Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices www.rsc.org/MaterialsC



ISSN 2050-7526



PAPER Yan-Bo Wu, Tao Wu *et al.* Exploring Mn²⁺-location-dependent red emission from (Mn/Zn)–Ga–Sn–S supertetrahedral nanoclusters with relatively precise dopant positions



Journal of Materials Chemistry C



View Article Online

PAPER



Cite this: J. Mater. Chem. C, 2016, 4, 10435

Exploring Mn²⁺-location-dependent red emission from (Mn/Zn)–Ga–Sn–S supertetrahedral nanoclusters with relatively precise dopant positions[†]

Qian Zhang,^a Jian Lin,^a Yun-Tao Yang,^b Zhen-Zhen Qin,^b Dongsheng Li,^c Shuao Wang,^d Yipu Liu,^e Xiaoxin Zou,^e Yan-Bo Wu*^b and Tao Wu*^a

Mn²⁺-Doped semiconductor nanocrystals or quantum dots have been extensively studied as potential vellow/orange/red phosphors due to the stable Mn²⁺-related emission tuned by its tetrahedral coordination environment in host lattices. However, it is still very difficult to objectively explore the location-performance relationship in conventional Mn²⁺-doped nanomaterials since the precise location information on Mn²⁺ dopants is generally unavailable due to their random distribution in host lattices. Herein, we purposely selected a specific supertetrahedral-nanocluster-based molecular crystal (OCF-40-ZnGaSnS, composed of isolated supertetrahedral T4-ZnGaSnS nanoclusters (NCs) with the formula $[Zn_4Ga_{14}Sn_2S_{35}]^{12-})$ as a host lattice, and effectively controlled the relatively precise position of Mn^{2+} dopants in host lattices of T4-ZnGaSnS NCs by *in situ* substitution of Zn^{2+} sites by Mn^{2+} ions, and investigated the Mn²⁺-location-dependent red emission properties. The current study clearly indicates that a long-lifetime (~170 µs) red emission centred at 625 nm at room temperature for lightly-doped $[Zn_{\tau}MnGa_{14}Sn_{2}S_{\tau_{5}}]^{12-}$ NCs with one Mn²⁺ dopant in its surface centre is very sensitive to temperature and dramatically red-shifts to 645 nm at 33 K upon the excitation of 474 nm. However, heavily-doped OCF-40-MnGaSnS (composed of T4-MnGaSnS NCs with the formula [Mn₄Ga₁₄Sn₂S₃₅]¹²⁻, in which four Mn^{2+} dopants are accurately located at its core in the form of Mn₄S) gives the temperature-insensitive red emission with a longer wavelength (641 nm) and a shorter lifetime (42 µs) at room temperature. This phenomenon is pretty uncommon compared to other heavily Mn²⁺-doped semiconductors. Such differences in their PL properties are ascribed to Mn²⁺-location-induced lattice strain to different degrees in two Mn²⁺-doped supertetrahedral NCs. In addition, the Mn²⁺-related red emission of both samples can be predominantly induced by the direct excitation of Mn^{2+} ions and secondarily by indirect excitation through exciton energy transfer from host lattices to Mn²⁺ dopants. Consistently, the DFT calculations suggest that the emission of NCs originated from the transition from the low spin excited state of Mn^{2+} (⁴T₁) to its high spin ground state (⁶A₁). The calculation results also revealed that the emission wavelength of lightly-doped $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NCs is not obviously affected by the temperature-induced thermal effect, but by temperature-induced structural contraction, while that of heavily-doped [Mn₄Ga₁₄Sn₂S₃₅]¹²⁻ NCs is affected by both effects. The total temperature cooling effect on the emission of $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NCs is the red-shift, while that on the emission of $[Mn_4Ga_{14}Sn_2S_{36}]^{12-}$ NCs is negligible, which is akin to the experimental results. This research opens up a new perspective and provides a feasible method to explore the location-performance relationship of other Mn²⁺-doped NCs.

^a College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Jiangsu 215123, China. E-mail: wutao@suda.edu.cn

Received 5th September 2016, Accepted 26th September 2016

DOI: 10 1039/c6tc03844a

www.rsc.org/MaterialsC

^b The Key Laboratory of the Materials for Energy Storage and Conversion of Shanxi Province, Institute of Molecular Science, Shanxi University, Taiyuan 030006, Shanxi, China. E-mail: wyb@sxu.edu.cn

^c College of Materials and Chemical Engineering, Key Laboratory of Inorganic Non-metallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, China

^d School for Radiological and Interdisciplinary Sciences (RAD-X), Soochow University, Jiangsu 215123, China

e State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Joint Research Laboratory of Nano-Micro Architecture Chemistry,

College of Chemistry, Jilin University, Changchun 130012, P. R. China

[†] Electronic supplementary information (ESI) available: EDX, XRD, EPR and PL spectra of Mn2+-doped samples. See DOI: 10.1039/c6tc03844a

Introduction

For the last few decades, doped semiconductor nanocrystals¹ have been attracting great attention since the intentionally inserted dopants can tune the optical,^{2,3} electronic,⁴ magnetic⁵ and even the catalytic⁶ properties of host materials. Transition metal ions can serve as one class of frequently studied dopants in the doping processes of the II-VI binary or I-III-VI ternary semiconductor hosts. Among them, an optically and magnetically active Mn²⁺ dopant has been widely investigated as a result of intriguing features of Mn²⁺-related emission, such as a long photoluminescence (PL) lifetime,⁷ high PL quantum yield (QY),^{8,9} wide Stokes shift, and various potential applications, such as LEDs,¹⁰ luminescence sensors,¹¹ spintronics,¹² lightemitting sources in optoelectronic devices¹³ or in biomedical imaging.14 Early studies mainly focused on Mn2+-doping behaviour in the bulk semiconductor hosts,^{2,15} nanocrystals and core-shell quantum dots with sizes larger than 2 nm.^{1,16,17} Recently, there has been gradually increasing research interest in the Mn²⁺-doped magic-sized NCs less than 2 nm.18,19 It is generally accepted that Mn²⁺-related emission is attributed to the spin-forbidden relaxation between ${}^{4}T_{1}$ and ${}^{6}A_{1}$ states of the Mn²⁺ ion, and its peak position is mainly determined by the coordination environment of the Mn²⁺ ion, i.e. the nature of the surrounding ligand (L), Mn-L distance and coordination field symmetry, which have a drastic influence on the lattice strain, subsequently affecting the ${}^{4}T_{1}$ and ${}^{6}A_{1}$ energy state splitting.²⁰ Therefore, identifying the precise position of the Mn²⁺ ion in the crystal lattice and its coordination environment plays a vital role in deeply understanding the direct and subtle correlation between Mn²⁺-related emission and its corresponding structure.

Unfortunately, despite the big progress in tuning Mn^{2+} -related emission, it is still very difficult to establish such correlation because Mn^{2+} dopants are prone to randomly distribute in the host lattice, regardless of nanocrystals or magic-sized nanoclusters, through traditional doping processes (*i.e.* nucleation and growth).²¹ Current structure characterization techniques are powerless for probing the precise location information on randomly distributed Mn^{2+} dopants in the host lattice, such as the coordination environment of a single Mn^{2+} ion and the relative location of adjacent Mn^{2+} ions in heavily-doped host lattices. Thus far, only one example has been reported, which discussed the tunable Mn^{2+} -related emission affected by the location of Mn^{2+} ions in the nanocluster.²²

Recently, we realized the precise doping of Cu⁺ and Mn²⁺ ions into the core site of the supertetrahedral chalcogenide molecular NC with the edge size of 2 nm and a vacancy in the centre of the NC (denoted as T5-CdInS, here "T" means tetrahedral, "5" is the number of metal layers in the cluster followed by the composition of the cluster).^{23,24} The unexpected successes make us clearly realize that the investigation on Mn²⁺-related emission from the Mn²⁺-doped NC can help us to explore the Mn²⁺-location–performance relationship. This is because easy crystallization of a negatively charged Mn²⁺-doped NC into a NC-based molecular crystal facilitates the characterization of the coordination environment of Mn²⁺ dopants and their relatively precise position in the host lattice through the single-crystal X-ray diffraction (SCXRD) technique. It is to be noticed that, in the above successful case, post-modified doping treatment on the coreless T5-CdInS NC allows only a single Mn^{2+} ion to be trapped at its core site, which prevents a systematic study on the Mn^{2+} -related emission tuned by the dopant concentration and the location in the NC.

Herein, we deliberately chose the previously reported NC-based semiconductor molecular crystal (denoted as OCF-40-ZnGaSnS, composed of supertetrahedral T4-ZnGaSnS NCs with the formula $[Zn_4Ga_{14}Sn_2S_{35}]^{12-}$ and an edge length of 1.5 nm) as the host lattice,²⁵ and effectively controlled the relatively precise location of Mn^{2+} dopants in the NC through *in situ* substitution of the Zn²⁺ site by the Mn^{2+} ion, and investigated the Mn^{2+} -location-dependent red emission from those Mn^{2+} -doped NCs.

Experimental

Chemicals

Sulfur powder (S, 99.99%, metal basis), zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O, AR, 99\%)$, manganese(II) acetate tetrahydrate $(Mn(Ac)_2 \cdot 4H_2O, AR, 99.99\%)$, metal basis), gallium nitrate hydrate (Ga(NO₃)₃·xH₂O, AR, 99.9%), stannous chloride (SnCl₂, AR, 99%) and piperidine (PR, 99%). All chemicals of analytical grade were obtained commercially and used without any further purification.

Syntheses

Synthesis of Mn^{2+} -doped sample ($Zn_{4-x}Mn_xGa_{14}Sn_2S_{35}$). S (72 mg, 2.245 mmol), SnCl₂ (35.0 mg, 0.184 mmol), Ga(NO₃)₃· xH_2O (253.0 mg, 0.988 mmol), Zn(NO₃)₂·6H₂O (76.9 mg, 0.259 mmol) and different doses of Mn(Ac)₂·4H₂O were added to the raw materials (see Table S1, ESI[†]); then they were mixed with H₂O (2.481 g, 137.8 mmol) and piperidine (PR, 2.023 g, 23.75 mmol) in a 23 mL Teflon-lined stainless steel autoclave and stirred for 30 min. The vessel was then sealed and heated to 200 °C for 10 days. After cooling to room temperature, a large amount of crystals were obtained.

Synthesis of $Mn_4Ga_{14}Sn_2S_{35}$. S (76.0 mg, 2.371 mmol), $SnCl_2$ (30.0 mg, 0.158 mmol), $Ga(NO_3)_3 \cdot xH_2O$ (272.0 mg, 1.062 mmol) and $Mn(Ac)_2 \cdot 4H_2O$ (34 mg, 0.139 mmol) were mixed with H_2O (2.481 g, 137.8 mmol) and piperidine (PR, 2.023 g, 23.75 mmol) in a 23 mL Teflon-lined stainless steel autoclave and stirred for 30 min. The vessel was then sealed and heated to 200 °C for 10 days, and a large amount of orange crystals were obtained.

(Note: the formula with neutral charge represents the sample discussed in the text, and the formula with -12 charge represents a nanocluster.)

Physical characterization

Powder X-ray diffraction patterns of as-synthesized crystalline samples were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-K α radiation operated at 30 kV and 10 mA. Elemental analyses for the molar ratio of Zn : Mn were carried out by energy-dispersive X-ray (EDAX) analysis on a scanning electron microscope (SEM) equipped with an energy

dispersive spectroscope (EDS) detector. An accelerating voltage of 25 kV and 40 s accumulation time were applied. A Varian 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine the concentrations of Zn^{2+} and Mn^{2+} . Electron paramagnetic resonance (EPR) measurements were carried out on powder samples at 9.06 GHz using an ER200-SRC Bruker X-band spectrometer at room temperature. Solid-state diffuse reflectance spectra were recorded on a SHIMADZU UV-3600 UV-vis-NIR spectrophotometer. The absorption spectra were calculated from the reflectance spectra by using the Kubelka–Munk function: $F(R) = \alpha/S = (1 - R)^2/2R$, where R, α , and S are the reflection, the absorption, and the scattering coefficient, respectively. PL and photoluminescence excitation (PLE) measurements and PLE vs. PL 2D mapping spectra were recorded using a HORIBA Scientific Fluorolog-3 steady state and time-resolved fluorescence spectrophotometer equipped with a 450 W xenon lamp. PL decays were recorded using an HORIBA Scientific Fluorolog-3 steady state fluorimeter with a time-correlated single-photon counting (TCSPC) spectrometer and a pulsed xenon lamp as the excitation source. Low temperature PL spectra were recorded on a HORIBA Scientific Fluorolog-3 spectrophotometer with a low temperature accessory. Single-crystal PL spectra were measured on the Craic Technologies micro-spectrophotometer with a 365 nm lamp excitation source.

Theoretical calculations

We studied two bare NCs $([Zn_3MnGa_{14}Sn_2S_{35}]^{12-})$ and $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$). Simultaneously, for each of these two NCs, 10 protons were also added to the S atoms in the four corners and the middle positions of six edges, resulting in protonated NCs $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$ and $[Mn_4Ga_{14}Sn_2S_{35}H_{10}]^{2-}$. The DFT calculations were performed for these four NCs at the B3LYP level with the 6-31G (d) basis set for H, S, Mn, Zn, and Ga and the SDD basis set with pseudo potential for Sn. For $[Zn_{3}MnGa_{14}Sn_{2}S_{35}]^{12-}$ and $[Zn_{3}MnGa_{14}Sn_{2}S_{35}H_{10}]^{2-}$ NCs, there is only one Mn²⁺ with five d electrons in each NC. The high spin state (Mn²⁺ adopts the ⁶A₁ configuration) should be the ground state and the low spin state (Mn^{2+} adopts the ${}^{4}T_{1}$ configuration) should be the excited state; for $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ and $\left[Mn_4Ga_{14}Sn_2S_{35}H_{10}\right]^{2-}$ NCs, the ground state should have four Mn²⁺ with ⁶A₁ configuration, while the excited state should have three Mn^{2+} with ${}^{6}A_{1}$ configuration and one Mn^{2+} with ${}^{4}T_{1}$ configuration. Remarkably, we checked two possibilities of the ground electronic state, *i.e.* spin multiplicity (S) = 1 and 21. Here, S = 1 denotes the so-called anti-ferromagnetic singlet (AFMS) state. The AFMS state was realized by the division of the whole NC into six fragments: the S atom in the centre is fragment 1, four Mn²⁺ atoms are fragments 2–5, and all other atoms are composed of fragment 6. During the initial guess of wavefunction, the spin multiplicity of the whole NC was assigned as a singlet (open shell), fragments 1 and 6 were also assigned as a singlet, and those of fragments 2-5 as a sextet. Note that two Mn^{2+} ions were assigned as the α spin, and the other two Mn^{2+} ions as the β spin. The reader can consult the keyword "Guess" and its option "Fragment" in the manual of the Gaussian package for the details of AFMS state calculation.²⁶ The energy of Mn²⁺-related emission was defined as differences between the energy of the excited state (a Mn²⁺ ion adopts the low spin state) and that of the ground state both in the optimized structure of the excited state. The Gibbs free energy corrections were considered during the calculation of emission energies. Note that the current geometry optimization can only obtain the structures at 0 K. All calculations were performed using the Gaussian 09 package.²⁷

Results and discussion

Doping process and structure characterization

The host material used in this study is a NC-based semiconductor molecular crystal named OCF-40-ZnGaSnS, composed of supertetrahedral NCs with the formula [Zn₄Ga₁₄Sn₂S₃₅]¹²⁻ (denoted as T4-ZnGaSnS).²⁵ Its structure and composition have been accurately characterized through SCXRD structure refinement and elemental analyses. There are twenty metal sites in the supertetrahedral T4-ZnGaSnS NC, in which two of the four vertices are occupied by Sn⁴⁺ ions, and each face centre in the supertetrahedron is occupied by one Zn²⁺ ion, and Ga³⁺ ions are located at other fourteen metal sites. The typical Mn²⁺-doping process was carried out via an in situ solvothermal method by directly mixing a certain amount of manganese source with other raw reagents, typically used in the synthesis of the host material OCF-40-ZnGaSnS. Due to the similar ionic radii (0.80 Å for Mn²⁺ and 0.74 Å for Zn^{2+} , being much larger than 0.61 Å for Ga^{3+} and 0.69 Å for Sn^{4+}) and the same ionic charge, the Mn^{2+} ion can theoretically and preferentially replace the Zn²⁺ site, instead of Ga³⁺ and Sn⁴⁺ sites. Ideally, the stepwise substitution of four Zn²⁺ ions in one T4-ZnGaSnS NC by Mn2+ ions can lead to the formation of four types of $[Zn_{4-x}Mn_xGa_{14}Sn_2S_{35}]^{12-}$ (x = 1, 2, 3 and 4) NCs (Fig. 1). Therefore, the dopant concentration can be tuned by systematically controlling the amount of manganese salts added. In principle, for a single T4-ZnGaSnS NC, when all four Zn sites in the face centre of the supertetrahedron are replaced by Mn²⁺ ions, Mn²⁺ doping concentration can reach its theoretical maximum value, which is the right case observed in the previously reported sample named OCF-40-MnGaSnS composed of T4-MnGaSnS NCs with the formula [Mn₄Ga₁₄Sn₂S₃₅]¹²⁻ and a well-defined structure.²⁵ However, to explicitly ascertain the possible subtle difference in PL emission caused by Mn²⁺ location in the NC, we may tend to compare two extreme cases, i.e. a lightly-doped NC ([Zn₃MnGa₁₄Sn₂S₃₅]¹²⁻) and a heavilydoped NC ([$Mn_4Ga_{14}Sn_2S_{35}$]¹²⁻). On the one hand, the big distinction in the Mn2+ coordination environment between $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ and $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ could maximise the difference in the Mn²⁺-related emission; on the other hand, it is also experimentally more feasible and more controllable to obtain the Mn²⁺-doped sample fully/mainly composed of $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NCs, instead of $[Zn_2Mn_2Ga_{14}Sn_2S_{35}]^{12-}$ and $[ZnMn_3Ga_{14}Sn_2S_{35}]^{12-}$ NCs, by strictly controlling the amount of Mn²⁺ salt added during the doping process.

We have set up four group experiments to prepare lightly Mn^{2+} -doped samples. To properly label these doped samples



with different doping concentrations, they are named Zn_{4-x}-Mn_xGa₁₄Sn₂S₃₅. Four samples were obtained and used for the following discussion, which are denoted as Zn_{2.89}Mn_{1.11}Ga₁₄Sn₂S₃₅, $Zn_{3.06}Mn_{0.94}Ga_{14}Sn_2S_{35}$, $Zn_{3.22}Mn_{0.78}Ga_{14}Sn_2S_{35}$ and $Zn_{3.46}$ - $Mn_{0.54}Ga_{14}Sn_2S_{35}$. The molar ratio of Zn: Mn in these Mn²⁺-doped samples was determined by EDS (Fig. S1, ESI⁺) and ICP-OES analyses (Table S1, ESI⁺), which are greater than or very close to 3. These results mean that the $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NC perhaps dominates in the final sample. However, as we all know, the crystallization process of multiple components is usually complicated because it may lead to phase separation or new phase formation. For the currently discussed in situ doping process, we have proved that it did not change the structure of the host lattice because the powder X-ray diffraction (PXRD) patterns of doped samples are very similar to that of the original host material, as shown in Fig. S2 (ESI⁺). Nevertheless, the fact is that on an unchanged host lattice one cannot be sure of the coexistence of ${\rm Zn}^{2+}$ and ${\rm Mn}^{2+}$ ions in the same single NC, as exhibited in Fig. 1. These divalent metal ions may be located at different single crystals or at different NCs of one single crystal. To rule out these cases as much as possible, we firstly carried out EDS measurements on some randomly selected single crystal of the Mn²⁺-doped sample, which indicates that both Zn²⁺ and Mn²⁺ ions coexist in a single crystal and no phase separation is observed (Fig. S1, ESI⁺). To further verify that both Zn²⁺ and Mn²⁺ ions coexist in one NC, not just in one crystal, we attempted to perform mass spectroscopy (MS) measurements. Unfortunately, the low solubility and instability of NCs under MS test conditions made it fail to directly prove the existence of four types of NCs. In addition, the single-crystal X-ray diffraction

technique also failed to identify the coexistence of Zn²⁺ and Mn²⁺ ions in a single NC due to their similar scattering factor. As we all know, Mn ··· Mn exchange interactions between the adjacent Mn²⁺ ions are different in heavily-doped and lightlydoped samples, we can employ X-band electron spin resonance (ESR) spectroscopy to further verify the environment (isolation or aggregation) of each Mn²⁺ ion. From the EPR signals (Fig. S3, ESI[†]), we can see a broad signal for the heavily-doped $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ NC, which is caused by the aggregation of Mn^{2+} in the core in the form of Mn_4S , and the $Mn \cdots Mn$ interactions lead to a reduction of the electron-nuclear spin interactions in an individual Mn²⁺ ion.²⁸ However, for lightlydoped samples, apparently six-line hyperfine splitting patterns can be seen, which indicates that the $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NC is the predominant form in the lightly-doped sample. Each Mn²⁺ ion is separated in different NCs. No Mn²⁺ pairs are formed in one single NC, and no spin-spin interactions happen within the neighbouring Mn²⁺ ion. These EPR signals made us believe that we got our expected results.

Absorption spectra and optical band gap

The solid-state optical diffuse reflection spectra of OCF-40-ZnGaSnS, OCF-40-MnGaSnS and four Mn²⁺-doped samples were measured at room temperature. The absorption spectra (α/S) derived with the Kubelka–Munk function and their corresponding Tauc plots are shown in Fig. 2a and Fig. S4a (ESI⁺), respectively. Obviously, heavily-doped OCF-40-MnGaSnS displays five absorption peaks (2.12 eV, 2.25 eV, 2.41 eV, 2.62 eV, and 2.85 eV), which is not apparently observed in lightly Mn²⁺-doped samples (Fig. 2b) and even they are absent in OCF-40-ZnGaSnS. Those absorption peaks are tentatively attributed to the transition from the ${}^{6}A_{1}({}^{6}S)$ ground state of the Mn²⁺ ion to the ${}^{4}E({}^{4}D), {}^{4}T_{2}({}^{4}D), [{}^{4}E({}^{4}G), {}^{4}A_{1}({}^{4}G)], {}^{4}T_{2}({}^{4}G), and {}^{4}T_{1}({}^{4}G)$ excited states, respectively.^{5,20} The optical band gaps of OCF-40-ZnGaSnS and OCF-40-MnGaSnS obtained by extrapolating the linear portion of the absorption edge are estimated at 3.47 eV and 3.02 eV, respectively. In addition, from Tauc plots of Mn2+-doped samples (Fig. S4b, ESI[†]), we can see that the band gaps red-shift from 3.48 eV to 2.84 eV with increasing Mn^{2+} doping content.

Photoluminescence properties

We noticed that PL emission intensity of OCF-40-MnGaSnS and Mn^{2+} -doped samples is not so strong at room temperature. Therefore, their PL and PL excitation (PLE) spectra were purposely tested in the low temperature region. The polycrystalline OCF-40-MnGaSnS sample clearly exhibits five excitation peaks (396 nm, 438 nm, 474 nm, 509 nm and 545 nm, as shown in Fig. 3a) at 33 K. In comparison to OCF-40-MnGaSnS, the polycrystalline $Zn_{2.89}Mn_{1.11}Ga_{14}Sn_2S_{35}$ sample has a blue-shifed PLE curve with five peaks centred at 393 nm, 435 nm, 470 nm, 502 nm, and 540 nm, respectively. Notably, the excitation measurement provides direct information on the energy level structure of Mn^{2+} ions in such a specific supertetrahedral NC. These peaks can also be assigned to transitions from the ${}^{6}A_{1}({}^{6}S)$ ground state to ${}^{4}E({}^{4}D), {}^{4}T_{2}({}^{4}D), {}^{4}T_{2}({}^{4}G),$ and ${}^{4}T_{1}({}^{4}G)$, respectively, being consistent with peaks in the





Fig. 2 (a) UV-vis absorption spectra of OCF-40-ZnGaSnS and OCF-40-MnGaSnS at room temperature, inset: optical images of OCF-40-ZnGaSnS and OCF-40-ZnMnGaSnS sample; (b) UV-vis absorption spectra of Mn^{2+} -doped samples with different doping concentrations at room temperature, inset: optical images of Mn^{2+} -doped sample.

absorption spectra. From Fig. 3b and c, we can also find that both lightly-doped Zn_{2.89}Mn_{1.11}Ga₁₄Sn₂S₃₅ and heavily-doped OCF-40-MnGaSnS can be easily excited through the direct excitation of the Mn²⁺ ion itself. It is to be noticed that such a direct excitation mechanism is just observed in some heavily Mn²⁺-doped chalcogenides.²⁹ However, for most lightly Mn²⁺-doped II–VI semiconductor materials, they are predominantly excited through exciton energy transfer from the host lattice to dopant Mn²⁺ ions, and hardly excited by the direct excitation of Mn²⁺ ions due to the spin- and parity-forbidden nature of Mn²⁺ d–d transitions.

As usual, PL emission intensity of OCF-40-MnGaSnS as well as the $Zn_{2.89}Mn_{1.11}Ga_{14}Sn_2S_{35}$ sample is very sensitive to temperature and dramatically enhances at low temperatures, as shown in Fig. 4. They also display a large red-shifted emission band with the peak position greater than 620 nm, compared to typical Mn^{2+} -doped II–VI semiconductor materials with a Mn^{2+} -related emission peak in the range of 580–600 nm. It is to be noticed that upon the excitation at 474 nm, polycrystalline OCF-40-MnGaSnS shows a maximum emission peak at 641 nm at room temperature (Fig. 4a), which only slightly red-shifts to 645 nm at 33 K. Such temperature-insensitive PL property is seldom observed in other heavily Mn^{2+} -doped chalcogenide nanocrystals. However, the emission peak position of the lightly Mn^{2+} -doped sample ($Zn_{2.89}Mn_{1.11}Ga_{14}Sn_2S_{35}$) is very sensitive

Fig. 3 (a) PLE spectra of OCF-40-MnGaSnS and $Zn_{2.89}Mn_{1.11}Ga_{14}Sn_2S_{35}$ with E_m = 642 nm at 33 K; (b) 2D PLE spectra of the OCF-40-MnGaSnS sample; (c) 2D PLE spectra of the $Zn_{2.89}Mn_{1.11}Ga_{14}Sn_2S_{35}$ sample.

to temperature, which is red-shifted from 625 nm at room temperature to 645 nm at 33 K (Fig. 4b).

Besides the PL measurements on polycrystalline samples, we also investigated the PL properties of randomly-selected single-crystal OCF-40-ZnGaSnS, OCF-40-MnGaSnS and Mn²⁺ doped samples for the purpose of ascertaining doping uniformity. Due to the limitation on the available lamp sources, only the



Fig. 4 PL spectra of the polycrystalline host material OCF-40-MnGaSnS (a) and $Zn_{2.89}Mn_{1.11}Ga_{14}Sn_2S_{35}$ (b) at different temperatures.

365 nm excitation light is used to study single-crystal PL properties. The single-crystal PL spectrum of OCF-40-MnGaSnS displays a narrow and symmetric emission band with the peak at 642 nm (Fig. 5a), which is also insensitive to temperature. However, for the single crystal of the Zn_{2.89}Mn_{1.11}Ga₁₄Sn₂S₃₅ sample, its PL spectrum gives a weak emission band in the range of 400-500 nm and a broad and symmetric strong emission band centred at 623 nm at 293 K. The former emission is attributed to PL emission from the host lattice or undoped T4-ZnGaSnS NC in the Mn²⁺-doped sample (Fig. S5, ESI[†]), and the latter temperature-sensitive Mn2+-related emission red-shifts to 652 nm at 113 K. These PL data for the single-crystal are slightly different from those obtained for polycrystalline samples (625-645 nm). This is possibly caused by the different detection system. However, the variation tendency is consistent for polycrystalline and single-crystal samples. Other three Mn²⁺-doped single-crystal samples also show similar temperature-sensitive PL properties with the emission peak in the range of 621-650 nm (Fig. S6, ESI[†]). It is easily concluded that the more the content of dopant concentration, the bigger the red shift of the Mn²⁺-related emission peak. It is to be noticed that the current results show that those Mn2+-doped samples can also be excited through an energy-transfer mechanism because the energy of the excitation incident beam (365 nm, i.e. 3.40 eV) is less than the band gap of its corresponding host material.



Fig. 5 Single-crystal PL spectra of OCF-40-MnGaSnS (a) and Zn_{2.89}- $Mn_{1.11}Ga_{14}Sn_2S_{35}$ (b) at different temperatures under the excitation of a 365 nm laser.

Wavelength (nm)

PL dynamics

To further gain an insight into the PL properties of OCF-40-MnGaSnS and other Mn²⁺-doped samples, it is essential to study time-resolved PL dynamics. The time-correlated single photon-counting (TCSPC) experiments were performed, and all time-dependent PL curves were fitted to a multi-exponential function of $I(t) = \sum A_i \exp(-t/\tau_i)$. The average lifetimes are determined by the expression of $\tau_{ave} = \sum A_i \tau_i^2 / \sum A_i \tau_i$. Fig. 6 shows the decay curve of the 642 nm emission for OCF-40-MnGaSnS at different temperatures upon excitation at 474 nm with 1.2 ms width. Fitting the decay curves by a bi-exponential can give average decay lifetimes of 42 µs at room temperature and 181 µs at 63 K. The lifetime of OCF-40-MnGaSnS at 642 nm emission increases with the temperature decreasing (Table S2, ESI⁺). The decay time of the Zn_{2.89}Mn_{1.11}Ga₁₄Sn₂S₃₅ sample monitored at 642 nm emission upon 474 nm excitation at room temperature is around 170 µs. It is clear that the decay time of four lightly-doped samples changes little, which is much longer than that of the heavily-doped OCF-40-MnGaSnS (Table S3 and Fig. S7, ESI⁺). This shortening of decay time for a heavily-doped sample is caused by magnetic coupling between neighbouring Mn²⁺ pairs (Fig. S8, ESI†), which partially lifts the spin selection rule in exchange coupled Mn²⁺ pairs.^{30,31}



Fig. 6 PL decay curve of OCF-40-MnGaSnS under pulsed 474 nm excitation and 642 nm emission at different temperatures. The inset pattern shows the temperature-dependent PL lifetime.

Mn²⁺-location-dependent PL property

Based on the big differences in PL properties between OCF-40-MnGaSnS and the Mn^{2+} -doped sample, it is reasonable for us to believe that the lightly Mn^{2+} -doped single crystal is predominantly composed of $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NCs, instead of the coexistence of $[Zn_4Ga_{14}Sn_2S_{35}]^{12-}$ and $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ NCs. Although we cannot absolutely rule out the possibility of the coexistence of other three types of NCs in the lightly-doped crystals, they should be minor components.

It is generally accepted that the Mn²⁺-related emission band and the decay lifetime can be tuned by Mn²⁺ dopant concentration. The strong Mn · · · Mn exchange interaction between the adjacent Mn²⁺ ions are easily found in the heavily doped sample, which usually leads to a red-shift of Mn²⁺-related emission and shortening of the lifetime.^{32,33} Such variation tendency is also apparently and even more intuitively observed in heavily-doped OCF-40-MnGaSnS with strong Mn ... Mn interaction and the lightly-doped Zn₃MnGa₁₄Sn₂S₃₅ sample nearly without Mn···Mn interaction. To explain why the emission peak position of Zn₃MnGa₁₄Sn₂S₃₅ is sensitive to temperature in comparison to OCF-40-MnGaSnS, we propose a possible mechanism for the splitting of Mn²⁺ excitation energy states induced by the symmetry of coordination field. As shown in Scheme 1, the coordination environment of Mn^{2+} ion in the face centre of the $[Mn_4Ga_{14} Sn_2S_{35}$ ¹²⁻ NC is different from that at the $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NC. Low temperatures may result in the possible contraction of the NC due to the shrinkage of Mn-S, Ga-S and Zn-S bonds. For a relatively high-symmetric [Mn₄Ga₁₄Sn₂S₃₅]¹²⁻ NC with a Mn₄S core, slight and synchronous contraction of four Mn-S bonds cannot lead to a significant change in the symmetry of ligand field. Therefore, the energy gap between the ${}^{4}T_{1}$ excitation state and the ⁶A₁ ground state changes little. However, it is obvious that the bond shrinkage of one Mn-S bond and three Zn-S bonds in different degrees can generate higher lattice strain in the non-symmetric NC of [Zn₃MnGa₁₄Sn₂S₃₅]¹²⁻ than that in the relatively symmetric [Mn₄Ga₁₄Sn₂S₃₅]¹²⁻ NC. Large crystal lattice distortion generally makes the Mn²⁺ ions undergo further



 $Scheme\,1$ Coordination environment of the Mn^{2+} ion in $[Mn_4Ga_{14}-Sn_2S_{35}]^{12-}$ and $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NCs.

ligand-field splitting, and drastically reduces the energy difference between the ${\rm Mn}^{2+}$ excitation states (especially the ${}^4{\rm T_1}$ state) and the ${}^6{\rm A_1}$ state, which correspondingly red-shifts ${\rm Mn}^{2+}$ -related red emission to low energy regions. This also explains why the absorption peak of OCF-40-MnGaSnS is little bit red-shifted in comparison to that of Zn_{2.89}Mn_{1.11}Ga₁₄Sn₂S₃₅ (Fig. 3a).

In addition, noticeably, the Mn²⁺-related red emission can be realized in two different excitation ways for both heavilydoped and lightly-doped T4-ZnGaSnS NC. The first way is to directly excite the Mn²⁺ ion in its own excitation levels. The electron from the ground-state of Mn²⁺ is excited to the higher energy levels of Mn²⁺, the excited free electron then relaxes through a radiative transition from the ⁴T₁ excited-state to the ${}^{6}A_{1}$ ground-state giving rise to the red emission of Mn²⁺. The second option is to excite firstly the host lattice, followed by efficient exciton energy transfer from the host lattice to the Mn^{2+} ion, which also results in the red emission of Mn^{2+} . The direct excitation method is commonly observed in the heavily Mn²⁺-doped sample, seldom in the lightly-doped sample. Noticeably, it can also be realized in the lightly-doped Zn₃MnGa₁₄Sn₂S₃₅ sample. Although we cannot give a clear explanation about it so far, it should be related to the coordination environment of the Mn²⁺ ion in such specific supertetrahedral nanostructure.

It is to be noticed that the NC-based doping process in tuning the Mn^{2+} location in the NC is always accompanied by the enhancement of dopant concentration. So, the PL properties of Mn^{2+} -doped samples seem to be affected by the concentration of Mn^{2+} in the nanocluster. However, the expression of concentration-dependent emission does not point out the contribution of the dopant location in tuning the Mn^{2+} -related emission. Therefore, we adopt the description of location-dependent emission. In addition, the currently reported Mn^{2+} -doped samples exhibit weak PL emission at room temperature. Such low PL efficiency may be caused by some intrinsic anti-site defects induced by the

random distribution of Sn and Ga ions in the corner of the T4 nanocluster. At room temperature, the defect-dominated de-excitation pathway overwhelmingly surpasses that of excited Mn^{2+} ions. That is why Mn^{2+} -related emission quenches fast with the temperature increasing to room temperature. In addition, an *in situ* doping method applied in the current study generally results in several types of Mn^{2+} -doped nanoclusters co-existing in the final microcrystal. The different crystal lattice strain from different NCs will cause the different gap between ${}^{4}T_{1}$ and ${}^{6}A_{1}$ for excited Mn^{2+} ions. This could explain the wide full-width of Mn^{2+} -related emission from doped samples.

Theoretical calculations

We also performed the DFT calculations to explain the mechanism of Mn²⁺-related emission. First, we tried to verify the ground state of the NCs with four Mn²⁺ atoms. With the consideration of Gibbs free energy corrections, the AFMS state is lower than the 21-et (S = 21) state by 0.098 eV for $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ and by 0.104 eV for $[Mn_4Ga_{14}Sn_2S_{35}H_{10}]^{2-}$. Thus, the ground state of the NCs with four Mn²⁺ atoms should be the AFMS state. This is consistent with the results of the variable temperature (2.0-300.0 K) magnetic susceptibility study (see Fig. S8, ESI⁺), which indicates the antiferromagnetic effect. The optimized structures in the ground state are shown in Fig. S9 (ESI[†]). The distances between the corner S atoms are around 15 Å (1.5 nm), which is similar to the crystal structures. However, such distances for bare NCs $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ and $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ are longer than those of the protonated NCs [Zn₃MnGa₁₄Sn₂S₃₅H₁₀]²⁻ and $[Mn_4Ga_{14}Sn_2S_{35}H_{10}]^{2-}$ by 0.81 and 0.66 Å, respectively, suggesting the significant Coulomb explosion effect in bare NCs.

The optimized structures for excited state NCs (see Fig. 7) are similar to the ground state structure regarding the size of NCs. The emission energies were calculated based on excited state structures. Shown in Table 1 are the energy differences between the ground state and the excited state at different temperatures and the corresponding emission wavelengths. As the table shows, the predicted emission energies for the bare NC $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ ($\Delta G_1 = G_{S=4} - G_{S=6}$) at different temperatures range from 2.09599 to 2.09430 eV, which correspond to the emission from 591.5 to 592.0 nm. In contrast, the ΔG_1 for the protonated NC $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$ ranges from 1.93149 to 1.92600 eV, corresponding to the emission from 641.9 to 643.7 nm. It can be seen that the emission wavelength of the NCs $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ and $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$ is not obviously related to the thermal effect of different temperatures, but to the variation of structures. Generally, with the temperature decreasing, the contraction of the structure around Mn²⁺ will lead to the red shift of Mn²⁺-related emission. Current calculation results provide indirect evidence for supporting this theory: the bare NC $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ is highly negatively charged, thus the structure will suffer from the so-called Coulomb expansion effect; as a comparison, that of the protonated NC $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$ will not obviously suffer from such an effect. Consistently, the average S-Mn bond length in the NC [Zn₃MnGa₁₄Sn₂S₃₅]¹²⁻ is 2.409 Å, which is 0.053 Å longer than that in the NC $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$ (2.356 Å). We think it is the shortening



Fig. 7 Optimized structures in excited states for bare and protonated NCs.

Table 1 The predicted emission energies (ΔG , in eV) and the corresponding emission wavelengths (λ , in nm) with regard to the variation of temperatures (T, in K)

		Bare NC		Protonated NC	
	$T(\mathbf{K})$	ΔG	λ	ΔG	λ
$[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$	293	2.09599	591.5	1.93149	641.9
	263	2.09585	591.6	1.93070	642.2
	233	2.09569	591.6	1.92989	642.4
	203	2.09547	591.7	1.92902	642.7
	173	2.09517	591.8	1.92809	643.0
	143	2.09479	591.9	1.92708	643.4
	113	2.09430	592.0	1.92600	643.7
$[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$	293	1.79437	691.0	1.77467	698.6
	263	1.81514	683.1	1.78308	695.3
	233	1.83590	675.3	1.79149	692.1
	203	1.85661	667.8	1.79987	688.9
	173	1.87710	660.5	1.80820	685.7
	143	1.89712	653.5	1.81647	682.6
	113	1.91642	647.0	1.82466	679.5

of the S–Mn bond lengths that leads to the elongation of the emission wavelength after the protonation. We note that the emission of the pronated NC $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$ around 643 nm is very close to the experimentally recorded value of 645 nm at a low temperature of 113 K. We can conclude that the emissions of NCs $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ and $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$ originated from the transition from the low spin state of Mn^{2+} (⁴T₁, S = 4 for the whole NC) to its high spin state (⁶A₁, S = 6 for the whole NC).

The predicted results for heavily-doped NCs $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ and $[Mn_4Ga_{14}Sn_2S_{35}H_{10}]^{2-}$ are obviously different. As shown in Table 1, with the temperature decreasing from 293 to 113 K, the predicted emission energies ($\Delta G_2 = G_{S=19} - G_{S=1(AMFS)}$)

for $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ increase from 1.79437 to 1.91642 eV. Correspondingly, the emissions shifted from 691.0 to 647.0 nm. Similarly, with the temperature decreasing from 293 to 113 K, the ΔG_2 values of $[Mn_4Ga_{14}Sn_2S_{35}H_{10}]^{2-}$ increase from 1.77467 to 1.82466 eV, leading to a blue-shift of emissions from 698.6 to 679.5 nm. Given that the optimized structure is not changed, the predicted results suggested that the emissions of NCs with four Mn²⁺ ions are significantly affected by the thermal effect, leading to the blue-shift. Simultaneously, the emissions of these NCs are also slightly affected by the temperature-induced structural contractions, which lead to the red-shift. Indirect evidence can be obtained from the comparison of bare and protonated NCs. The averge S-Mn bond length in $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ is 2.456 Å, which is 0.020 Å longer than that in $[Mn_4Ga_{14}Sn_2S_{35}H_{10}]^{2-1}$ (2.436 Å). The difference of 0.020 Å is obviously smaller than that between $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ and $[Zn_3MnGa_{14}Sn_2S_{35}H_{10}]^{2-}$, which is consistent with our deduction from the discussion on experimental parts. Nevertheless, the red-shift caused by temperature-induced structural constractions can be a counter factor to the blue-shift caused by the temperature-induced thermal effect. Therefore, the total effect of temperature on the emission wavelength of NCs with four Mn²⁺ will be negligible. Therefore, though the predicted emission wavelengths are a little longer than the experimentally recorded ones, we can conclude that the emission of NCs $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ and $[Mn_4Ga_{14}Sn_2S_{35}H_{10}]^{2-}$ also originated from the transition from the low spin excited state of a Mn^{2+} (⁴T₁, S = 19 for the whole NC) to its high spin ground state $(^{6}A_{1}, \text{AFMS for the whole NC}).$

Conclusions

In summary, a NC-based semiconductor material is deliberately selected as a host material to investigate the Mn²⁺-locationdependent PL emission. When a single Zn²⁺ ion in the $[Zn_4Ga_{14}Sn_2S_{35}]^{12-}$ supertetrahedral NC with a Zn_4S core in its centre is replaced by a Mn²⁺ ion, the formed lightly-doped [Zn₃MnGa₁₄Sn₂S₃₅]¹²⁻ NC exhibits tempertature-sensitive PL emission with the peak position changing from 625 nm at room temperature to 645 nm at 33 K. However, for a heavilydoped $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ NC with four Mn^{2+} ions residing at the Zn^{2+} sites, its emission band is insensitive to temperature. Such big differences in PL emission properties are mainly due to the different coordination environment of Mn^{2+} ions, *i.e.* the discrete Mn²⁺ ion in the asymmetric NC and aggregated Mn²⁺ ions in the symmetric NC. The current study on Mn²⁺-related emission from supertetrahedral NCs with a well-defined structure and relatively precise dopant position facilitates a deep understanding of the Mn²⁺-location-performance relationship, which cannot be easily observed in the conventional Mn²⁺-doped II-VI semiconductor nanocrystal with a random distribution of dopants. The DFT calculations suggest that the PL emission of NCs originated from the transition of the low spin excited state of a Mn^{2+} (⁴T₁) to its high spin ground state (⁶A₁). The emission wavelength of a lightly-doped [Zn₃MnGa₁₄Sn₂S₃₅]¹²⁻ NC is not obviously affected by the temperature-induced thermal effect,

but by the temperature-induced structural contractions, while that of the heavily-doped $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ NC is affected by both effects. Therefore, the total temperature cooling effect on the emission of the lightly-doped $[Zn_3MnGa_{14}Sn_2S_{35}]^{12-}$ NC is the red-shift, but that on the emission of the heavily-doped $[Mn_4Ga_{14}Sn_2S_{35}]^{12-}$ NC is negligible. Further investigation on Mn^{2+} -related emission of other Mn^{2+} -doped NCs is underway.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21271135, 21671142 and 21273140), a start-up fund (Q410900712) from Soochow University, the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Young Thousand Talented Program, the Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase), and the Program for the Innovative Talents of Higher Learning Institutions of Shanxi Province.

References

- 1 N. Pradhan, Chem. Phys. Chem., 2016, 17, 1087-1094.
- 2 R. N. Bhargava, D. Gallagher, X. Hong and A. Nurmikko, *Phys. Rev. Lett.*, 1994, **72**, 416–419.
- 3 S. L. Shen and Q. B. Wang, Chem. Mater., 2013, 25, 1166-1178.
- 4 J. Lin, Y. Dong, Q. Zhang, D. Hu, N. Li, L. Wang, Y. Liu and T. Wu, *Angew. Chem., Int. Ed.*, 2015, **54**, 5103–5107.
- 5 W. Q. Peng, S. C. Qu, G. W. Cong, X. Q. Zhang and Z. G. Wang, *J. Cryst. Growth*, 2005, **282**, 179–185.
- 6 G. Y. Zhao, J. Li, X. R. Niu, K. Tang, S. P. Wang, W. S. Zhu, X. Q. Ma, M. Y. Ru and Y. Z. Yang, *New. J. Chem.*, 2016, 40, 3491–3498.
- 7 A. A. Bol and A. Meijerink, Phys. Rev. B., 1998, 58, 15997-16000.
- 8 Z. Deng, L. Tong, M. Flores, S. Lin, J. X. Cheng, H. Yan and Y. Liu, *J. Am. Chem. Soc.*, 2011, 133, 5389–5396.
- 9 R. Zeng, M. Rutherford, R. Xie, B. Zou and X. Peng, *Chem. Mater.*, 2010, 22, 2107–2113.
- 10 W. Lv, W. Lu, N. Guo, Y. Jia, Q. Zhao, M. Jiao, B. Shao and H. You, *Dalton Trans.*, 2013, **42**, 13071–13077.
- 11 X. M. Zhai, Y. Q. Gong, W. Yang, H. Kang and X. Zhang, *RSC Adv.*, 2015, 5, 63458–63464.
- 12 R. Beaulac, P. I. Archer, S. T. Ochsenbein and D. R. Gamelin, *Adv. Func. Mater.*, 2008, **18**, 3873–3891.
- 13 L. Peng, D. Li, Z. Zhang, K. Huang, Y. Zhang, Z. Shi, R. Xie and W. Yang, *Nano Res.*, 2015, **8**, 3316–3331.
- B. Zhao, Y. Yao, K. Yang, P. Rong, P. Huang, K. Sun, X. An,
 Z. Li, X. Chen and W. Li, *Nanoscale*, 2014, 6, 12345–12349.
- 15 J. K. Furdyna, J. Appl. Phys., 1988, 64, R29.
- A. Nag, R. Cherian, P. Mahadevan, A. V. Gopal, A. Hazarika,
 A. Mohan, A. S. Vengurlekar and D. D. Sarma, *J. Phys. Chem. C*, 2010, **114**, 18323–18329.
- 17 C. Gan, Y. Zhang, D. Battaglia, X. Peng and M. Xiao, *Appl. Phys. Lett.*, 2008, **92**, 241111.
- 18 J. Eilers, E. Groeneveld, C. M. Donega and A. Meijerink, J. Phys. Chem. Lett., 2012, 3, 1663–1667.

- 19 J. Yang, R. Fainblat, S. G. Kwon, F. Muckel, J. H. Yu, H. Terlinden, B. H. Kim, D. Iavarone, M. K. Choi, I. Y. Kim, I. Park, H. K. Hong, J. Lee, J. S. Son, Z. Lee, K. Kang, S. J. Hwang, G. Bacher and T. Hyeon, *J. Am. Chem. Soc.*, 2015, 137, 12776–12779.
- 20 C. J. Duan, A. C. A. Delsing and H. T. Hintzen, *Chem. Mater.*, 2009, **21**, 1010–1016.
- 21 N. Pradhan, D. Goorskey, J. Thessing and X. G. Peng, *J. Am. Chem. Soc.*, 2005, **127**, 17586–17587.
- 22 C. B. Khadka, A. Eichhöfer and F. Weigend, J. F. Corrigan Inor. Chem., 2012, **51**, 2724–2756.
- 23 T. Wu, Q. Zhang, Y. Hou, L. Wang, C. Y. Mao, S. T. Zheng, X. H. Bu and P. Y. Feng, *J. Am. Chem. Soc.*, 2013, **135**, 10250–10253.
- 24 J. Lin, Q. Zhang, L. Wang, X. Liu, W. Yan, T. Wu, X. Bu and P. Y. Feng, J. Am. Chem. Soc., 2014, 136, 4769–4779.
- 25 T. Wu, L. Wang, X. H. Bu, V. Chau and P. Y. Feng, J. Am. Chem. Soc., 2010, 132, 10823–10831.

- $26\ http://www.gaussian.com/g_tech/g_ur/k_guess.htm.$
- 27 M. J. Frisch, *et al.*, *Gaussian 09, Rev. D.01*, Gaussian Inc., Wallingford CT, 2013, see ESI[†] for the full form of this reference.
- 28 P. T. K. Chin, J. W. Stouwdam and R. A. J. Janssen, *Nano Lett.*, 2009, 9, 745–750.
- 29 C. J. Duan, A. C. A. Delsing and H. T. Hintzen, *Chem. Mater.*, 2009, **21**, 1010–1016.
- 30 C. Barthou, J. Benoit, P. Benalloul and A. Morell, J. Electrochem. Soc., 1994, 141, 524–528.
- 31 J. F. Suyver, S. F. Wuister, J. J. Kelly and A. Meijerink, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5445–5448.
- 32 N. Yamashita, S. Maekawa and K. Nakamura, *Jpn. J. Appl. Phys.*, 1990, **29**, 1729–1732.
- 33 A. Ishizumi, E. Jojima, A. Yamamoto and Y. Kanemitsu, J. Phys. Soc. Jpn., 2008, 77, 053705.