Synthesis of alloyed Zn$_{1-x}$Mn$_x$S nanowires with completely controlled compositions and tunable bandgaps

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This study reported the successful synthesis of Zn$_{1-x}$Mn$_x$S nanowires with completely controlled compositions ($0 \leq x \leq 1$). The $x$ values could be well controlled by tuning the feeding ratio of [(C$_4$H$_9$)$_2$NCS$_2$]$_2$Zn to [(C$_4$H$_9$)$_2$NCS$_2$]$_2$Mn precursors. The bandgaps of Zn$_{1-x}$Mn$_x$S nanowires showed nonlinear bowing character versus the composition. This result provided an effective route for designing Mn-based ternary chalcogenide nanowires with specific bandgaps, which is significant for their better application in photonics and spintronics.

Introduction

Mn$^{2+}$ doped semiconductor nanomaterials have attracted great attention in photonics and spintronics due to their unique optical and magnetic properties, such as orange photoluminescence emission and photo-induced magnetization. Many factors could affect their optical or magnetic properties, including the temperature, dopant location and composition/dopant concentration. As is well known, the composition is a key factor affecting the bandgaps of semiconductor nanomaterials, e.g. the ternary Zn$_x$Cd$_{1-x}$S nanowires showed tunable bandgaps versus the composition. Hence, the synthesis of composition completely controlled Mn-based ternary chalcogenide nanomaterials is significant to explore the relationship between their bandgaps and composition. Many methods have been employed to synthesize Mn$^{2+}$ doped chalcogenide nanomaterials, such as the nucleation and growth doping methods as well as the ionic diffusion and exchange doping methods, however, it remains challenge for synthesizing composition completely controlled Mn-based ternary chalcogenide nanomaterials, especially for the one dimensional nanostructures such as Zn$_{1-x}$Mn$_x$S nanowires.

The solution-solid-solid (SSS) growth has shown great convenience in synthesis of various binary chalcogenide nanowires and even ternary Zn$_x$Cd$_{1-x}$S nanowires with superionic conductors such as Ag$_2$S, Ag$_2$Se and Cu$_2$S as catalysts. Previously, we have synthesized the ZnS nanowires via the SSS route using Ag$_2$S nanoparticles as the catalyst, and the adopted precursors were metalorganic [(C$_{4}$H$_{9}$)$_2$NCS$_2$]$_2$Zn and [(C$_{4}$H$_{9}$)$_2$NCS$_2$]$_2$Mn, respectively. The two precursors are of similar structures, and their decomposing rates and conditions might be similar, thus co-decomposing [(C$_{4}$H$_{9}$)$_2$NCS$_2$]$_2$Zn and [(C$_{4}$H$_{9}$)$_2$NCS$_2$]$_2$Mn was probably very suitable for the synthesis of composition completely controlled Zn$_{1-x}$Mn$_x$S nanowires.

Herein, by adopting the [(C$_{4}$H$_{9}$)$_2$NCS$_2$]$_2$Zn and [(C$_{4}$H$_{9}$)$_2$NCS$_2$]$_2$Mn precursors with different molar ratios, we successfully synthesized the ternary alloyed Zn$_{1-x}$Mn$_x$S nanowires with tunable composition ($0 \leq x \leq 1$) through the Ag$_2$S nanoparticle mediated growth. The composition, morphology and structure of the Zn$_{1-x}$Mn$_x$S nanowires were determined by powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), the inductively coupled plasma-mass spectrometry (ICP-MS), energy dispersive spectroscopy (EDS) and the electron paramagnetic resonance (EPR) analysis. The optical properties of the Zn$_{1-x}$Mn$_x$S nanowires were investigated using the ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectrophotometries.

Experimental section

Materials

The used chemical reagents include AgNO$_3$ (99%), Mn(NO$_3$)$_2$·4H$_2$O (97.5%), Zn(NO$_3$)$_2$·6H$_2$O (98%), 1-dodecanethiol (98%), 1-dodecylamine (CP), dibutylamine (99%), methanol (99.7%), ethanol (99.7%), carbon disulfide (AR), NaOH (96%), HNO$_3$ (65–68%), cyclohexane (99.5%). These reagents were used as received without any further purification. And the deionized water was used to prepare the solution for the chemical experiments.

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ultrapure water were collected from Milli-Q Advantage, Millipore.

Synthesis of the \([(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Zn and}\ [\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Mn}\text{ precursors and Ag}_2\text{S nanoparticles. The approaches of synthesis of metal dibutyldithiocarbamate complexes }\[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Ag, }[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Zn and }[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Mn}\text{ precursors and Ag}_2\text{S nanoparticles have followed the similar procedures as reported in our previous study.}^{16,25}

Synthesis of the Zn\(_{1-x}\)Mn\(_x\)S (0 \leq x \leq 1)\) nanowires. In a typical preparation, the metal dibutyldithiocarbamate complexes \([\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Ag, }[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Zn and }[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Mn}\text{ precursors with the feeding molar fraction of Mn/(Mn + Zn) precursors, i.e. }[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Mn/\[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Zn and }[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Mn, at 0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5% and 100% were added into a round bottom flask, respectively. Then the mixed solvent of 1-dodecylamine and 1-dodecanethiol with the volume ratio of 1 : 1, and the Ag\(_2\)S nanoparticles suspension in cyclohexane with fixed amount, were all added into the flask. Then this mixture solution were stirred at 40 °C for 10 min by a magnetic stirrer. After that the flask were pumped, and quickly heated to 120 °C and kept there for 10 min. Following on, the products were carefully washed and centrifuged with methanol and cyclohexane respectively for at least five times. Finally the solid products from the centrifuge were collected and dried for further characterization.

Characterization. The products were identified by X-ray diffraction (XRD, Cu target, \(\lambda_{Cu} = 1.5418 \text{ Å}\)) with the step size of 0.02° and scan speed of 0.5 s per step. Their morphology, structure and composition were characterized by high resolution transmission electron microscopy (HRTEM, JEM-2100F) attached with an energy dispersive spectroscopy (EDS). Their composition were also determined using the inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500), and ICP-MS analysis, the samples were first dissolved by 10 mL 7% HNO\(_3\) solution and then diluted to 80 mL using 2% HNO\(_3\) solution. The absorption spectra were recorded by an ultraviolet-visible absorption spectrometer (UV-Vis, Rayleigh WFX-120B). The photoluminescence (PL) spectra were collected by laser confocal photoluminescence microscopy (LabRam HR Evolution) at room temperature with the 532 nm laser as the excitation source, and the products were scattered and flattened on a glass wafer before analysis. The electron paramagnetic resonance (EPR) experiments were performed on an X-band Bruker EMX spectrometer.

Results and discussions

The Ag\(_2\)S nanoparticles were prepared similarly to our previous reports,\(^{16,25}\) the morphology and structure of the nanoparticles were characterized by [HR]TEM as shown in Fig. S1a–c.\(^\dagger\) The diameters of the Ag\(_2\)S nanoparticles were uniform with the average size of ca. 12.6 ± 1.7 nm as shown by Fig. S1d.\(^\dagger\) All of these obtained Ag\(_2\)S nanoparticles were stocked in cyclohexane for further use.

In the preparation of ternary Zn\(_{1-x}\)Mn\(_x\)S nanowires, the \([[\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Zn and }[(\text{C}_4\text{H}_9\text{H}_3\text{NCS}_2\text{Mn}\text{ precursors with specific molar fraction of Mn/(Mn + Zn) at 0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5% and 100% were respectively mixed with unchanged amount of Ag\(_2\)S catalysts and the solvent of 1-dodecylamine and 1-dodecanethiol. Then after reaction, the nine products were collected and labelled as 1\# to 9\#, respectively. The XRD patterns of these samples have been shown in Fig. 1. It can be seen that the pattern of sample 1\# coincided with the hexagonal ZnS phase (JCPDS: 36-1450), and that of sample 9\# was consistent with the hexagonal γ-MnS phase (JCPDS: 40-1289). The diffraction peaks in 2–8\# exhibited similar patterns to those of 1\# (ZnS) and 9\# (MnS). Meanwhile the corresponding single peak, such as the [110] peak, of the nine samples evolved progressively from the high 2θ angle towards the low 2θ angle from samples 1\# to 9\#, suggesting their increased lattice parameters (Table S1†). This result indicated that the samples 2–8\# were composed of alloyed Zn\(_{1-x}\)Mn\(_x\)S phase instead of phase-separated phases. And because the lattice constant of MnS is larger than that of ZnS, the increased lattice constants from 1–9\# could be attributed to the increased Mn\(^{2+}\) concentration in the samples from 1–9\#. Besides, the x values can be estimated following the eqn (1) based on the Vegard’s law,\(^{34}\)

\[
x = \frac{a_x - a_{\text{ZnS}}}{a_{\text{MnS}} - a_{\text{ZnS}}}
\]

where \(a_{\text{MnS}}, a_{\text{ZnS}}\) and \(a_x\) are the lattice parameters of hexagonal MnS, ZnS and Zn\(_{1-x}\)Mn\(_x\)S, respectively. The calculated x values were 0.10, 0.23, 0.32, 0.47, 0.64, 0.70 and 0.83 for samples 2–8\#, respectively.

![Fig. 1 XRD patterns of the samples 1–9\#. The standard ZnS pattern (JCPDS: 36-1450) and MnS pattern (JCPDS: 40-1289) were shown on the bottom and top, respectively.](image-url)
The morphologies of the samples 1, 3, 5, 7, 9# were characterized by the TEM microscopy as shown in Fig. S2† a and b. It can be seen that the products were composed of matchstick-like heteronanostructures, which were constructed by a nanowire stem and a terminated nanoparticle. The average diameters of nanowires were ca. 6.5 ± 1.4 nm, 6.9 ± 1.0 nm, 6.9 ± 1.2 nm, 6.9 ± 1.3 nm, 6.7 ± 1.3 nm for samples 1, 3, 5, 7, 9#, respectively, without consideration of the terminated nanoparticles (Fig. S2†). The sample 5# was selected as the typical example for further analysis. EDS result (Fig. 2c) indicated that the Zn, Mn, Ag and S elements existed in the sample 5#, and the atomic ratio of elements Zn to Mn was 21.2 : 21.9 (inset of Fig. 2c), coincided well with Zn0.53Mn0.47S phase as indicated by the XRD analysis (Fig. 1). Fig. 2e, g and h showed that the measured interplanar distances of the nanowire was 3.38 Å coinciding well with the d_{100} spacing (3.373 Å) of Zn_{0.53}Mn_{0.47}S phase (Table S1†), and the growth direction of the nanowire was along [110] direction, which were also supported by the FFT pattern of the nanowire (Fig. 2f). However, this nanowire was not straight but seemed flexible, thus the direction of the lattice fringes with the same Miller index slightly changed along the nanowire as shown in Fig. 2g and h. Nevertheless, the interplanar distances along the nanowires (Fig. 2e, g and h) were unchanged which indicated the homogeneous composition along the nanowire, otherwise different interplanar distance could be found for the planes with the same Miller indices. Fig. S3† indicated that the terminated nanoparticle was composed of monoclinic Ag2S phase (JCPDS: 14-0072). These results suggested the formation of ternary alloyed Zn_{0.53}Mn_{0.47}S nanowire catalyzed by the Ag2S nanoparticle for sample 5#. And it could also suggest that the Ag2S nanoparticles can act as the catalysts for the growth of ternary alloyed Zn_{0.53}Mn_{0.47}S nanowires.
ternary Zn$_{1-x}$Mn$_x$S nanowires via SSS route in this case, similar to the reported Ag$_2$S nanoparticles catalyzed growth of ZnS and MnS nanowires.$^{16,24,25,35}$

To obtain the accurate composition $x$ of Zn$_{1-x}$Mn$_x$S nanowires, the typical samples 3, 5, 7# were characterized by ICP-MS and the molar fraction of Mn/(Mn + Zn) was measured at 0.23, 0.48 and 0.69, respectively (denoted by $\star$ in Fig. 3). Besides, the composition $x$ for all samples determined by Vegard’s law based on the XRD spectra were also drawn in Fig. 3 (denoted by $\bullet$), as well as the composition for sample 5# determined by EDS analysis (denoted by $\diamond$). It can be seen that all these analysis methods have provided the similar results, indicating the $x$ values determined by Vegard’s law could be used to approximately represent their composition. In other words, the nanowires of samples 1–9# were composed of ZnS, Zn$_{0.90}$Mn$_{0.10}$S, Zn$_{0.77}$Mn$_{0.23}$S, Zn$_{0.66}$Mn$_{0.34}$S, Zn$_{0.53}$Mn$_{0.47}$S, Zn$_{0.33}$Mn$_{0.64}$S, Zn$_{0.30}$Mn$_{0.70}$S, Zn$_{0.17}$Mn$_{0.83}$S and MnS phase, respectively.

Besides, Fig. 3 has also shown that the experimental determined $x$ values coincided well with the feeding molar ratio of Mn/(Mn + Zn) precursors, which suggested that this route was very effective in the synthesis of composition controlled Zn$_{1-x}$Mn$_x$S nanowires.

The optical properties of these products were examined by UV-Vis and PL spectroscopies. The absorbance spectra of the samples in Fig. 4a all showed the discernible shoulder peaks. The bandgaps of the samples were extracted (Fig. 4b) using the method similar to the literatures.$^{20,36,37}$ It was interesting that the extracted bandgaps of Zn$_{1-x}$Mn$_x$S nanowires did not shown a linear relationship with the composition $x$, but exhibited a nonlinear optical bowing effect (Fig. 4c) similar to that reported in PbS$_{1-x}$Se$_x$ nanocrystals$^{38}$ and ZnSe$_{1-x}$Te$_x$ nanowires,$^{20}$ etc. Taking into accounts of the optical bowing effect, the quadratic eqn (2) below were used to fit the bandgaps of Zn$_{1-x}$Mn$_x$S nanowires,

$$E_g(x) = E_g(ZnS) + Bx(1-x)$$

Fig. 4 (a) Absorption spectra of the typical samples 1–9#, which are denoted by different colors. (b) The extracted peaks for the samples 1–9#. For example, in the sample 1#, the top solid dark line was original absorbance curve. The top dashed grey line was the fitted baseline. The bottom solid grey peak was extracted by subtracting baseline from the absorbance curve. The bottom dashed dark curve was the fitted Gaussian plot, which displayed the shoulder peak located around 318 nm. The method to extract the shoulder peak was similar to that in the literatures$^{20,36,37}$ (c) The relationship between the bandgap energy of Zn$_{1-x}$Mn$_x$S nanowires and the composition $x$. 

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where $E_g^A$ and $E_g^B$ are the bandgaps of two binary phases A and B, $b$ is the bowing parameter. Thus the bandgaps of the obtained Zn$_{1-x}$Mn$_x$S nanowires was fitted as the eqn (3),

$$E_g (eV) = xE_g^A + (1 - x)E_g^B - bx(1 - x)$$

(2)

where the fitted bowing character $b$ was $0.74 \pm 0.07$ eV. The bowing effects, similar to the literatures, could arise from the differences in electronegativities, atomic radii, and also the lattice constants between MnS and ZnS, and the larger differences may lead to the larger bowing parameters. Compared with the reported PbS$_{1-x}$Se$_x$ nanocrystals and ZnSe$_{1-x}$Te$_x$ nanowires (Table S2†), the differences in electronegativities, atomic radii and lattice constants for the Zn$_{1-x}$Mn$_x$S nanowires in this study are generally larger than those for PbS$_{1-x}$Se$_x$ nanocrystals, but smaller than those for ZnSe$_{1-x}$Te$_x$ nanowires, which might render the Zn$_{1-x}$Mn$_x$S nanowires exhibit a moderate bowing character $b$ value among the three chalcogenide nanomaterials. The fitted equation gives the bandgap minimum of Zn$_{1-x}$Mn$_x$S nanowires at $x = 0.64$, suggesting the bandgaps of Zn$_{1-x}$Mn$_x$S nanowires ranging from 3.58–3.88 eV. This result indicated the SSS growth could be very effective in design the growth of Zn$_{1-x}$Mn$_x$S nanowires with specific bandgap.

The PL properties of the samples 1, 3, 5, 7, 9# were examined (Fig. S4†) in the range of 550–850 nm using the 532 nm laser as the excitation source. It can be seen that the samples 1# (ZnS) and 9# (MnS) show featureless PL spectra, however, the ternary Zn$_{1-x}$Mn$_x$S samples of 3, 5, 7# show clear characteristic yellow emission at 576 nm from the $^4T_2 \rightarrow ^6A_1$ transition of Mn$^{2+}$ dopant, which indicated the formation of ternary alloyed Zn$_{1-x}$Mn$_x$S compound. Besides, the EPR spectra of the typical samples of 3, 5, 7# were also collected as shown in Fig. S5†. The increased EPR intensity from samples 3# to 7# indicated the increased amount of Mn$^{2+}$ in the Zn$_{1-x}$Mn$_x$S nanowires, and the hyperfine structure of Mn$^{2+}$ cannot be resolved due to the high Mn$^{2+}$ concentration for these samples. These features are similar to those reported in Cd$_{1-x}$Mn$_x$Se nanocrystals. The results also supported the formation of ternary alloyed Zn$_{1-x}$Mn$_x$S nanowires.

In conclusion, the ternary alloyed Zn$_{1-x}$Mn$_x$S nanowires were controlled synthesized via the Ag$_2$S nanoparticle mediated growth under vacuum by the co-decomposition of [(C$_{6}$H$_{5}$)$_{2}$NCS$_{2}$]$_{2}$Zn and [(C$_{6}$H$_{5}$)$_{2}$NCS$_{2}$]$_{2}$Mn precursors. The diameters of the alloyed Zn$_{1-x}$Mn$_x$S nanowires were uniform. The composition of the nanowires could be well tuned over the entire range ($0 \leq x \leq 1$). The relationship between the bandgaps and composition $x$ of the Zn$_{1-x}$Mn$_x$S nanowires were examined, and thus the bandgaps were found to exhibit the nonlinear bowing character versus the composition $x$. The results could provide new opportunities for modulating the bandgaps of Mn-based ternary chalcogenide nanowires and promote their further application in photonics and spintronics.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**