Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Material

Controlled Growth of Semiconductor Nanofilms within TiO_2 Nanotubes for Nanofilm Sensitized Solar Cells

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Description of experimental procedures:

Fabrication and transfer of the TiO_2 nanotubes. Prior to electrochemical anodization, the pure titanium foil (400 μm thick, 99.7% purity, Ding Ding Baoji Titanium Products Co., Ltd.) was ultrasonically cleaned in a sequence of acetone, ethanol and deionized water, and then dried with an air gun. TiO_2 nanotubes (NTs) were grown at 20 ^oC by an anodic oxidation of Ti foil at 60 V for 1.5h in an electrolyte mixture containing 0.5 wt % NH_4F (98%, Alfa) and 2.0 vol % deionized H_2O dissolved in ethylene glycol (Sinopharm Chemical Regent Co.,Ltd, AR). After anodization, the membrane was ultrasonically washed in methanol solution to remove the electrolytes, followed by annealing at 450 ℃ for 30min. The as-annealed film was anodized again in the same stock electrolyte for 1.5min with a bias of 60 V. After being rinsed with methanol, the secondary anodized Ti foil was then immersed in 0.5wt% $H_2C_2O_4$ solution for 2h to resolve the underlayer amorphous TiO_2. As a result, the TiO_2 NTs of the first layer were separated from the substrate to form a freestanding membrane. Large-area noncurling crystallized free-standing TiO_2 NTs then obtained.

The free-standing TiO_2 nanotube membranes were transferred onto the fluorine-doped tin oxide (FTO, 7Ω, Nippon Sheet Glass, Japan) substrates which coated a thin layer of the TiO_2 paste and dried for 2 h at 40 ℃. The resulting materials were then successively heated at 325 ℃ for 15 min, at 375 ℃ for 15 min, at 450 ℃ for 15 min and at 500 ℃ for 15 min in air. The TiO_2 nanotubes sticked strongly to the FTO substrate were thus obtained.

ALD growth of II-VI semiconductor nanofilms (ALD-NFs) and SILAR growth of QDs (SILAR-QDs) within TiO_2 NTs. The II-VI semiconductor nanofilms were deposited by atomic layer deposition in a Savannah S100 system (Cambridge Nanotech, Cambridge MA) at a pressure of ~ 1 Torr. Dimethyl cadmium (DMCd, 99.99%, NATA Optoelectronic Materials Co. Ltd.), diethyl zinc (DEZn, 99.99%, NATA Optoelectronic Materials Co. Ltd.), bis(trimethylsilyl)sulfide (BTMSS, 98.0%, Alfa Aesar) and bis(trimethylsilyl)selenide (BTMSSe, 97%, Gelest, Inc.) were used as precursors and sequentially introduced into the reactor using N_2 gas as a carrier gas (20 sccm). The reaction was carried out at 150 ℃ and the precursors were hold at 25 ^{o}C except BTMSSe (40^{o}C).

ALD growth of CdS. Typically, DMCd and BTMSS are sequentially introduced into the reaction chamber. Following the 50 ms DMCd or 300 ms BTMSS pulse, the precursors are confined inside the ALD reactor for 10 s (soak step) to ensure a complete exposure inside the TiO_2 nanotubes. The reaction chamber was then purged with N_2 gas for 10s.

The growth of CdSe or ZnS film was identical to the CdS except the pulse time of the prescursor (DMCd:50ms, DEZn:200ms, BTMSS:300ms, BTMSSe:250ms).

SILAR growth of QDs. In a controlled experiment, the staggered CdS/CdSe QDs were assembled onto the surface of TiO_2 NTs using a SILAR method, as described in a previous report.[1] The resulting composites were then used as the photoanodes of SILAR-QDSC device.

Assembly of solar cell devices. The semiconductor sensitized solar cells were assembled using the composites of the TiO_2 NTs functionalized by NFs and QDs as photoanodes, and Cu_2S as the counter electrodes, made according to the procedure reported by Hossain et al,[2] in a sandwiched fashion by inserting a hot-melt Surlyn film (Meltonix 1170-60, 60 μm, Solaronix SA) as spacer between the two electrodes. The inter electrode space was filled with an electrolyte composed of 1 M S, 1 M $Na_2S•9H_2O$ and 0.1M NaOH in Milli-Q ultrapure water.

Optical and electrical characterization. UV-Vis absorption spectra of all samples were recorded on a Varian Cary 5000 UV-vis spectrophotometer. Scanning electron microscopy (SEM) images were obtained from FEI Quanta 200F microscope operated at an accelerating voltage of 20 kV. Elemental analysis of the electrodes were conducted using an energy dispersive X-ray spectroscopy (EDS) analyzer (QUANTA 200FEG) attached to the FEI Quanta 200F SEM microscope. Transmission electron microscopy (TEM) and high resolution (HR) TEM were carried out with a FEI TECNAI F30 microscope operating at 300 kV. X-ray diffraction (XRD) analyses were performed at a scanning rate of 2 °/min on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation source (λ = 1.54 Å) operating at 40 kV and 200 mA. Photovoltaic measurement was recorded with a Newport Oriel class AAA solar simulator (model 92250A-1000) equipped with a class A 300 W xenon light source powered by a Newport power supply (model 69907). The power output of the lamp was calibrated to 1 Sun (AM1.5G, 100 mW/cm^2) using a certified Si reference cell (SRC−1000−TC−QZ, VLSI standard, S/N 10510-0031). The current-voltage characteristics of each cell were recorded with a Keithley digital source meter (model 2400). Photovoltaic performance was measured using a mask with an aperture area of 0.1256cm^2. The incident photon-to-current conversion efficiency (IPCE) was measured as a function of excitation wave-length using the incident light from a 150 W tungsten lamp (model CHTT 150W), which was focused through an QEM24-D 1/4m double monochromator (model DK242) onto the photovoltaic cell under measurement. Electrical impedance spectroscopy (EIS) experiments were carried out using an electro-chemical workstation (IM6 Zahner, Germany) with a frequency range of 40 mHz ~400 kHz and a potential modulation of 10 mV under dark conditions.

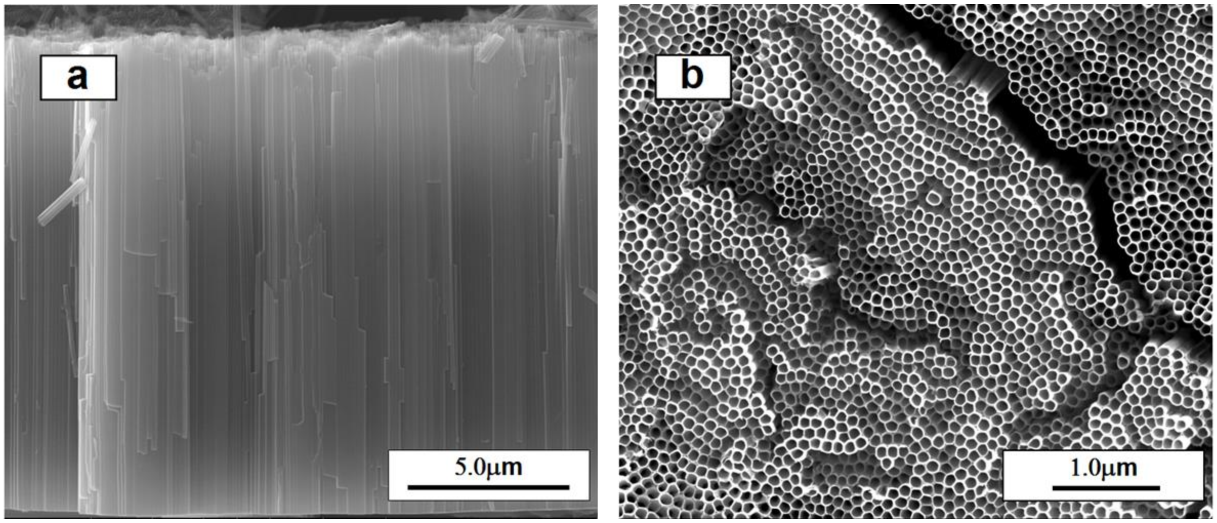
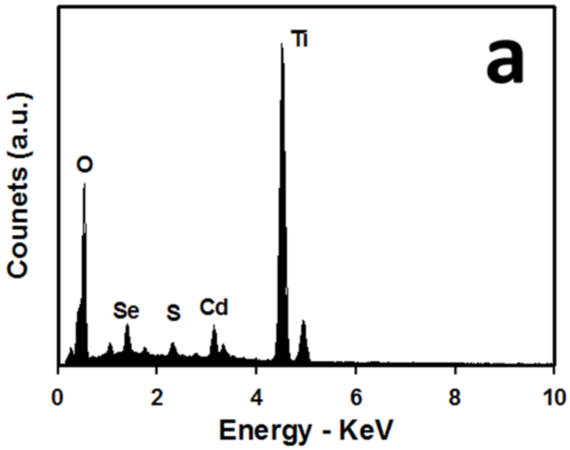


Figure S1. SEM images: (a) cross-section view, (b) top-view of the TiO_2 NTs. SEM analysis reveals that the TiO_2 film was composed of well-aligned nanotubes of about 15 μm in length and a uniform size distribution of ~100 nm in diameter.



b

Element	Wt%	At%
OK	48.86	75.85
SeL	3.16	1.00
SK	0.57	0.45
CdL	6.38	1.41
TiK	41.03	21.29

FigS2. (a) EDS, and (b) the corresponding element contents of the TiO_2 NTs subject to ALD of CdS/CdSe.

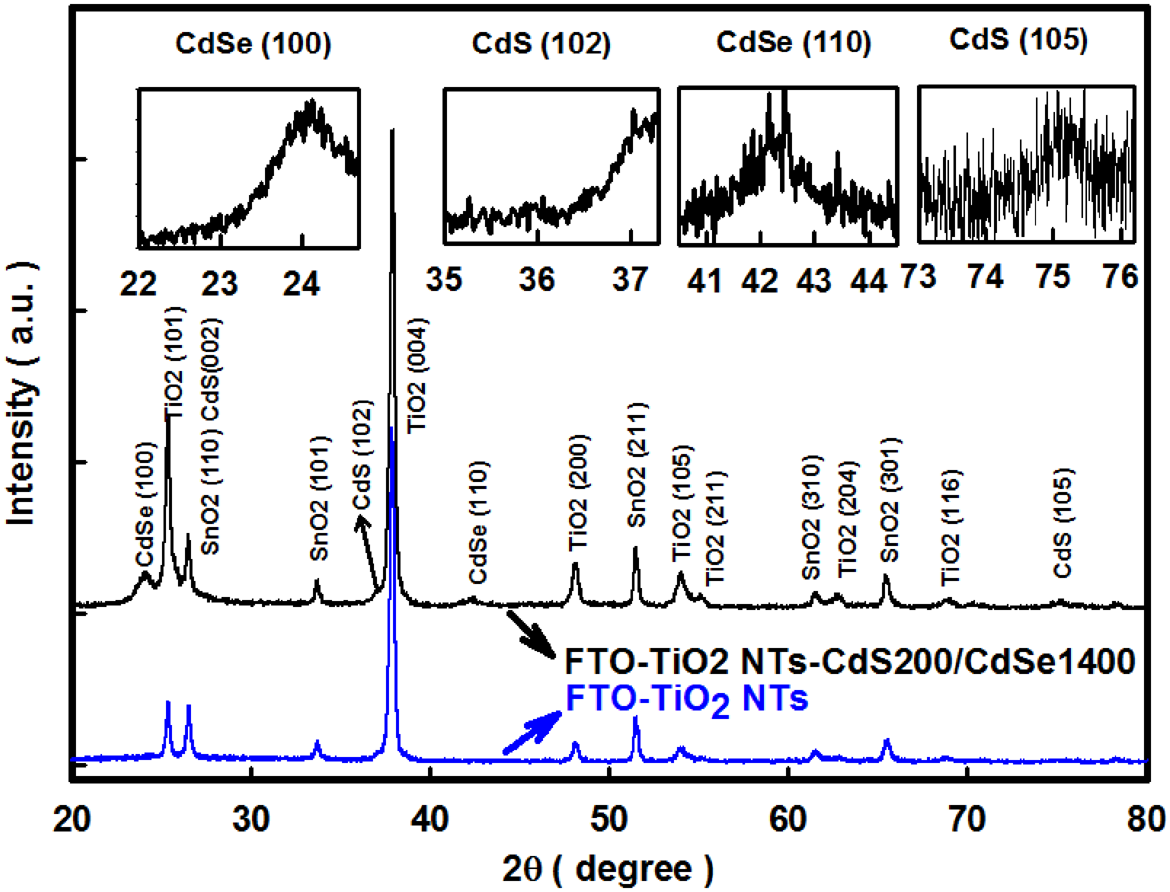
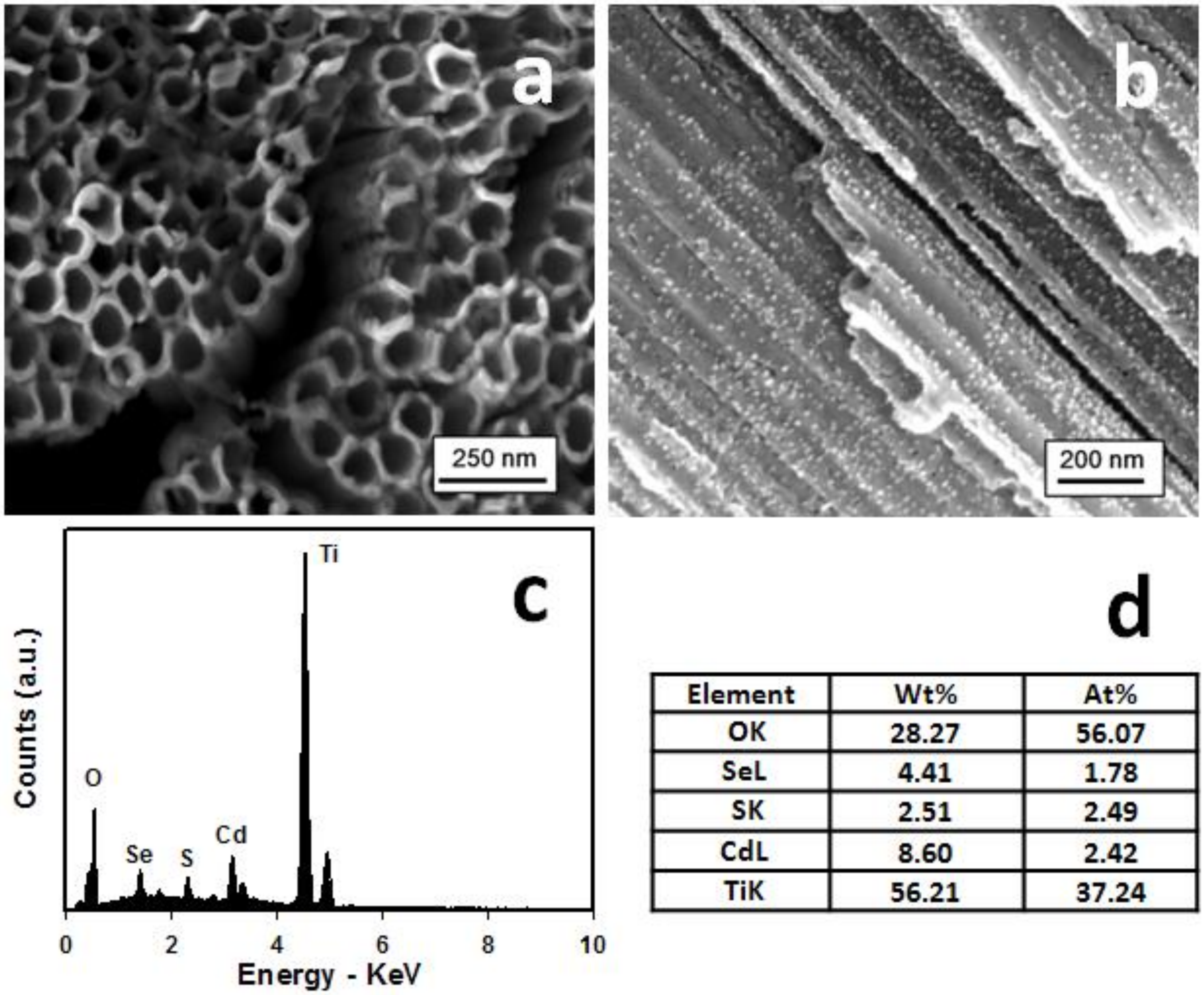


Figure S3. X-ray diffraction patterns of the FTO-TiO_2 NTs (a) before and (b) after ALD of CdS/CdSe deposition. The insets are the magnified XRD patterns of the ALD CdS/CdSe sample.

The peaks located at 36.62° and 75.34° are attributed to the hexagonal CdS (JCPDS No. 65-3414) and the peaks located at 23.90° and 41.97° to the hexagonal CdSe, (JCPDS No.08-0459).



Element	Wt%	At%
OK	28.27	56.07
SeL	4.41	1.78
SK	2.51	2.49
CdL	8.60	2.42
TiK	56.21	37.24

Figure S4. (a) top-view, (b) cross-section view SEM images of the TiO_2 NTs coated with CdS/CdSe QDs prepared by SILAR.

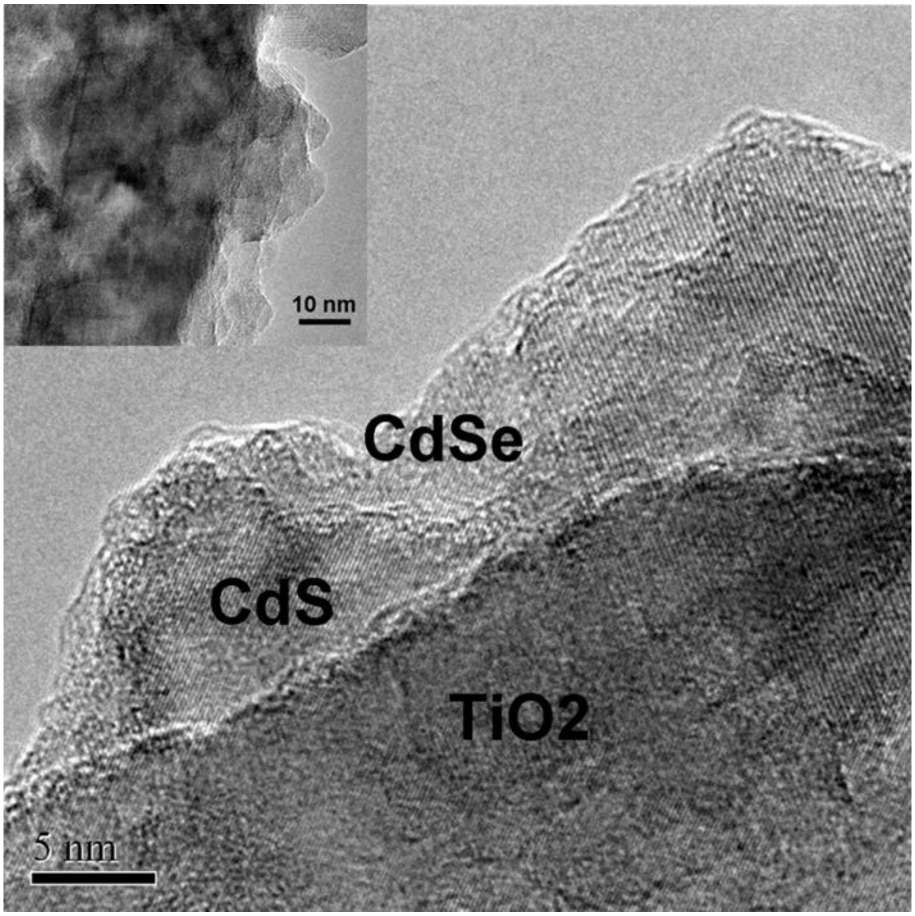


Figure S5. TEM (inset) and HRTEM images of the TiO_2 NTs coated with CdS/CdSe QDs prepared by SILAR.

The photoanode prepared by SILAR has a rough surface with aggregated CdS and CdSe nanocrystals.

Table S1. Photovoltaic Parameters of ALD-NFSC.

Sample	**V_{OC}/V**	**J_{SC}/mA cm^{-2}**	**FF(%)**	**PCE (%)**
B2.00	**0.43(±0.01)**	**6.66(±0.20)**	**50.70(±0.63)**	**1.43(±0.05)**
B1.97	**0.44(±0.01)**	**8.62(±0.11)**	**49.20(±0.54)**	**1.86(±0.01)**
B1.91	**0.44(±0.01)**	**9.80(±0.30)**	**51.08(±3.77)**	**2.20(±0.07)**
B1.81	**0.47(±0.01)**	**11.54(±0.07)**	**49.26(±2.05)**	**2.70(±0.15)**
B1.76	**0.41(±0.01)**	**11.75(±0.29)**	**42.83(±0.87)**	**2.06(±0.04)**

The standard deviation of the properties is based on the data of five cells.

Note: ZnS passivation was *not* applied for these samples.

Table S2. Photovoltaic Parameters of five cells based on the ALD-NFSC.

Sample	**V_{OC}/V**	**J_{SC}/mA cm^{-2}**	**FF(%)**	**PCE (%)**
Cell-1	0.51	17.83	50.81	4.62
Cell-2	0.52	17.59	49.83	4.56
Cell-3	0.51	17.72	49.00	4.42
Cell-4	0.50	17.44	49.88	4.35
Cell-5	0.51	16.30	50.81	4.22

Table S3. Photovoltaic Parameters of five cells based on the SILAR-QDSC.

Sample	**V_{OC}/V**	**J_{SC}/mA cm^{-2}**	**FF(%)**	**PCE (%)**
Cell-1	0.52	11.69	48.23	2.93
Cell-2	0.49	11.72	50.31	2.89
Cell-3	0.50	11.84	45.49	2.69
Cell-4	0.50	11.33	48.11	2.73
Cell-5	0.49	10.87	49.02	2.61

1. Lee, Y. L.; Lo, Y. S., *Adv. Func. Mater.* **2009,** *19*, 604.
2. Hossain, M. A.; Jennings, J. R.; Koh, Z. Y.; Wang, Q., *ACS Nano* **2011,** *5*, 3172.