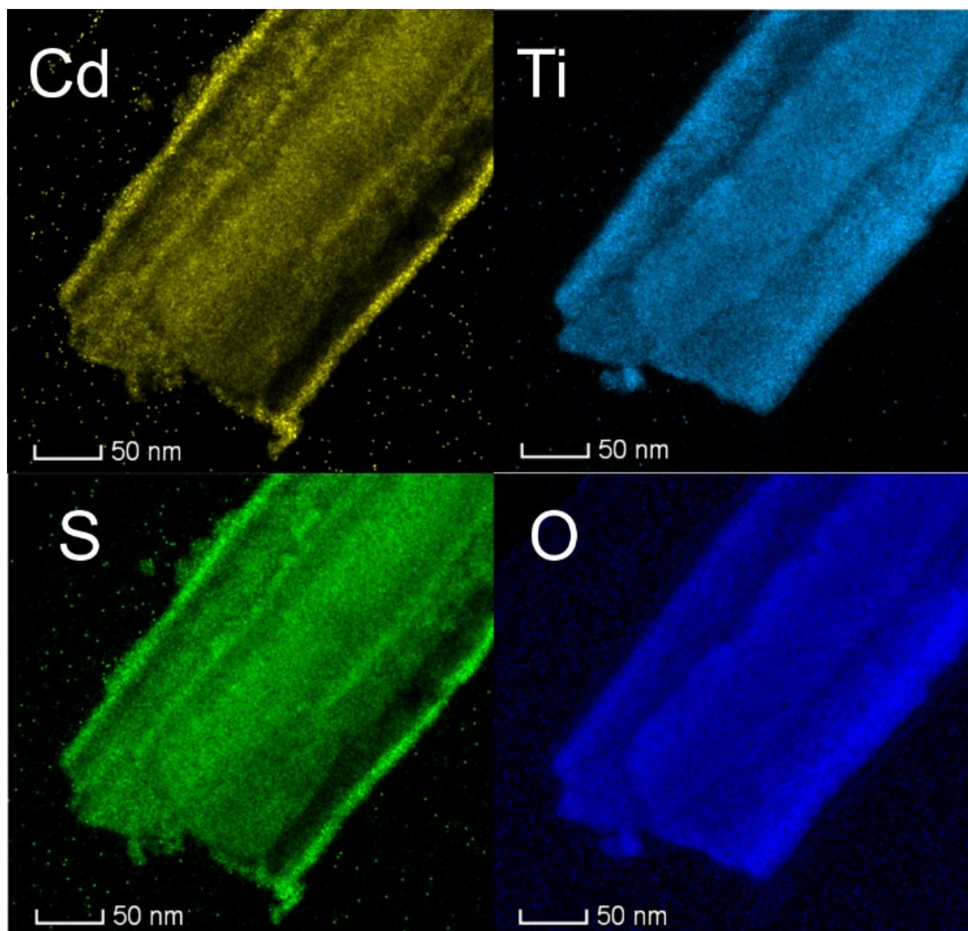


**Fig. S2.** Elemental STEM/EDX maps of a fragment of a single 130 μm $TiO_2$ nanotube coated with 5 nm of CdS.

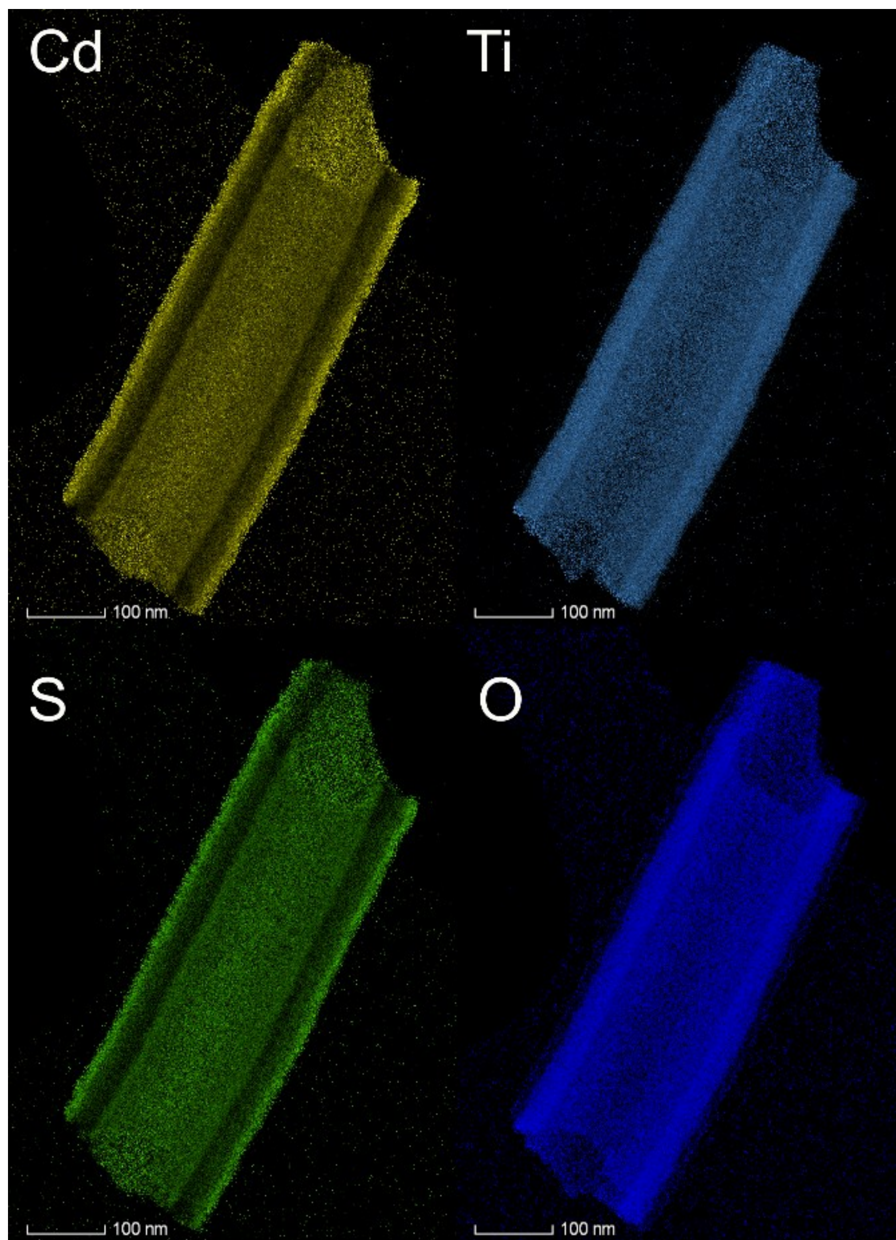


**Fig. S3.** Elemental STEM/EDX maps of a fragment of a single 20 μm $TiO_2$ nanotube coated with 10 nm of CdS.

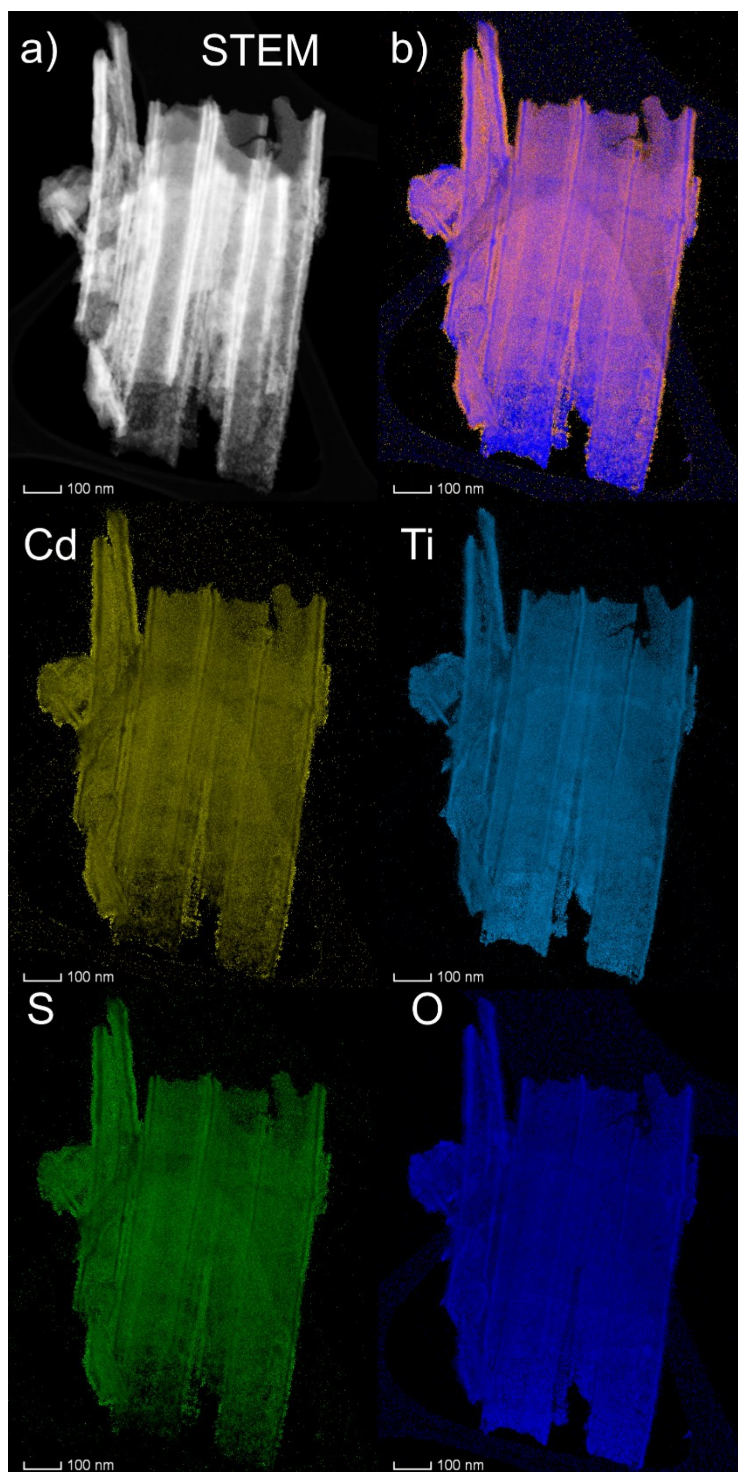


**Fig. S4.** A HAADF-STEM image of (a) a bundle of 130 μm thick $TiO_2$ nanotube layer coated with 5 nm of CdS, and (b) corresponding overall STEM/EDX elemental map. Other images show STEM/EDX maps for individual elements.

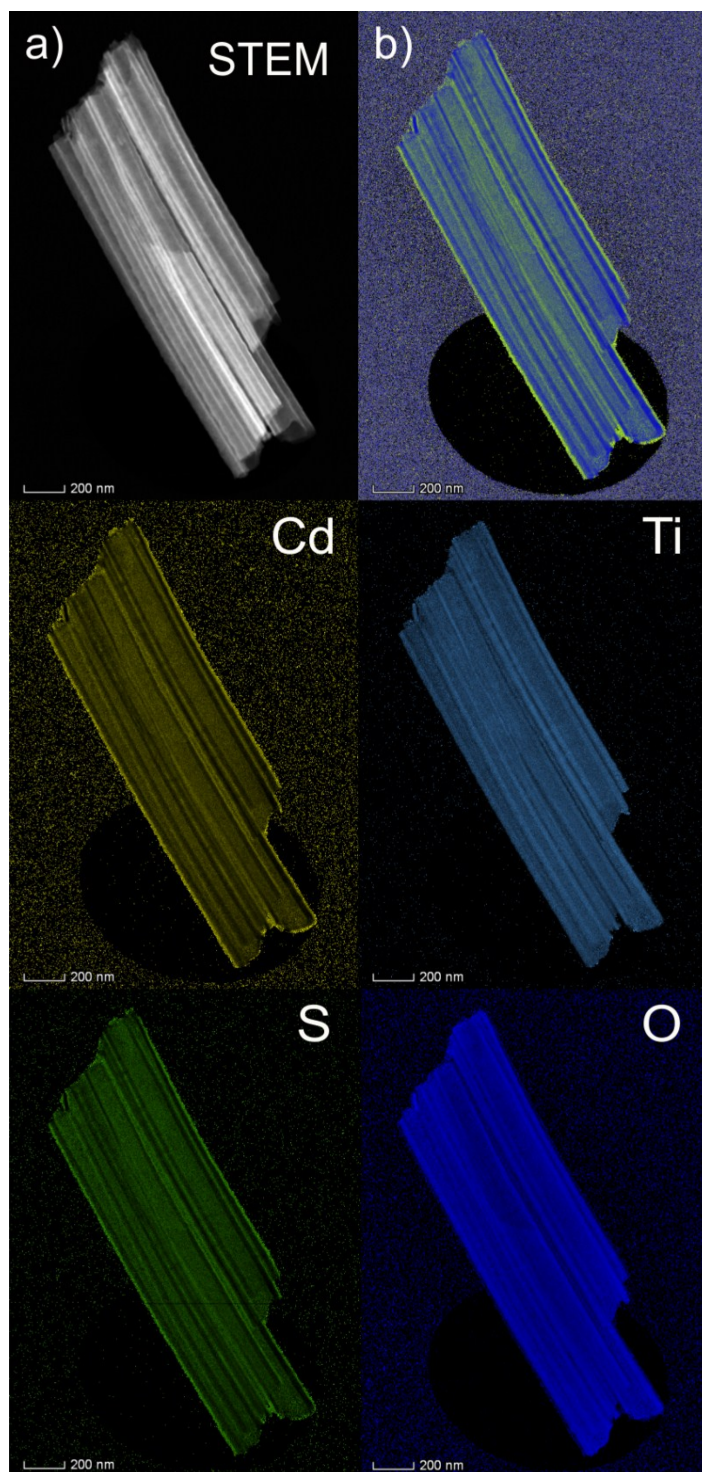


**Fig. S5.** A HAADF-STEM image of (a) a bundle of 20 μm thick $TiO_2$ nanotube layer coated with 10 nm of CdS, and (b) corresponding overall STEM/EDX elemental map. Other images show STEM/EDX maps for individual elements.

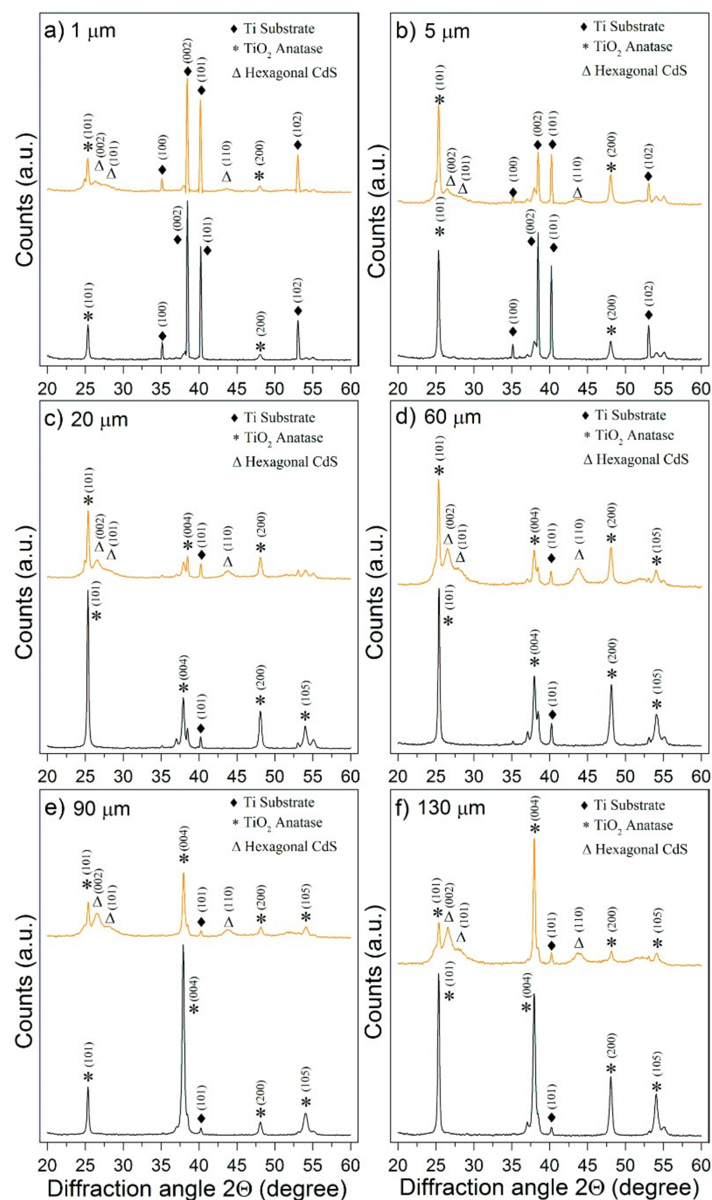


**Fig. S6.** XRD patterns of blank (lower black lines) and CdS coated (upper orange lines) $TiO_2$ nanotube layers (a) 1μm, (b) 5μm, (c) 20μm, (d) 60μm, (e) 90μm, and (f) 130 μm thick.

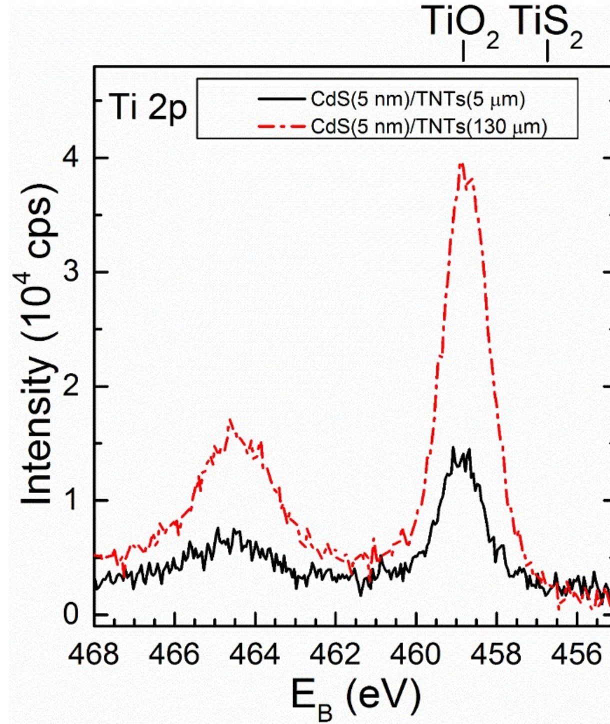


**Fig. S7.** XPS Ti 2p spectra of Cds coated $TiO_2$ nanotube layers 1μm (black solid line) and 130 μm thick (red dashed line). The binding energy of Ti-O and Ti-S bonds are indicated at the top axis. The spectra show the absence of Ti-S bond.

<u>CdS/TNT band alignment determined by XPS</u>

The band offsets at the $CdS/TiO_2$ interface were determined by XPS following the concept introduced by Kraut et al. [1]. The valence band offset (VBO) at $CdS/TiO_2$ interface was determined according to following relation:

$$VBO = -\left(EB_{Ti2p} - VBM_{TiO2}\right)^{(i)} + \left(EB_{Cd3d} - VBM_{CdS}\right)^{(ii)} + \left(EB_{Ti2p} - EB_{Cd3d}\right)^{(iii)} \quad (1)$$

where $EB_{Ti2p}$ and $EB_{Cd3d}$ are binding energies of Ti $2p_{3/2}$ and Cd $3d_{5/2}$ core level lines, respectively, and $VBM_{TiO2}$ and $VBM_{CdS}$ are valence band maxima of $TiO_2$ and CdS, respectively, collected from $TiO_2$ reference, CdS reference, and $CdS/TiO_2$ interface as illustrated

in Fig. S8. Blank, 2.5 nm CdS coated, and 10 nm CdS coated TNT layers were used as $TiO_2$ reference, interface, and CdS reference, respectively. Based on obtained values listed in Table S1 the valence band of $TiO_2$ is found to lie (1.2 ± 0.2) eV below valence band of CdS at CdS/$TiO_2$ interface. The conduction band offset (CBO) was calculated using the conventional bulk band gap values of anatase $TiO_2$ (3.2 eV) and CdS (2.4 eV) to be (0.4 ± 0.2) eV.

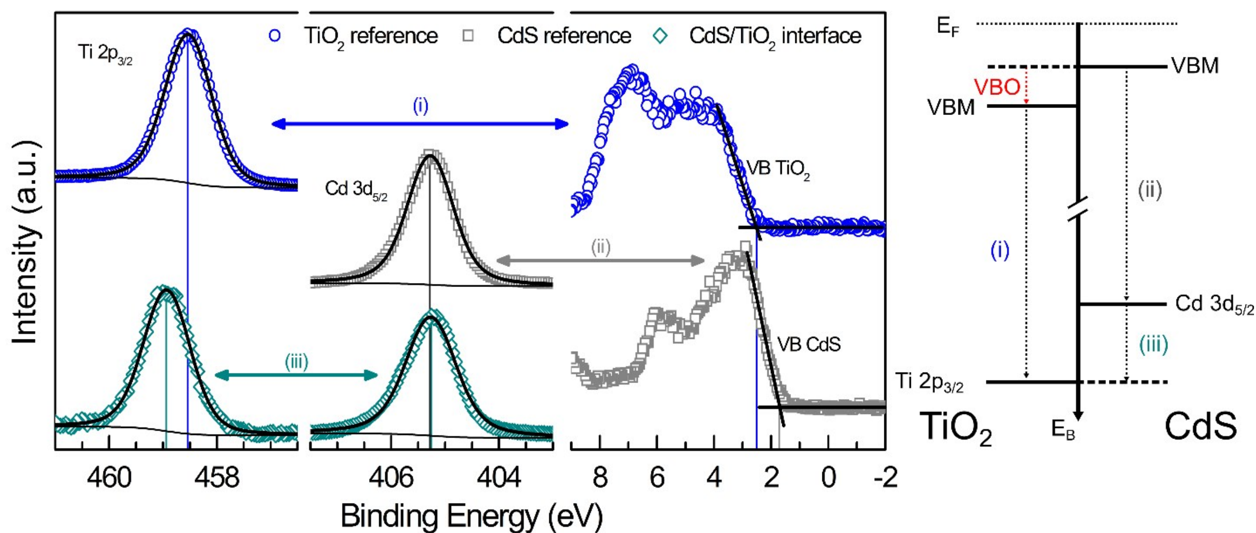


**Fig. S8:** Determination of valence band offset at CdS/$TiO_2$ interface using XPS. Valence band offset calculated based on binding energies of Ti2$p_{3/2}$ and Cd 3$d_{5/2}$ core levels and valence band maxima measured on $TiO_2$ reference, CdS reference, and CdS/$TiO_2$ interface.

**Table S1:** Binding energy values obtained by XPS from CdS reference, $TiO_2$ reference, and CdS/$TiO_2$ interface for calculation of valence and conduction band offsets.

| | **Binding Energy (eV)** | | |
|---|---|---|---|
| | **Ti 2$p_{3/2}$** | **Cd 3$d_{5/2}$** | **VBM** |
| **CdS reference** | x | 405.26 | 1.70 |
| **$TiO_2$ reference** | 458.53 | x | 2.52 |
| **CdS/$TiO_2$ interface** | 458.93 | 405.27 | x |

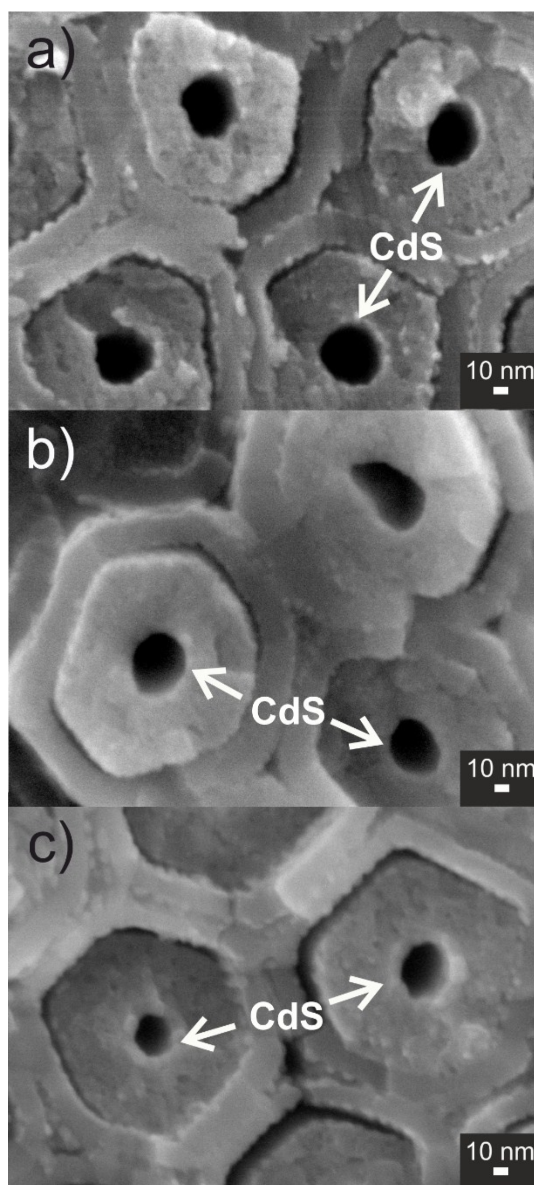


**Fig. S9.** SEM images of the bottom part of 20 μm thick $TiO_2$ nanotube layers with CdS coating of different thickness: a) 2.5 nm, b) 5 nm, and c) 10 nm.

References

1 E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, in *Precise Determination of the Valence-Band Edge in X-Ray Photoemission Spectra: Application to Measurement of Semiconductor Interface Potentials*, Phys. Rev. Lett., 1980, 44, pp. 1620–1623.