



Low temperature synthesis, photoluminescence, magnetic properties of the transition metal doped wurtzite ZnS nanowires

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ABSTRACT

In this paper, we synthesized the transition metal ions (Mn, Cu, Fe) doped and co-doped ZnS nanowires (NWs) by a one-step hydrothermal method. The results showed that the solid solubility of the Fe²⁺ ions in the ZnS NWs was about two times larger than that of the Mn²⁺ or Cu²⁺ ions in the ZnS NWs. There was no phase transformation from hexagonal to cubic even in a large quantity transition metal ions introduced for all the samples. The Mn²⁺/Cu²⁺/Fe²⁺ related emission peaks can be observed in the Mn²⁺, Cu²⁺ and Fe²⁺ doped ZnS NWs. The ferromagnetic properties of the co-doped samples were investigated at room temperature.

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1. Introduction

Since the unique superiority of the Zn-containing nanocrystals (NCs) over the Cd-containing NCs is their low cytotoxicity in the field of biological applications, preparing of the doped ZnS NCs by transition metal ions have received increasing attentions [1–4]. Transition metal ions are the most interesting impurities as they introduce deep levels in the gap region, which can influence not only the optical, but also the electrical and magnetic properties thus influencing their practical applications [5–7]. In addition, theoretical works have predicted that the transition metal ions doped ZnS NCs could exhibit the high Curie temperature for applications as practical commercial devices [8,9]. More importantly, the interaction between the transition metal ions and the charge carriers of the ZnS host is stronger in the confined space of the NCs compared with that in the bulk counterparts, leading to the excellent properties. However, different and even contradictory results were reported for the ZnS based samples prepared by different methods. The organic phase growth method can produce the high quality ZnS NCs with good monodisperse and high PL quantum yield (QY), which usually require high temperature and hazardous organometallic precursors that have an

adverse impact on the environment [10,11]. To date, researchers have not stopped trying to employ environmental friendly, simple, and low-cost methods in the fabrication of NCs. The aqueous synthesis has been proved to be a simpler, cheaper, and less toxic method to prepare the water-soluble NCs, however, usually suffered from some problems such as poor crystallinity and low PL QYs [12,13]. From the practical point of view, the hydrothermal method requires a relatively low temperature, cheap precursors of low toxicity and makes easy the introduction of the transition metal ions into the ZnS lattice [14,15].

In this paper, we report the transition metal ions (Mn, Cu, Fe) doped wurtzite ZnS nanowires (NWs) synthesized by a one-step hydrothermal method at low temperature. No phase transformation from hexagonal to cubic can be observed even in a large quantity introduced. Also, we observe the ferromagnetic properties of the co-doped ZnS NWs at room temperature, which are less obtained by many scientists. The solid solubility, the detailed microstructure, and the optical-magnetic properties will be investigated.

2. Experimental section

Zinc nitrate, manganese nitrate, copper nitrate, iron nitrate, thiourea, ethylenediamine (EN) are all analytical grade (Shanghai Chemical Reagents Co.) and used without further purification. In a

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typical process, $1-x$ mmol of zinc nitrate and x mmol of nitrate were dissolved in 16 ml EN and water (1:1 in volume ratio). After stirring for 1 h, 3 mmol of thiourea were put into the resulting complex. After stirring for 2 h, the colloid solution was transferred into a 20-ml Teflon-lined autoclave and kept at 180 °C for 12 h. After the reaction, the autoclave was taken out and cooled down to room temperature. The product was washed with ethanol and deionized water for several times and separated by centrifugation, and then dried at 80 °C for 1 h to get a white powder.

3. Characterization of products

X-ray diffraction (XRD) pattern was collected on a MAC Science MXP-18 X-ray diffractometer using a Cu target radiation source. Transmission electron micrographs (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on JEM-2100 electron microscope. The specimen was prepared by depositing a drop of the dilute solution of the sample in ethanol on a carbon-coated copper grid and drying at room temperature. UV–vis absorption spectrum was measured on UV-3101PC UV spectrometer. The specimen for the measurement was dispersed in ethanol and placed in a 1 cm quartz cell, and ethanol served as the reference. Photoluminescence (PL) measurement was carried out at room temperature, using 325 nm as the excitation wavelength, He–Cd Laser as the source of excitation. Magnetic hysteresis loop was measured by a Lake Shore 7407 vibrating sample magnetometer (VSM) with the maximum field of 6 kOe.

4. Results and discussion

As seen from XRD patterns (Fig. 1), all the diffraction peaks for the ZnS NWs (black line) can be well indexed as the hexagonal wurtzite phase structure, which are consistent with the standard card (JCPDS no. 36-1450). No impurity phase can be found in the spectrum, indicating the formation of the pure wurtzite phase ZnS. It is possible to predict the growth direction by performing comparison of the full width at half maximum (FWHM) for

different XRD peaks. It is noticeable that the (002) diffraction peak is stronger and narrower than the other peaks, suggesting a preferential growth direction along the c -axis [16]. After doping the $\text{Cu}^{2+}/\text{Fe}^{2+}/\text{Mn}^{2+}$ ions into the ZnS NWs, there is no extra diffraction peak from the doped ions observed for all the samples in Fig. 1, suggesting that the $\text{Cu}^{2+}/\text{Fe}^{2+}/\text{Mn}^{2+}$ ions are incorporated into the ZnS lattice and the maximum concentration of the Cu^{2+} , Fe^{2+} , Mn^{2+} ions in the ZnS NWs is 10%, 13%, 10%, the maximum concentration of the Mn^{2+} ions in the $\text{ZnS}:\text{Cu}^{2+}$ (1%) and $\text{ZnS}:\text{Fe}^{2+}$ (1%) NWs is 10%, 10%, respectively. For the $\text{ZnS}:\text{Cu}^{2+}$ NWs (green line), the diffraction peaks show clearly shift to the higher degree as compared to that for the ZnS NWs, indicating that the lattice constants of the $\text{ZnS}:\text{Cu}^{2+}$ NWs are decreased with the Cu^{2+} doped ratio increased. Since that the ionic radius of the Cu^{2+} ions (0.72 Å) is smaller than that of the Zn^{2+} ions (0.74 Å), the lattice contraction would be happen if the Cu^{2+} ions substituted for the Zn^{2+} sites in the ZnS NWs. For the $\text{ZnS}:\text{Fe}^{2+}$ NWs (blue line), there is no shift of the diffraction peaks caused by the lattice expansion or contraction as the Fe^{2+} doped ratio increased. Since that the ionic radius of the Fe^{2+} ions (0.74 Å) is the same as that of the Zn^{2+} ions (0.74 Å). For the $\text{ZnS}:\text{Mn}^{2+}$ NWs (cyan line), a clearly shift to the lower angle in the peak position of the XRD patterns indicates that the lattice constants of the $\text{ZnS}:\text{Mn}^{2+}$ NWs are increased with the Mn^{2+} doped ratio increased. Since that the ionic radius of the Mn^{2+} ions (0.83 Å) is 10% larger than that of the Zn^{2+} ions (0.74 Å), the lattice expansion can be observed if the Mn^{2+} ions substituted for the Zn^{2+} sites in the ZnS NWs. For the $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{S}:\text{Mn}^{2+}$ (red line) and $\text{Zn}_{0.99}\text{Fe}_{0.01}\text{S}:\text{Mn}^{2+}$ (magenta line) NWs, an obvious shift to the lower angle can also be observed as the Mn^{2+} doped ratio increased, indicating the increased lattice constants for the $\text{Cu}^{2+}/\text{Mn}^{2+}$ and $\text{Fe}^{2+}/\text{Mn}^{2+}$ co-doped ZnS NWs. According to the Bragg equation [17], the lattice constants of the $\text{Cu}^{2+}/\text{Fe}^{2+}/\text{Mn}^{2+}$ ions doped and co-doped ZnS NWs were calculated (see Table 1), which further proved that the $\text{Cu}^{2+}/\text{Fe}^{2+}/\text{Mn}^{2+}$ ions have been incorporated into the ZnS NWs. Unlike the earlier reports [18,19], we have not observed the phase transformation from hexagonal to cubic even in a large quantity introduced. On the basis of the molecular dynamics and thermodynamics analysis, the temperature for the transformation from cubic to hexagonal ZnS NCs is 25 °C when the average size is 7 nm, dramatically lower than that observed in the bulk material (1020 °C) [20]. Moreover, the small size and some particular morphology can enhance the stability of the structure by tuning the surface energy density and the free energy of formation [21]. For the Cu doped and co-doped ZnS NWs (red and green line), the relative intensity ratio of the (110) and (112) diffraction peak with respect to the (103) diffraction peak is larger than that of the other samples. So, the doping element (the Cu^{2+} ions in this paper) would have an important effect on the growth of the different lattice plane.

Table 1

Lattice constants of the $\text{Zn}_{1-x}\text{TM}_x\text{S}$ ($\text{TM}=\text{Mn}$, Fe , and Cu) NWs calculated from XRD.

Sample lattice parameter (Å)	
ZnS	$a=3.812$, $c=6.246$
$\text{Zn}_{0.90}\text{Cu}_{0.10}\text{S}$	$a=3.806$, $c=6.233$
$\text{Zn}_{0.99}\text{Fe}_{0.01}\text{S}$	$a=3.811$, $c=6.246$
$\text{Zn}_{0.87}\text{Fe}_{0.13}\text{S}$	$a=3.813$, $c=6.243$
$\text{Zn}_{0.99}\text{Mn}_{0.01}\text{S}$	$a=3.815$, $c=6.249$
$\text{Zn}_{0.90}\text{Mn}_{0.10}\text{S}$	$a=3.826$, $c=6.265$
$\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Mn}_{0.01}\text{S}$	$a=3.814$, $c=6.240$
$\text{Zn}_{0.89}\text{Cu}_{0.01}\text{Mn}_{0.10}\text{S}$	$a=3.830$, $c=6.265$
$\text{Zn}_{0.98}\text{Fe}_{0.01}\text{Mn}_{0.01}\text{S}$	$a=3.821$, $c=6.262$
$\text{Zn}_{0.89}\text{Fe}_{0.01}\text{Mn}_{0.10}\text{S}$	$a=3.828$, $c=6.256$

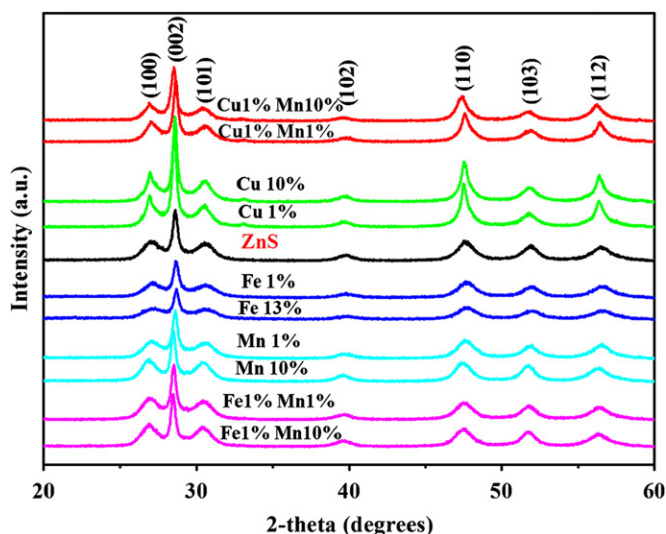


Fig. 1. XRD patterns of (black line) ZnS; (green line) $\text{ZnS}:\text{Cu}^{2+}$ (1%), $\text{ZnS}:\text{Cu}^{2+}$ (10%); (red line) $\text{ZnS}:\text{Cu}^{2+}$ (1%) Mn^{2+} (1%), $\text{ZnS}:\text{Cu}^{2+}$ (1%) Mn^{2+} (10%); (blue line) $\text{ZnS}:\text{Fe}^{2+}$ (1%), $\text{ZnS}:\text{Fe}^{2+}$ (13%); (cyan line) $\text{ZnS}:\text{Mn}^{2+}$ (1%), $\text{ZnS}:\text{Mn}^{2+}$ (10%); (magenta line) $\text{ZnS}:\text{Fe}^{2+}$ (1%) Mn^{2+} (1%), $\text{ZnS}:\text{Fe}^{2+}$ (1%) Mn^{2+} (10%) NWs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

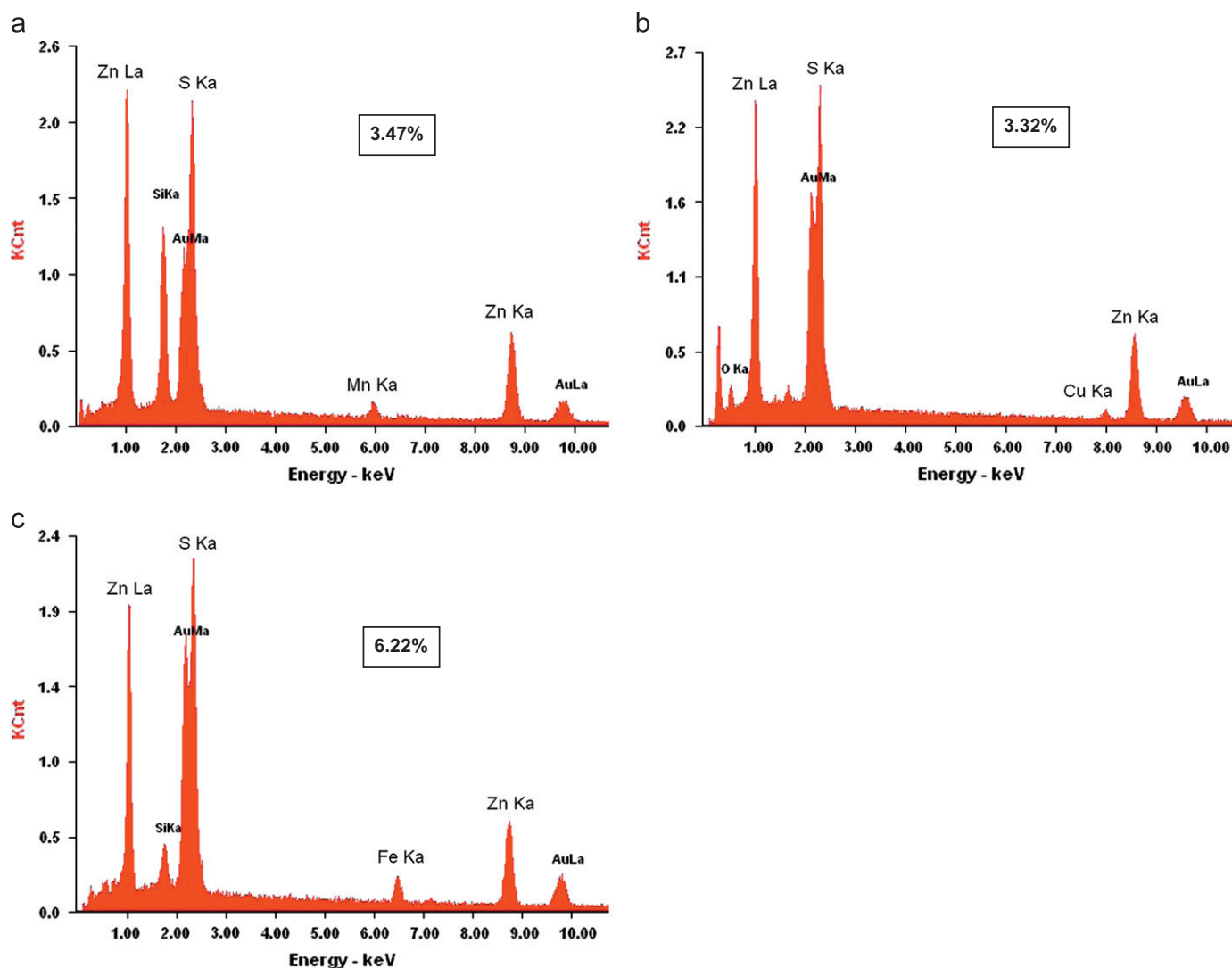


Fig. 2. EDAX images of (a) ZnS:Mn²⁺ (10%); (b) ZnS:Cu²⁺ (10%); (c) ZnS:Fe²⁺ (13%) NWs.

The compositional analysis of the ZnS:Mn²⁺ (10%), ZnS:Cu²⁺ (10%), ZnS:Fe²⁺ (13%) NWs are performed by EDAX, which can be seen in Fig. 2. The amount of the Mn, Cu, Fe element detected is much less than those actually added during synthesis. Only 3.47% Mn, 3.32% Cu and 6.22% Fe is detected for the ZnS:Mn²⁺ (10%), ZnS:Cu²⁺ (10%), ZnS:Fe²⁺ (13%) NWs. The results show that the solid solubility of the Fe²⁺ ions in the ZnS NWs is about two times larger than that of the Mn²⁺ or Cu²⁺ ions in the ZnS NWs.

The detailed microstructures of the prepared samples are characterized using transmission electron microscopy. Fig. 3 display the TEM, HRTEM, FFT and SAED images of the ZnS:Mn²⁺, ZnS:Cu²⁺, ZnS:Fe²⁺ NWs. The HRTEM images (Fig. 3b, e and h) were taken from the area marked by the red rectangle in Fig. 3a, d and g. It can be seen that the ZnS:Mn²⁺ NWs are smooth and the diameter is about 10 nm, which exhibit a well oriented along the (002) direction and good crystallization (Fig. 3a–b). Considering our XRD study and close observation of the FFT (see inset image of Fig. 3b) and SAED images (Fig. 3c), it can be concluded that the diffraction rings represent the wurtzite ZnS structure. Moreover, few streaky spots are found in the FFT image, which may come from the defects in the lattice. As for the ZnS:Cu²⁺ NWs, the average diameter is about 5 nm (Fig. 3d) and no lattice disorder is observed (Fig. 3e). It is worth to note that the incorporation of the

Cu²⁺ ions does not degrade the crystallinity of the ZnS NWs, and the single crystal nature of the ZnS:Cu²⁺ NWs can be verified based on their regular diffraction spots in the SAED image (Fig. 3f). The growth direction of the ZnS:Cu²⁺ NWs is perpendicular to the lattice fringes, and the *d* spacing of the 002 plane is about 0.31 nm. Compared with the Mn²⁺/Cu²⁺ case, the average diameter of the ZnS:Fe²⁺ NWs is about 8 nm (Fig. 3g). Close inspection of the HRTEM image (Fig. 3h) shows that the NWs exhibit two kinds of lattice fringes in the blue and green rectangle region. Since that both the Zn and S atom in wurtzite and cubic ZnS are four coordinated, where the wurtzite ZnS has the simple ABABAB close-packed stacking order, the cubic ZnS has the ABCABC close-packed stacking order. So, it requires only a minor rearrangement of atoms to change the lattice arrangement. Since that the diffraction rings corresponding to the wurtzite and cubic ZnS is overlapping as shown in Fig. 3i. Consequently it is difficult to determine whether the structure transformation occurred from the SAED analysis. Seen from the FFT images of the Mn²⁺/Cu²⁺/Fe²⁺ doped ZnS NWs (see inset images of Fig. 3b, e and h), the shape of the unit cell (marked by the yellow dots) is different for the Mn²⁺/Cu²⁺/Fe²⁺ doped ZnS NWs, indicating that doing Mn²⁺/Cu²⁺/Fe²⁺ ions into the ZnS lattice would have an important effect on the growth of the different lattice plane, which is in consistent with the XRD results.

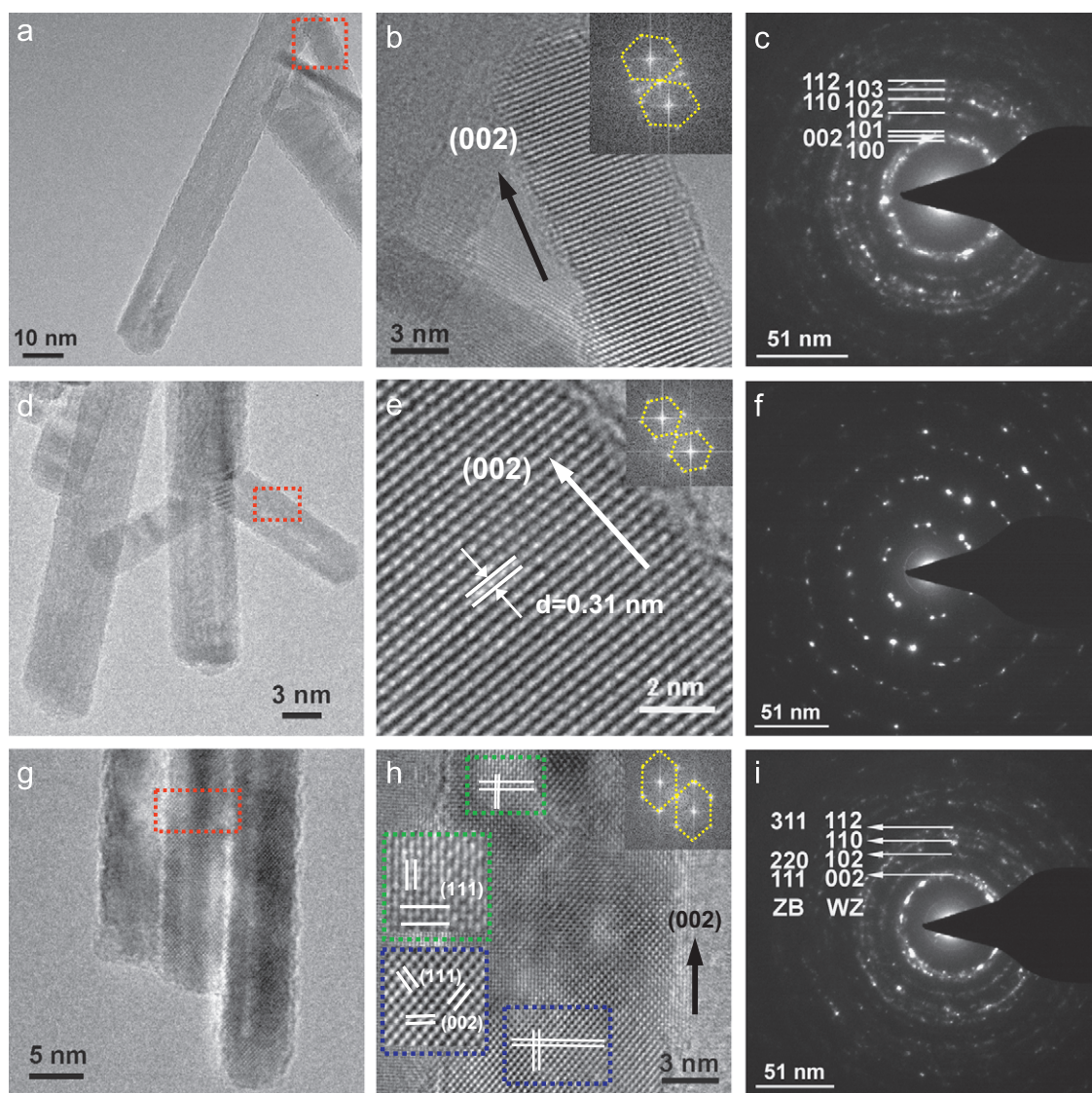


Fig. 3. (a) (b) (c) TEM, HRTEM (FFT) and SAED images of the ZnS:Mn²⁺(1%) NWs; (d) (e) (f) TEM, HRTEM (FFT) and SAED images of the ZnS:Cu²⁺(1%) NWs; (g) (h) (i) TEM, HRTEM (FFT) and SAED images of the ZnS:Fe²⁺(1%) NWs. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

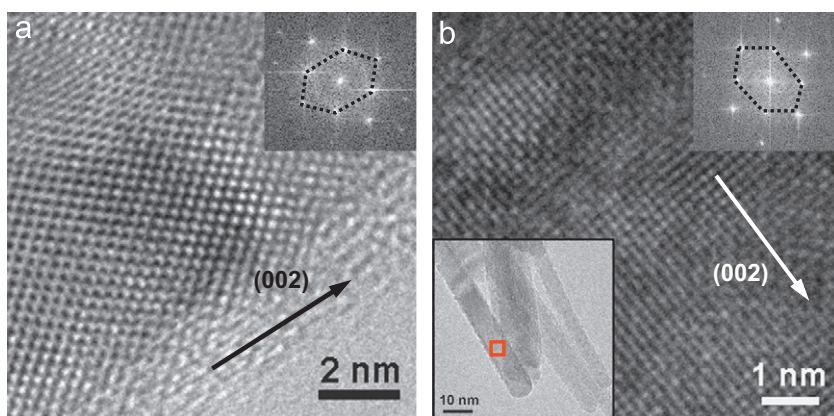


Fig. 4. (a) HRTEM and FFT images of the ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs; (b) TEM, HRTEM and FFT images of the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs.

The TEM and HRTEM images of the Mn/Cu and Mn/Fe co-doped ZnS NWs can be seen in Fig. 4. The diameter of the Mn/Fe co-doped NWs (see the inset image of Fig. 4b) are the same as those of the single-metal doped NWs (Fig. 4a and g). The HRTEM

and FFT images of both the Mn/Cu and Mn/Fe co-doped ZnS NWs in Fig. 4a and Fig. 4b show that the co-doped ZnS NWs also grow along the (002) direction. Note that the degree of the lattice expand is different, which can be seen clearly in Fig. 4a. Since that

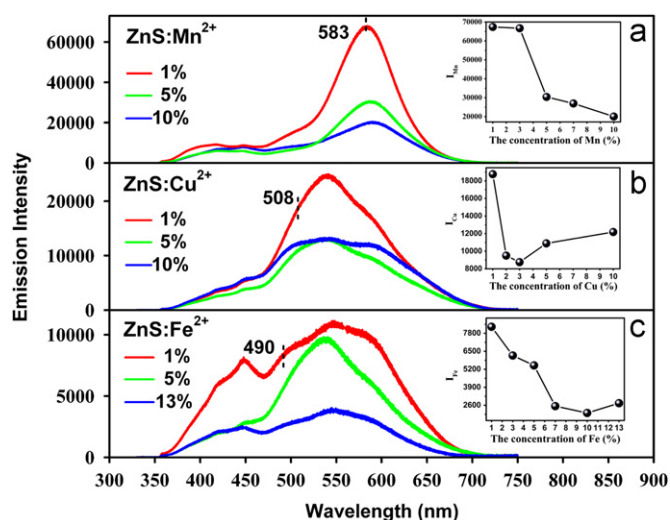


Fig. 5. Room temperature PL spectra of the (a) ZnS:Mn²⁺(1%) (red line), ZnS:Mn²⁺(5%) (green line) and ZnS:Mn²⁺(10%) (blue line) NWs; (b) the ZnS:Cu²⁺(1%) (red line), ZnS:Cu²⁺(5%) (green line) and ZnS:Cu²⁺(10%) (blue line) NWs; (c) the ZnS:Fe²⁺(1%) (red line), ZnS:Fe²⁺(5%) (green line) and ZnS:Fe²⁺(13%) (blue line) NWs; the inset figures in (a) (b) (c) is the intensity of the Mn/Cu/Fe-related PL peak on the Mn²⁺/Cu²⁺/Fe²⁺ concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

there are two kinds of doped ions with different ion radius substituted for the Zn²⁺ sites simultaneously.

Fig. 5 show the room temperature photoluminescence (PL) spectra of the ZnS:TM²⁺ (TM=Mn, Cu, Fe) NWs. The PL spectrum of the ZnS:Mn²⁺ (1%) NWs (Fig. 5a red line) shows a strong yellow-orange emission peak at 583 nm (corresponding to the Mn²⁺ ⁴T₁–⁶A₁ transition) and a weak broad blue–green emission band (coming from the defect states emission: S vacancy, Zn vacancy and surface states [22,23]), indicating that the Mn²⁺ ions have been successfully incorporated into the ZnS lattice [24]. For the ZnS:Cu²⁺ (1%) NWs (Fig. 5b red line), the green emission peak centered at 508 nm arises from the shallow donor level (sulfur vacancy) to the t₂ level of Cu²⁺ ions [25,26], a strong green emission peak centered at 540 nm corresponds to the sulfur species on the surface of ZnS NWs [27], and an orange emission band (transition from the deep defect to the Cu (t₂) states [19]) is rarely reported so far. Compared with the ZnS:Cu²⁺ (1%) NWs (Fig. 5b red line), the PL spectrum of the ZnS:Fe²⁺ (1%) NWs (Fig. 5c red line) shows the Fe-related emission peak centered at 490 nm. It is worth to note that the PL intensity of the ZnS:Fe²⁺ NWs is lower than that of the Mn²⁺ or Cu²⁺ doped ZnS NWs, indicating that the Fe²⁺ ions mainly act as the quenching centers of fluorescence, which is in agreement with the literatures [28,29]. In the inset figures in Fig. 5a–c, the concentration quenching effect can be observed in the ZnS:TM²⁺ (TM=Mn, Cu, Fe) NWs, which can be attributed to the migration of the excitation energy between the transition ions pairs in the case of doping. During the concentration quenching process, the excitation energy transferred from one transition ion to its nearest transition ion by the nonradiative transition process and via a number of transfer steps, finally to a quenching site (e.g. defect state). Moreover, the peak position of the Mn²⁺/Cu²⁺/Fe²⁺ related emission band shift to the lower energy with the doped ratio increased. When the Mn²⁺/Cu²⁺/Fe²⁺ ions are incorporated into the ZnS lattice, the lattice distortion is induced by the different size between the Zn²⁺ (0.74 Å) and Mn²⁺ (0.83 Å)/Cu²⁺ (0.72 Å)/Fe²⁺ (0.74 Å) ions thus influencing the energy level structure of the ZnS NWs [30].

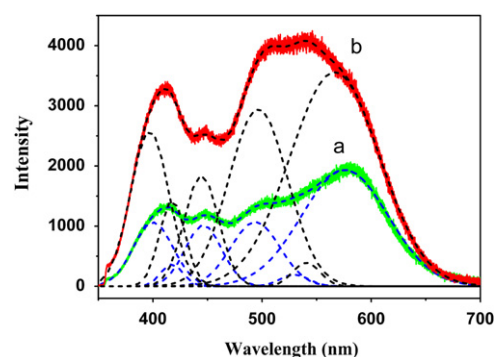


Fig. 6. Room temperature PL spectra of the (a) ZnS:Cu²⁺(1%)Mn²⁺(10%) (green line) and (b) ZnS:Fe²⁺(1%)Mn²⁺(10%) (red line) NWs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For the Cu/Mn or Fe/Mn co-doped ZnS NWs, the PL spectra (Fig. 6) are different from those of Mn²⁺, Cu²⁺ and Fe²⁺ doped ZnS NWs (Fig. 5). The PL spectra of both the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs (Fig. 6 red line) and ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs (Fig. 6 green line) show a broad emission band between 350–650 nm, which can be decomposed into six Gaussian peaks centered at 397, 418, 445, 496, 540, 567 nm (black dot line) and 400, 418, 445, 493, 527, 575 nm (blue dot line), respectively. The observed broad spectra of the ZnS:Fe²⁺(1%)Mn²⁺(10%) and ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs compared with the ZnS:Fe²⁺(1%) and ZnS:Cu²⁺(1%) NWs can be attributed to the change of the energy band structure due to the TM–TM interaction at higher TM concentrations in ZnS NWs. The localized energy level of the excitation states of the Fe²⁺, Cu²⁺ and Mn²⁺ ions would be different by changing the impurity mole ratios of the Fe²⁺, Cu²⁺ and Mn²⁺ ions in ZnS NWs. Moreover, the PL intensity of the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs (Fig. 6 red line) is about two times higher than that of the ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs (Fig. 6 green line). Based on the luminescence mechanism of the co-doped ZnS NWs [31], there would be more electrons excited in the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs compared with the ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs when Fe²⁺, Cu²⁺ and Mn²⁺ ions are doped into the ZnS lattice.

Fig. 7 show the magnetic hysteresis loops of the ZnS:Fe²⁺(1%)Mn²⁺(10%) and ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs measured at room temperature. It can be seen that the coercivity of the ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs ($H_c=343$ Oe) is about two times larger than that of the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs ($H_c=168$ Oe), the saturation magnetization of the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs is about 100 times larger than that of the ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs. So, the magnetic property of the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs is nearly paramagnetic [32]. Since Mn itself is anti-ferromagnetic, so the extrinsic ferromagnetism cannot be induced even if the Mn clustering occurs [33], whereas Fe is a kind of magnetic element, so it can be easily observed the ferromagnetic properties of the ZnS:Fe²⁺ NWs at room temperature due to its high Curie temperature (1043 K) [8,34]. As the Mn²⁺ doped ratio increased to 10% for the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs, the enhanced antiferromagnetic interaction caused by the increased Mn²⁺ ions would suppress the ferromagnetic ordering caused by the Fe²⁺ ions, which would induce the paramagnetic-like behavior. Chen et al. [1] have studied the magnetic properties of the ZnS NWs doped with one or two transition metal atoms (Cr, Mn, Fe, Co, and Ni) using first-principles calculations. They found that the hybridization between the transition metal atoms and S atoms played an important role in the formation of the induced magnetic moments, the Cr atoms induced antiferromagnetism interactions,

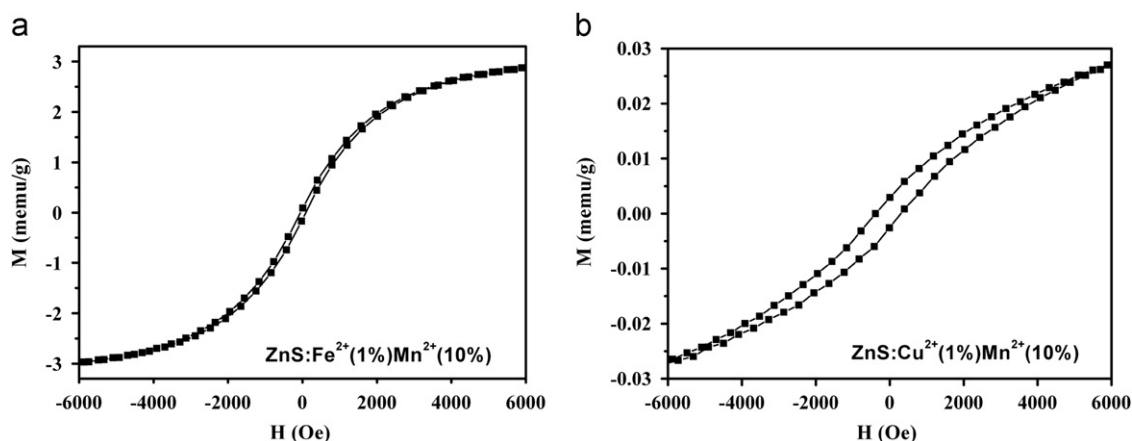


Fig. 7. Magnetic hysteresis loops of (a) the ZnS:Fe²⁺(1%)Mn²⁺(10%) NWs; (b) the ZnS:Cu²⁺(1%)Mn²⁺(10%) NWs.

whereas Mn, Fe, Co and Ni atoms induced ferromagnetism interactions. For all the doped samples under study, the spin-up *d* bands are occupied for all the *TM* (*TM*=Mn (3*d*⁵), Fe (3*d*⁶) Cu (3*d*⁹)) elements, whereas the spin-down states are partially occupied. As proved by our XRD, EDAX and PL results, it can be suggested that the Mn²⁺/Cu²⁺/Fe²⁺ ions are incorporated into the ZnS NWs. Consequently, the degenerate Mn²⁺/Cu²⁺/Fe²⁺ 3*d* states split into the triply degenerate *p*–*d* bonding *t*_{2g} states and doubly degenerate non-bonding *e*_g states. The triply degenerate *t*_{2g} and doubly degenerate *e*_g states are separated due to the strong *p*–*d* exchange interaction between *TM* (Mn²⁺ Fe²⁺ Cu²⁺) *d* and anion (*s*^{2–}) *p* orbitals [35]. Based on the Anderson's super exchange [36], due to the hybridization interaction between the Mn²⁺ (3*d*³) Cu²⁺(3*d*⁷) (or Fe²⁺ (3*d*⁴)) ion's *d* shell and S^{2–}(3*p*⁶) ion's *p* shell, these spin-down states become partly occupied and consequently the spin-up states of the S ions become more occupied than the spin-down states and induced the magnetic moments of the S ions parallel to that of the Mn and Cu (or Fe) ions [37]. In addition, the presence of the intrinsic point defects, clusters, and the structural ordering would also contribute to the ferromagnetic behavior at room temperature. Consequently, much more theoretical and experimental work should be performed to clarify the mechanism of the ferromagnetism at room temperature.

5. Conclusions

In this paper, we have synthesized the transition metal ions doped ZnS NWs with the solid solubility of the Mn²⁺, Cu²⁺, Fe²⁺ ions being 3.47%, 3.32%, and 6.22% respectively. We did not observe the phase transformation from hexagonal to cubic for all the samples even in a large quantity introduced. The PL intensity of the Mn/Cu/Fe-related emission peak reached the highest value when the doped ratio equaled 1%. The ferromagnetism of the Mn/Cu and Mn/Fe co-doped ZnS NWs was observed around room temperature.

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