Rational and scalable fabrication of high-quality WO$_3$/CdS core/shell nanowire arrays for photoanodes toward enhanced charge separation and transport under visible light

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High-quality one-dimensional WO$_3$/CdS core/shell nanowire arrays used as photoanodes in photoelectrochemical (PEC) cells were for the first time prepared via a rational, two-step chemical vapor deposition process. The narrow band-gap CdS shell was homogeneously coated on the entire surface of as-grown WO$_3$ core nanowire arrays, forming coaxial heterostructures. The one-dimensional core/shell heterostructure facilitates the photogenerated electron–hole pair separation and the electron transfer from CdS to WO$_3$ nanowires under visible light illumination. Moreover, the core nanowire arrays provide a direct pathway for the electron transport. The present results imply that the WO$_3$/CdS core/shell heterostructure nanowire arrays may be useful in the design of nanomaterial photoanodes toward highly efficient PEC cells.

Introduction

Nanomaterials and nanostructures have been extensively investigated and applied as fundamental building blocks for the development of next generation solar energy conversion devices. One-dimensional nanostructures, such as nanowires, nanorods and nanotubes, provide a direct pathway for charge transport and high electron mobility for efficient electronic devices due to their high aspect ratio and high surface to volume ratio. Furthermore, one-dimensional nanostructure arrays generally have the advantage of low reflectance because of light scattering and trapping over a wide spectrum range, endowing them with superior optical absorption properties compared with thin films. Therefore, one-dimensional nanomaterials could be used as promising photoanodes for photoelectrochemical (PEC) or solar cells, which require effective light harvesting, low recombination of photogenerated carriers, and fast diffusion for efficient photoinduced performance. Relative to single-material nanowires, the composite core/shell nanowires can take advantage of each material and compensate for their individual shortcomings to show synergistic effects. Construction of a junction heterostructure between the narrow bandgap semiconductor shell and the wide bandgap semiconductor nanowire core provides significant advantages both for light absorption and charge separation.

Owing to these benefits, several types of core/shell heterostructures, such as ZnO/ZnS$_x$Se$_{1-x}$, ZnO/Cd$_x$Se$_{1-x}$, ZnO/Zn$_x$Cd$_{1-x}$Se$_x$, TiO$_2$/Cd$_x$S$_{1-x}$, and TiO$_2$/CdS$_x$ have been demonstrated as potential candidates for solar energy conversion, which could absorb visible light and enhance the charge separation of photogenerated electrons and holes by transferring photoelectrons from shell to core.

With the ability to further extend into the visible-blue region of the solar spectrum as compared to UV-light active TiO$_2$ and ZnO, WO$_3$ has been studied extensively as a visible-light-responsive photocatalyst and photoelectrode. Heterojunction films have been extensively investigated, such as WO$_3$/Fe$_2$O$_3$, WO$_3$/BiVO$_4$, InVO$_4$/WO$_3$ and WO$_3$/Cu$_2$O, which improved the efficient carrier separation in the heterojunction, resulting in promising photoelectrochemical activity. CdS is a well-known semiconductor material that has been widely used as a visible-light active photocatalyst, and also as a photosensitizer for various wide bandgap semiconductor photoanodes due to its narrow direct bandgap (~2.4 eV). CdS
nanoparticle modified WO₃ nanowhiskers showed enhanced visible light absorption and improved photodecomposition efficiencies.

In this paper, the high-quality WO₃/CdS core/shell nanowire arrays as promising photoanodes of PEC cells were successfully prepared via a rational, two-step chemical vapor deposition (CVD) method. The high-density arrays of monoclinic single-crystalline WO₃ nanowires were grown directly on a tungsten foil substrate through a CVD route, leading to a considerable decrease in defects and improvement in the transport of carriers. Then the WO₃ nanowires were sheathed with the narrow bandgap semiconductor CdS shell deposited by a subsequent CVD. The vapor-phase growth is desirable not only for the synthesis of high-crystallinity nanowires but also for the achievement of high-density nanowire arrays on a substrate, which is crucial for their solar energy conversion. Compared to the pristine WO₃ nanowire arrays, the WO₃/CdS core/shell nanowire heterostructures exhibit enhanced visible light absorption, efficient charge separation, and high transfer efficiency of photogenerated electrons due to the presence of a nanometer-size heterointerface between the semiconductor shell and the nanowire core. To the best of our knowledge, this is the first report to synthesize WO₃ nanowire arrays sheathed with CdS.

**Experimental**

**Fabrication of WO₃ nanowires**

In a typical synthesis, WO₃ powder (99.9% purity) was placed in a quartz tube located in a conventional horizontal furnace, acting as a source material. Tungsten foil used as a substrate was cleaned with alcohol, acetone and deionized water in an ultrasonic cleaner, and then positioned at the low temperature zone, downstream of the source material. After the quartz tube was pumped down to a vacuum of ~80 Pa, the temperature of the tube was increased from room temperature to 1000 °C. During the whole heating process, a carrier gas of high-purity Ar (99.999% purity) was passed through the quartz tube at a rate of 300 sccm (standard cubic centimetres per minute). After being grown for 6 h, the furnace was naturally cooled to room temperature in the flowing carrier gas. The samples were annealed in air at 500 °C for 1 h to obtain WO₃ nanowires.

**WO₃/CdS core/shell and CdS nanowire synthesis**

For deposition of the CdS outer layers, the WO₃ nanowire arrays grown on the substrate were placed a few cm apart from the CdS (99.9% purity) powder, inside a quartz tube. With ~100 sccm of high-purity Ar gas, the furnace temperature was raised to 850 °C. During growth, the pressure in the quartz tube was controlled at ~50 Pa. After 20 min of deposition, the furnace was allowed to cool to room temperature under the argon flow, resulting in the successfully uniform coating of CdS on the WO₃ nanowires. As a comparison, we also synthesized random CdS nanowires on a tungsten substrate under the same growth conditions.

**Characterizations**

Crystallographic phases and purity information of the prepared samples were investigated by X-ray diffraction (XRD) at room temperature. The XRD pattern was recorded on a Rigaku-D/Max 2500 V/PC X-ray diffractometer using Cu Kα radiation (λ = 1.54056 Å) at 40 kV and 200 mA. The field emission scanning electron microscopy (FE-SEM) images were obtained on an XL30 ESEM FEG scanning electron microscope operating at 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were observed on a JEM 200CX TEM instrument. X-ray photoelectron spectroscopy (XPS) spectra were collected on an ESCALab MKII X-ray photoelectron spectrometer, using a non-monochromatized Mg K X-ray as the excitation source. The binding energies were corrected for specimen charging by calibrating the C 1s peak to 284.6 eV. A Shimadzu UV-2550 UV-vis spectrometer fitted with an integrating sphere was used to investigate the optical absorption of the samples. UV-visible absorption spectra of powder samples were recorded using a pure BaSO₄ pellet as the reference.

**Photoelectrochemical measurements**

The photoelectrochemical properties were examined in a standard three-electrode configuration in a Pyrex glass cell by using an electrochemical analyzer (CHI-633C, Shanghai Chenhua). The WO₃ nanowires, CdS nanowires, and WO₃/CdS core/shell nanowires were used as the working electrode, or photoanode, a Pt foil and an Ag/AgCl electrode were used as the counter and the reference electrode, respectively. A xenon lamp (500 W) was used as a light source and a 420 nm cutoff filter was used to obtain visible light. Phosphate aqueous solution (0.1 M, pH ≈ 7.0) was used as buffer, and a 0.1 M Na₂S electrolyte (pH ≈ 7.0) was used for the PEC measurements. Electrochemical impedance spectroscopic (EIS) curves of the samples were also observed with a PAR2273 workstation (Princeton Applied Research, USA). The frequency range was from 50 mHz to 100 kHz.

**Photoluminescence decay measurements**

The 800 nm output of a 76 MHz, picosecond Ti:Sapphire laser was used to get the excitation wavelength of 400 nm from the second generation processes. A 400 nm laser beam with a power density of ~100 W cm⁻² and at an incident angle of ~45° relative to the normal direction was focused onto the samples at room temperature. The fluorescence signal was collected vertically from the sample surface by a 60× microscope objective and sent through a 0.5 m spectrometer to a charge-coupled-device camera for spatial and spectral PL characterizations or to an avalanche photo diode for the PL decay measurements using a time-correlated single-photon counting system with a time resolution of ~250 ps.

**Results and discussion**

The XRD patterns of WO₃ nanowires, CdS nanowires, and WO₃/CdS core/shell nanowires show that the as-grown pristine WO₃
nanowire arrays correspond to the monocline phase of WO3 (JCPDS 43-1035) (Fig. 1). The random CdS nanowires are identical to the hexagonal structure of CdS (JCPDS 41-1049). In the case of WO3/CdS core/shell nanowires, besides the differentiation peaks assigned to WO3, all additional ones are wellmatched to the hexagonal structure of CdS, indicating the presence of a CdS shell coated on the WO3 nanowire core.

The photographs of the WO3 nanowires, WO3/CdS core/shell nanowires and CdS nanowires are shown in Fig. 2a–c, compared with the pristine WO3 nanowires, the color of the as-grown WO3/CdS core/shell nanowires obviously changed to orange. The FE-SEM images observably reveal the high density and uniform vertical alignment of WO3 nanowires grown on a tungsten foil substrate (Fig. 2d). The individual WO3 nanowires have a smooth lateral surface and uniform diameter along their entire length (Fig. 2g), which qualitatively favor the formation of heterostructures with an abrupt interface. The initial alignment of the WO3 nanowires was largely maintained after the formation of WO3/CdS core/shell nanostructures (Fig. 2e). As compared with the pristine WO3 nanowires, the WO3/CdS core/shell nanowires exhibit a rougher surface after CdS deposition (Fig. 2h). In addition, the surface of the CdS shell along the length of the nanowires is markedly similar, and nearly all the nanowires are uniformly coated (Fig. 2h), implying the formation of high-quality core/shell nanostructures. The dimensions of the as-prepared random CdS nanowires are highly uniform, and the surface is clearly smooth (Fig. 2f and i). The spatial chemical compositions of WO3, CdS and WO3/CdS nanowires were further identified by EDS spectra (Fig. 2j–l), confirming the presence of Cd and S elements on WO3 nanowires. The EDS elemental mapping of WO3/CdS core/shell nanowires identifies that the outer layers of the WO3 core nanowires are homogeneously composed of Cd and S elements (Fig. 3a–e). The EDS line-scanning also reveals the presence of W and O elements in the core part and Cd and S elements in the shell part (Fig. 3f).

The TEM image shows that the surface of a pristine WO3 nanowire is clearly smooth, and the lattice spacing of WO3 is 0.372 nm, which corresponds to the [020] plane of monoclinic WO3 (Fig. 4a), which is in good agreement with the result of the fast Fourier transform (FFT) pattern of WO3 nanowires (the inset in Fig. 4a), confirming that the WO3 nanowires were grown with the [020] orientation. For WO3/CdS core/shell nanowires, the entire surface of the WO3 nanowires was homogeneously coated with a thin CdS shell, displaying typical core/shell nanostructures (Fig. 4b). The CdS shell is of uniform thickness along the length of the WO3 nanowires. Moreover, the shell in the head end has the same thickness with that in the body (the inset in Fig. 4b), which demonstrated that the CdS shell layer continuously covered the entire surface of the WO3 nanowires core. The high magnification TEM (HRTEM) image of the WO3/CdS core/shell nanowires shows that the CdS shell grows directly on the WO3 nanowires (Fig. 4c). The TEM image of the random CdS nanowire reveals that the nanowire is relatively uniform (Fig. 4d). The HRTEM image and FFT pattern of the CdS nanowire reveals that the CdS nanowires are single crystal.

**Fig. 1** XRD patterns of the (a) WO3, (b) WO3/CdS and (c) CdS samples.

**Fig. 2** Optical image of (a) WO3 nanowires, (b) WO3/CdS core/shell nanowires and (c) CdS nanowires. Low magnification SEM images and cross-sectional SEM images (the inset) of (d) WO3 nanowires, (e) WO3/CdS core/shell nanowires, and (f) CdS nanowires. High magnification SEM images of (g) WO3 nanowires, (h) WO3/CdS core/shell nanowires, and (i) CdS nanowires. EDS results of (j) WO3 nanowires, (k) WO3/CdS core/shell nanowires, and (l) CdS nanowires.

**Fig. 3** (a) SEM image of WO3/CdS core/shell nanowires. EDS elemental (b–e) mapping and (f) line-scan reveal the presence of W, O, Cd and S elements.
and the measured lattice spacing is about 0.332 nm, which is well-matched to the (002) lattice plane of hexagonal CdS (the inset of Fig. 4d).

Fig. 5 shows the XPS spectrum of the pristine WO3 nanowires and WO3/CdS core/shell nanowires. The strong peak binding energies were observed at 35.5, 37.5, and 41.3 eV, which correspond to spin-orbit splitting of the W4f7/2, W4f5/2 and W5p3/2 components, respectively, in tungsten oxides (Fig. 5a), suggesting that the W6+ ions are dominant in the product, and the XPS O 1s core-level binding energies of the tungsten oxide samples correspond to 531.0 eV (Fig. 5b).44,45 In addition, the XPS spectra of the WO3/CdS nanowires show the presence of peaks at 404.5 eV and 411.3 eV corresponding to Cd2+ and at 161.0 eV corresponding to S2− (Fig. 5c and d),46,47 further confirming the formation of the CdS shell. Furthermore, the peaks of W4f and W4p for WO3/CdS core/shell nanowires were not clearly observed, as shown in Fig. 5e, implying that the entire surface of the WO3 nanowires continuously and homogeneously sheathed with the CdS shell layer. On the basis of the above analysis results, it can be concluded that high-quality WO3/CdS core/shell heterostructure nanowire arrays were successfully fabricated using this rational, two-step CVD process.

To examine the optical properties of WO3, CdS and WO3/CdS core/shell nanowires, the spatial UV-vis diffuse reflection absorption spectra were studied (Fig. 6). It is clear that the densely deposited CdS on WO3 nanowires has a significant effect on the optical property of light absorption. Relative to the absorption edge of the pristine WO3 nanowires near 440 nm, the spectral position of the absorption edge red shifts to about 550 nm for the WO3/CdS core/shell nanowires (Fig. 6a), which exhibit obviously enhanced light absorption capacity in the visible light region. The band gap, $E_g$, could be determined using the equation48

$$ (a h \nu)^n = A(h \nu - E_g) $$

where $\alpha$ is the absorption coefficient, $h \nu$ is the light energy, $A$ is a constant, $E_g$ is the optical band gap energy, and $n$ is equal to 1/2 for an indirect band gap and 2 for a direct band gap. The transition of WO3 and CdS is indirect and direct, respectively. According to eqn (1), the band gaps of the WO3, CdS and WO3/CdS nanowires were estimated to be 2.77, 2.36 and 2.32 eV from the onset of the absorption curves (Fig. 6b and c), respectively, which are consistent with the bulk values,48 indicating that the absorption range of WO3 nanowires was enhanced by coupling of narrow band-gap CdS.

Due to the importance of photoelectrochemical cells as solar energy conversion devices, we employed WO3/CdS core/shell

![Fig. 4](image-url)  
(a) TEM image of WO3 nanowires; the inset is the corresponding HRTEM image and the FFT pattern. (b) TEM image of WO3/CdS core/shell nanowires. The inset is the enlarged head ends of the WO3/CdS core/shell nanowires. (c) HRTEM image of the WO3/CdS core/shell nanowires. (d) TEM image of CdS nanowires; the inset is the corresponding HRTEM image and the FFT pattern.

![Fig. 5](image-url)  
XPS spectra analysis of the WO3 and WO3/CdS core/shell nanowires: narrow scan for (a) W element, (b) O element, (c) Cd element and (d) S element; (e) wide scan for WO3/CdS core/shell nanowires.

![Fig. 6](image-url)  
(a) UV-visible absorption spectra of bare WO3 nanowires, WO3/CdS core/shell nanowires, and CdS nanowires. The band edge of (b) WO3 nanowires, and (c) WO3/CdS core/shell nanowires and CdS nanowires.
nanowires as photoanodes in a three-electrode PEC system with pristine WO3 nanowire arrays and random CdS nanowires as comparison references. As shown in Fig. 7I, the photocurrent–time (I–t) curves of the pristine WO3 nanowires, CdS nanowires and WO3/CdS core/shell nanowires photoanodes at 0 V versus Ag/AgCl under visible light illumination (λ ≈ 420 nm) on and off were measured. The changes of both “on” and “off” currents are nearly vertical, implying that charge transport in the WO3/CdS core/shell nanowires proceeds very quickly. Moreover, as shown in Fig. 7I, the photoelectric sensitivity defined as ($I_{\text{light on}} - I_{\text{light off}}$)/$I_{\text{light on}}$ for WO3 nanowires, CdS nanowires and WO3/CdS core/shell nanowires was found to be ~8.7%, ~17.4% and 189.9%, respectively. It means that the photocurrent densities of WO3/CdS core/shell nanowires possess the highest response under visible light, which may result from the arrayed nanostructure and the band energy alignment of WO3/CdS core/shell nanowires, i.e. one-dimensional WO3/CdS core/shell nanowire arrays have low reflectance due to light scattering and trapping, and the narrow band-gap CdS shell improves visible light harvesting.

The energy band diagram for WO3/CdS core/shell nanowires could be explained by the possible mechanism for the enhanced photosensitivity under visible light irradiation. Such core/shell nanowire heterostructures of WO3/CdS should form type-II band alignment (as shown in the schematic diagram in Fig. 7II). As the conduction band (CB) level and valence band (VB) level of pristine WO3 nanowires, WO3/CdS core/shell nanowires and CdS nanowires are more negative than the corresponding bands of WO3, the electron–hole pairs are photogenerated in a CdS shell under visible light illumination, and the photoexcited electrons in a CdS shell favorably transfer from the CB of the CdS shell to that of the WO3 core due to the potential difference, in turn suppressing the recombination of the electron–hole pairs, and they act as a catalyst for reductive reaction. Furthermore, the WO3 nanowires provide a direct pathway for electron transport from WO3 to the tungsten substrate, in which facile electron transfer also would reduce the chance of recombination with holes. On the other hand, the photogenerated holes theoretically travel in the opposite direction from VB of WO3 to that of CdS and participate in the oxidation reaction, and the opportunities for electron–hole recombination can be substantially reduced.

Electrochemical impedance spectroscopy (EIS) is a powerful tool to investigate charge separation/transfer and recombination processes in PEC and solar cells. Fig. 8 shows the impedance spectra of WO3, CdS and WO3/CdS core/shell nanowires at the applied potential of 0 V vs. Ag/AgCl in 0.1 M Na2S electrolyte (pH ≈ 7) under visible light illumination. The charge transfer occurs on the photoanodes, and the radius of the arc is correlated with the charge-transfer ability at the interface of the photoelectrode–electrolyte.49–52 The efficient charge transfer at the interface of the photoelectrode–electrolyte reduces the charge recombination and results in the facile charge transport of electrons through the films.43,44 As a result, the arc radius of the WO3/CdS core/shell nanowires is remarkably smaller than those of the WO3 and CdS nanowires (Fig. 8), which indicates that the WO3/CdS core/shell nanowires have a very good efficiency of charge transfer and a more effective charge separation.

The room-temperature photoluminescence decay of the pristine WO3 nanowires, WO3/CdS core/shell nanowires and CdS nanowires shows that the WO3/CdS nanowires exhibit a longer PL lifetime (~1.74 ns) than the WO3 (~0.26 ns) and CdS (~1.50 ns) nanowires (Fig. 9). This result is in accordance with the amperometric I–t curve data (Fig. 7I) and the CB edge position of the different electrodes (Fig. 7II). As both the VB and CB edges of CdS are higher than those of WO3 in the type-II WO3/CdS core/shell nanowires, the energy gradient existing at the interfaces tends to spatially separate electrons and holes on different sides of the heterojunction, favorable for reducing the combination of electron–hole pairs. As a result, the photogenerated carrier lifetime could be significantly enhanced. These long-lived charge-separated states make the core/shell nanorods most suitable for photovoltaic or photoconduction applications.

![Fig. 7](image7.png) (I) Amperometric I–t curves of (a) pristine WO3 nanowires, (b) WO3/CdS core/shell nanowires, and (c) CdS nanowires at a zero bias versus Ag/AgCl voltage with visible light (λ ≈ 420 nm) on/off cycles. (II) WO3/CdS core/shell nanowire photoanode structure (left) and the charge transfer process (right).

![Fig. 8](image8.png) Nyquist plots of measured EIS spectra of pristine WO3 nanowires, CdS nanowires, and WO3/CdS core/shell photoelectrodes under visible light (λ ≈ 420 nm).
Conclusion

High-quality WO$_3$/CdS core/shell nanowire array heterostructures were successfully synthesized through a rational, two-step CVD method. The CdS shell is uniformly deposited on the entire surface of the WO$_3$ nanowires along the whole length to form the core/shell heterostructures. The photoelectric sensitivity of the WO$_3$/CdS core/shell nanowires is higher than that of WO$_3$ and CdS nanowires under visible light illumination. The WO$_3$/CdS core/shell nanowires also exhibit lower charge transfer resistances and longer decay times than the pure WO$_3$ and CdS nanowires. The spatial separation of the charges and facile charge transfer progress enhance lifetime and photoelectric sensitivity. The attractive one-dimensional core/shell heterostructures offer a promising strategy for improving PEC cell efficiencies.

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