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**Highly Efficient Photoanode Based on Cascade Structural Semiconductor of Cu2Se/CdSe/TiO2: A Multifaceted Approach to Achieving Microstructural and Compositional Controls**

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Highly Efficient Photoanode Based on Cascade Structural Semiconductor of Cu$_2$Se/CdSe/TiO$_2$: A Multifaceted Approach to Achieving Microstructural and Compositional Controls

Baohe Chong, abc Wen Zhu, abc Yong Liu, a Li Guan b and George Z. Chen *b

Hydrogen produced by splitting water is receiving significant attention due to the rising global energy demand and growing climate concern. The photocatalytic decomposition of water converts solar energy into clean hydrogen, and may help mitigate the crisis of fossil fuel depletion. However, the photocatalytic hydrogen production remains challenging to obtain high and stable photoconversion efficiency. Here, we report a highly efficient photoanode based on coaxial heterogeneous cascade structure of Cu$_2$Se/CdSe/TiO$_2$ synthesized via a simple room-temperature and low-cost electrochemical deposition method. The microstructure and composition of the Cu$_2$Se top layer are regulated and controlled by doping Cu with various amounts in different zones of the CdSe/TiO$_2$ coaxial heterojunction and then using a simple integral annealing process. Surprisingly, a little effort made to achieve the Cu$_2$Se top layer utilizing such doped CdSe/TiO$_2$ exhibits a significant enhancement in photocatalytic activity. The maximum stable photocurrent density of the sample with the optimal copper zone and doping concentration has reached up to 28 mA/cm$^2$, which can be attributed to the success in the uniform dispersion of the three-layer heterogeneous nanojunctions among the anatase nanotube wall from top to bottom. This results in a stepwise structure of band-edge levels in the Cu$_2$Se/CdSe/TiO$_2$ photoelectrode that is conducive to enhancing effectively the separation of the photogenerated electron-hole pair.

Introduction

The photocatalytic decomposition of water, which uses solar energy to split water and produce cheap hydrogen as a clean energy carrier, is believed to be able to help mitigate the crisis of fossil fuel depletion. Since Fujishima and Honda firstly reported in 1972 the use of TiO$_2$ photoanode for the photocatalytic water splitting, extensive studies have been carried out on TiO$_2$ based nanomaterials due to their high photocatalytic activity, photochemical stability, nontoxicity and low cost. Various nanostructured TiO$_2$ materials such as nanorods, nanoparticals, nanotubes and nanowires have been fabricated. In comparison with the traditional TiO$_2$ nanocrystal-based photoelectrodes, vertically oriented TiO$_2$ nanotube arrays (NTAs) prepared on a Ti foil by electrochemical anodization can offer larger specific surface areas without a concomitant decrease in geometric and structural order. Most importantly, the highly ordered one-dimensional nanostructure provides a unidirectional electrical channel for charge transfer, so that photoinduced electron-hole pairs can be effectively separated. However, TiO$_2$ is a large band-gap semiconductor (3.2 eV), and its activation is limited only in the UV region, which accounts for only 4-5% of the spectrum of solar energy. To extend the photoresponse into the visible light region, sensitizing TiO$_2$ NTAs with a narrow band-gap semiconductor is deemed to be a promising strategy.

Transition-metal chalcogenides semiconductors such as CdS, Cu$_2$S, CuInS$_2$, CdSe, Cu$_2$Se, Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$ as the sensitizer of TiO$_2$ are of current interest to energy-related research due to their narrow band-gap properties. Among these semiconductors, CdSe has been extensively considered for application in sensitizing TiO$_2$ NTAs on account of its excellent energy band-gap (1.7eV) and good electron mobility (800 cm$^2$/V•s). Currently, the compound semiconductor heterojunction research of CdSe/TiO$_2$ NTAs focuses mainly on the formation of single-junction nano-materials, which generally use
CdSe nanoparticles or single layer nanofilm as the sensitizer.\textsuperscript{42} However, the photocatalytic activity of these composite heterojunctions needs improvement, because such single-junction nano-materials often result in rapid charge-carrier recombination that limits electron harvesting.\textsuperscript{31} Recently, the conceptual design of multi-junction photoanodes with a multilayered semiconductor co-sensitization structure has demonstrated greater efficiency than the corresponding single-junction photoanodes.\textsuperscript{43, 44} Merging the multilayered narrow-band-gap and the TiO\textsubscript{2} large-band-gap semiconductors can result in the formation of multi-heterostructures and produce a novel photocatalyst with continuously changed band gap, thereby effectively enhancing the photoresponse.

Cu\textsubscript{2}Se is a typical p-type semiconductor with highly conducting and semi-transparent features. So far there are several interesting reports on using Cu\textsubscript{2}Se as an absorber material in photovoltaic devices.\textsuperscript{35-39, 45} A widely varying range of band gap energy for Cu\textsubscript{2}Se from indirect band gap of 1.1-1.5 eV to direct band gap of 2.0-2.3 eV have been reported. The ability to tailor the band gap energy is directly related to its capability of microscopic controls in composition and structure. This is helpful to achieve the best energy band match in the formation of multi-junction nano-materials. However, for special highly structured TiO\textsubscript{2} NTAs substrates, it has been proven difficult to use the conventional methods for an accurate control of the microstructure and composition of the multilayered coatings that play a critical role in determining the resultant photocatalytic activity. In the present study, we illustrate the growth of a double-layer structure.

Cu\textsubscript{2}Se/CdSe nanofilms were grown on TiO\textsubscript{2} NTA electrodes to form a coaxial heterogeneous cascade structure (Scheme 1) using a simple room-temperature, low-cost electrochemical deposition method. Scheme 1 shows the Cu\textsubscript{2}Se/CdSe/TiO\textsubscript{2} coaxial heterogeneous structure and the charge-transfer mechanism in a single coaxial heterogeneous structure. The holes migrate to the sensitizer-electrolyte interface and participate in the oxygen production reaction of water splitting. The electrons are transferred to the core material and travel to the back-contact, where they are conducted through the circuit to the counter electrode to participate in the hydrogen production reaction. Such a structure is designed to help improve the contact area between the sensitizer and the TiO\textsubscript{2} surface, exciting the photoelectrons in the sensitizer and smoothly injecting them into the conduction band of TiO\textsubscript{2} NTAs.\textsuperscript{46}

The top layer of Cu\textsubscript{2}Se is formed by doping Cu in different zone of CdSe/TiO\textsubscript{2} coaxial heterojunction and then using a simple integral annealing process. The microstructural and compositional characteristics of the materials can be controlled and manipulated by simply changing the doping position and the doping quantity. This relatively inexpensive and simple synthesis technique is suitable for industrial production.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme1.png}
\caption{Cross section of the Cu\textsubscript{2}Se/CdSe/TiO\textsubscript{2} coaxial heterogeneous cascade structure with two-junction and the charge-transfer mechanism.}
\end{figure}

\section*{Experimental}
\subsection*{Preparation of TiO\textsubscript{2} NTAs.}
Synthesis of highly ordered TiO\textsubscript{2} NTAs followed the typical two-step anodic oxidation method.\textsuperscript{44} Titanium foils (99.8\% purity) were mechanically ground using emery papers with different types and polished with the metallographic abrasive paper successively, then ultrasonically cleaned orderly with acetone, distilled water and ethanol, followed by drying in ambient air (at laboratory temperature...
and common ambient pressure). The anodization of titanium foil was carried out in an electrolyte comprised of NH$_4$F (0.32 wt. %) and distilled H$_2$O (2.0 vol %) in ethylene glycol at room temperature using platinum foil as the counter electrode. The two-step anodic oxidation was conducted as follow: step-1, the titanium foil was firstly anodized at 60 V for 20 min. in the electrolyte, followed by rinsing with ethanol and drying in ambient air, and then by annealing at 700°C in a muffle furnace for 1 h with heating rate of 7°C/min; step-2, the sample was re-soaked into the electrolyte and suffered the second anodization for 11 h, then was annealed again at 450°C in the muffle furnace for 2 h at a heating rate of 2°C/min after rinsing with ethanol and drying in an oven at 100°C for 1 h.

**Fabrication of CdSe/TiO$_2$ and Cu$_2$Se/CdSe/TiO$_2$ Coaxial Heterogeneous Nanojunction.**

For electrochemical deposition of CdSe on TiO$_2$ NTAs, CdSO$_4$ and SeO$_2$ of the analytical reagent grade were used as the sources of Cd and Se, respectively. EDTA-2Na (C$_{10}$H$_{12}$O$_8$N$_2$Na$_2$•2H$_2$O) and NH$_4$OH were used to complex the ions and adjust the pH value for obtaining a proper electrodeposition potential. The solutions were freshly prepared just before the beginning of each series of measurements. The electrochemical deposition was carried out using a computer controlled electrochemical workstation that was connected to a three-electrode system comprised of Ti foil as working electrode (WE), Pt foil as counter electrode (CE) and Hg$_2$Cl$_2$/KCl (SCE) as reference electrode (RE). For copper doping, CuSO$_4$ (2 mM) solution was used as Cu source.

**Characterizations.**

The morphologies of the samples were studied by field emission scanning electron microscopy (FESEM) (Nova NanoSEM 450) and transmission electron microscopy (TEM) (JEOL JEM-2100). The X-ray diffraction (XRD) (X’Pert PRO) measurement was performed on a Bruker D8 diffractometer with Cu Kα radiation operated at 40 kV, 40 mA. UV-Vis absorption spectra were collected at room temperature using the Lambda 35 UV-vis spectrophotometer. For the incident-photon-to-current-conversion efficiency (IPCE) measurement, light source was generated by a 300W xenon lamp of Newport (Oriel,69911) and then split into specific wavelength using Newport oriel cornerstone 130 1/8 Monochromator (Oriel,model 74004).

The optical response performance of the samples was investigated in a photoelectrochemical cell with a platinum foil counter electrode and the SCE reference electrode. 0.5 M Na$_2$S was used as the electrolyte in photoelectrochemical measurements. The CorrtestTM CS350 electrochemical workstation was also used to control the potential and record the photocurrent generated. The optical response of the samples was investigated in a photoelectrochemical cell with a platinum foil counter electrode and the SCE reference electrode. 0.5 M Na$_2$S was used as the electrolyte in photoelectrochemical measurements. The CorrtestTM CS350 electrochemical workstation was also used to control the potential and record the photocurrent generated. The optical response of the samples was investigated in a photoelectrochemical cell with a platinum foil counter electrode and the SCE reference electrode. 0.5 M Na$_2$S was used as the electrolyte in photoelectrochemical measurements.

**Results and discussion**

This research focuses on synthesis of multi-junction nano-materials coated with highly ordered structure through a modified electrochemical atomic layer deposition (ALD) route, and on studying and manipulating their microstructural and compositional properties. The electrochemical ALD method as reported in the literature is based on underpotential deposition (UPD). UPD is a surface-limited phenomenon in which the deposition of one element occurs at a potential that precedes the Nerstian equilibrium value, so that the resulting deposit is generally limited to one atomic layer. Electrochemical ALD utilizes alternating UPD of the elements that form the compound semiconductor in a cycle. Each deposition cycle can form only a monolayer of heterogeneous elements, and the thickness of the deposit is controlled by the number of deposition cycles. To date, this method has been extensively used to grow highly crystalline nanofilms of transition-metal chalcogenides at ambient temperature and pressure and is convenient for industrial production. Before electrochemical ALD, it is pivotal to find the suitable UPD potential of each compositional element of the compound. This can be determined by cyclic voltammetry (CV). The electrochemistry behaviour of Se(IV) was investigated in an ammonia buffer medium. In this regime, two competitive processes were observed: the first led to the formation of Se(0), and the second resulted in further reduction of Se(0) to HSe$^-$. Thus, it is important to understand which process dominates in the competition, and which exerts a direct impact on the Se UPD behaviour. Apparently, the competition can be affected by a number of factors, such as the type of electrolyte and buffers, pH, complexing agent, temperature, and so on. Therefore, in this study, the addition of EDTA as a complexing agent, the content variation of the ammonia buffer, and a resultant suitable pH value are used to adjust the UPD potential of Se and Cd for the deposition of the CdSe layer. Figure 1 shows the cyclic voltammograms (CVs) of the TiO$_2$ NTA electrode in the solution of mixed CdSO$_4$ and SeO$_2$. The X-ray diffraction (XRD) (X’Pert PRO) measurement was performed on a Bruker D8 diffractometer with Cu Kα radiation operated at 40 kV, 40 mA. UV-Vis absorption spectra were collected at room temperature using the Lambda 35 UV-vis spectrophotometer. For the incident-photon-to-current-conversion efficiency (IPCE) measurement, light source was generated by a 300W xenon lamp of Newport (Oriel,69911) and then split into specific wavelength using Newport oriel cornerstone 130 1/8 Monochromator (Oriel,model 74004).

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Figure 1. Cyclic voltammograms of the TiO$_2$ nanotube electrode recorded at 10 mV/s in the solution containing (green line) 10 mM CdSO$_4$ + 0.1M EDTA, pH = 8.5; or (blue line) 2 mM SeO$_2$ + 0.1M EDTA, pH = 8.5.

Figure 2a shows XRD patterns of the pure TiO$_2$ NTAs and the as-prepared CdSe/TiO$_2$ NTAs samples. All diffraction peaks on the black line can be well-indexed to the anatase TiO$_2$ phase and the Ti metal phase. After decoration of the TiO$_2$ NTAs with CdSe, the intensity of diffraction peaks of the TiO$_2$ phase decreased, indicating that the CdSe had been attached onto the TiO$_2$ NTAs. Meanwhile, some new diffraction peaks located at 24.13°, 42.34°, 49.93° appeared (see red line in Figure 2a). These new peaks were correspondingly attributed to (100), (110), (112) of the hexagonal CdSe (JCPDS No. 03-065-3415), confirming that the deposited CdSe layer possessed the hexagonal crystal structure. Figure 2b shows the EDX quantitative analysis of the CdSe coated or sensitized TiO$_2$ NTAs. Both Ti and O peaks came from the TiO$_2$ NTAs, while Cd and Se peaks that were clearly visible on the EDX spectrum came from the CdSe deposit. Quantitative analysis of the EDX spectrum revealed that the atomic ratio of Cd (2.39%) versus Se (2.53%) was nearly 1, indicating that the deposited CdSe had the expected 1:1 stoichiometry.
Figure 2. (a) XRD diffractograms of samples: (black line) pure TiO$_2$; (red line) CdSe(7h)/TiO$_2$. (b) EDX spectrum and the corresponding element content of CdSe(7h)/TiO$_2$.

The photocurrent-potential curves measured on a series of CdSe/TiO$_2$ NTAs samples are shown in Figure 3. The CdSe layers in these samples were fabricated using five different deposition times; data for the corresponding pure TiO$_2$ NTAs substrate before sensitization is also provided. The stable photocurrent density of pure TiO$_2$ NTAs was about 2.0mA/cm$^2$ (the current density is measured against the projected area of the TiO$_2$ NTAs). After deposition of CdSe on the TiO$_2$ NTAs using the electrochemical ALD method, the improvement of photocurrent densities of CdSe/TiO$_2$ NTAs were obvious. Especially, a noteworthy enhancement in the photocurrent density was found for the CdSe(7h)/TiO$_2$ sample in which the CdSe layer was deposited for 7 h. As shown in Figure 3, the photocurrent density increases in the wake of the increasing CdSe deposition time within 7 h. However, when the deposition time was further increased to 9 h, the photocurrent density dropped, indicating that the sensitized CdSe layer was too thick after 9 h of deposition. Excessive CdSe deposition causes reduced light absorption because of the increase of the transmission distance of photons.

Figure 3. Optical response of CdSe/TiO$_2$NTAs samples in which the CdSe layers are fabricated using different deposition times compared with pure TiO$_2$.

The CdSe(7h)/TiO$_2$ electrode was then selected as the optimal seed layers on account of its best photocurrent density in this work. Before doping Cu into the CdSe nanofilm, a suitable potential for Cu deposition on the CdSe underlayer should be determined. Figure 4 features the CV of CdSe substrate in the Cu ion solution. For comparison, the CV of CdSe in the blank solution (without Cu ion) is also provided in Figure 4 (green line). A relatively broad anodic stripping peak A1 was observed between -0.55 and -0.3 V. This strip peak means the decomposition of CdSe from the TiO$_2$ substrate if an applied potential is more positive than -0.55 V. The blue line shows the first CV cycle of CdSe/TiO$_2$ in the Cu$^{2+}$ solution, in which the region C between -0.6 to -0.35 V indicates the UPD region of Cu on the CdSe substrate. When the scan region extends negatively to -1.0 V, two anodic peaks A2 at -0.3 V and A3 at 0.2 V correspond to the oxidative stripping of Cu deposited at the Nernst potential and via UPD, respectively (pink line). To avoid decomposition of the CdSe substrate during the Cu deposition process, the deposition potential of -0.6 V was selected.
Figure 4. Cyclic voltammogram of CdSe(7h)/TiO$_2$ nanotube electrode recorded at 10 mV/s in solutions containing (green line) 0.5 M Na$_2$SO$_4$; (blue and pink line) 2 mM CuSO$_4$.

Figure 5a shows the XRD patterns of a sample with a structural formula of CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$. This Cu-doped sample was prepared according to the following procedure. Firstly, CdSe was deposited on the TiO$_2$ NTAs substrate for 6 h using the electrochemical ALD method. Then, copper was deposited on the CdSe(6h)/TiO$_2$ substrate upon consumption of a charge of 0.6 C. After drying slightly, the Cu covered sample was re-immersed into the CdSe reaction solution and subjected to electrochemical ALD for 1 h. Before testing, the sample was integrally annealed at 450 °C in nitrogen (ambient pressure) for 2 h with heating and cooling rate of 2 °C/min. As shown in Fig. 5a, in comparison with the XRD pattern of CdSe(7h)/TiO$_2$ shown in Figure 2, the Cu-doped sample gave new peaks, located at 26.79° and 44.45°, that were attributed to (111) and (220) of Cu$_2$Se, respectively. Energy dispersive X-ray spectroscopy (EDS) analysis confirmed the presence of Cd, Cu and Se elements in the Cu-doped sample (Figure 5b). Subtracting the amount of Cd that is the same as the amount of Se in the CdSe compound, the atomic ratio of Cu to the remaining Se was very close to 2:1, in consistence with the stoichiometry of Cu$_2$Se, indicating the effectiveness of the integral annealing process for the formation of the Cu$_2$Se compound.
Figure 5. (a) XRD diffractograms of sample CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$; (b) EDX spectrum and the corresponding element content of sample CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$

The FE-SEM images of as-prepared samples including the pure TiO$_2$ NTAs, CdSe/TiO$_2$ NTAs and Cu-doped CdSe/TiO$_2$ NTAs also are shown in Figure S1. The pure TiO$_2$ NTAs sample presented a highly uniform array of nanotubes of 100 nm in diameter and about 8 nm in wall thickness. These nanotubes were oriented in the vertical direction to the titanium foil substrate. The hollow nature makes both inner and outer surface areas accessible for modification with a narrow band-gap semiconductor. FE-SEM images of the CdSe sensitized TiO$_2$ NTAs sample revealed that well modified coaxial structures have been obtained successfully using the electrochemical ALD method (Figure S1c,d). The tube inner diameter was shrunken and the wall was thickened relative to those in Figure S1a,b. After CdSe electrodeposition, the average inner diameter of the tubes was ~80 nm, suggesting that the CdSe coating layer was ~10 nm thick (the pure TiO$_2$ NT substrate had an average inner diameter of 100 nm). Figure S1(e, f) present the FE-SEM images of Cu-doped CdSe/TiO$_2$ NTAs sample. The tube inner diameter and wall thickness were not significantly different from those of the only CdSe sensitized sample. Because there was an addition of a certain amount of copper, the constant wall thickness suggested that copper has diffused into adjacent CdSe layer, resulting in the formation Cu$_2$Se during the integral annealing process.

Figure S2 shows the cross-sectional FE-SEM images of as-prepared samples including the pure TiO$_2$ NTAs, CdSe/TiO$_2$ NTAs and Cu-doped CdSe/TiO$_2$ TNAs. Cross-sectional FE-SEM image (Figure S2a) reveals that the pure TiO$_2$ TNAs have a rather smooth wall surface. As shown in Figure S2(b,c) when semiconductor was deposited on the TiO$_2$ TNAs using the electrochemical ALD method, both the interior and exterior surfaces of TiO$_2$ NTAs were homogeneously coated with sensitizer without any obvious particle agglomerations, suggesting the electrochemical ALD method in our work is rather efficient to grow well dispersed nanofilms among the whole nanotube wall.

The prepared samples were further investigated using transmission electron microscopy (TEM). Figure 6a features a single tube wall of the pure TiO$_2$ nanotube sample that shows a hollow nanostructure and has a wall thickness of about 8 nm. The wall is smooth without any stuff covered. Figure 6b and 6c show the TEM images of samples after semiconductor sensitized, which reveal that the semiconductor were uniformly grown on the TiO$_2$ nanotube inner and outer of wall. The high resolution TEM images (HRTEM) shown in Figure 6d-6f reveal a well-defined cascade structure with uniformly dispersed two and three-layer heterogeneous nanojunction among the anatase nanotube wall has been obtained. In Figure 6f, the d spacing in the outer nanocrystal layer was measured to be 0.32 nm, which matched well the interplanar spacing of Cu$_2$Se (111) plane and was consistent with the XRD measurement result shown in Figure 5. The d spacing in the interlayer was 0.37 nm and was assignable to the interplanar spacing of the CdSe (100) plane, while the d spacing of 0.35 nm in the inner layer was identifiable to the interplanar spacing of the TiO$_2$ (101) plane. This result demonstrates that the double-layer Cu$_2$Se and CdSe co-sensitized TiO$_2$ NT electrodes with a coaxial heterogeneous cascade structure of Cu$_2$Se/CdSe/TiO$_2$ can be successfully formed by doping Cu in CdSe/TiO$_2$ NTAs followed by the simple integral annealing process.
To investigate an appropriate copper doping zone, Cu was loaded in different deposition period of CdSe. Three different sites were chosen to deposit Cu, including near the inner layer, the intermediate layer and near the outer layer, with corresponding structural formula of CdSe(6h)/Cu(0.3C)/CdSe(1h)/TiO$_2$, CdSe(3.5h)/Cu(0.3C)/CdSe(3.5h)/TiO$_2$ and CdSe(1h)/Cu(0.3C)/CdSe(6h)/TiO$_2$, respectively. The amount of charge for deposition of Cu was 0.3 C, while the total deposition time of CdSe was 7 h. Figure 7 shows the measured photocurrent density of three Cu-doped samples with different copper doping sites. The sample of CdSe(1h)/Cu(0.3C)/CdSe(6h)/TiO$_2$ achieved the maximum stable photocurrent density of 20 mA/cm$^2$ among the samples investigated. In contrast, the sample of CdSe(6h)/Cu(0.3C)/CdSe(1h)/TiO$_2$ showed only a photocurrent density of 7 mA/cm$^2$ that was even less than the 7.5 mA/cm$^2$ level obtained from undoped CdSe(7h)/TiO$_2$ (see Figure 3). It is generally believed that the charge transfer rate is governed by the energy band alignment at the heterointerfaces. Fermi-level alignment between TiO$_2$, CdSe and Cu$_2$Se was proposed to construct a stepwise structure of band-edge levels in the Cu$_2$Se/CdSe/TiO$_2$ photoelectrode (Scheme 2). Such stepwise energy band structure is advantageous to the electron injection and hole recovery in the system. When the copper doping site is chosen near the outer layer, it gives rise to the formation of Cu$_2$Se at the top level during the integral annealing process. As a result, a suitable architecture of Cu$_2$Se/CdSe/TiO$_2$ can be obtained, which is favourable for reducing the charge-carrier recombination probability. On the contrary, doping copper near the inner layer produces an architecture of CdSe/Cu$_2$Se/TiO$_2$ that does not conform to this stepwise band edge level alignment and as a result hinders the photogenerated charge-carrier transfer. A similar effect has been found in the CdSe and CdS co-sensitized TiO$_2$ semiconductor photoelectrodes in which the photocurrent density of the CdSe/CdS/TiO$_2$ electrode is higher than that of the CdS/CdSe/TiO$_2$ electrode. By means of the time-resolved photoluminescence technique, the impact of energy band structure on the charge-carrier transfer has been fully explained.
Figure 7. Optical response of Cu-doped CdSe(7h)/TiO$_2$ with various copper doping zone. The Cu deposition coulomb was 0.3 C, while the total deposition time of CdSe was 7 h.

Scheme 2. Ideal step band edge structure for efficient transports of photogenerated charge-carriers in Cu$_2$Se/CdSe/TiO$_2$ electrode.

Furthermore, the effect of copper doping concentration was studied by adjusting the amount of Cu deposition charge. The variation of photocurrent density as a function of the amount of copper doping in CdSe/TiO$_2$ is shown in Figure 8. The stable photocurrent densities of four samples with various copper doping concentrations of Cu (0.3 C), Cu (0.6 C), Cu (1.2 C), and Cu (1.8 C) were 20, 28, 17 and 13 mA/cm$^2$, respectively. The maximum photocurrent density can be obtained from the 0.6 C sample. In comparison with TiO$_2$ NTA, the CdSe(1h)/Cu(0.6C)CdSe(6h)/TiO$_2$ electrode showed a 14-fold enhancement in photocurrent density.

Practical photoelectrolysis system consists of two electrolyte immersed electrodes with the bias voltage applied between the working and counter electrodes, the overall chemical reaction in such a system is made of two independent half reactions. To understand the chemical changes at the photoelectrode, in laboratory water photoelectrolysis experiments a three-electrode geometry is used to measure photocurrent. This geometry involves a working electrode (photocathode or photoanode), a counter electrode that generally is platinum and a reference electrode that is SCE electrode in our work. To investigate the difference of photoconversion efficiency between the two-electrode and three-electrode configuration, the photochemical measurement was carried out. Figure S3 shows the measurement results of CdSe/TiO$_2$ and Cu$_2$Se/CdSe/TiO$_2$ in different configuration. The photocurrent density curves of both CdSe/TiO$_2$ and Cu$_2$Se/CdSe/TiO$_2$ (Figure S3 a,b) shift to positive about 1.2V in the two-electrode configuration with respect to the three-electrode configuration, which attributes to the reference electrode SCE. The photoconversion efficiencies (Figure S3 b,d) calculated according to the corresponding equation shows that the photoconversion efficiency measured in three-electrode configuration have a slight exaggeration (no significant) with respect to the photoconversion efficiency value measured in two-electrode configuration. This result agrees with the literature published previous.$^{36}$ Grimes
explained that the voltage measured between the working and the counter electrodes gives the actual applied bias voltage $V_{app}$. This voltage multiplied by the cell current gives the electrical energy supplied by the electrical power supply. But in practice, where a potentiostat is used to apply an external bias to the photoelectrode, this actual voltage $V_{app}$ (between the working and counter electrodes) may slightly exceed the bias voltage measured as $V_{app} = V_{meas} - V_{aoc}$ with respect to the reference electrode. Thus, the measurement tested in three-electrode configuration can show a slightly higher efficiency value than that tested in two-electrode configuration.

Figure 8. Optical response of different Cu deposition coulomb in CdSe(1h)/Cu/CdSe(6h)/TiO$_2$ sample.

To quantify the photoresponse of prepared samples, incident-photon-to-current-conversion efficiency (IPCE) measurements were made to examine their photoresponses as a function of incident light wavelength. As revealed in Figure 9a, the CdSe/TiO$_2$ NTAs showed a pronounced response in the visible light region, with a maximum IPCE value of 31.9% obtained around 500 nm. The photoresponses of CdSe/TiO$_2$ NTAs were drastically extended to the all visible light region of the solar spectrum after doping Cu into CdSe/TiO$_2$ NTAs, indicating that semiconductor Cu$_2$Se can efficiently promote the photoresponse owing to its narrow band-gap. Overall, the IPCE of CdSe/TiO$_2$ NTAs and Cu$_2$Se/CdSe/TiO$_2$ NTAs revealed significant photoresponses in the visible light region, which is consistent with their corresponding UV-Vis absorption spectra. Figure 9b shows the UV–Vis absorption curves of the pure TiO$_2$ NTAs, the CdSe/TiO$_2$ NTAs and the Cu$_2$Se/CdSe/TiO$_2$ NTAs. The pure TiO$_2$ NTAs had an absorption onset at about 400 nm that was determined by linear extrapolation from the inflection point of the curve toward the baseline. The calculated band-gap is 3.1 eV, corresponding to the typical band-gap value of TiO$_2$. It can be seen that CdSe deposition atop TiO$_2$ NTAs has a red-shifted absorption edge into the visible region, extending the absorption tail to 650 nm with a band-gap about 1.9 eV. After Cu doping and annealing, the absorption was further red-shifted and has an absorption tail to 800 nm, gaining a band-gap value of 1.5 eV. In addition, the absorbance of the cascade structural Cu$_2$Se/CdSe/TiO$_2$ NTAs film is apparently stronger than that of the CdSe/TiO$_2$ film in the visible region from 400 to 800 nm. The enhanced absorption is believed to result from the formation of the Cu$_2$Se top layer, which has a narrower band-gap to harvest solar energy in almost the entire visible light zone.
Conclusions

In this paper, we have proposed and demonstrated a new method for the fabrication of a novel semiconductor photoanode with a unique Cu$_2$Se/CdSe/TiO$_2$ nanostructure. The fabrication is developed on the TiO$_2$ NTAs substrate in three steps. Firstly, the CdSe inner layer was successfully deposited on pure TiO$_2$ nanotubes substrate to form a nanotube-array coaxial heterogeneous structure by electrochemical ALD. It was found that CdSe deposition for 7 h had led to a significant improvement in the photocurrent density, reaching 7.5 mA/cm$^2$. Secondly, the CdSe(7h)/TiO$_2$ nanotubes were selected as the optimal seed layer for Cu doping. Finally, integral annealing was applied, and the sample with the structural formula of CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$ showed the best photoelectrochemical performance.

The product possessed a cascade of multiple heterogeneous junctions formed in the coaxial manner on the TiO$_2$ NTAs substrate. An accurate control and manipulation in microstructure and composition of the materials could be achieved by simply changing the

Figure 9. (a) TEM image of sample CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$. (b) UV-vis absorbance spectra of pure TiO$_2$ (black line); CdSe(7h)/TiO$_2$ (red line); CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$ (green line).
doping position and concentration, which is helpful to achieve a best energy band match for splitting water utilizing solar energy. The as-prepared photoanode combines the multifaceted advantages, including the directed vertical electric transport of TiO$_2$ nanotubes, the good contacts between Cu$_2$Se and CdSe films, and the significantly enhanced light-harvesting and carrier transporting ability arising from the stepwise band edge level alignment in the resultant cascade structural semiconductor. In comparison with the pure TiO$_2$ NTAs, the as-prepared Cu$_2$Se/CdSe/TiO$_2$ NTAs photoanode showed a 14-fold enhancement in photocurrent density. It is actually encouraging and opens up an avenue for the development of water splitting materials.

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Electronic Supplementary Information

Highly Efficient Photoanode Based on Cascade Structural Semiconductor of Cu$_2$Se/CdSe/TiO$_2$: A Multifaceted Approach to Achieving Microstructural and Compositional Controls
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Figure S1. FESEM images of top-surface: (a,b) pure TiO$_2$, (c,d) CdSe(7h)/TiO$_2$, (e,f) CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$
Figure S2. Cross-sectional FSEM images of pure TiO$_2$ (a), CdSe/TiO$_2$ (b) and CdSe(1h)/Cu(0.6C)/CdSe(6h)/TiO$_2$ (c).
Figure S3. (a) Photocurrent density curves of CdSe/TiO$_2$ NTAs in different configuration, (b) Photocurrent density curves of Cu$_2$Se/CdSe/TiO$_2$ NTAs in different configuration.