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ZnO/ZnS\textsubscript{x}Se\textsubscript{1-x} core/shell nanowire arrays as photoelectrodes with efficient visible light absorption

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ZnO/ZnS\textsubscript{x}Se\textsubscript{1-x} core/shell nanowires have been synthesized on n\textsuperscript{+}-type silicon substrate via a two-step chemical vapor deposition method. Transmission electron microscopy reveals that ZnS\textsubscript{x}Se\textsubscript{1-x} can be deposited on the entire surface of ZnO nanowire, forming coaxial heterojunction along ZnO nanowire with very smooth shell surface and high shell thickness uniformity. The photoelectrode after deposition of the ternary alloy shell significantly improves visible light absorption efficiency. Electrochemical impedance spectroscopy results explicitly indicate that the introduction of ZnS\textsubscript{x}Se\textsubscript{1-x} shell to ZnO nanowires effectively improves the photogenerated charge separation process. Our finding opens up an efficient means for achieving high energy conversion devices. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4745918]

In recent years, due to their high efficiency charge carrier transport and surface charge carrier transfer/separation,\textsuperscript{1-3} core/shell structure nanowires with type II band offsets have attracted much attention as fundamental building blocks for the development of next generation solar energy conversion devices. As one of the most important metal oxides, ZnO nanowires are widely used as photoanode materials, due to its obvious advantages of longer carrier lifetime, higher electronic mobility which is favorable for electron transport, easier to synthesize than other metal oxides (e.g., TiO\textsubscript{2}).\textsuperscript{1,4} However, its wide bandgap (3.37 eV) prevents efficient absorption to sunlight in the visible region, thus brings a low overall solar energy conversion efficiency. To resolve this problem, constructing the core/shell heterostructure with narrower band gap semiconductor is considered as one promising way to extend the absorption of sunlight to the visible region. Meanwhile, core/shell architectures provide a large interfacial area to ensure the rapid charge separation and consequently increase the carrier collection efficiency.\textsuperscript{5} Furthermore, the core nanowires afford a direct electrical pathway for the photogenerated carriers to rapidly transport to the photoelectrode, and the shell allows the holes to flow in the opposite direction.\textsuperscript{6-8} The core/shell structures can also effectively prevent the nonradiative recombination of the electrons in core nanowires with electrolyte and the corrosion of core nanowires from electrolyte as well.\textsuperscript{9} Based on above consideration, many kinds of type II radial heterojunctions such as ZnO/ZnSe,\textsuperscript{10,11} ZnO/Cl-ZnO,\textsuperscript{12} ZnO/CdS,\textsuperscript{13} ZnO/In\textsubscript{2}S\textsubscript{3},\textsuperscript{14} ZnO/CdTe\textsuperscript{15} and so on have been fabricated by growing thin layer of semiconductor materials with different bandgaps on a ZnO nanowire array. We recently have synthesized ZnO/C\textsubscript{3}N\textsubscript{4} and TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} nanoparticle core/shell photocatalyst and demonstrated that both UV light photocatalytic activity and visible light photocatalytic activity were greatly improved due to the enhanced charge separation.\textsuperscript{16-18}

As compared with binary semiconductor shell with fixed composition and absorption edge, ternary alloy semiconductors have great advantages of tunable composition and band gap, for solar cell device application. These merits offer the opportunities to achieve higher conversion efficiency by having a wider range of band gaps that match the solar spectrum. Li et al. prepared a composition-graded Zn\textsubscript{C}\textsubscript{1-x}Cd\textsubscript{x}Se@ZnO core/shell nanowire array photoelectrodes via a temperature-gradient chemical vapor deposition (CVD) method,\textsuperscript{19} which yield a continuous absorption edge from 460 nm to 700 nm across the sample surface. Wu et al. also synthesized a type II ZnO/Zn\textsubscript{C}\textsubscript{1-x}Cd\textsubscript{x}Se ternary alloy nanocables with tunable shell composition and band gaps to cover almost the entire visible spectrum using an ion-exchange route.\textsuperscript{20} Additionally, TiO\textsubscript{2}/CdSSe ternary semiconductor system also have been detail-edly investigated.\textsuperscript{21} ZnS\textsubscript{x}Se\textsubscript{1-x} alloy semiconductors have significant importance in photonics and electronics, since their absorption edge (E\textsubscript{g}) can be tuned over a range of from 340 nm to 460 nm (0 ≤ x ≤ 1),\textsuperscript{22-24} partially in visible light region. However, no attempts have been made to synthesize ZnS\textsubscript{x}Se\textsubscript{1-x}-sheathed ZnO nanowires using CVD method. In this study, we report our effort in exploring low-cost and high efficient photoelectrodes made of ZnS\textsubscript{x}Se\textsubscript{1-x} ternary semiconductor compound sheathed ZnO nanowires on a heavily doped n-type silicon substrate. We synthesized the ZnO/ZnS\textsubscript{x}Se\textsubscript{1-x} core/shell nanowires via a two-step CVD method. ZnO nanowires were grown directly on a silicon substrate. Then, a continuous ZnS\textsubscript{x}Se\textsubscript{1-x} layer was deposited on the pre-grown ZnO nanowires. By optimizing the deposition parameters, we achieved ZnO/ZnS\textsubscript{x}Se\textsubscript{1-x} coaxial hetero-junction with very smooth shell surface and high shell thickness uniformity. The core/shell structure photoelectrode demonstrates a great visible light photoresponse. The charge transfer and recombination processes were also investigated by electrochemical impedance spectroscopy (EIS).
The core/shell heterojunction was prepared by a two-step CVD method. For ZnO nanowires growth, nominal 5 nm thick gold layer were deposited on the heavily doped n-type Si(100) substrate as the vapor-liquid-solid (VLS) growth catalyst. A mixture of ZnO powder and graphite powder (200 mesh size from Alfa Aesar) with a molar ratio of 1:1.2 ZnO/C was loaded at the end of a quartz cuvette as the source. And then the substrate was placed in the upstream 6 cm away from the source. With 20 sccm of argon, the furnace temperature was raised to 1100 °C at a rate of 50 °C/min. During the growth, 20 sccm of oxygen was used as the reaction gas under the same carrier gas flow. After reaction for 40 min, the furnace was allowed to cool to room temperature under the argon flow. For the ZnSxSe1-x coating on ZnO nanowires, the source materials were prepared by physically mixing the high-purity ZnS and ZnSe powders (Alfa Aesar, 99.99%) with the molar ratio of ZnS to ZnSe of 3:7. The mixture of ZnS and ZnSe powders were placed in a quartz boat. The substrates with pre-grown ZnO nanowires were placed in the downstream in the boat 8 cm away from the source. The furnace was heated to 1100 °C with a heating rate of 75 °C/min and then cooled to room temperature with 20 sccm of argon carrier gas.

The morphology and microstructures of the as-prepared ZnO/ZnSxSe1-x core/shell nanowires were examined using Hitachi S-4800 field-emission scanning electron microscopy (FE-SEM) and FEI Tecnai F20 high resolution transmission electron microscopy (HRTEM). The photoluminescence (PL) measurement of the ZnO/ZnSxSe1-x core/shell photoelectrodes served as the working electrode, a Pt wire as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The photocurrents with light on and off were measured in electrolytes containing 0.1 M Na2SO4 at 0.0 V versus SCE. UV light (λ = 254 nm) and visible light (λ > 420 nm) were used as the light sources with the intensity of 714 μW/cm² and 377 mW/cm², respectively. Visible irradiation was obtained from a 500 W Xenon lamp (Beijing China Education Au-light Co. Ltd.) with a 420 nm cutoff filter.

Fig. 1(a) shows a typical SEM image of the high-density ZnO/ZnSxSe1-x core/shell nanowires on a heavily doped n-type silicon substrate. Due to the higher secondary electron emission efficiency of ZnO than ZnSxSe1-x under electron beam of SEM, we can clearly see the brighter ZnO nanowires surrounded by ZnSxSe1-x shells. The diameters of ZnO nanowires are in the range of 50–150 nm in the inset of Fig. 1(a) and increase up to the range of 100–250 nm after coating the ZnSxSe1-x alloy shell, as shown in Fig. 1(a). An x-ray energy-dispersive spectrum (EDS) acquired from the ZnO/ZnSxSe1-x sample clearly exhibits S and Se peaks with an approximate atomic ratio of 0.87:2.49, close to 1:3, as shown in Fig. 1(b). The microstructure and crystallinity of the ZnO/ZnSxSe1-x nanostructure is further investigated by TEM and HRTEM. Fig. 1(c) shows the sample has typical core/shell structures. It can be seen that, under the optimized deposition condition, the alloy shell is deposited on the entire surface of the ZnO nanowire. Moreover, the alloy shell has uniform thickness along the length of ZnO nanowire and exhibits a smooth and dense surface. It is worth noting the shell in the head end has same thickness with that in the body, as shown in the inset of Fig. 1(c). In particular, the ZnSxSe1-x shell thickness can be controlled by deposition time. These characteristics mentioned above will be quite beneficial to surface charge separation and transfer for the photoelectrochemical applications.19 The TEM image Fig. 1(d) explicitly reveals the diameter of a typical single ZnO nanowire is ~70 nm, and the thickness of the ZnSxSe1-x shell is ~70 nm. The HRTEM image of the core/shell structure...
further reveals that ZnO nanowire is grown with a preferential [0001] orientation as indicated by the white arrow in Fig. 1(e). The crystal structure was further confirmed by selected area electron diffraction (SAED) pattern, shown in the inset of Fig. 1(e). Meanwhile, we notice the shell exhibits an amorphous structure. These characteristics demonstrate the two-step CVD method is an effective fabrication approach for core/shell heterostructure.

Fig. 2 shows the normalized room temperature PL spectra of pristine ZnO nanowires, pristine ZnS$_{x}$Se$_{1-x}$ nanowires with same growth condition to that of the alloy shell coating ZnO, and ZnO/ZnS$_{x}$Se$_{1-x}$ core/shell nanowires, respectively. The ZnO/ZnS$_{x}$Se$_{1-x}$ core/shell nanowire exhibited efficient and broad PL emissions in the visible light region (green curve in Fig. 2). The ZnO/ZnS$_{x}$Se$_{1-x}$ nanowires show an obvious shoulder peak at ~440 nm, which can be ascribed to the near band edge (NBE) emission of ZnS$_{x}$Se$_{1-x}$. The ZnO/ZnS$_{x}$Se$_{1-x}$ nanowires also yield other emission peaks at the range ~460 nm (460 nm, corresponding to the peak of ZnSe when x = 0), which can be attributed to the defect-assisted recombination in ZnS$_{x}$Se$_{1-x}$ alloy shell.25 It should be noted that the strong NBE emission peak of ZnO nanowire at ~380 nm (red curve in Fig. 2) is not observed in ZnO/ZnS$_{x}$Se$_{1-x}$ core/shell nanowires, which may be attributed to three reasons.10 First, ZnO/ZnS$_{x}$Se$_{1-x}$ heterojunction has type II band offsets between ZnO and ZnS$_{x}$Se$_{1-x}$ and the shell has a narrower band gap than ZnO, as shown in the inset of Fig. 2. The charge separation between the core/shell of type-II band alignment results in a low hole concentration and recombination rate in ZnO. Second, the alloy shell absorbs the excitation laser and prevents ZnO efficient absorption to excitation laser. Third, even if the ZnO yields emission, the shell will absorb the emission light from ZnO, keeping the emission from been detected.

Alloying of binary II–VI semiconductors is an important method to obtain tunable bandgap emissions through composition modulation. For the ZnS$_{x}$Se$_{1-x}$ system, the nonlinear variation of the energy gaps with x can be fitted by a quadratic function as follows:

\[ E_g(x) = xE_g(ZnS) + (1-x)E_g(ZnSe) - x(1-x)b, \]

where $E_g(x)$, $E_g(ZnS)$, and $E_g(ZnSe)$ are the energy gaps of ZnS$_{x}$Se$_{1-x}$, ZnS, and ZnSe, respectively, and b is the bowing parameter, which was found to be in the range from 0.40 to 0.65 eV.26 To get the value of $E_g(x)$, we performed PL of the pristine ZnS$_{x}$Se$_{1-x}$ nanowires (blue curve in Fig. 2) and the peak is 442 nm. Here, we set $b = 0.6$.22 $E_g(x)$, $E_g(ZnS)$, and $E_g(ZnSe)$ are 2.80 eV, 3.66 eV, and 2.67 eV, respectively. Then x is calculated to be 0.24, i.e., the composition of ZnS$_{x}$Se$_{1-x}$ is ZnS$_{0.24}$Se$_{0.76}$, which is consistent with the measured value by EDS, as shown in Fig. 1(b).

Considering the importance of photoelectrochemical cells (PEC) as solar energy conversion devices, PEC measurements of the pristine ZnO and ZnO/ZnS$_{x}$Se$_{1-x}$ core/shell nanowires as photoanodes were carried out. In order to ensure rigorous control experiments of before and after coating ZnS$_{x}$Se$_{1-x}$ shell, we performed the PEC measurements using the same ZnO nanowire substrate. Fig. 3 shows amperometric I-t curves of the ZnO/ZnS$_{x}$Se$_{1-x}$ core/shell nanowires and pristine ZnO nanowires photoelectrodes at a 0.0 V versus SCE with the illumination on and off. The changes of both “on” and “off”...
currents are quite sharp, which indicates that charge transport in these as-prepared sample proceeds very quickly. Upon UV illumination with a density of 714 $\mu$W/cm$^2$, pristine ZnO and ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires have similar photocurrent density $\sim$0.075 $\mu$A/cm$^2$. Under dark condition, they have similar dark current $\sim$0.006 $\mu$A/cm$^2$ as well. This indicates the Zn$_{1-x}$S$_x$/Se$_{1-x}$ shell does not reduce the UV light absorption efficiency at a same UV density as shown Fig. 3(a). From Fig. 3(b), one can see that ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires have great improvement to the adsorption of visible light ($\lambda > 420$ nm). The photocurrent density of ZnO nanowire photoanode has no clear response, but that of ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ nanowire photoanode vertically changes from $\sim$0.01 to $\sim$0.19 $\mu$A/cm$^2$ with visible light of 377 mW/cm$^2$ on. These results suggest that the photoelectrode after deposition of the alloy shell significantly improved visible light absorption efficiency, meanwhile does not obviously reduce the absorption efficiency of UV light. In ZnO and Zn$_{1-x}$S$_x$/Se$_{1-x}$ type II band alignment system, when the Zn$_{1-x}$S$_x$/Se$_{1-x}$ shells absorb the visible light to generate the electron-hole pair in the shell, the photogenerated electrons can be transferred to the conduction band of ZnO nanowires, which facilitates the charge separation and transfer processes.

It is well known that EIS is a powerful tool to study charge separation/transfer and recombination processes in solar cells. Here, EIS was performed to investigate the photogenerated charge separation processes of ZnO and ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires under UV and visible light irradiation as shown in Fig. 4. In the two cases, the arc EIS planes clearly suggest charge transfer happens on the photoelectrodes. The radius of the arc on the EIS spectra represents the electron transfer resistance at the surface of electrodes. In Fig. 4, the arc radius on EIS Nyquist plot of the ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires is smaller than that of the ZnO nanowires under both UV and visible light irradiation, which suggest that Zn$_{1-x}$S$_x$/Se$_{1-x}$ shell leads to a more effective charge separation and a faster interfacial charge transfer. It is worth noting that the arc radius on EIS Nyquist plot of the ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires is also smaller than that of the ZnO nanowires without light irradiation, which imply that the Zn$_{1-x}$S$_x$/Se$_{1-x}$ shell could change the charge distribution of ZnO nanowires and result in an easier charge transfer process as shown in Fig. 4(c). These EIS results clearly indicate that the introduction of Zn$_{1-x}$S$_x$/Se$_{1-x}$ shell to ZnO nanowires can effectively improve the photogenerated charge separation process.

In summary, we demonstrated a facile, low-cost two-step CVD method to synthesize ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanostructures as photoelectrodes. TEM results explicitly reveal that Zn$_{1-x}$S$_x$/Se$_{1-x}$ is deposited on the entire surface of ZnO nanowire to form the heterojunction along the whole nanowire with very smooth shell surface and high shell thickness uniformity. The PEC measurements suggest that the photogenerated charge separation process.28 It is well known that EIS is a powerful tool to study charge separation/transfer and recombination processes in solar cells. Here, EIS was performed to investigate the photogenerated charge separation processes of ZnO and ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires under UV and visible light irradiation as shown in Fig. 4. In the two cases, the arc EIS planes clearly suggest charge transfer happens on the photoelectrodes. The radius of the arc on the EIS spectra represents the electron transfer resistance at the surface of electrodes. In Fig. 4, the arc radius on EIS Nyquist plot of the ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires is smaller than that of the ZnO nanowires under both UV and visible light irradiation, which suggest that Zn$_{1-x}$S$_x$/Se$_{1-x}$ shell leads to a more effective charge separation and a faster interfacial charge transfer. It is worth noting that the arc radius on EIS Nyquist plot of the ZnO/Zn$_{1-x}$S$_x$/Se$_{1-x}$ core/shell nanowires is also smaller than that of the ZnO nanowires without light irradiation, which imply that the Zn$_{1-x}$S$_x$/Se$_{1-x}$ shell could change the charge distribution of ZnO nanowires and result in an easier charge transfer process as shown in Fig. 4(c). These EIS results clearly indicate that the introduction of Zn$_{1-x}$S$_x$/Se$_{1-x}$ shell to ZnO nanowires can effectively improve the photogenerated charge separation process.

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