Supporting Information

Cascade Quantum Dots Sensitized TiO_2 Nanorod Arrays for Solar Cells Application

Liang-Yih Chen,*[a] Zusing Yang,[b] Chia-Ying Chen,[b] Tsung-Yeh Ho,[a] Wei-Cyuan Jhu,[a] Po-Wei Liu[a] and Huan-Tsung Chang*[b]

*Corresponding author. sampras@mail.ntust.edu.tw; changht@ntu.edu.tw

Synthesis of TiO_2 nanorod arrays photoanode.

TiO_2 nanorod arrays were grown by using hydrothermal autoclave method, developed by Liu and Aydil. 12.5 mL of deionized water (DI-H_2O) and 15 mL HCl were mixed together at ambient condition. In order to confine the lateral surfaces of TiO_2 nanorods, saturated aqueous sodium chloride solution was added into the growth solution of 2.5 mL. After stirring for 5 min, 0.35 mL of titanium (IV) isopropoxide (TTIP, Sigma-Aldrich, 97 %) was dropped into the mixed solution. Two pieces of FTO glass substrates (F:SnO_2, 10 Ω/□, Nippon Sheet Glass Co. Ltd) were cleaned by using ultrasonic bath in detergent, DI-H_2O, and iso-propanol (IPA) for 30 min by each. After cleaning, TiO_2 nanocrystallines were coated on FTO substrates as seedlayer to enhance the vertical alignment situation and density of TiO_2 nanorods. The TiO_2 seedlayer was prepared by $TiCl_{4(aq)}$ of 0.2 M at 30 ^oC for 12 Hr. After seedlayer coating, the surface modified FTO substrates were placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 200 ^oC for 9-12 Hr in an electric oven. After synthesis, the autoclave was cooled to room temperature under ice bath, which took approximately 30 min. The

TiO_2 nanorod arrays samples were taken out, cleaned extensively with DI-H_2O several times and allowed to dry in ambient air. In order to increase the crystallinity of TiO_2 nanorod arrays, the as-synthesized samples were annealed at 500 ^oC for 30 min.

Decoration of CdS/CdSe/ZnS quantum dots.

TiO_2 NARs with an effective area of 0.25 cm^2 was immersed into a solution containing $Cd(NO_3)_2$ (0.5 M) for 5 min, rinsed with ultrapure H_2O, and dried with an air gun. They were then dipped for 5 min into a solution of 0.5 M Na_2S aqueous solution, rinsed with ultrapure H_2O, and dried with an air gun. The process was repeated up to three cycles. These as-prepared electrods are herein represented as CdS photoanodes.

The CdSe photoanodes were then dipped into a solution of $Cd(NO_3)_2$ (0.5 M) for 5 min at room temperature and then immersed into 0.08 M Na_2SeSO_3 aqueous solution at 50 °C for 30 min followed by rinsing with ultrapure H_2O and then dried with an air gun. The process was repeated up to six cycles. These as-prepared electrodes are represented henceforth as CdS/CdSe photoanodes. To reduce charge recombination between quantum dots (QDs) and electrolyte, the as-prepared CdS/CdSe photoanodes were immersed into $ZnSO_4$ solution (0.5 M) for 5 min, rinsed with ultrapure H_2O, and dried with an air gun. They were then dipped for 5 min into 0.5 M Na_2S aqueous solution, followed by rinsing with ultrapure H_2O and dried with an air gun. After the whole CdS/CdSe/ZnS decoration process, the QDs sensitized TiO_2 nanorod arrays photoanodes were post-annealed at 300 ^oC for 30 min in ambient air condition.

Preparation of CoS counter electrode.

$Co(NO_3)_2$ (0.232 g), thioacetamide (0.05 g) and PVP (0.014 g) were added to ultrapure H_2O (final volume 10 mL) in a glass bottle. The solution was subjected to sonication for at least 30 min. After addition of 0.5 N NaOH (2.4 mL) to the mixture, the resulting solution was then heated at 100 ^oC for 60 min. The resulting mixture (1 mL) was finally subjected to two centrifugation-wash cycles (6,000 rpm for 10 min; 0.5 mL ethanol as precipitant). The CoS nanocomposites were then dispersed in ethanol solution (1.0 mL) prior to the use for fabrication of counter electrodes. A drop-dry strategy was then used to deposit CoS onto FTO substrates (effective area of 0.25 cm^2). In brief, required drops (0.05 mL) of the dispersed solution (0.6 mg in 1 mL ethanol) were added onto the substrates. The substrates were then subjected to dry in an oven at 100 ^oC for 10 min to obtain CoS counter electrodes.

Energy dispersive X-ray spectroscopy (EDX, Oxford, equipped with Philips Tecnai G^2 F20 FEI-TEM)

The composition of the decoration CdS/CdSe/ZnS QDs was determined by EDX experiments, which were carried out in the TEM. Figure S1 shows the typical EDX spectra, in which spectrum is obtained from CdS/CdSe/ZnS-deposited TiO_2 NRAs. Cd, Zn, S and Se peaks are visible, which agrees with the fact that CdS/CdSe/ZnS QDs were formed during SILAR deposition process.

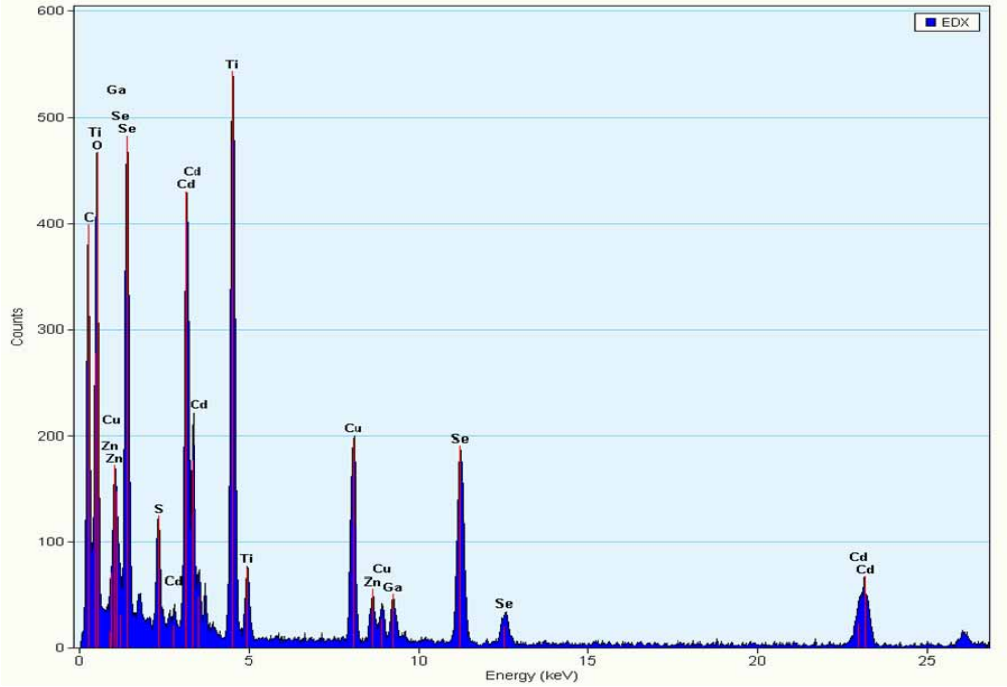

Figure S1. EDX spectrum of CdS/CdSe/ZnS QDs decoration on TiO_2 NRAs.

X-ray diffraction (XRD, BRUKER, D8 DISCOVER SSS Multi Function High Power X-Ray Diffractometer, source: Cu-Kα).

XRD analysis was carried out to determine the structure of the samples. Figure S2(a) is an experimental XRD peak profile taken from FTO substrate. Figure 2(b) is another experimental XRD profile taken from CdS/CdSe/ZnS decorated TiO_2 NRAs. Compared with Figure S2(a), additional peaks appear which may be attributed to cubic CdSe phase (JCPDS file No. 19-0191) and rutile TiO_2 phase (JCPDS file NO. 88-1074). The broad peaks associated with cubic CdSe phase suggest that

the sizes of the CdSe QDs are very small. In addition, the TiO_2 phase has higher peak intensity on (002) phase, indicating that as-synthesized TiO_2 NRAs has preferred orientation in the direction of [001]. The result is consistent with X-TEM observation.

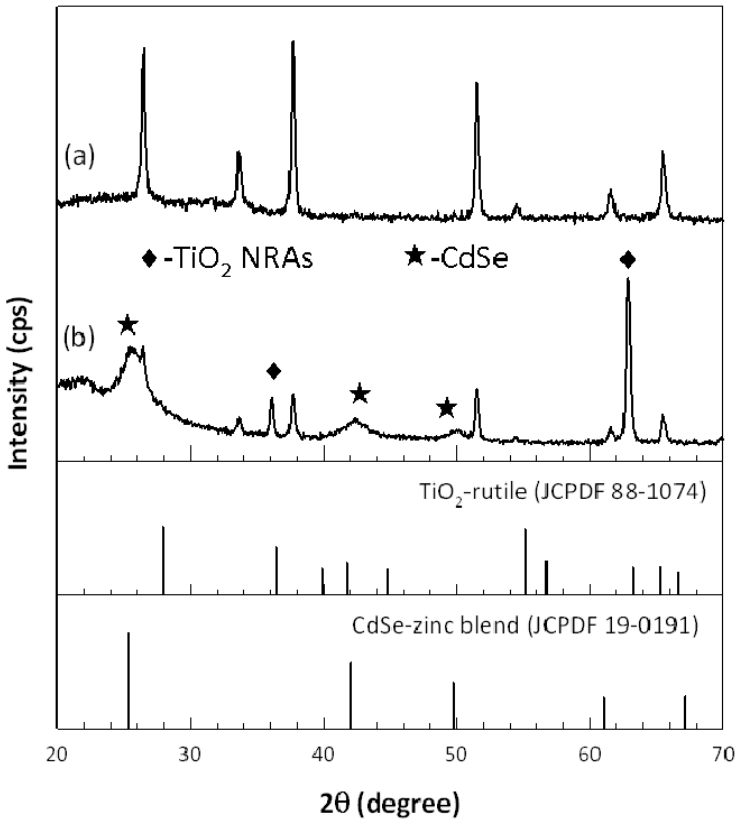

Figure S2. XRD analysis results taken from (a) FTO substrate, (b) CdS/CdSe/ZnS decorated TiO_2 NRAs.

Raman spectroscopy (Uni-Ram, Protrustech Corporation Limited, 532 nm diode laser excited Raman scattering).

An investigation of crystalline structure using Raman spectrum was carrier out for TiO_2 nanorods, as shown in Figure S3. Peaks in the Raman spectrum are assigned to B_{1g} (143 cm^{-1}), E_g (449 cm^{-1}), A_{1g} (610 cm^{-1}) and combination modes (235 cm^{-1}) of the rutile phase.

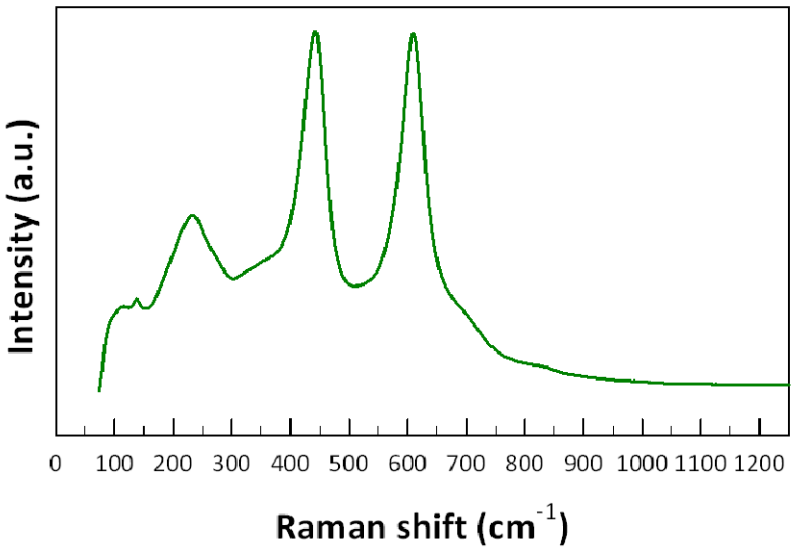

Figure S3. Raman spectrum of rutile phase TiO_2 NRAs

Fabrication of CdS/CdSe/ZnS Quantum Dots-Sensitized Solar Cells.

Solar cells were fabricated by assembling one of the CdS/CdSe/ZnS photoelectrodes, a CoS counter electrode, and a spacer of 30 μm thickness (SX 1170-25, Solaronix SA) in a sandwich configuration. The devices were annealed at 100 °C for 25 min. The electrolyte was a polysulfide solution: 2.0 M Na_2S (Acros, >90%), 0.5 M S (Acros), and 0.2 M KCl (Acros, >99%) in methanol/water (7:3, v/v). Two holes were then made in the counter electrode and a drop of the polysulfide electrolyte was put on the hole. The polysulfide was introduced into the cell via vacuum backfilling. Finally, the hole was sealed using a hot-melt film. In order to have a good electrical contact for the connection to the measurement setup, copper tapes were used on the edge of the FTO substrate outside of the cell. The QDs-sensitized solar cells properties of the TiO_2 NRAs photoanodes were measured as follows. The photocurrent density (J) and photovoltage (V) of the cell were measured with an active TiO_2 NRAs electrode having an area of 0.25 cm^2 under AM 1.5 G simulation sunlight which as produced by a 150 W Class A Solar Simulator (Model 92250A, Oriel)

with an illumination intensity of 100 mW/cm^2. The incident light intensity was calibration by a standard crystalline silicon solar cell (Oriel reference cell, 91550V). A power source meter (Keithley 2400) was used to measure the response of the solar cells. Before J-V measurement, masking is required to avoid optical artifacts such as light piping in the conducting glass used as top electrode, which inflate the photocurrent resulting an overestimating of the conversion efficiencies.[S1]

[S1] Seigo Ito, Md. Khaja Nazeeruddin, Paul Liski, Pascal Comte, Raphaël Charvet, Péter Péchy Marie Jirousek, Andreas Kay, Shaik M. Zakeeruddin and Michael Grätzel, *Prog. Photovolt: Res. Appl*. **2006**, *14*, 589-601.

The diameter distribution of TiO_2 nanorods and average spacing estimation.

From tilt view and cross-sectional images of scanning electron microscopy (Figure S4(a)~(b)), we can obtain the diameter distribution of TiO_2 nanorods, as shown in Figure S4(c). The average diameter of TiO_2 nanorods is 45 nm and the average spacing is between 80~100 nm in this work.

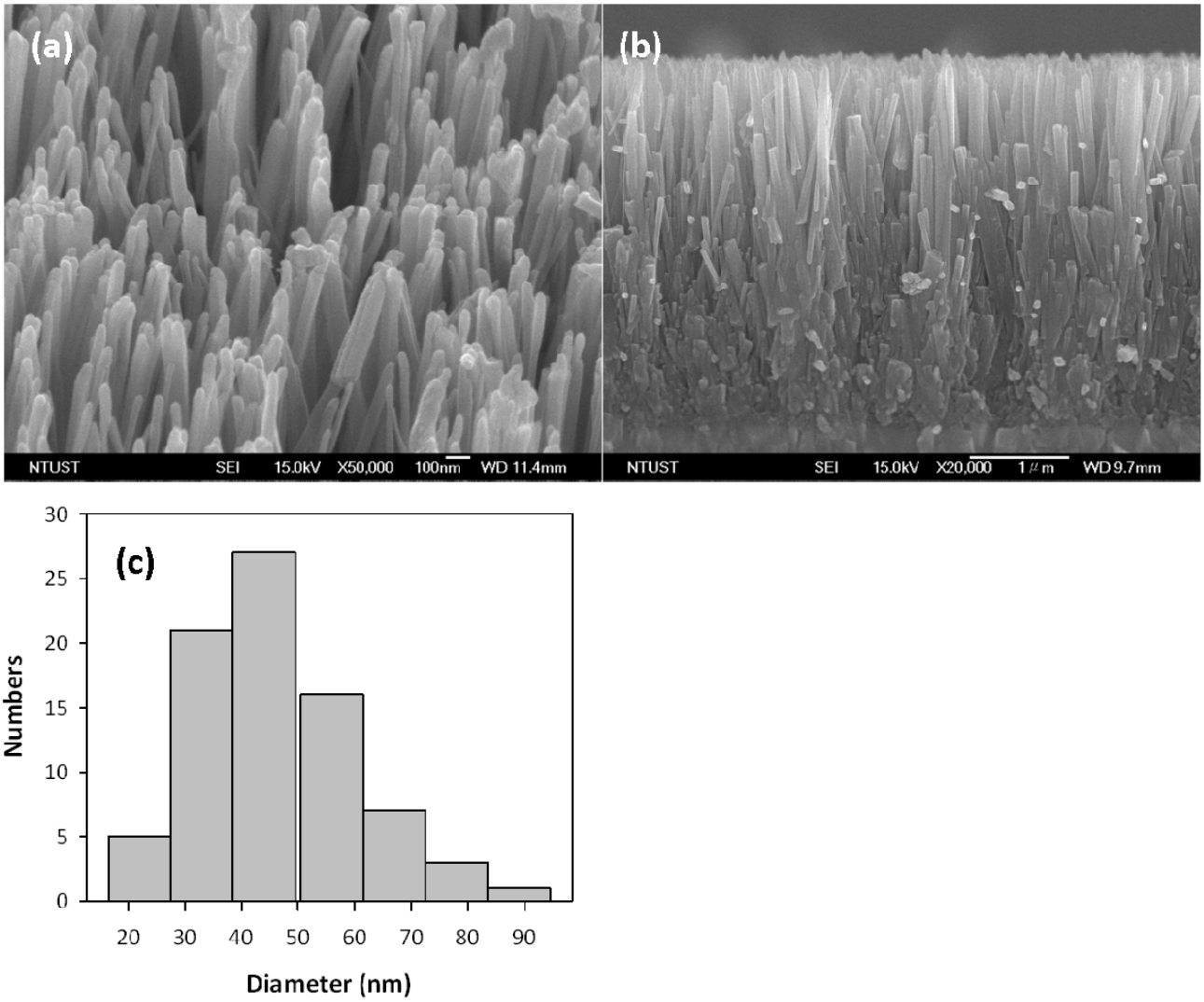

Figure S4. (a) tilt-view; (b) cross-sectional SEM images of TiO_2 nanorods. (c) The diameter distribution of TiO_2 nanorods.

High-resolution transmission electron microscopy images for CdS/CdSe/ZnS QDs sensitized TiO_2 photoanode. (Philips Tecnai G2 F20 FEI-TEM, 200 KV)

The interfacial structure between TiO_2 nanorod and cascade QDs was characterized by high-resolution transmission electron microscopy (HR-TEM). The following HR-TEM image, Figure S5, was taken at the interface between TiO_2 nanorod and cascade QDs**.**

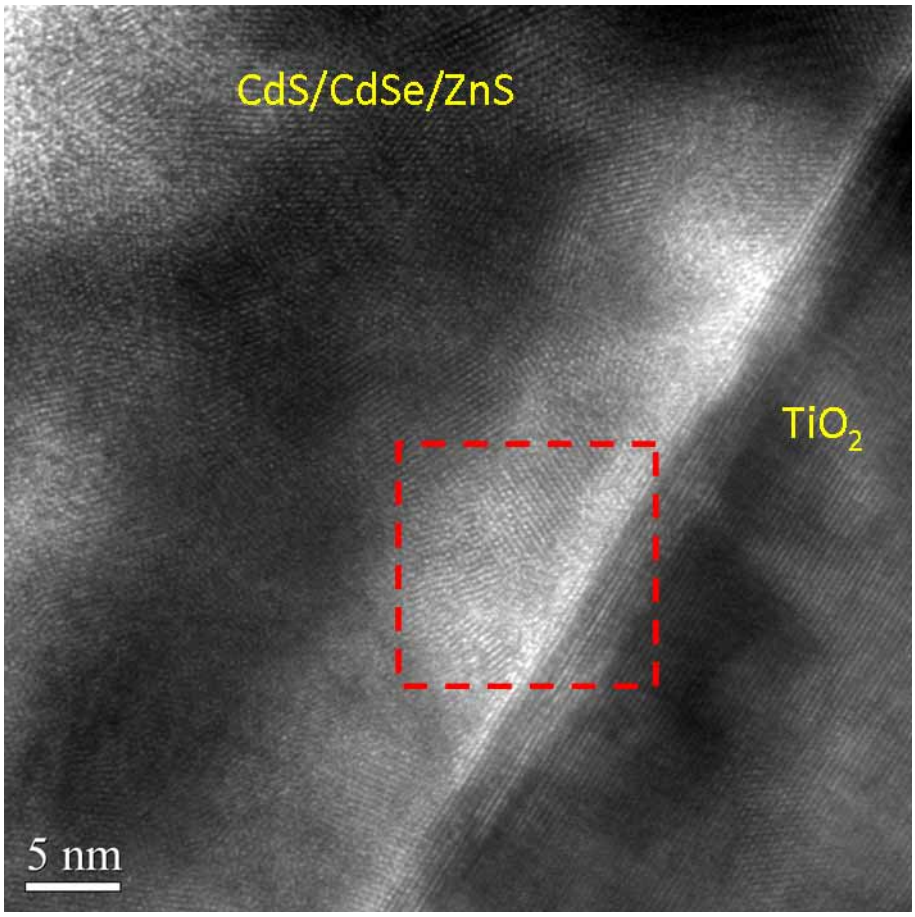

Figure S5. High-resolution TEM image of the interface between TiO_2 nanorod and cascade QDs.

In order to analyze the nanostructure furthermore, we enlarged the area (the square area) and shown in Figure S6(a). Herein, we draw a line profile to estimate the plane distance of (b) and (c). The line profile analyses are shown in Figure S6(b) and Figure S6(c). From analysis result, we can find the plane distance of (b) is about 3.62 Å, which is similar to the value of CdSe (111) (JCPDS file no.

19-0191, 3.51 Å). Otherwise, the plane distance of (c) is about 3.37 Å, which is similar to the value of CdS (111) (JCPDS file no. 80-0019, 3.35 Å)

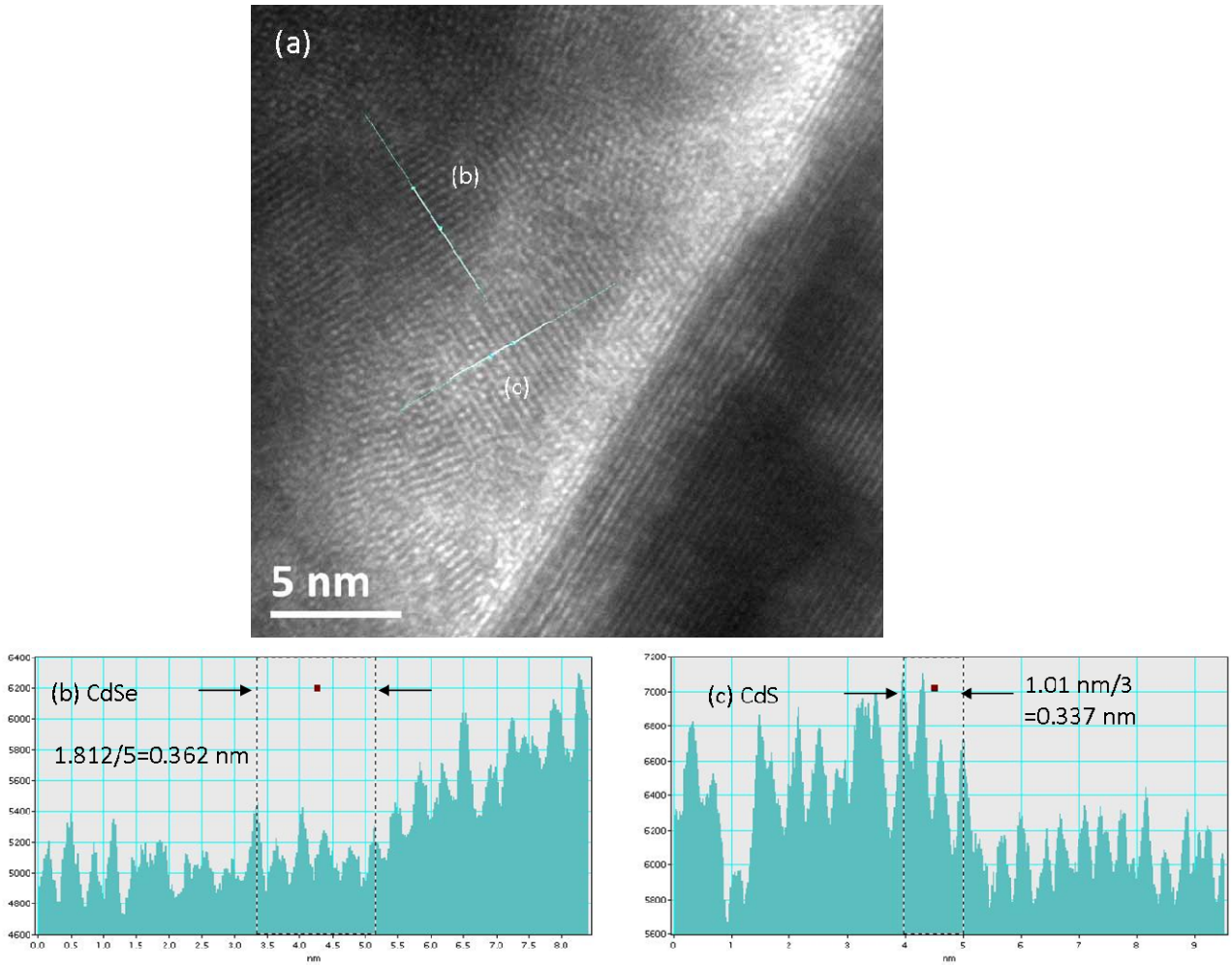

Figure S6. (a) Magnifying square area of Figure S4 to estimate the plane distances of QDs. The line profile of (b) and (c) are shown in the following figures, respectively.