

Electronic Supplementary Information (ESI)

Heating-up synthesis of pure phase kesterite Cu₂ZnSnS₄ nanocrystals using simple coordinating sulphur precursor

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ESI 1:

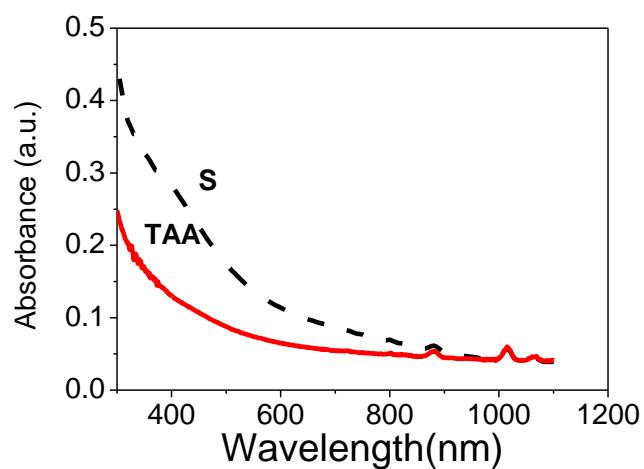
Overview of formulation and size distribution of colloidal CZTS NCs reported by different groups^a

	Method	Precursors	Stabilizers solvents	Reaction conditions	Phase Size (nm)	Authors
Hot- injection		Cu(acac) ₂ , Zn(OAc) ₂ Sn(OAc) ₄ , S	OAm TOPO	Injection of S, metal precursor in OAm into TOPO at 300 °C	KS 13	Riha <i>et al.</i> ¹
		CuCl ₂ 2H ₂ O, ZnCl ₂ SnCl ₄ 5H ₂ O, DDT	OAm OA DDT	Injection of metal precursor solutions into OAm, OA and DDT at 240 °C	WZ 2-5	Lu <i>et al.</i> ²
		CuCl ₂ , ZnCl ₂ , SnCl ₄ , S	OAm	-	KS 7-9	Saha <i>et al.</i> ³
		Cu(acac) ₂ , Zn(OAc) ₂ Sn(OAc) ₄ , tert-DDT	DDT TOPO ODE	-	WZ 35×11 rods	Singh <i>et al.</i> ⁴
		Cu(acac) ₂ , Zn(acac) ₂ Sn(acac) ₂ Br ₂ S	OAm	Injection of S in OAm into metal precursor in OAm at 225 °C	KS 15-25	Guo <i>et al.</i> ⁵
		Cu(acac) ₂ , Zn(OAc) ₂ SnCl ₂ 2H ₂ O, S	OAm	110 °C for 30 min, then 280 °C for 1 h	KS 12	Steinhagen <i>et al.</i> ⁶
Heating -up		CuI, ZnCl ₂ , SnI ₄ , S	OAm		KS 7-35	Rath <i>et al.</i> ⁷
		CuI, ZnCl ₄ , Sn(EtXn) ₂ DDT	OAm DDT	280 °C for 30 min	KS 5-8	Chesman <i>et al.</i> ⁸
		CuI, SnCl ₄ 5H ₂ O ZnCl ₂ , CS ₂	OAm DDT		KS 2-8	Chesman <i>et al.</i> ⁹
		Cu(OAc) ₂ , Zn(OAc) ₂ Sn(OAc) ₄ , S	OAm	240 °C	Spherical 5-6	Kameyama <i>et al.</i> ¹⁰
		Cu(OAc) ₂ , Zn(OAc) ₂ Sn(OAc) ₄ , S, DDT	OA OAm ODE		KS WZ	Zou <i>et al.</i> ¹¹
		Cu(acac) ₂ , Zn(acac) ₂ Sn(acac) ₄ , DDT	OAm	220 °C for 1-8 h	WZ 10-40	Li <i>et al.</i> ¹²
Thermal decomposition.		CuCl ₂ , ZnCl ₂ , SnCl ₂ thiourea	OAm	235 °C for 30 min	KS	Wei <i>et al.</i> ¹³
		Cu(acac) ₂ , Zn(OAc) ₂ SnCl ₂ , S	OAm	110 °C for 30 min	KS 10.6 ± 1.9	Yang <i>et al.</i> ¹⁴
		Cu(dedc) ₂ , Zn(dedc) ₂ Sn(dedc) ₄		Injection of OAm into the precursor solution	KS 2-7	Khare <i>et al.</i> ¹⁵
Solvothermal		CuCl ₂ 2H ₂ O, ZnCl ₂ SnCl ₄ 4H ₂ O, CH ₄ N ₂ S		230 °C for 24 h in ethylene glycol	KS 100	Zhou <i>et al.</i> ¹⁶
Hydrothermal		Cu(OAc) ₂ , Zn(NO ₃) ₂ SnCl ₂ 2H ₂ O, CH ₄ N ₂ S		180 °C for 4-8 h in water /ethylenediamine	KS 3-10	Liu <i>et al.</i> ¹⁷

^aKS: kesterite, WZ: wurtzite, DDT: dodecanethiol, OAm: oleylamine, OA: oleic acid, TOPO: trioctylphosphine, ODE: octadecene.

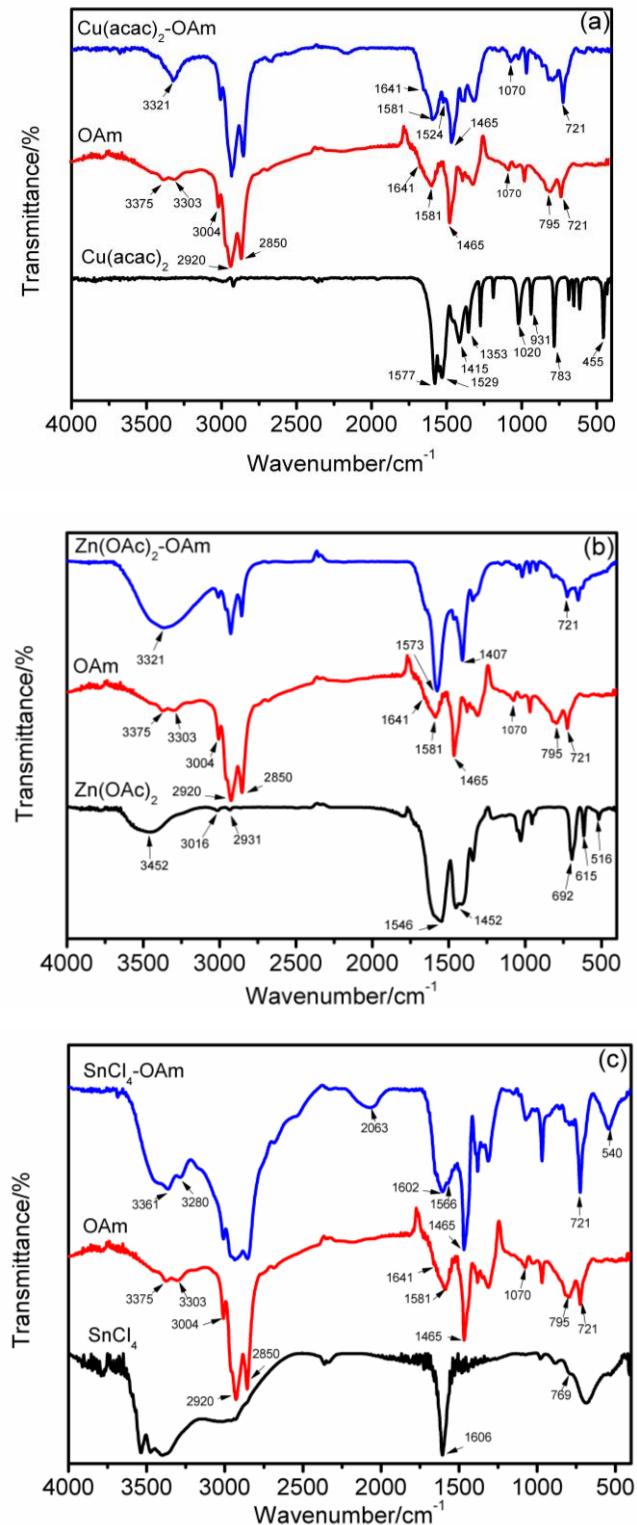
ESI 2:

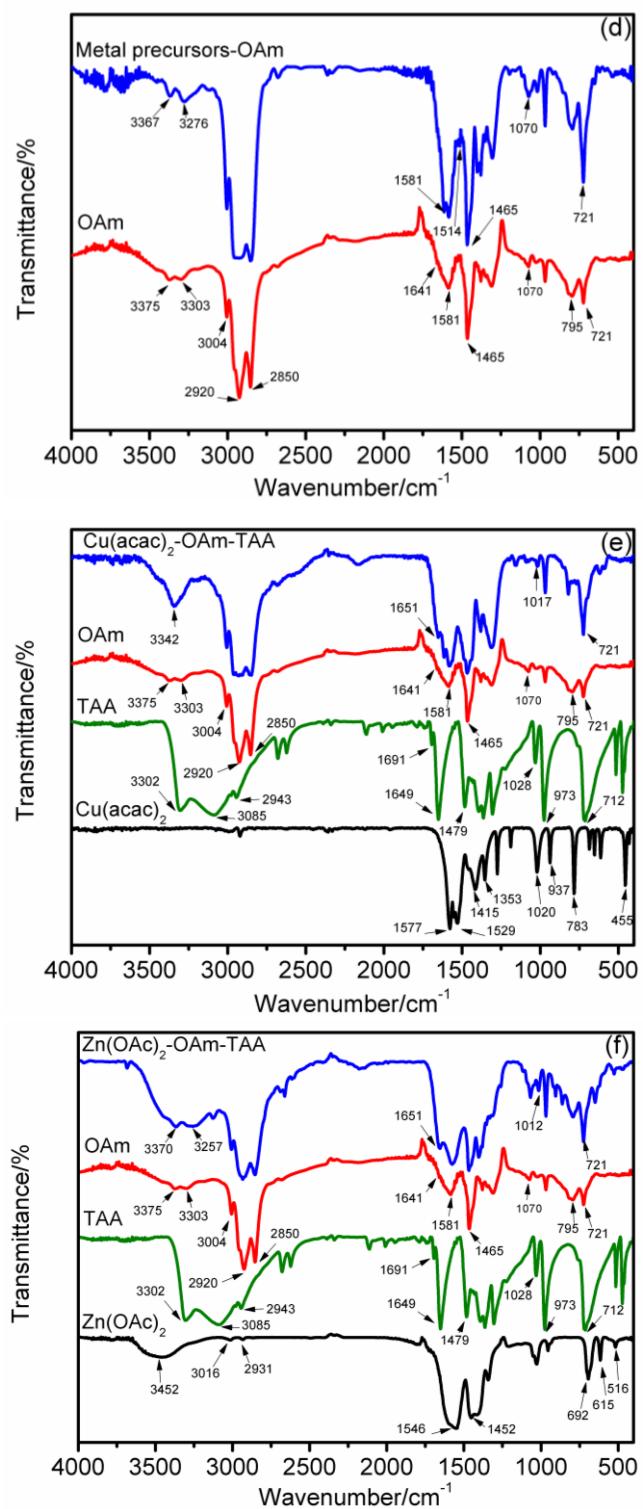
UV-vis absorption spectra of the samples synthesized using sulfur powder and TAA as sulphur sources with the reaction time of 1 hour.

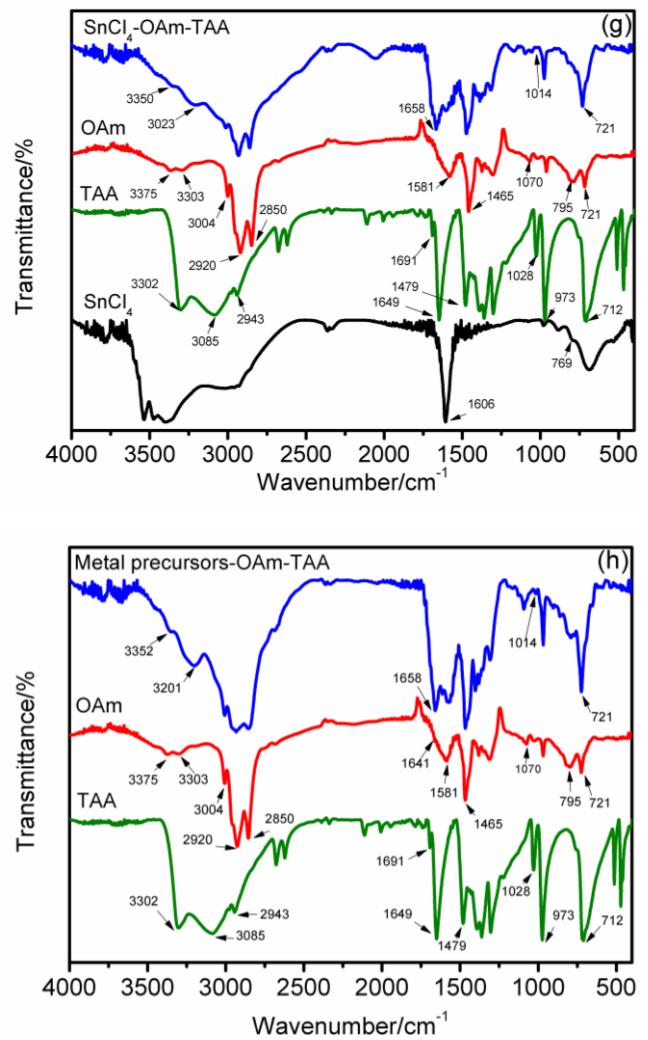


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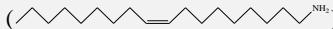
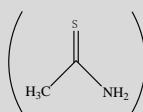
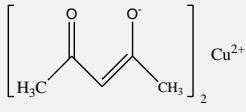
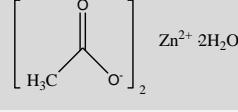
ESI 3a. FT-IR spectra of metal ion precursors mixed with OAm or with OAm plus TAA. (a) Cu(acac)₂+OAm, (b) Zn(OAc)₂ 2H₂O+OAm, (c) SnCl₄+OAm, (d) all the metal ion precursors+OAm, (e) Cu(acac)₂+OAm+TAA, (f) Zn(OAc)₂ 2H₂O+OAm+TAA, (g) SnCl₄+OAm+TAA, (h) all the metal ion precursors+OAm+TAA.







ESI 3b. Infrared vibrational assignments for various components in the precursor solutions ^a

	Vibrational modes ^a	Frequency (cm ⁻¹)
OAm ¹⁸⁻²⁰ (	$\nu(\text{NH}_2)$ $\delta(\text{C-H})$ $\nu_{\text{as}}(\text{C-H})$ and $\nu_{\text{s}}(\text{C-H})$ $\delta(-\text{C}=\text{C})$ $\delta(\text{NH}_2)$ $\delta(\text{CH}_3)$ $\delta(\text{C-N})$ $\delta(\text{C-C})$	3375, 3303 3004 2920, 2850 1641, 795 1581 1465 1070 721
TAA ²¹ 	$\nu(\text{NH}_2)$ $\nu_{\text{as}}(\text{CH}_3)$ $\nu(\text{C-N})$ $\delta(\text{N-H})$ $\nu(\text{C=S})$ $\nu(\text{C-H})$ and $\nu(\text{CH}_3)$ $\nu(\text{C}\text{---}\text{C})$ coupled with $\nu(\text{C}\text{---}\text{O})$ $\nu(\text{C}\text{---}\text{O})$ coupled with $\nu(\text{C}\text{---}\text{C})$ $\delta_{\text{d}}(\text{CH}_3)$ $\delta_{\text{s}}(\text{CH}_3)$	3302, 3085 2943 1691, 1479 1649 1028, 973, 712 2929 1577, 931 1529 1415 1353
Cu(acac) ₂ ^{22, 23} 	$\nu(\text{C-CH}_3)$ + $\nu(\text{C}\text{---}\text{C})$ $\rho_{\text{r}}(\text{CH}_3)$ $\pi(\text{CH})$ $\nu(\text{C-CH}_3)$ + ring def. $\nu(\text{Cu-O})$ $\pi\left(\text{H}_3\text{C}-\text{C}\begin{array}{l} \diagup \\ \diagdown \end{array}\text{O}\right)$ $\nu(\text{C-CH}_3)$ + $\nu(\text{Cu-O})$	1274 1020 783 684 651 640 455
Zn(OAc) ₂ 2H ₂ O ^{24, 25} 	$\nu(\text{H-OH})$ $\nu_{\text{as}}(\text{C-H})$ and $\nu_{\text{s}}(\text{C-H})$ $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO}^-)$ $\nu(\text{Zn-O})$	3452 3016, 2931 1546, 1452 692 - 516
SnCl ₄	$\nu(\text{Sn-Cl})$	1614, 769

^a ν_{s} = symmetric stretching vibration; ν_{as} = asymmetric stretching vibration; δ = bending vibration.

ESI 3c.

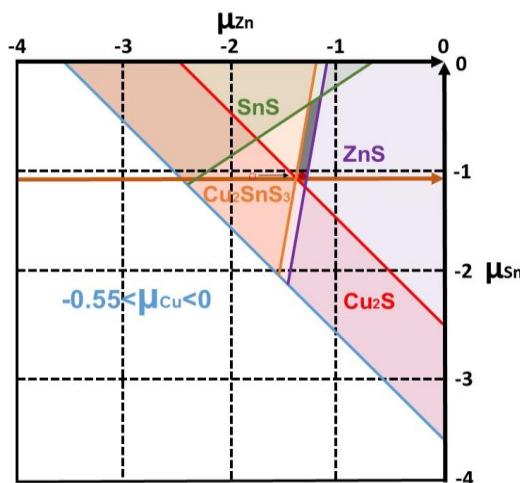
Analysis of ESI 3a and ESI 3b.

In order to detect the interactions of OAm with the metal ions, including Cu^{2+} , Zn^{2+} , and Sn^{4+} , the FT-IR spectra of the mixture solutions of OAm with each metal ion precursor, *i.e.* $\text{Cu}(\text{acac})_2$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, SnCl_4 , and with all of the metal ion precursors have been analyzed respectively as shown in the ESI 3a. The assignments of the characteristic FTIR absorption bands for each component were summarized in ESI 3b.¹⁸⁻²⁵ In the case of mixture of OAm with $\text{Cu}(\text{acac})_2$ (ESI 3a(a)), or that with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (ESI 3a(b)), the IR peaks at 3375 cm^{-1} and 3303 cm^{-1} attributed to the stretching vibration of $-\text{NH}_2$ group moved to 3321 cm^{-1} , and for the mixture of OAm with SnCl_4 (ESI 3a(c)), these peaks shifted to 3361 cm^{-1} and 3280 cm^{-1} respectively, indicating the coordination of $-\text{NH}_2$ group with the metal ions. It is noteworthy to emphasize that this peak-shift phenomenon can also be observed for the mixture solution of OAm with all of the metal ion precursor (ESI 3a(d)). In addition, a new peak at around 1524 cm^{-1} and 1566 cm^{-1} appeared in ESI 3a(a) and ESI 3a(c) respectively, which can be assigned to the stretching vibration of Cu-N and Sn-N bonds. As for the mixture of OAm with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, the difference in the wavenumbers, *i.e.* $\Delta\nu_{\text{a-s}} = \nu_{\text{a}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$, increased, suggesting that the bonding force of COO^- with Zn^{2+} cation decreased, which also shows evidence for the coordination between Zn^{2+} and OAm.

As sulfur source, TAA may also coordinate with metal ions with $-\text{NH}_2$ and C=S groups to form metal-TAA complexes.²⁶ FT-IR spectra of mixture solution of TAA with metal ion precursors with exist of OAm were measured as well (ESI 3a(e), 3a(f), 3a(g), and 3a(h)). For the mixture solutions of OAm, TAA with $\text{Cu}(\text{acac})_2$ (ESI 2a(e)), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (ESI 2a(f)) or SnCl_4 (ESI 2a(g)), the absorption peak at 1028 cm^{-1} assigned to the stretching vibration of C=S group for TAA shifted to 1017 cm^{-1} , 1012 cm^{-1} , and 1014 cm^{-1} respectively, which suggested that C=S group have been coordinated with the metal ions. On the other hand, the absorption peak at 1649 cm^{-1} assigned to the bending vibration of NH_2 group for TAA shifted to 1651 cm^{-1} for the mixture of $\text{Cu}(\text{acac})_2 + \text{OAm} + \text{TAA}$ as well as that of $\text{Zn}(\text{OAc})_2 + \text{OAm} + \text{TAA}$, and to 1658 cm^{-1} for the mixture of $\text{SnCl}_4 + \text{OAm} + \text{TAA}$, which can be attributed to the coordination of NH_2 group in TAA with the metal ions. However, it can be observed during the synthesis process that at a temperature around 80°C , TAA was decomposed, and H_2S was released at the meantime.

ESI 4:

Schematic diagram of the stable chemical-potential region for $-0.55 < \mu_{\text{Cu}} < 0$, and the gray area is the stable region of CZTS.²⁷



Reference

- 1 S. C. Riha, B. A. Parkinson and A. L. Prieto, *J. Am. Chem. Soc.*, 2009, **131**, 12054-12055.
- 2 X. T. Lu, Z. B. Zhuang, Q. Peng and Y. D. Li, *Chem. Commun.*, 2011, **47**, 3141-3143.
- 3 S. K. Saha, A. Guchhait and A. J. Pal, *Phys. Chem. Chem. Phys.*, 2012, **14**, 8090-8096.
- 4 A. Singh, H. Geaney, F. Laffir and K. M. Ryan, *J. Am. Chem. Soc.*, 2012, **134**, 2910-2913.
- 5 Q. J. Guo, H. W. Hillhouse and R. Agrawal, *J. Am. Chem. Soc.*, 2009, **131**, 11672-11673.
- 6 C. Steinhagen, M. G. Panthani, V. Akhavan, B. Goodfellow, B. Koo and B. A. Korgel, *J. Am. Chem. Soc.*, 2009, **131**, 12554-12555.
- 7 T. Rath, W. Haas, A. Pein, R. Saf, E. Maier, B. Kunert, F. Hofer, R. Resel and G. Trimmel, *Sol. Energy Mater. Sol. Cells*, 2012, **101**, 87-94.
- 8 A. S. R. Chesman, N. W. Duffy, S. Peacock, L. Waddington, N. A. S. Webster and J. J. Jasieniak, *Rsc Adv.*, 2013, **3**, 1017-1020.
- 9 A. S. R. Chesman, J. van Embden, N. W. Duffy, N. A. S. Webster and J. J. Jasieniak, *Cryst. Growth Des.*, 2013, **13**, 1712-1720.
- 10 T. Kameyama, T. Osaki, K. Okazaki, T. Shibayama, A. Kudo, S. Kuwabata and T. Torimoto, *J. Mater. Chem. A*, 2010, **20**, 5319-5324.
- 11 Y. Zou, X. Su and J. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 18377-18384.
- 12 M. Li, W. H. Zhou, J. Guo, Y. L. Zhou, Z. L. Hou, J. Jiao, Z. J. Zhou, Z. L. Du and S. X. Wu, *J. Phys. Chem. C*, 2012, **116**, 26507-26516.
- 13 A. Walsh, S. Y. Chen, S. H. Wei and X. G. Gong, *Adv. Energy Mater.*, 2012, **2**, 400-409.
- 14 H. Yang, L. A. Jauregui, G. Zhang, Y. P. Chen and Y. Wu, *Nano Lett.*, 2012, **12**, 540-545.
- 15 A. Khare, A. W. Wills, L. M. Ammerman, D. J. Norris and E. S. Aydil, *Chem. Commun.*, 2011, **47**, 11721-11723.
- 16 Y. L. Zhou, W. H. Zhou, Y. F. Du, M. Li and S. X. Wu, *Mater. Lett.*, 2011, **65**, 1535-1537.
- 17 W. C. Liu, B. L. Guo, C. Mak, A. D. Li, X. S. Wu and F. M. Zhang, *Thin Solid Films*, 2013, **535**, 39-43.
- 18 J. L. S. Zhang, R. S.; Misra, R. D. K., *Langmuir*, 2007, **23**, 6342-6351.

- 19 S. Moudikoudis and L. M. Liz-Marzan, *Chem. Mater.*, 2013, **25**, 1465-1476.
- 20 N. Shukla, C. Liu, P. M. Jones and D. Weller, *J. Magn. Magn. Mater.*, 2003, **266**, 178-184.
- 21 M. Y. Maryam Ranjbar, Robabeh Nozari, Shabnam Sheshmani, *Int. J. Nanosci. Nanotechnol.*, 2013, **9**, 203-212.
- 22 R. A. Y. Moreno, R. Saavedra, J-Y Pivan, O. Pena, T. Roisnell, *J. Chil. Chem. Soc.*, 2013, **58**, 2122-2124.
- 23 R. M. Mahfouz, S. Al-Ahmari, A. Al-Fawaz, Z. Al-Othman, I. K. Warad and M. R. H. Siddiqui, *Mater. Res-Ibero-Am. J.*, 2011, **14**, 7-10.
- 24 Y. Wang, Y. Li, Z. Zhou, X. Zu and Y. Deng, *J. Nanopart. Res.*, 2011, **13**, 5193-5202.
- 25 M. Vafaei and M. S. Ghamsari, *Mater. Lett.*, 2007, **61**, 3265-3268.
- 26 Y. X. Sun, H. J. Zheng, X. C. Li, K. Zong, H. Wang, J. B. Liu, H. Yan and K. W. Li, *Rsc. Adv.*, 2013, **3**, 22095-22101.
- 27 S. Y. Chen, J. H. Yang, X. G. Gong, A. Walsh and S. H. Wei, *Phys. Rev. B*, 2010, **81**, 245204.