

Supplementary Information

Novel nanowire array based highly efficient quantum dot sensitized solar cell

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1. Morphologies of ZnO nanowire (NW), CdS/ZnO NW, and CdSe/CdS/ZnO NW

The morphology changes and crystalline structures of the bare ZnO NW, CdS/ZnO NW, and CdSe/CdS/ZnO NW array were investigated. Figure S1a-c show the morphology changes of the ZnO NWs using a field-emission gun scanning electron microscope (SEM), and they provide some evidences of morphological changes such as significant surface roughening or diameter increases. TEM images provide more detailed information about modification of ZnO NW array. Figure S1d-f are conventional TEM images and figure S1g-i are high-resolution TEM images taken from the marked regions in figure S1d-f. Figure S1d and S1g are taken from bare ZnO NW, showing a single crystalline structure of ZnO NW. Shown in figure S1e and S1f indicate that the uniform CdS shell of thickness ~10 nm covered ZnO NW surface and CdSe nanoparticle (NP) (~ 6.5 nm) was deposited on the CdS/ZnO shell/core NW. High-resolution images of (h) the CdS/ZnO and (i) the CdSe/CdS interface regions indicate that the polycrystalline CdS shell and CdSe NPs were deposited on single crystalline ZnO NW.

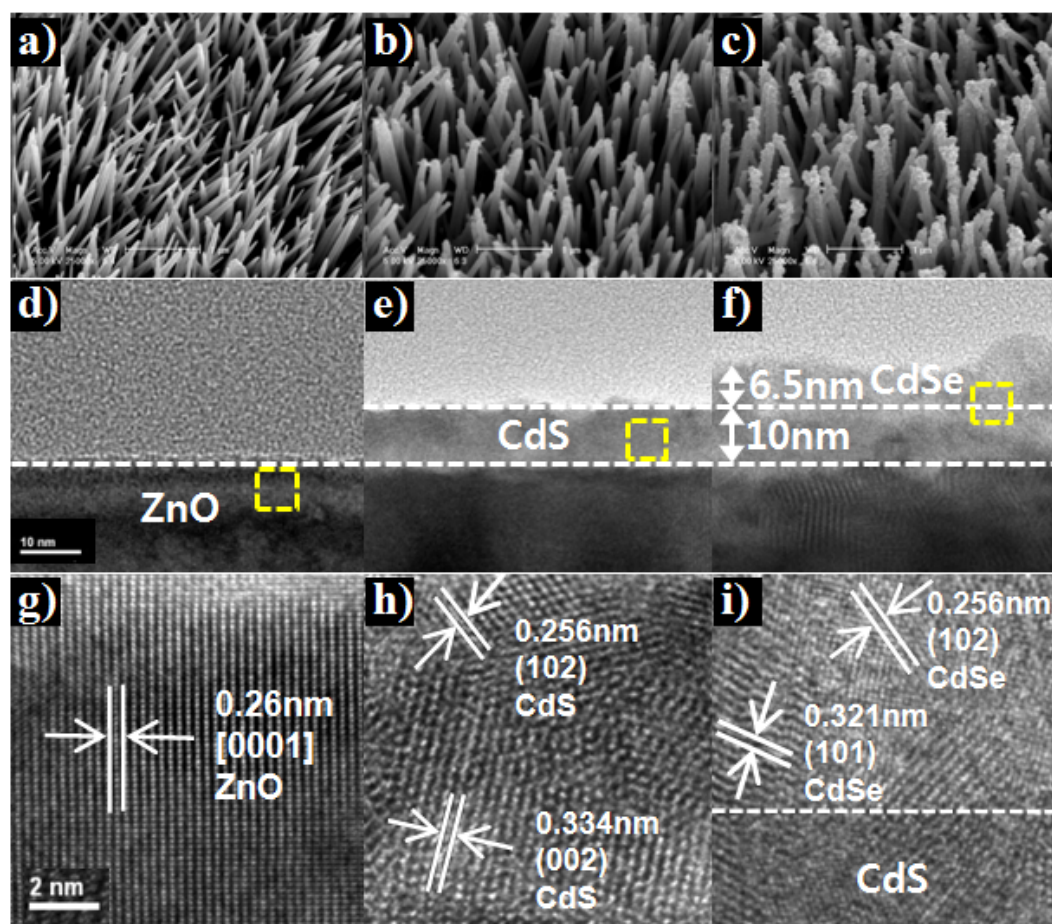
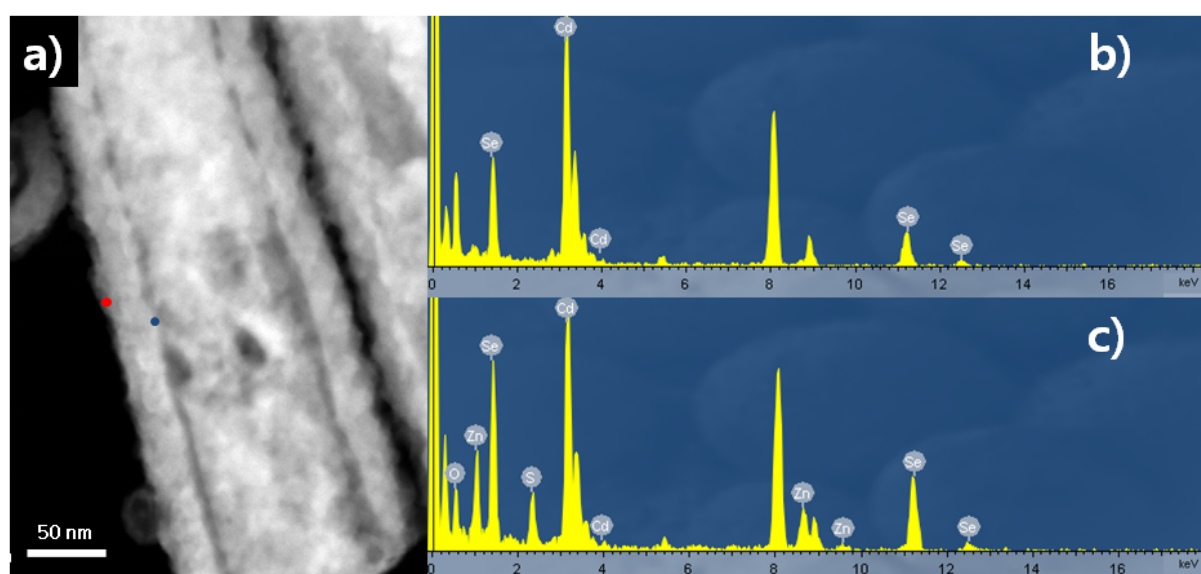


Figure S1. Tilted SEM images of (a) ZnO NW array, (b) CdS/ZnO NW, (c) CdSe/CdS/ZnO NW. (d-f) TEM images corresponding to (a-c), respectively. (g-h) High-resolution TEM images of the ZnO, the CdS/ZnO, and the CdSe/CdS/ZnO NW array taken from the marked square region in (d), (e), and (f), respectively.

2. EDS analysis

Energy dispersive spectra (EDS) experiments were carried out to determine the chemical composition of CdSe/CdS shell. Shown in figure S2 are high angle annular dark field (HAADF) scanning transmission electron microscope (STEM) image and selective area EDS analysis data. Only Cd and Se atoms were detected in the EDS of the outer part of the CdSe/CdS shell (red spot), whereas the inner part of the CdSe/CdS shell shows S and Zn and O in addition to Cd and Se (blue spot). It confirms that CdSe NPs are deposited on the CdS shell layer.



3. Additional TEM images of CdSe/CdS/ZnO NW

Additional TEM images of CdSe/CdS/ZnO NW are shown in figure S3. Figure S3 (a) and (b) shows that CdSe/CdS shell layer has rough surface due to the CdSe NP layer. Figure S3 (c) and (d) are HAADF STEM and bright field (BF) STEM images of a CdSe/CdS/ZnO NW, which clearly shows that there are contrast differences between the core and the shell layer, and the outer part of the CdSe/CdS shell consists of the CdSe NPs.

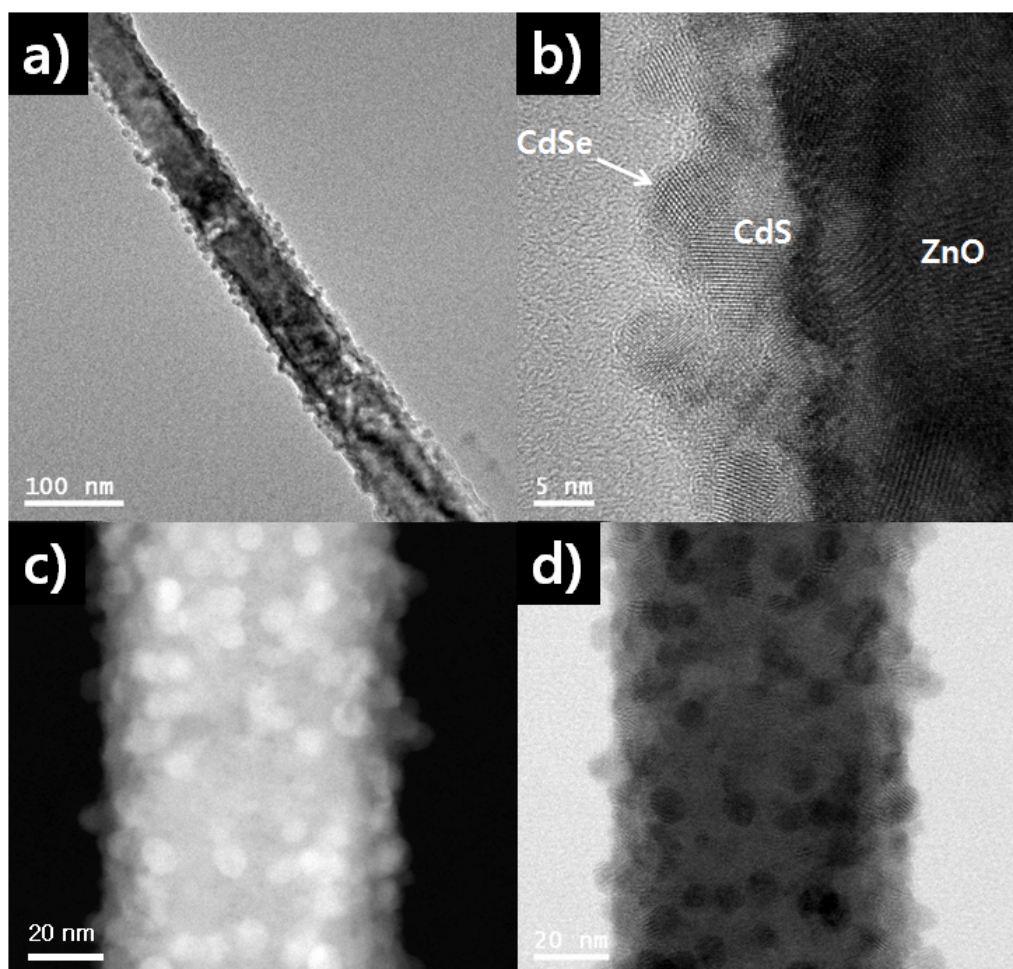


Figure S3. (a) TEM image of a single CdSe/CdS/ZnO NW; (b) HRTEM image of CdSe/CdS shell; (c) HAADF STEM image of a CdSe/CdS/ZnO NW; (d) bright field (BF) STEM image of a CdSe/CdS/ZnO NW.

4. Description of cell structure and fabrication procedure

As shown in figure S4, a sandwich structure cell was fabricated by assembling the nanowires photoanode with an Au-coated FTO counter electrode prepared by thermal evaporation. A 60 μm thick sealing material (SX-1170-60, Solaronix SA) was inserted between the photoanode and the counter electrode to glue them and make a space for the electrolyte. A polysulfide electrolyte composed of 0.5 M Na_2S , 2 M S, 0.2 M KCl in a methanol/water (7:3 by volume)¹ was injected through the hole on the counter electrode.

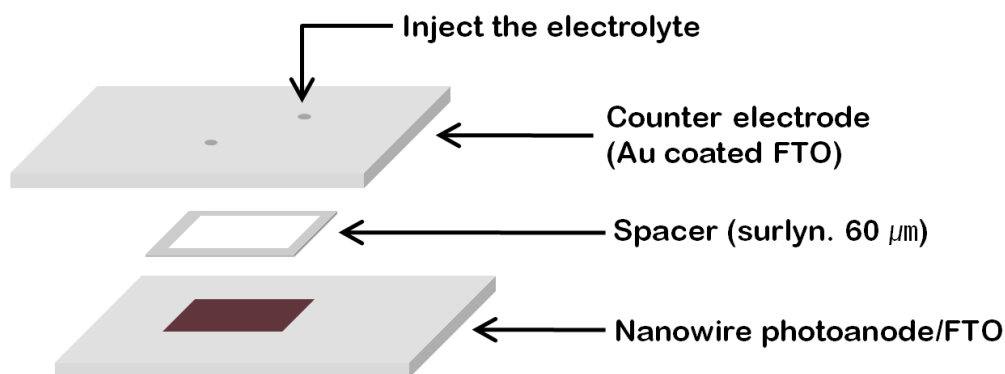


Figure S4. Schematic diagram of the cell fabrication.

5. Effects of electrolyte on the cell performances

Effects of electrolyte on the cell performances have been studied and the results are shown in figure S5 and tables S1, S2. Figure S5 (a) is the photocurrent density-voltage graph of the cells with two different electrolytes; polysulfide and polyiodide. Polyiodide is a conventionally used electrolyte in dye sensitized solar cell (DSSC). For comparison, we used the same 7.5 μm -long CdSe/CdS/ZnO NW arrays as photoanodes and Pt-coated FTO as counter electrodes. A cell with a polyiodide electrolyte showed slightly lower V_{oc} and remarkably lower J_{sc} than a cell with a polysulfide electrolyte. We believe this is because for quantum dot sensitized solar cells (QDSSCs), polyiodide electrolyte causes a decay of quantum dots (QDs), which makes a rapid decrease of the photocurrent generation. Thus, in case of QDSSCs, especially with cadmium chalcogenide QDs, polysulfide is a suitable electrolyte for stabilizing QDs. In our system, we applied an electrolyte solution composed of 0.5 M Na_2S , 2 M S, 0.2 M KCl in a methanol/water (7:3 by volume). KCl was added for enhancing the conductivity of the electrolyte. Figure S5 (b) is the photocurrent density-voltage curve of the cells with a polysulfide electrolyte with and without KCl. For comparison, we used the same 9 μm -long CdSe/CdS/ZnO NW arrays as photoanodes and Au-coated FTO as counter electrodes. When KCl was added in the electrolyte, J_{sc} and V_{oc} increased slightly but fill factor enhanced noticeably. We believe this is because of the increasing conductivity of the electrolyte with addition of KCl.

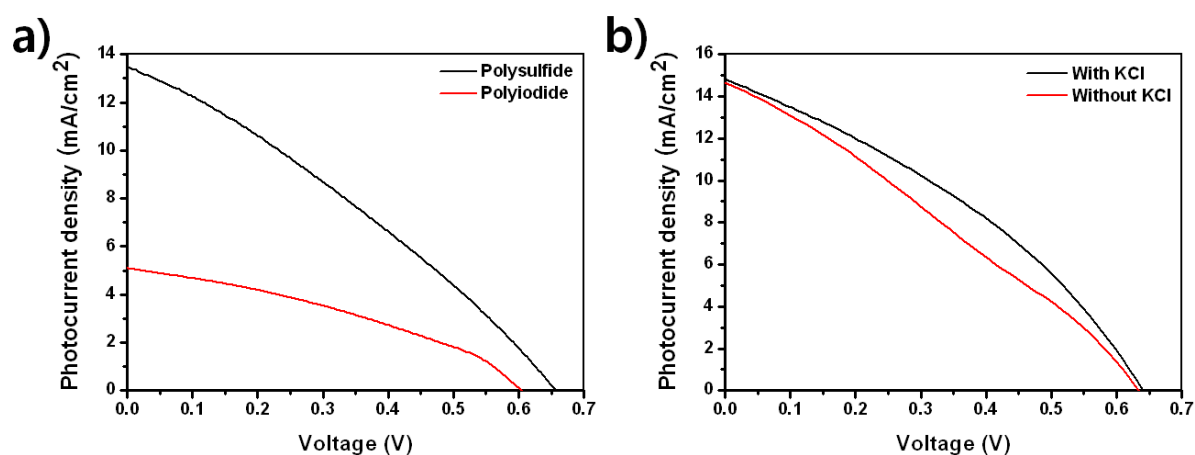


Figure S5. (a) Photocurrent density-voltage curves of the CdSe/CdS/ZnO NWs cells with two different electrolytes; polysulfide (black line) and polyiodide (red line). (b) Photocurrent density-voltage curves of the CdSe/CdS/ZnO NWs cells with (black line) and without (red line) KCl in the polysulfide electrolyte.

Table S1. Effects of electrolytes on the cell performances.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)
Polysulfide	0.657	13.5	0.30	2.66
Polyiodide	0.606	5.1	0.36	1.11

Table S2. Effects of the additive of electrolytes on the cell performances.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)
With KCl	0.638	14.8	0.36	3.40
Without KCl	0.638	14.6	0.28	2.61

6. Effects of ZnO NWs length on the cell performances

The effects of the length of ZnO NW arrays on the QDSSC performances were investigated. Three different samples were tested for 7.5, 9, and 16 μm -long CdSe/CdS/ZnO NW arrays. The results were shown in Figure S6 and Table S3. With increased NWs length, photocurrent generation was enhanced and the cell conversion efficiency increased. Longer NWs provide higher surface area, on which amounts of QDs deposited increased and consequently the light absorption is enhanced. However, further increase of the NW length showed a decrease of the cell efficiency, which is thought to be due to the decreased charge collection efficiency through a long charge pathway.

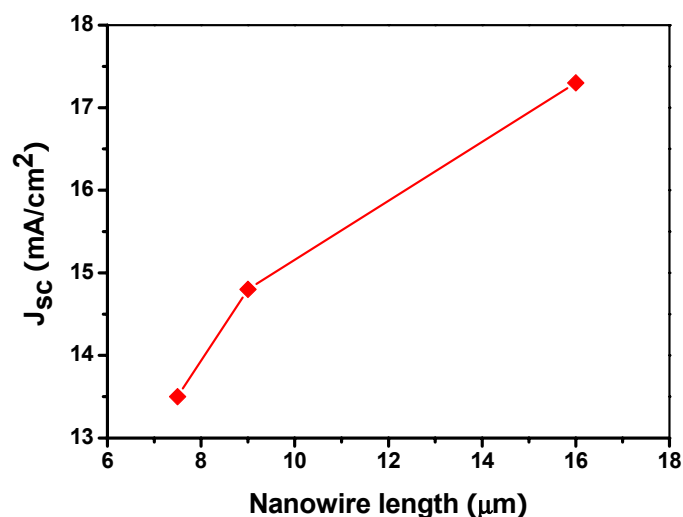


Figure S6. Graph plotting nanowire length vs J_{sc} .

Table S3. Effects of ZnO NWs length on the cell performances.

NW length (μm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	$\eta(\%)$
7.5	0.657	13.5	0.30	2.66
9	0.638	14.8	0.36	3.40
16	0.627	17.3	0.38	4.12

<Reference>

1. Y. L. Lee, C. H. Chang, *J. Power Sources*, 2008, **185**, 584.