Water Splitting

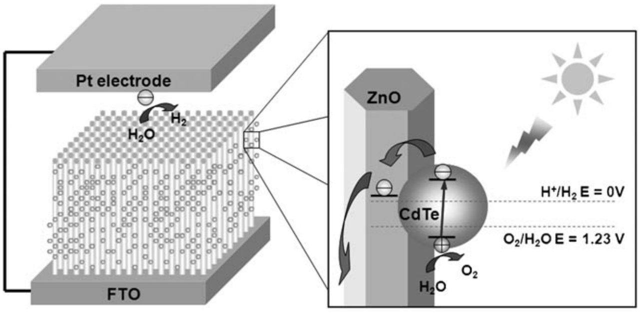
DOI: 10.1002/anie.201001827

Quantum Dot Monolayer Sensitized ZnO Nanowire-Array Photoelectrodes: True Efficiency for Water Splitting**

Hao Ming Chen, Chih Kai Chen, Yu-Chuan Chang, Chi-Wen Tsai, Ru-Shi Liu, Shu-Fen Hu, Wen-Sheng Chang, and Kuei-Hsien Chen*

Increasing demand for clean energy has motivated considerable effort to exploit the properties of various materials in photovoltaics and related solar-harvesting devices.[1] Splitting of water by sunlight to generate hydrogen is one of the forms of energy production with the most potential. Metal oxides such as TiO_2, ZnO, and WO_3 with various morphologies have been investigated for use in splitting water.[2–6] However, most of these metal oxides have large band gaps, which limit light absorption in the visible region and overall efficiency. To reduce the band gaps of nanostructured metal oxides, doping and utilization of transition metals, carbon, or nitrogen have been investigated.[7–9] One possibility is the use of semiconductor nanocrystals, known as quantum dots (QDs), as an alternative to photosensitive dyes. Quantum dots generally offer various significant advantages over dyes.[10] It was recently established that QDs generate multiple electron–hole pairs per photon, improving device efficiency.[11] Quantum dot sensitized nanostructures are widely studied for use in solar cells.[12,13] However, little work has been done on metal oxide and semiconductor QD-based composite structures for use in water-splitting nanodevices.

To elucidate this fundamental issue, we examined a combination of CdTe QDs and ZnO nanowires for splitting water photoelectrochemically (Scheme 1). One-dimensional nanostructures offer the additional potential advantage of improved charge transport over zero-dimensional nanostructures such as nanocrystals.[6] Additionally, the typical electron mobility in ZnO is 10–100 times higher than that in TiO_2, so the electrical resistance is lower and the electron-transfer efficiency higher.[14] However, since the overall water-splitting reaction is tough, sacrificial reagents are commonly adopted to evaluate the photocatalytic activity for water splitting. When the photocatalytic reaction is carried out in an aqueous solution that contains a reductant, electron donors, or hole scavengers such as sulfide ions or selenium ions, photogenerated holes irreversibly oxidize the reductant rather than the water. Employment of CdTe QDs in water splitting system has major advantages. CdTe with a more favorable conduction band energy ($E_{CB} = -1.0$ V vs. NHE) can inject electrons into ZnO faster than CdSe ($E_{CB} = -0.6$ V vs. NHE). In addition, monolayer deposition of CdTe QDs on the surface of ZnO nanowires would further improve the stability in electrochemical reaction, by avoiding anodic decomposition/corrosion of CdTe and thus enhancing the overall water-splitting performance. During the photoirradiation of CdTe, two reactions can be expected to dominate after initial charge separation [Eqs. (1) and (2)].[15]



Scheme 1. Sketch showing ZnO nanowires decorated with CdTe QDs and charge-transfer processes.

$$\text{Anodic decomposition}:\ \mathrm{CdTe}\ (\mathrm{e}+\mathrm{h}) \rightarrow \mathrm{Cd}^0 + \mathrm{Te}^0 \quad (1)$$

$$\text{Anodic corrosion}:\ \mathrm{CdTe}\ (\mathrm{h}) \rightarrow \mathrm{Cd}^{2+} + \mathrm{Te}^{\bullet -} \quad (2)$$

Monolayer deposition of QDs can facilitate transfer from CdTe to ZnO and improve QD stability, so that the efficiency in the overall water-splitting reaction can be exactly measured in aqueous phase without sacrificial reagents.[16,17] To the best of our knowledge, this is the first demonstration of sensitizing ZnO nanowires with CdX (X = S, Se, Te) QDs in a non-sacrificial electrolyte.

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[*] Dr. H. M. Chen, C. K. Chen, Y.-C. Chang, C.-W. Tsai, Prof. Dr. R. S. Liu
Department of Chemistry, National Taiwan University
Taipei, Taiwan 106 (Taiwan)
Fax: (+886) 2369-3121
E-mail: rsliu@ntu.edu.tw
Prof. Dr. S. F. Hu
Department of Physics, National Taiwan Normal University
Taipei, Taiwan 106 (Taiwan)
Dr. W.-S. Chang
Energy & Environment Research Laboratories
Industrial Technology Research Institute
Hsinchu, Taiwan 300 (Taiwan)
Prof. Dr. K. H. Chen
Institute of Atomic & Molecular Sciences Academia Sinica
Taipei, Taiwan 106 (Taiwan)

[**] The authors gratefully acknowledge the financial support of the Institute of Atomic & Molecular Sciences Academia Sinica (Contract No. AS-98-TP-A05), National Science Council of Taiwan (Contract Nos. NSC 97-2112M-003-007-MY3 and NSC 97-2113M-002-012-MY3), Bureau of Energy, Ministry of Economic Affairs (Contract No. MOEA 8455DC6100) and Petroleum Foundation, Taiwan.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201001827.

The photogenerated electrons and holes cause redox reactions similarly to electrolysis. To obtain our nanodevice, we grew ZnO nanowires on F-doped SnO_2 (FTO) substrates using a modified hydrothermal method.[18] Scanning electron microscopy (SEM) images of pristine ZnO nanowires (Figure 1) reveal high surface density (ca. 4×10^6 wires$\,cm^{-2}$). Figure 1b shows a cross-sectional image of ZnO nanowires, which have lengths of about 4 μm and diameters of about 150 nm.

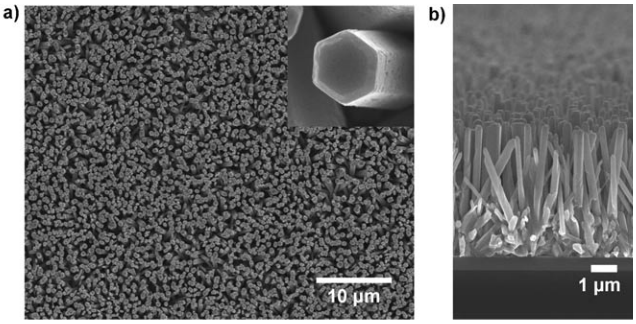

Figure 1. a) SEM image of ZnO nanowires on FTO substrate. b) Cross-sectional image of ZnO nanowires.

To obtain the exact efficiency for the water-splitting reaction under light illumination, we conducted all photoelectrochemical (PEC) studies in a 0.5 M aqueous solution of Na_2SO_4 with a pH of 6.8 without sacrificial reagents (e.g., Na_2S, K_2SO_3). Figure 2a shows a set of linear-sweep voltammograms recorded on pristine ZnO nanowires and ZnO nanowires loaded with CdTe QDs after various deposition times under illumination of 100 mW$\,cm^{-2}$. A dark scan from −0.5 to +1.1 V showed a small current in the range of 10^{-6} A$\,cm^{-2}$. The photocurrent increased drastically with deposition time up to 24 h. ZnO nanowires loaded with QDs (24 h) showed a pronounced photocurrent starting at about 0 V, which increased to 2.0 mA$\,cm^{-2}$ at +1.0 V under illumination. In comparison to pristine ZnO nanowires, photocurrent density of QD-loaded ZnO nanowires (24 h) was about three times greater (ca. 2.0 mA$\,cm^{-2}$) than that of pristine ZnO nanowires of similar thickness (ca. 0.7 mA$\,cm^{-2}$) at 1.0 V, which suggested that nanowires loaded with CdTe QDs can harvest solar light more effectively than unloaded nanowires. To quantitatively address the photoactivity of QD-sensitized nanoanodes, percentage efficiency η is calculated by an equation in which the contribution due to applied potential is subtracted from the total efficiency.[7,8] The plot of efficiency versus deposition time (Figure 2b) showed a maximum photoconversion efficiency of 1.83%, while a maximum of $\eta\approx0.66\%$ was observed for the reference ZnO nanowires sample under similar conditions of illumination. Thus, the efficiency of the QD-loaded ZnO nanowires was enhanced by a factor of three compared to pristine ZnO nanowires. Unexpectedly, the efficiency decreased drastically with further increasing deposition time up to 168 h. Further analyses were performed to elucidate this effect (see below).

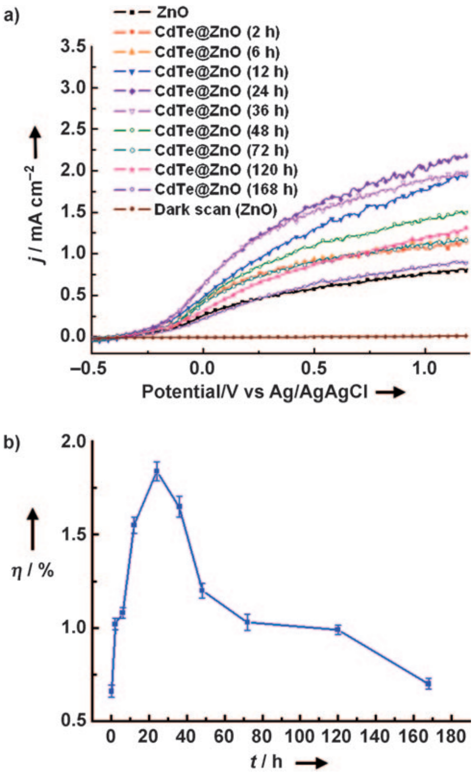

Figure 2. a) Linear-sweep voltammograms from pristine ZnO nanowires, ZnO nanowires loaded with CdTe QDs at various deposition times, and dark scan. b) Photoconversion efficiency of the pristine ZnO nanowires and ZnO nanowires loaded with CdTe QDs for various deposition times.

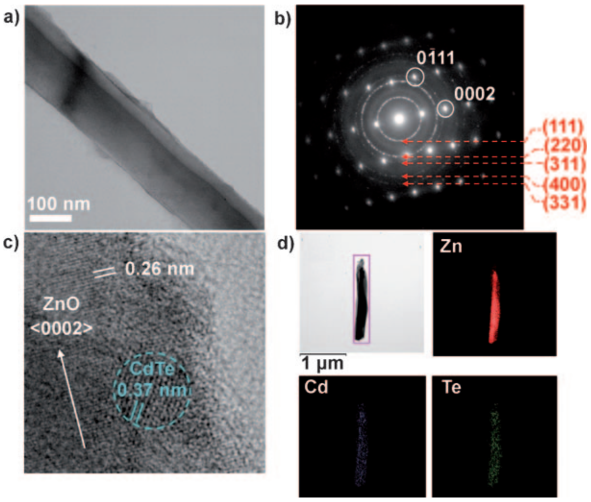

Figure 3. a) TEM image of ZnO nanowires decorated with CdTe QDs. b) Corresponding electron diffraction pattern of a). c) HRTEM image of a ZnO nanowire decorated with CdTe QDs. d) Elemental mapping images of Zn, Cd, and Te.

A transmission electron microscopy (TEM) image (Figure 3a) of ZnO nanowires decorated with an ensemble of CdTe QDs (24 h) reveals that they are uniform in diameter (ca. 150 nm). The selected-area electron diffraction pattern (Figure 3b) is characteristic of the two-component crystalline nature. The set of spots can be indexed to the ZnO wurtzite structure along the $[2\bar{1}\bar{1}0]$ zone axis, which shows single-crystalline nature (white circles). The set of rings reveals a typical face-centered-cubic polycrystalline structure corresponding to bulk CdTe, and probably associated with the large amount of CdTe QDs on the surface of the ZnO nanowires. These results indicate that QDs were successfully attached to the surface of ZnO nanowires. The high-resolution TEM image of the edge of a nanowire (Figure 3c) provides more compelling evidence that QDs are attached to the nanowire surface. An abrupt transition is observed between the (0002) lattice planes of the ZnO nanowires and the (111) lattice planes of the CdTe QD. The lattice spacing between the (111) planes of 0.37 nm is also in agreement with that of CdTe bulk crystal (JCPDS no. 89-3053). Figure 3d shows a TEM image of a CdTe/ZnO nanowires heterostructure and corresponding elemental mapping of Zn, Cd, and Te. Zinc is uniformly distributed along the nanowires, while Cd and Te are found on the spots corresponding to the position of nanoparticles.

High-resolution TEM images of ZnO nanowires after a deposition time of 120 h are shown in Figure 4. After sensitization with CdTe QDs, HRTEM images verified that individual ZnO nanowires are covered with nanoparticle aggregates of thickness about 15–30 nm. After longer deposition times, large amounts of CdTe nanocrystals aggregated and became a continuous film which covered upon the surface of the ZnO nanowires. The film aggregates consisted of a number of QDs with average diameter of 3–8 nm, and this specific structure resulted in degradation of photocurrent response owing to anodic decomposition and corrosion. After incident photons are absorbed by the QDs, photoexcited electron–hole pairs are confined within the nanocrystal. Photogenerated electron and hole may transfer to the neighboring CdTe nanocrystals, which may lead to the occurrence of anodic decomposition and corrosion. Thus, it was found that the color of the photoanodes (120 h) became gray after long-term photoirradiation because of anodic decomposition and corrosion.

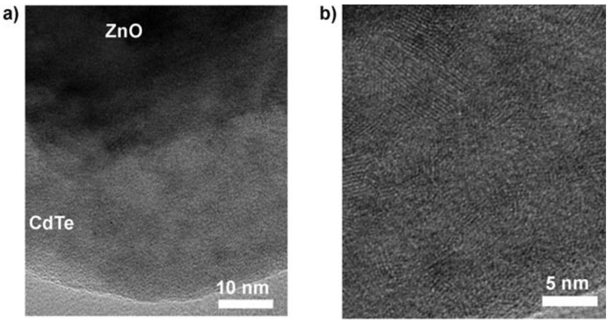

Figure 4. HRTEM images of ZnO nanowires after a deposition time of 120 h.

To examine the photoresponse of this structure over time, the *I–t* curve of ZnO nanowires loaded with CdTe QDs (24 h) at $+0.5$ V was measured (Figure 5a). Upon illumination with light, a spike in the photoresponse was observed owing to the transient effect in power excitation, and the photocurrent then quickly returned to a steady state.[19,20] This result further confirm that photogenerated electrons are quickly transported from CdTe QDs to ZnO nanowires. In the long term, the chemical stability of this structure could be addressed by depositing a monolayer on the ZnO nanowires. Figure 5b shows that the photocurrent response was almost identical over 50 cycles and thus demonstrates very good stability of this structure. The achieved high efficiency and stability can be attributed to two major improvement. First, monolayer deposition of CdTe QDs allows fast and efficient transfer of the photogenerated electrons from CdTe to the ZnO nanowires, which leads to much reduced anodic decomposition/corrosion and greatly improved stability of photodevices. Second, the QDs afford multiple excitons from single photon.

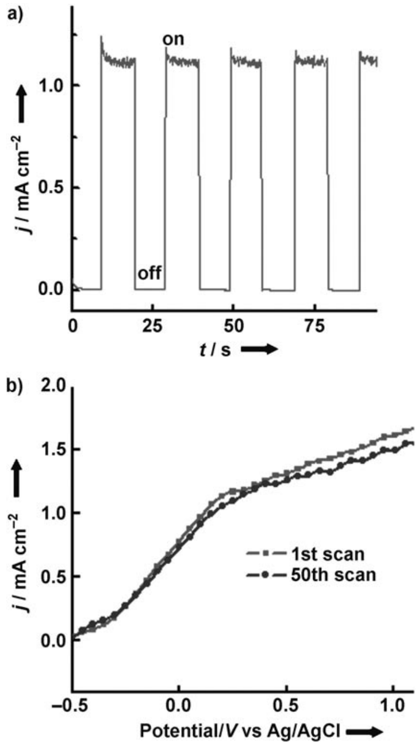

Figure 5. a) Amperometric *I–t* curves of the ZnO nanowires with/without CdTe QDs at 100 $\mathrm{mW\,cm^{-2}}$ with on/off cycles. b) Stability of PEC performance after 50 scans.

To further quantify the PEC performance, measurements of incident photon to current conversion efficiency (IPCE) were made to study the photoresponse of pristine and CdTe-sensitized ZnO nanowires as a function of incident light wavelength (Figure 6). The IPCE was determined at zero bias voltage by Equation (3)[21]

$$\mathrm{IPCE} = (1240\,I)/(\lambda\,J_{\mathrm{light}}) \tag{3}$$

where I is the photocurrent density, λ the incident light wavelength, and J_{light} the measured irradiance. Pristine ZnO had strong photoresponse in the near-UV region but little photoresponse above 400 nm. However, the sensitized samples show substantial photoactivity in the visible-light region from 400 to 530 nm in addition to strong photoresponse in the near-UV. The IPCE of QD sensitized photoanode shows a clearly resolved peak at 480 nm which aligns exactly with the position of the absorption of CdTe (see UV absorption spectra in Supporting Information). Broadening of the peak at about

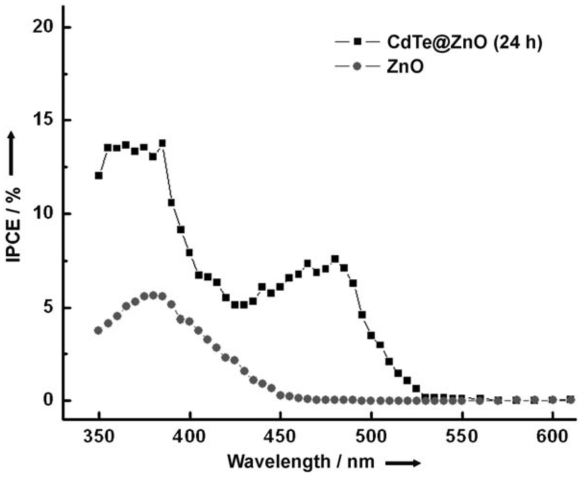

Figure 6. Measured IPCE spectra of pristine ZnO nanowires and ZnO nanowires loaded with CdTe QDs (24 h) in the region of 350–600 nm at a potential of 0 V versus Ag/AgCl.

480 nm can be attributed to photocorrosion of the CdTe QDs after repeated PEC measurements.[9] These results clearly confirm that CdTe sensitization improves visible-light absorption, and photogenerated electrons in CdTe QD can be transferred to ZnO nanowires, which significantly increases the IPCE throughout the entire visible region for the CdTe@ZnO photoanode.

In summary, we have demonstrated a quantum dot sensitized nanowire photodevice based on photosensitization of ZnO nanowires with CdTe QDs. This is the first demonstration of sensitizing ZnO nanowires with CdX QDs in a nonsacrificial electrolyte. The significant photocurrent and efficiency achieved here confirm that this structure can facilitate the stability and provide the true efficiency for the overall water-splitting reaction. The maximum photoconversion efficiency of 1.83 %is more than 200 % higher than that of pristine ZnO nanowires. Thus, this structure can be used as a photoanodes which is relatively stable in the photooxidation process in aqueous solution. Although this study concerned the CdTe system, we believe that this strategy can also be extended to other photoanode systems.

Experimental Section

Zinc nitrate, absolute ethanol, zinc acetate, and Te powder were purchased from Sigma-Aldrich. Sodium borohydride and hexamethylenetetramine (HMT) were obtained from Acros Organics. Cadmium chloride and mercaptopropionic acid (MPA) were purchased from Fluka. 100 mL of a 0.06 M solution of zinc acetate in absolute ethanol was mixed with ultrasonic agitation. The FTO substrates were wetted with zinc acetate solution for 10 s, and then blown dry with stream of argon. The substrates were annealed at 350 °C for 30 min to yield a layer of ZnO seeds. The seeded substrates were suspended horizontally in a reagent solution containing 0.06 M zinc nitrate and 0.06 M HMT in a Teflon vessel, and then sealed in an autoclave and heated to 110 °C for nanowire growth. The nanowire substrate was removed from the autoclave and thoroughly washed with distilled water after 24 h of growth, and then dried in air. $NaBH_4$ (0.08 g) was treated with Te powder (0.127 g) in water (1.0 mL) to produce sodium hydrogen telluride (NaHTe, 0.99 M). The NaHTe solution (0.5 mL) was then added to a N_2-saturated mixture (74.8 mL, pH 11.2) of MPA (38 mM) and $CdCl_2$ (16 mM) to give a final Cd^{2+}/MPA/HTe^- molar ratio of 1:2.4:0.5. This mixture was then heated under reflux at 90 °C for 6 h. The color of the solution changed from dark red to orange-yellow. A nanowire substrate was baked at 450 °C for 30 min. After cooling in air the substrate was placed with the nanowire side up on the bottom of the vial containing the CdTe QD dispersion. After 24 h the nanowire substrate was removed from the QD dispersion and thoroughly washed with distilled water. A water-splitting photoelectrode was used as the working electrode, a platinum plate as counterelectrode, and Ag/AgCl as reference electrode. All PEC studies were operated in a 0.5 M Na_2SO_4 (pH 6.8) solution as supporting electrolyte medium. The water-splitting photoelectrode was illuminated with a xenon lamp equipped with PE300BF filters to simulate the AM1.5 spectrum (390–770 nm in visible region). Amperometric *I*–*t* curves of ZnO nanowires decorated with CdTe QDs were recorded at an applied voltage of +0.5 V at 100 mW cm^{-2}. The nanowires were studied with a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive spectroscopy (EDS) probe. HRTEM images, electron diffraction patterns, and elemental maps were collected on a JEOL JEM-2100F electron microscope.

Received: March 27, 2010

Keywords: electrochemistry · nanostructures · photochemistry · quantum dots · water chemistry

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