Composition-Tuned ZnO/Zn$_x$Cd$_{1-x}$Te Core/Shell Nanowires Array with Broad Spectral Absorption from UV to NIR for Hydrogen Generation

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**ABSTRACT:** For highly efficient photoelectrodes, the materials used must have both a broad absorption range and large separation efficiency of photogenerated electron−hole pairs. Type II heterostructures with a ternary shell meet these two requirements and thus are recognized as being an ideal material system for application in photocatalytic hydrogen production. Here, a ZnO/Zn$_x$Cd$_{1-x}$Te core/shell nanowires array with a broad absorption edge from UV (380 nm) to NIR (855 nm) was fabricated via a chemical vapor-deposition method. More importantly, the ZnO/Zn$_x$Cd$_{1-x}$Te core/shell nanowires array are highly single crystalline, and the composition can be continuously tuned by optimizing the deposition temperature, making the design of the desired photocatalyst possible. As expected, the single-crystalline ternary Zn$_x$Cd$_{1-x}$Te shell greatly enhances the charge separation efficiency and prolongs the lifetime of photogenerated charge carriers, which contribute to the high photocatalytic and photoelectrocatalytic activity under light irradiation. In addition, ZnO/Zn$_x$Cd$_{1-x}$Te core/shell structure show remarkable photocatalytic H$_2$-production activity and high H$_2$-production capability because of the synergistic light absorption of the ternary Zn$_x$Cd$_{1-x}$Te shell and the formation of a type II heterostructure at the interface between the ZnO core and Zn$_x$Cd$_{1-x}$Te shell. This work provides a new material platform for the design of highly efficient solar-fuel devices that demonstrate a broad and controllable absorption from the UV to NIR wavelengths.

**KEYWORDS:** ZnO/Zn$_x$Cd$_{1-x}$Te nanowires array, controllable band gap, broad absorption, type II heterostructure, hydrogen production

**INTRODUCTION**

The one-dimensional (1D) ZnO semiconductor has attracted considerable interest as the photoelectrode material for the conversion of water into the hydrogen because of its distinct merits of long photogenerated carrier lifetime, high electronic mobility, and facile synthesis.$^1$ However, its large band gap (3.37 eV) restricts its absorption in the ultraviolet region, which accounts for only 5% of the entire solar spectrum. As a result of the development of band-gap engineering, the absorption range of the 1D ZnO-based photoelectrode material has been extended to the visible light region by constructing type II core/shell heterostructure nanowires arrays with a narrower band-gap semiconductor such as CdS$^2$ or CdSe.$^3$ Importantly, the type II core/shell heterostructure nanowires array possesses four advantages: (1) the type II core/shell heterojunctions formed in the interfacial area of the core/shell heterostructures profoundly improve the separation efficiency of photogenerated electron−hole pairs,$^4$ (2) the large interfacial area of the core/shell heterostructure warrants fast charge separation and thus enhances the charge-collection efficiency,$^5$ (3) the shell of the heterostructure not only blocks nonradiative recombination of the electrons in ZnO cores with electrolyte but also provides protection of the ZnO cores from electrolyte-mediated corrosion,$^6$ and (4) the special topology of the 1D
nanostructure array offers a direct electric pathway for the rapid transport of photogenerated carriers to a conductive substrate. As a result, much effort has been devoted to fabricating ZnO-based type II core/shell architecture nanowires arrays as photoelectrodes, including heterostructures with a binary shell, such as ZnO/CdS, ZnO/CdTe, and ZnO/ZnSe, and with a ternary shell, such as ZnO/ZnSxSe1-x and ZnO/ZnCd1-xS.

In comparison to heterostructures with a binary shell, ZnO-based core/shell heterostructures with a ternary shell are more attractive because of their adjustable composition and band gap, which make the design of the desired photoelectrodes possible. Several synthesis techniques have been exploited to manufacture ternary shells. For example, an ion-exchange route has been applied to synthesize a ZnxCd1−xSe shell on a ZnO nanocables array, which demonstrated absorption covering almost the entire visible light region by modulating the shell composition. Solvothermal methods have also been used to fabricate a ZnxCd1−xS shell on a ZnO nanorods array, and their band gap can be controlled by regulating the Zn/Cd ratio during the synthesis process. However, these methods involve complicated chemical reactions. In this way, the shell composition is strongly dependent on multiple chemical or physical factors such as chemical reagent concentration, solution temperature, and reaction time, which make it difficult to control the shell composition precisely. Thus, new strategies are required that can facilely and precisely adjust the chemical composition of a ternary shell.

The chemical-vapor deposition (CVD) technique provides an opportunity for the rational design of a ternary semiconductor shell with spatially graded compositions by simply controlling the deposition temperature. For example, a composition-tunable ZnxCd1−xTe ternary shell has been fabricated onto a pregrown ZnO nanowires array by temperature-gradient CVD. Our group has also synthesized a ZnSxSe1−x ternary shell on a pregrown ZnO nanowires array by CVD. However, the absorption edges of the ZnO/ZnCd1−xSe and ZnO/ZnSxSe1−x nanowires array only cover a narrow region of visible light because of the intrinsic large band gaps of these materials. Therefore, for highly efficient photoelectrodes, it is crucial to find a superior material to fabricate a ternary shell that has a much broader light absorption ability. The ZnxCd1−xTe alloy shows a tunable band gap over a wide range from 2.25 to 1.45 eV and thus exhibits significant application potential for use in optoelectronics. Consequently, ZnO/ZnCd1−xTe core/shell nanowires may show superior performance for water splitting. However, nothing has been reported on the growth of a composition-graded ZnxCd1−xTe shell on a ZnO nanowires array or its application in photocatalytic hydrogen production.

In this work, a ternary alloy semiconductor with a ZnxCd1−xTe shell was constructed by a simple CVD method on a ZnO nanowires array. By optimizing the experimental conditions, the Zn content of the ZnCd1−xTe shell can be gradually adjusted from 0 to 1 by simply controlling the deposition location in the CVD furnace. The absorption edge of this ZnO/ZnxCd1−xTe core/shell nanostructure can be extended from the UV (380 nm) to the NIR (855 nm) region with an increase of the Cd composition, which covers nearly 22% of the entire solar spectrum. In addition, the synthesized...
Zn₇Cdₓ⁻ₓTe shell is highly crystalline, which favors the fast transport of photogenerated carriers. Electrochemical impedance spectroscopy (EIS) was employed to investigate the charge-transfer and recombination processes. The results demonstrate that the Zn₇Cdₓ⁻ₓTe shell-decorated ZnO nanowires array has an enhanced photoelectrochemical (PEC) performance. Significantly, the Zn₇Cdₓ⁻ₓTe shell profoundly enhances the yield of hydrogen from the ZnO nanowires array. The ZnO/Zn₇Cdₓ⁻ₓTe nanowires array developed in our work provides a new platform for the design of highly efficient solar cells and photocatalysts.

**EXPERIMENTAL SECTION**

**ZnO/Zn₇Cdₓ⁻ₓTe Core/Shell Nanowires Array Synthesis.** The ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires array was prepared on ITO substrates by a two-step process: growth of the ZnO nanowires array by a hydrothermal method and deposition of the Zn₇Cdₓ⁻ₓTe shell on the pregrown ZnO nanowires array by CVD. In the first step, the ITO substrates were chemically cleaned by ethanol and then exposed to UV irradiation. After that, the ITO substrates were seeded by a ZnO suspension. In a typical H₂-production experiment, two pieces of pure Zn₇Cdₓ⁻ₓTe nanowires on the ITO substrate, three pregrown samples (P1–P3) were placed at the bottom of a furnace was heated at 700 °C. After the growth of ZnO nanowires on the ITO substrate, three pregrown samples (P1–P3) were placed downstream of the gas flow. A mixture of high-purity ZnTe and CdTe powders (Alfa Aesar, 99.99%) with a ratio of 2:1 was placed in the center of the furnace as the vapor source. The distance between the ITO substrate and source ranged from 8 to 12 cm. A schematic diagram of the reactor setup is shown in Figure 1a. The furnace was heated at 700 °C by two steps as follows: first from room temperature to 500 °C at a rate of 70 °C/min and then from 500 to 700 °C with a rate of 100 °C/min. Once sample heating was completed, the furnace was cooled to room temperature rapidly under an argon gas atmosphere at a flow rate of 100 sccm.

**XRD and Absorption Measurements.** Elemental composition analysis was determined by X-ray diffraction (XRD) on an (Philips X’Pert Pro Super) X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). UV–vis–NIR diffuse reflectance spectroscopy (DRS) of the ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires array was performed with a Hitachi U-3100 in diffuse reflection mode with a range of 300–1100 nm.

**Photoelectrochemical Measurements.** Photoelectrochemical properties of the ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires array were determined on a CHI660D electrochemical system (Shanghai, China). All photoelectrochemical measurements were taken in a rectangular quartz reactor electrolyte solution with a standard three-electrode system: ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires array, working electrode; Pt wire, counter electrode; and standard calomel electrode (SCE), reference electrode. The as-prepared electrode was immersed into a 0.1 M Na₂SO₄ electrolyte solution with an area of 2 × 3 cm². The photocurrents were measured under a 500 W xenon lamp (Beijing China Education Au-light Co. Ltd.) with a 420 nm cutoff filter at 0.0 V versus SCE. Here, the incident light intensity is maintained at 377 mW/cm².

**Photocatalytic H₂ Evolution Measurements.** The photocatalytic H₂ evolution by water-splitting experiments was conducted in a 300 mL pyrex reactor under photoirradiation conditions that was coupled with a gas chromatograph (TianmeiGC-7900) equipped with a thermal conductivity detector. A 300 W xenon lamp with a cutoff filter (250 < λ < 780 nm, 751.6 m W/cm²) was used to irradiate the suspension. In a typical H₂-production experiment, two pieces of pure ZnO, P1–P3 samples, respectively, were placed at the bottom of a quartz reactor containing 80 mL of a mixed aqueous solution with 0.25 M Na₂SO₄ and 0.35 M Na₂S as sacrificial agents. Before irradiation, the system was bubbled with Argon for 1 h to remove the air and to ensure that the system was under anaerobic conditions. A certain amount of gas was sampled through the septum. Meanwhile, the generated H₂ was analyzed by gas chromatography.

**RESULTS AND DISCUSSION**

The morphology and microstructure of the as-prepared ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires array were examined by Hitachi S-4800 field-emission scanning electron microscopy (FE-SEM) and FEI Tecnai F20 high-resolution transmission electron microscopy (HRTEM). A typical SEM image of ZnO nanowires grown on ITO substrates is shown in Figure 1b. The diameters of pristine ZnO nanowires ranged from 50 to 150 nm. After coating with Zn₇Cdₓ⁻ₓTe, the diameters of the ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires array increased to 100–200 nm, as displayed in Figure 1c, and the surface of the pristine ZnO nanowires became rough. Figure 1d shows an X-ray energy-dispersive spectrum (EDS) acquired from sample P2. The peak intensities of Cd and Te gives their atomic ratio as 0.89 to 1.58. The elements Cd and Te likely come from the ternary Zn₇Cdₓ⁻ₓTe shell. To obtain further information on the microstructure and crystallinity of the ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires array, TEM and HRTEM were carried out on sample P2. In Figure 1e, it can be clearly seen that the ZnO nanowire is covered by a 50 nm thick Zn₇Cdₓ⁻ₓTe shell with a distinct interface between the ZnO nanowire and Zn₇Cdₓ⁻ₓTe shell. Note that the Zn₇Cdₓ⁻ₓTe shell is highly crystalline with an interplanar spacing of 0.253 nm, as exhibited in Figure 1f. The highly crystalline nature of the Zn₇Cdₓ⁻ₓTe shell is beneficial for the separation and transfer of photogenerated carriers. The measured interplanar spacing of the ZnO core is 0.26 nm, which is consistent with that of the (001) plane of ZnO.

To analyze the elemental composition of the different samples, XRD of all samples was performed, as shown in Figure 2a. For comparison, the XRD patterns of a pristine ZnO nanowires array grown on ITO substrate, pure CdTe powder, and pure ZnTe powder are also shown. Samples P1–P3 all show weak peaks at 23.6° (marked by black squares), corresponding to the (111) plane of cubic CdTe (JCPDS 65-1082). They also display peaks at 65.8° (black stars) which is consistent with (331) plane of cubic ZnTe (JCPDS 65-385). The presence of these two peaks on all samples proves that the shell is composed of ternary Zn₇Cdₓ⁻ₓTe. In addition, all samples show a peak at around 29.1°, which belongs to the (111) plane of cubic ZnTe. This peak gradually increases from 28.5° in P1 to 27.5° in P2 and 27.4° in P3 (labeled by black triangles). The trend is in accordance with Vegard’s law. It is known that the ionic radius of Cd²⁺ ions (95 pm) is slightly longer than that of Zn²⁺ ions (74 pm). As more Zn²⁺ ions are substituted by Cd²⁺ ions in samples P1–P3, the interplanar spacing of the (111) plane gradually increases. As a result, the diffraction angle continuously decreases. In addition, all samples exhibit peaks at 31.8, 34.5, 36.2, and 56.6°, which are indexed to the (100), (002), (101), and (110) planes of hexagonal ZnO (JCPDS 89-510), respectively. Obviously, these strong XRD peaks are caused by the ZnO nanowires core. The XRD peak of the ITO substrate at 30.4° also appears for all samples as well as the pristine ZnO nanowires array grown on the ITO substrate. To confirm the Zn content of different Zn₇Cdₓ⁻ₓTe shells further, UV–vis–NIR DRS of the ZnO/Zn₇Cdₓ⁻ₓTe core/shell nanowires was studied, as shown in Figure 2b. The presence of ZnO nanowires array on ITO substrates shows an absorption peak located at ~380 nm, corresponding to the expected band

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the ZnO/ZnS absorption of the ZnO/Zn

For comparison, XRD data of pristine ZnO nanowires, pure CdTe

The band gap of the ternary semiconductor compound can be
decrease step-by-step from 2.20 eV for P1 to 1.57 eV for P2 and
region. Importantly, the absorption edges of the samples
gap (3.3 eV). After coating with Zn$_x$Cd$_{1-x}$Te, the absorption of the ZnO/Zn$_x$Cd$_{1-x}$Te core/shell nanowires is extended to the entire visible light region and part of the NIR region. Importantly, the absorption edges of the samples decrease step-by-step from 2.20 eV for P1 to 1.57 eV for P2 and 1.48 eV for P3 with the increasing Cd content, indicating that the band gap of the ternary semiconductor compound can be adjusted through tuning the element composition. For the Zn$_x$Cd$_{1-x}$Te shells, nonlinear band gaps are dependent on the composition of Zn or Cd. Here, Zn content, $x$, can be fitted through a quadratic relationship as follows

$$E_g(x) = xE_g(ZnTe) + (1 - x)E_g(CdTe) - x(1 - x)b$$

(1)

where $E_g(x)$, $E_g(ZnTe)$, and $E_g(CdTe)$ are the band gaps of Zn$_x$Cd$_{1-x}$Te, ZnTe, and CdTe, respectively. According to the literature, the band gaps of ZnTe and CdTe are 2.25 and 1.45 eV, respectively, and $b$, the bowing parameter, is set as 0.76. Therefore, the Zn concentration, $x$, of samples P1–P3 is calculated to be 0.76, 0.21 and 0.07, respectively. Figure 2c shows the plots of Zn composition versus band gap of the Zn$_x$Cd$_{1-x}$Te shell. The band gap of the Zn$_x$Cd$_{1-x}$Te shell continuously increases with an increase of the Zn composition. Consequently, the band gap of the ZnO/Zn$_x$Cd$_{1-x}$Te core/shell nanowires can be modulated by controlling the deposition location of the samples.

Electrochemical measurements were performed to investigate the PEC properties of ZnO/Zn$_x$Cd$_{1-x}$Te electrodes under visible-light irradiation ($\lambda > 420$ nm). Figure 3a shows the amperometric current–time ($I - t$) curves of different samples (P1–P3) at 0 V versus SCE with the light on and off. When the light turns on, the photocurrent density of sample P1 sharply increases from 0.1 to 0.76 $\mu$A/cm$^2$. As for P2, the dark current density is 0.05 $\mu$A/cm$^2$, and the photocurrent density is 2.25 $\mu$A/cm$^2$. Sample P3 has the same dark current density as P2 but a higher photocurrent density, 5.45 $\mu$A/cm$^2$. However, the pregrown ZnO nanowires array photocathode has no distinct photoreresponse under visible-light irradiation because of its large band gap (3.3 eV). These results suggest that (1) compared with pristine ZnO nanowires photocathodes, the photoelectrodes coated by Zn$_x$Cd$_{1-x}$Te shells significantly improve visible-light absorption efficiency and (2) with the increase in Cd content from P1 to P3, the visible-light absorption range gradually increases, which is consistent with the results of UV–vis–NIR DRS. Electrochemical impedance spectroscopy (EIS) is considered to be a powerful tool to study charge-transfer and recombination processes of photoelectrodes. EIS Nyquist plots of ZnO and ZnO/Zn$_x$Cd$_{1-x}$Te photocathodes under visible-light irradiation are presented in Figure 3b. The arc radius of the ZnO/Zn$_x$Cd$_{1-x}$Te electrodes (P1–P3) is much smaller than that of the pristine ZnO electrode under visible-light irradiation, which suggests that the band gap of the Zn$_x$Cd$_{1-x}$Te shell on the ZnO nanowires array notably improves separation efficiency of photogenerated electron–hole pairs and thus reduces charge-transfer resistances. In addition, with the increase in Cd content from P1 to P3, the arc radius gradually decreases. This is likely because the visible-light absorption range of P3 is much larger than those of P2 and P1. As a result, more photogenerated carriers are produced inside sample P3, leading to smaller impedance.

Figure 4 shows the photocatalytic H$_2$-production activity of samples P1–P3 from an aqueous solution containing Na$_2$S and Na$_2$SO$_3$ under UV–vis irradiation together with that of pristine ZnO nanowires for comparison. As shown in Figure 4a, the photocatalytic H$_2$-production activity of pure ZnO nanowires is revealed during 5 h of light illumination. With the presence of Zn$_x$Cd$_{1-x}$Te, the H$_2$-evolution property is remarkably enhanced. The amount of H$_2$ generated on the basis of sample P3 reaches 1.326 mmol/g, which is over 2-fold greater than that of pure ZnO nanowires (0.522 mmol/g). Note that the amount of H$_2$ generated increases with the increase in the Cd content, which is consistent with the PEC results. Moreover, the rate of H$_2$ evolution of the samples in Figure 4b shows a value of 265 $\mu$mol h$^{-1}$ g$^{-1}$ for sample P3. The pristine ZnO nanowires on ITO substrate, however, give an evolution rate of 104 $\mu$mol h$^{-1}$ g$^{-1}$. These results demonstrate that the presence of the Zn$_x$Cd$_{1-x}$Te crystalline shell is crucial for the improved
The performance of these photocatalysts. As a result, the H₂-production efficiency increase by ~2.6-fold when exposed to UV−vis irradiation when Na₂S/Na₂SO₃ are used as hole scavengers. Furthermore, with variation of x in ZnₓCd₁−ₓTe from 0.76 to 0.07, the photocatalytic activity increases from 226 to 265 μmol h⁻¹ g⁻¹ because of the enhancement of visible-light absorption efficiency. Throughout the testing cycles displayed in Figure 4c, sample P3 exhibits a persistent high H₂-production capability. Therefore, the crystalline ZnₓCd₁−ₓTe shell protects the ZnO nanowires to some extent during the light irradiation. The mechanism of the H₂-production performance of ZnO/ZnₓCd₁−ₓTe electrodes (P1−P3) can be elucidated by the schematic illumination of electron−hole separation and transport at the ZnO/ZnₓCd₁−ₓTe interface in Figure 4d. As known, the light-absorption capability of a semiconductor is a crucial factor for photocatalytic H₂ production. The ZnO/ZnₓCd₁−ₓTe core/shell structure remarkably extends the absorption range of light from UV to NIR, which greatly enhances the light-absorption capability in comparison with pure ZnO nanowires. However, it is worth noting that photogenerated carriers will recombine fast, leading to a low photocatalytic H₂ production. In this work, a single crystalline ZnₓCd₁−ₓTe shell and well-aligned ZnO/ZnₓCd₁−ₓTe interface were achieved by optimizing the CVD conditions. Thus, the built-in field formed at the type II heterostructure interface favors the vertical transfer of photogenerated electrons from the CB of ZnₓCd₁−ₓTe to the CB of ZnO, which provides a direct path for electron transfer. The H⁺...
in the solution is then reduced to a hydrogen molecule with the photogenerated electrons collected on ITO substrates. Meanwhile, the holes are transferred to the valence band (VB) of the Zn\textsubscript{1-x}Cd\textsubscript{x}Te shell and then consumed by the sacrificial agents (S\textsuperscript{2-} and SO\textsubscript{2} \textsuperscript{2-}). Consequently, the photogenerated charge-separation efficiency is improved because of the declining charge-recombination rate.\textsuperscript{29} Moreover, the increase of the spectra absorption range mentioned above is also crucial to obtain better H\textsubscript{2}-production performance of the ZnO/Zn\textsubscript{1-x}Cd\textsubscript{x}Te nanowires.\textsuperscript{30} For the ZnO/Zn\textsubscript{1-x}Cd\textsubscript{x}Te core/shell nanostructure, a significant advantage should be noted: the ternary shell Zn\textsubscript{1-x}Cd\textsubscript{x}Te band could be tuned over a large range from ZnTe (2.25 eV, \~ 550 nm) to CdTe (1.45 eV, \~ 855 nm) as the x value increases from 0 to 1, which enhances the visible-light absorption of the whole system. Although the position of the band changes as the x value decreases, we have to notice that the band alignment between the core and shell always keeps the type II structure.

\section*{Conclusions}

We have synthesized a composition-graded ZnO/Zn\textsubscript{1-x}Cd\textsubscript{x}Te core/shell nanowires array on ITO substrates via a hydrothermal method followed by a CVD method. Through controlling the deposition location, the Zn content of the shells can be continuously and exactly tuned from 0 to 1. TEM results explicitly reveal that the Zn\textsubscript{1-x}Cd\textsubscript{x}Te shell is highly crystalline and covers the entire surface of the ZnO nanowire. Importantly, the ZnO/Zn\textsubscript{1-x}Cd\textsubscript{x}Te core/shell nanowires array shows a broad absorption range from UV to NIR by adjusting the shell composition. The introduction of the Zn\textsubscript{1-x}Cd\textsubscript{x}Te shell to the ZnO nanowires also profoundly improves the photogenerated charge-separation process because of the formation of a type II heterojunction at the interface. As expected, an enhanced yield of hydrogen was observed after coating the ZnO nanowires with a Zn\textsubscript{1-x}Cd\textsubscript{x}Te shell. These results are of great significance for the design of composition-modulated core/shell electrodes with a large and well-controlled absorption range from UV to NIR.

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Notes

The authors declare no competing financial interest.

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