Crystalline ZnO/ZnS_xSe_{1-x} core–shell nanowire arrays for efficient visible-light photoelectrocatalysis†

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ZnO/ZnS_{x}Se_{1−x} core–shell nanowire arrays on a silicon substrate were successfully prepared via a hydrothermal method followed by chemical vapor deposition (CVD) of the ZnS_{x}Se_{1−x} shell. By optimizing the CVD growth conditions, a crystalline ZnS_{x}Se_{1−x} shell and well-aligned ZnO/ZnS_{x}Se_{1−x} interface were achieved, which plays an important role towards the enhanced performance of photocatalytic activity. The introduction of the crystalline, lattice-matched ZnS_{x}Se_{1−x} shell to ZnO nanowires significantly enhances the photocatalytic and photoelectrocatalytic activity under UV light irradiation. More attractively, after being combined with the ZnS_{x}Se_{1−x} shell, the visible light photoelectrocatalytic activity of the ZnO/ZnS_{x}Se_{1−x} core–shell nanowires is observed. The performance enhancement of ZnO/ZnS_{x}Se_{1−x} core–shell nanowires under irradiation is mainly due to matching lattice and band energy level alignment between the crystalline ZnS_{x}Se_{1−x} shell and ZnO nanowire core. The high crystal quality of the ZnS_{x}Se_{1−x} shell and the band alignment of the ZnO/ZnS_{x}Se_{1−x} core–shell greatly enhance the charge separation efficiency and prolong the life-time of photogenerated charge carriers. Our finding is expected to provide a new insight into the fabrication of novel and high performance nanowire based core–shell photocatalysts.

Introduction

Among various semiconductor photocatalysts, metal-oxides such as TiO_2 (3.4 eV) and ZnO (3.2 eV) have been extensively investigated due to their relatively high photocatalytic activity and low cost. However, the high photogenerated charge recombination rate and poor visible light response of these photocatalysts have hindered the large-scale industrial applications of photocatalysis (PC). Photoelectrocatalysis (PEC), driving the photogenerated electron to a counter electrode via an external bias potential, has shown higher efficiency in the destruction of contaminants when compared with photo-oxidation and photocatalysis.1–5 Compared with TiO_2, ZnO is also an important photocatalyst due to its superiority in higher electron mobility and higher removal of some specific organic contaminants.6–8 To improve the activity of a photoelectrode, one dimensional (1D) nanowires are emerging as a promising photoelectrode due to their large surface-to-volume ratio and rapid charge transport.9 ZnO nanowires have been widely used in photoelectrochemical cells10–11 and detection.12–15 To date, considerable efforts have been carried out to enhance the photogenerated charge separation efficiency and solar energy utilization of ZnO.16–22

Combining ZnO nanowires with another narrow band-gap semiconductor can introduce a visible light response. In addition, the charge transport from ZnO to another semiconductor can lead to efficient charge separation, hence reducing the probability of photogenerated electron–hole recombination.23 Various II–VI group semiconductors with narrow band gaps have been widely used in combination with ZnO nanowires, such as CdS,24 CdTe,26 and CdTe.27 Yong and co-workers synthesized a type-II CdS nanoparticle–ZnO nanowire heterostructure and achieved enhanced photocatalytic activity in dye decomposition.24 Significantly, combining ZnO nanowires with a uniform shell structure has demonstrated the advantages of high charge transport efficiency and surface charge separation. A lot of reports have demonstrated the advantages of the core–shell structure, which provide a large interfacial area to ensure rapid charge separation. Moreover, the core nanowires provide a direct electrical pathway for the photo-induced charge carriers to rapidly transfer to the substrate. Compared with binary compounds, ternary compounds have obvious advantages such as continuously tunable composition and band gap capability.

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† Electronic supplementary information (ESI) available: Large-scale SEM image (Fig. S1), PL spectra (Fig. S2), EIS Nyquist plots (Fig. S3) and the effect of external potential on MB degradation on ZnO/ZnS_{x}Se_{1−x} core–shell nanowires under UV irradiation (Fig. S4). See DOI: 10.1039/c4ta04293j
These merits provide the ability to cover a wider range of the solar spectrum and achieve higher solar utilization due to the tunable band gap and absorption.

It is notable that the crystalline shell of the 1D core–shell structure is beneficial for the transfer of photogenerated carriers due to its less defects when compared with an amorphous shell. But, designing a 1D core–shell structure with crystalline shell is full of challenges because of complicated synthetic procedures and rigorous experimental conditions. The crystalline and composition-tuned ternary shell improves the photoelectrochemical performance of the core–shell structure profoundly. The ternary semiconductors, ZnS$_x$S$_{1-x}$ alloy, as an important member of ternary II–VI semiconductors, have a tunable absorption edge ($E_a$) from 340 nm to 460 nm (0 ≤ $x$ ≤ 1), partially in the visible light region. Our group has developed a ZnO/ZnS$_x$S$_{1-x}$ core–shell nanowire using a two-step CVD method and achieves an efficient visible light absorption on this core–shell nanowire. However, the obtained ZnS$_x$S$_{1-x}$ shell was shown to be amorphous, which inhibited the higher efficiency of charge separation and transport.

In this study, we report our efforts in synthesizing crystalline ZnO/ZnS$_x$S$_{1-x}$ core–shell nanowires and exploring the application of this core–shell nanowire in PC and PEC water treatment. High density ZnO nanowires were grown on a Si substrate using a hydrothermal method. By optimizing the CVD growth conditions, a crystalline ZnS$_x$S$_{1-x}$ shell and well-aligned ZnO/ZnS$_x$S$_{1-x}$ interface were achieved. These interesting core–shell nanowires show enhanced PC and PEC performance due to the matching lattice and band energy level alignment between the crystalline ZnS$_x$S$_{1-x}$ shell and ZnO nanowire core. The successful achievement of such core–shell nanowires would be a good demonstration of novel and high performance photocatalysts.

**Experimental section**

**Preparation of the ZnO nanowires and ZnS$_x$Se$_{1-x}$ core–shell nanowires**

ZnO nanowires on a Si substrate were synthesized using a hydrothermal method. Heavily doped n-type Si (100) was chemically cleaned using a dilute HF solution in order to remove the naturally formed native oxide layer. Firstly, a ZnO seed layer was deposited on the Si substrate by a spin-coating method. Then, ZnO nanowires were synthesized in an aqueous solution of 0.0025 M zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) and 0.0025 M hexamethylenetetramine (HMT) heated at 90 °C for 9 h.

The ZnS$_x$Se$_{1-x}$ coating on ZnO nanowires was prepared by a CVD method based on our previous work. High-purity ZnS and ZnSe powders (Alfa Aesar, 99.99%) were mixed as the source materials (ZnS–ZnSe = 3 : 7). The mixed ZnS and ZnSe powders were placed in a quartz boat. The ZnO nanowires were placed downstream of the gas flow and placed 8 cm apart from the source. The furnace was heated to 1100 °C at a rate of 75 °C min$^{-1}$. Then, the furnace was cooled down to room temperature in 20 sccm of argon gas.

**Characterization**

The morphology and microstructure of the as-prepared samples were measured by an Hitachi S-4800 field-emission scanning electron microscopy (FE-SEM) and FEI Tecnai F20 high-resolution transmission electron microscopy (HRTEM). The Tecnai F20 transmission electron microscope was operated at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of the samples were measured on a (Philips X’Pert Pro Super) X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). Raman spectra were examined by a InVo-RENISHAW system at room temperature using 532 nm as the light source. UV-vis diffuse reflectance spectra (DRS) were measured by a UV-vis spectrometer (Hitachi U-3010).

**PC and PEC experiments**

The photoelectrochemical studies and PEC degradation experiments were performed in a rectangular quartz reactor (5 cm × 5 cm × 14 cm), which contained an 80 mL sample solution, allowing 2 cm × 2.3 cm of the as-prepared electrode to be immersed into the solution. All photoelectrochemical studies were performed on a CHI650D electrochemical system (Shanghai, China) equipped with a standard three-electrode system. The as-prepared ZnO nanowires and ZnS$_x$S$_{1-x}$ core–shell nanowires were used as the working electrode, a platinum wire as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. All photoelectrochemical measurements were performed in a 0.1 M Na$_2$SO$_4$ electrolyte solution. The photoresponse to UV light and visible light were measured at 0.0 V versus SCE. Electrochemical impedance spectra (EIS) were recorded under a sinusoidal AC perturbation signal of 5 mV over the frequency range of 0.05 to 10$^5$ Hz.

UV light was provided by an 11 W UV light lamp (λ = 254 nm) and the average light intensity was 1.1 mW cm$^{-2}$. Visible light was obtained from a 500 W xenon lamp (Beijing China Education Au-light Co. Ltd.) with a 420 nm cut-off filter and the light intensity was 280 mW cm$^{-2}$. The degradation of methylene blue (MB) dye (5 × 10$^{-6}$ mol L$^{-1}$) was used to test the PC and PEC activities of the as-prepared nanowires. The concentration of MB was measured by recording the absorbance at the characteristic band of 633 nm using a UV-756PC UV-vis spectrophotometer (Shanghai Sunny Hengping Scientific Instrument Co. Ltd).

**Results and discussion**

**Structure and morphology of the ZnO/ZnS$_x$S$_{1-x}$ core–shell nanowire arrays**

The ZnO/ZnS$_x$S$_{1-x}$ core–shell nanowire was synthesized using a two-step method and the fabrication process shown in Fig. 1a. Firstly, ZnO nanowires were grown directly on a Si substrate using a hydrothermal method. Then, a continuous ZnS$_x$S$_{1-x}$ shell was prepared via ZnS and ZnSe vapor deposition on the ZnO nanowires at 1100 °C. The morphology of the ZnO/ZnS$_x$S$_{1-x}$ core–shell nanowire arrays was investigated by SEM. Fig. 1b shows the typical SEM images of the high-density ZnO nanowires before ZnS$_x$S$_{1-x}$ coating.
nanowires were grown successfully on the substrate. As shown in Fig. 1c, a ZnS–ZnO nanowire array was shown in Fig. S1. The high-density and orderly ZnO/ZnS core–shell nanowires were further investigated by HRTEM and EDX. As can be seen, the ZnS-like LO mode has a low frequency tail, which is helpful for charge transport and high photocatalytic performance. Furthermore, the lattice-resolved TEM image of the shell suggests the good crystallinity of the ZnS-ZnSe core–shell shell, which is quite beneficial for the separation and transfer of photo-generated carriers. Moreover, the composition of the ZnS-ZnSe core–shell shell can be tuned by adjusting the distance from the source materials.

The Raman spectra of ZnO and the ZnO/ZnS–Se core–shell nanowire arrays are shown in Fig. 2d. The wurtzite structure of ZnO belongs to the C6v symmetry group. Except for the non-active Raman mode, ZnO has six optical modes (1A1(LO), 1A1(LO), 1E1(TO), 1E1(TO) and 2E1). The peak at 437 cm⁻¹ is characteristic of ZnO, which can be assigned to the E1 (high) optical mode. Moreover, among the Raman modes of ZnO, the E1 (LO) mode (583 cm⁻¹) is caused by lattice defects. The E1 (LO) mode could not be observed, indicating that the as-prepared ZnO nanowires have a high crystalline quality. After being coated by ZnS-ZnSe, three optical modes of ZnS-ZnSe can be observed in the Raman spectra. The optical modes depend on the ZnS-ZnSe compositions. The peaks at 208 cm⁻¹ and 243 cm⁻¹ are attributed to the ZnS-like TO and LO modes; the peaks at 315 cm⁻¹ are related to the ZnS-like LO mode. As can be seen, the ZnS-like LO mode has a low frequency tail, which corresponds to the alloy disorder effect.

UV-vis DRS spectra were performed to investigate the optical purity of the ZnO/ZnS–Se core–shell nanowires (Fig. 3). For direct bandgap semiconductors, the bandgap (Eg) follows eqn (1).
respectively. So, the band gap ($E_g$) which corresponds to a band gap of 3.1 eV. The band gap of $x$-region, which is beneficial for the utilization of solar energy.

PL measurements were also carried out to investigate the charge separation and transfer process; the results are shown in Fig. S2.† The intensity of the PL emission spectra are related to the recombination of photogenerated electron and hole pairs, the lower the PL intensity, the higher charge separation efficiency. The peak at about 380 nm corresponds to the near band edge emission of ZnO. Compared with that of pure ZnO, the PL intensity of ZnO/ZnS$_{1-x}$ decreases intensively, demonstrating the higher charge separation efficiency of the core–shell structure.

The XRD patterns of ZnO nanowires and the ZnO/ZnS$_{1-x}$ core–shell nanowire arrays are shown in Fig. 4. For pure ZnO nanowires arrays, all the diffraction peaks can be exactly indexed as the wurtzite ZnO structure (JCPDS 36-1451). After coating the ZnS$_{1-x}$–ZnSe$_{1-x}$ shell, four new diffraction peaks centered at 25.9°, 27.4°, 29.0° and 30.5° were observed, which can be indexed to the ZnS$_{1-x}$–ZnSe$_{1-x}$ structure. The peak positions of ZnS$_{1-x}$–ZnSe$_{1-x}$ shell are located between those of wurtzite-structured ZnS (JCPDS 89-2942) and ZnSe (JCPDS 89-2940), suggesting the formation of high-purity, single-phase ZnS$_{1-x}$–ZnSe$_{1-x}$.

**Photoelectrochemical properties**

Electrochemical measurements were performed to investigate the photoelectrochemical properties of the ZnO and ZnO/ZnS$_{1-x}$ electrodes. The current–time ($I$–$t$) curves of the as-prepared electrodes were measured with light on/off cycles at 0 V versus SCE under UV light ($\lambda = 254$ nm) (Fig. 5a) and visible light irradiation ($\lambda > 420$ nm) (Fig. 5b). The changes of “on” and “off” currents are fast and the photoresponse phenomenon is entirely reversible, indicating that charge transport in the as-prepared electrodes proceeds very quickly. Upon UV light irradiation, the photocurrent density of ZnO/ZnS$_{1-x}$ is 0.91 μA cm$^{-2}$, which is two times higher than that of pure ZnO. It is notable that a photocurrent spike could be seen in the ZnO electrode when the UV light was on. This is due to the recombination processes of holes accumulated at the surface and electrons from the ZnO conduction band. The rough surface of the ZnO/ZnS$_{1-x}$ core–shell structures may have a larger surface area and more active sites, which is beneficial for holes to react with reduced species in the electrolyte before they accumulated at the surface to recombine with electrons. Thus, a photocurrent spike cannot be observed in the ZnO/ZnS$_{1-x}$ core–shell structure. Upon visible light irradiation, ZnO shows no obvious response. Interestingly, ZnO/ZnS$_{1-x}$ shows a noticeable photocurrent response, which vertically changes from 0.02 μA cm$^{-2}$ (dark current) to 3.73 μA cm$^{-2}$ (photocurrent). The photocurrent enhancement of ZnO/ZnS$_{1-x}$ suggests an enhanced photogenerated electrons and holes separation process, which originates from visible light adsorption of ZnS$_{1-x}$ and the band-alignment between ZnO and ZnS$_{1-x}$.

EIS is a powerful tool to investigate the interface charge separation efficiency, which is a crucial factor for
photocatalysis. Fig. S3† shows the EIS Nyquist plots of the ZnO and ZnO/ZnS$_{1-x}$Se$_{1-x}$ photocatalysts under UV (a) and visible light (b) irradiation. The radius of the arc in the EIS spectra reflects the reaction rate occurring at the surface of the electrode, the smaller the radius, the better the charge transfer ability.

As shown in Fig. S3,† the arc radius of the ZnO/ZnS$_{1-x}$Se$_{1-x}$ electrode is much smaller than that of the ZnO electrode under both UV and visible light irradiation, which indicates that ZnO/ZnS$_{1-x}$Se$_{1-x}$ possess a more effective separation of photogenerated electron-hole pairs and lower charge-transfer resistance. ¹³⁻¹⁵ These EIS spectra indicate that the ZnS$_x$Se$_{1-x}$ shell can effectively enhance the photogenerated charge separation efficiency of the ZnO nanowires.

Enhancement of PC and PEC activity

The PC and PEC activity of ZnO and ZnO/ZnS$_{1-x}$Se$_{1-x}$ nanowires were evaluated using MB as a model pollutant under UV (λ = 254 nm) and visible light irradiation (λ > 420 nm) (Fig. 6). PC and PEC degradation processes obey pseudo-first-order kinetics; a linear relationship was observed in the plots of ln(C/C₀) of MB versus irradiation time (t) shown in Fig. 6. Where C represents the concentration of MB at irradiation time t; C₀ represents initial concentration of MB after absorption equilibrium. The slope of the linear line is the PC and PEC degradation apparent rate constant k; comparison of the value of the rate constant k is a quantitative way to evaluate the PC and PEC activity. The value of k was calculated and shown in the insert graph of Fig. 6a and b. The electro-oxidation (EC), UV light and visible light photolysis (in the absence of the photocatalyst) were performed as references. As can be seen from Fig. 6a, the EC process and UV photolysis almost played no role in MB degradation. Compared with ZnO nanowires, the PC and PEC activity of the ZnO/ZnS$_{1-x}$Se$_{1-x}$ core–shell nanowires were obviously enhanced. The rate constant k of PEC degradation of ZnO/ZnS$_{1-x}$Se$_{1-x}$ core–shell nanowires is 0.65 × 10⁻² min⁻¹, which was 54.8% higher than that of pristine ZnO nanowires. It is well known that ZnO could not be excited by visible light due to its wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap. ZnO PC degradation almost shows the same efficiency with visible light photolysis. A wide band gap.
nanowires is \(0.86 \times 10^{-2}\ \text{min}^{-1}\), which is 1.7 times as that of pristine ZnO nanowires. The coating of a ZnS,Se\(_{1-x}\) shell not only enhances the PEC activity of ZnO under UV light irradiation but also extends the light absorption range of the ZnO nanowires. It is worthy to note that the reaction rate constant of PEC degradation is larger than the sum of the electro-oxidation and PC degradation, indicating there may exist a synergetic effect between ZnS,Se\(_{1-x}\) and ZnO nanowires during PEC degradation. The effect of theexternal potential on PEC degradation of MB on ZnO/ZnS,Se\(_{1-x}\) nanowires under UV irradiation was investigated and shown in Fig. S4.\(^{+}\) As the external potential increases, the PEC activity of the ZnO/ZnS,Se\(_{1-x}\) nanowires increases gradually. The external potential could drive the photogenerated electrons to the counter electrode, leading to an inhibition of the recombination process of photogenerated charges. As a result, the PEC activity increases with an increase of external potential. When the external potential is under the water decomposition potential, the potential would drive the electrons to the counter electrode, leading to a promoted separation of the photogenerated electrons and holes. When the potential is higher than water decomposition potential, complex oxidation reactions can occur. At this time, the external potential not only can separate the holes and electrons but also can oxidize MB by active intermediates (such as hydroxyl radicals).

The mechanism for enhancement of PEC activity

A schematic for electron-hole separation and transport at the ZnO/ZnS,Se\(_{1-x}\) interface is shown in Fig. 7. As can be seen, the band position of ZnO and ZnS,Se\(_{1-x}\) has a type-II structure.\(^{12}\)

Under UV light irradiation, electrons in the valence bands (VB) of ZnO and ZnS,Se\(_{1-x}\) can be excited to their conduction bands (CB). According to our previous study,\(^{12}\) the VB position of ZnO is lower than that of ZnS,Se\(_{1-x}\). The photogenerated holes on ZnO could easily transfer to ZnS,Se\(_{1-x}\), reducing the probability of photoinduced charge recombination. Moreover, since the CB position of ZnO is lower than that of ZnS,Se\(_{1-x}\), the excited electrons of ZnS,Se\(_{1-x}\) could inject into the CB of ZnO. The external potential would drive the electrons to the counter electrode, further reducing the probability of photogenerated electron-hole recombination. The improvement of UV light PC and PEC activity is mainly due to the high efficiency of photogenerated charge separation induced by the ZnO and ZnS,Se\(_{1-x}\) type-II band alignment and external circuit.

As it is well known that ZnO cannot absorb visible light and only ZnS,Se\(_{1-x}\) can be excited by visible light. Since the CB potential of ZnS,Se\(_{1-x}\) is more negative than that of ZnO, the excited electrons of ZnS,Se\(_{1-x}\) could transfer to the CB of ZnO. The electrons would further transfer to the counter electrode via the external potential, leaving the holes on the ZnS,Se\(_{1-x}\) shell, leading to an enhanced photogenerated charge separation. The electrons and holes could react with water and dissolved oxygen to yield superoxide and hydroxyl radicals.\(^{25,36}\) The holes and radicals are able to degrade the MB due to their high oxidative capacity. Herein, a visible light PC and PEC activity is achieved due to the visible light adsorption of ZnS,Se\(_{1-x}\).

Conclusions

ZnO/ZnS,Se\(_{1-x}\) core–shell nanowire arrays were synthesized via a hydrothermal method followed by a CVD method. A crystalline ZnS,Se\(_{1-x}\) shell and well-aligned ZnO/ZnS,Se\(_{1-x}\) interface were achieved, which plays an important role in the enhanced performance of photocatalytic activity. Compared with pure ZnO nanowires, the ZnO/ZnS,Se\(_{1-x}\) core–shell nanowire arrays have enhanced PC and PEC activity under UV light irradiation. Moreover, PC and PEC activity of the ZnO/ZnS,Se\(_{1-x}\) core–shell nanowire arrays were also observed under visible light irradiation. The performance enhancement of the ZnO/ZnS,Se\(_{1-x}\) core–shell nanowires is mainly due to the matching lattice and band energy alignment between the crystalline ZnS,Se\(_{1-x}\) shell and ZnO nanowire core. Ternary narrow band gap compound coupling is demonstrated to be a promising approach to design visible light active photocatalysts.

Conflict of interest

The authors declare no competing financial interest.

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Notes and references

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