Photocatalytic CdSe QDs-decorated ZnO nanotubes: an effective photoelectrode for splitting water†

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Arrays of ZnO nanorods (NRs) were successfully converted into nanotubes (NTs), used as photoelectrodes in photovoltaic cells after their sensitization with CdSe quantum dots (QDs) and a strong correlation between the PEC performance and geometrical structure of ZnO NTs@CdSe(QDs) and ZnO NRs@CdSe(QDs) was established under the same conditions.

One-dimensional (1D) nanoarchitectures of wide-band-gap semiconductors (WBGS) (ZnO, TiO2, SnO2 and GaN) such as nanorods (NRs), nanotubes (NTs) and nanowires (NWs) exhibit excellent photon absorption and facilitate the efficient transport of photogenerated-charge carriers. Modified WBGS in shape and size have been used to improve the performance of optoelectronic devices. But most of the WBGS are sensitive to the UV portion of sunlight. Quantum dots (QDs) are added or band-engineering adopted to functionalize WBGS in the visible part of the sunlight. Quantum dots (QDs) are favored as sensitizers for WBGS because of their uniquely tunable particle size, their convenience of multiple charge carrier generation from a single high-energy photon, and their ability to modulate vectorial charge transfer. However, to date numerous QD (CdS, CdSe, CdTe, PbS, CuInS2, InP, Bi2S3) -sensitized nanostructures (most of which are TiO2-based) have been investigated for use in photovoltaics.

Recently, the arrays of CdSe nanofilms on ZnO nanowires have been studied as photoanodes in solar cells. The author’s group has stimulated research into the QDs decorated-1D ZnO nanodevices by investigating ZnO NRs@CdSe(QDs) and ZnO NWs@CdTe(QDs) arrays for the photoelectrochemical splitting of water, but ZnO NTs@CdSe(QDs) has not been reported for the same by anyone till now.

The uncooled ZnO samples (0 h) grew as rods and the array films in the mother solution were slowly cooled for different times to promote the hexagonal etching of NRs using NH4OH that was produced by the cleavage of HMT, facilitating their gradual conversion into NTs (Fig. 1). The ZnO NTs/NRs arrays films were washed with DIW, air-dried, annealed at 450 °C for 0.5 h. Hydrophobic oleic acid-encapsulated-CdSe QDs were produced using the method described by Qu and Peng et al. with some modifications, which adopted hydrophobic character upon the exchange of ligands (oleic acid with 3-mercaptopropionic acid (MPA)). Finally, the aggregates of MPA-escorted CdSe QDs were deposited on the surface of the ZnO NTs/NRs arrays by sequential layer-by-layer deposition and the as-obtained ZnO NRs or NTs@CdSe(QDs) samples were annealed at 350 °C for 0.5 h. UV-visible absorption spectroscopy and X-ray diffraction (XRD) study confirmed the aforementioned deposition (Fig. S2a, S2b, S3c, S3d, S3e and S4f), in close agreement with the high-resolution transmission electron microscope (HRTEM, JEM-2100F microscope) results (Fig. 2). HRTEM images (Fig. 2a,b,d) and their corresponding selected area electron diffraction spectroscopic (SAED) patterns (Fig. 2c) reconfirmed the 5–8 nm thick loading of 3 nm sized-CdSe QDs aggregate on the walls of the ZnO nano-surface.

Fig. 1 Gradual transformation of ZnO NRs to NTs on cooling.
shift peak B of the nanostructures toward higher energy. Han et al.\textsuperscript{20} explained this shift as a consequence of the shrinkage of the lateral lattice parameters \((a\) and \(b)\) by the surface effect (that the surface energy of ZnO planes 100 and 101 is lower than that of the 002 plane). The increase in lattice constant \(c\) as verified by the elongated SAED pattern is caused by the tendency to conserve the length of the Zn-O bonds with 1-D growth along the \(c\)-axis. XAS study also revealed the oxygen-rich tips for NRs and NTs.\textsuperscript{21}

The photovoltaic performance of the arrays of CdSe(QDs)-sensitized ZnO NRs (0 h cooling) and NTs (24 h cooling) in a conventional multi-electrode PEC cell was determined. The cell comprised a saturated calomel electrode (SCE) as a reference electrode, a Pt flag as a cathode and ZnO NRs/NTs@CdSe(QDs) arrays as a working anode-electrode. Photoreponses were measured under illumination by a 300 W Xe light source \((> 420 \text{ nm})\) with an intensity of 100 mW cm\(^{-2}\) (AM 1.5G) in aqueous solution of the hole scavenger-electrolyte 0.35 M Na\(_2\)S and 0.25 M K\(_2\)SO\(_3\) \((\text{pH} = 13.3)\)\textsuperscript{22} to suppress the photocorrosion of CdSe QDs. The optimal loading of CdSe QDs on ZnO nanotubes that maximized photocurrent density was measured and optimal efficient 28 mM CdSe QDs-loaded samples of ZnO were used for the comparative study. (See supporting information (SI) and Fig. S9.) An amperometric study for pristine ZnO NTs, ZnO NTs@CdSe(QDs) and annealed ZnO NTs@CdSe(QDs) was carried out, which revealed the stability of the above-mentioned samples for 600 s under light on/off cycles at an applied voltage \((V)\) of + 0.35 V and a power density of 100 mW cm\(^{-2}\) (Fig. 3). The photocurrent densities \((J)\) of pristine, CdSe(QDs)-sensitized and annealed CdSe(QDs)-sensitized samples of ZnO NRs (0 h cooling) and NTs (24 h cooling) were observed to be 0.54, 1.53 and 2.1 mA cm\(^{-2}\) and 0.897, 1.98 and 5.10 mA cm\(^{-2}\) at zero bias, respectively (Fig. 3 and S10\textsuperscript{5}). The corresponding recorded onset potentials for ZnO NTs were −0.77, −0.97 and −0.99 V. The photoresponses of the ZnO NTs samples are two times higher than those of the ZnO NRs@CdSe(QDs) arrays.\textsuperscript{14} The onset potentials typically depend on the pH \((E = E_0 − 0.59 \text{ pH})\) of the solution and are approximately equal to the conduction band (CB) edge potential \((E_c)\).\textsuperscript{23} The onset potential of ZnO NTs@CdSe(QDs) is more negative (−0.97 to −0.99 V) than that of NRs (−0.91 to −0.98) because the CB edge position of ZnO NTs is more negative than that of NRs, even though the band gaps of both ZnO NRs and NTs which were calculated from DRS observations (Fig. S2a and S2b\textsuperscript{5}) are almost equal to 3.37 eV. Higher surface area to volume ratio of ZnO NTs than ZnO NRs accounted for the enhancement in \(J\). Accordingly, ZnO NTs were more sensitive toward generated hydrogen than were ZnO NRs. Additionally, the high pH of the electrolyte used and the typical morphology of the ZnO nanostructures were responsible for the wide potential window \((≈ 1.5 \text{ V})\) in \(J-V\) plots, associated with effective electron-exchange.\textsuperscript{24}

The inherently anisotropic wurtzite crystal structure of ZnO, revealed by XAS, makes it ideal for 1D-hexagonal growth, providing a direct conduction path along the \(c\)-axis for electrons that are injected from CdSe quantum dots, reducing the electron-hole recombination. The uniform height
Morphological changes, a result of annealing, are visualized in Fig. S5.† Although HRTEM and XRD study cannot detect amorphous carbon in anode samples, the elemental analysis (Heraeus Vario EL-III, accuracy = 0.1%) of non-annealed and annealed ZnO NTs@CdSe(QDs) systems revealed the presence of 3.1 and 2.2% carbon, respectively, which is the evidence of autoignition of MPA by annealing. The photocurrent saturation25 that was detected in the J–V plots might be caused by the saturation of the sensitizing centers (or active sites) with CdSe QDs on tabular ZnO arrays, which causes the interfacial reaction to proceed more slowly than the migration of photogenerated electrons. The optimal concentration of CdSe QDs, used herein in the investigation, was 28 mM (Fig. S9), requiring the ZnO surface to be saturated with photoactive sites.

Notes and references