

# One-pot synthesis and third-order nonlinear optical properties of AgInS<sub>2</sub> nanocrystals†

Lu Tian,<sup>a</sup> Hendry Izaac Elim,<sup>b</sup> Wei Ji\*<sup>b</sup> and Jagadese J. Vittal\*<sup>a</sup>

Received (in Cambridge, UK) 2nd June 2006, Accepted 11th July 2006

First published as an Advance Article on the web 3rd August 2006

DOI: 10.1039/b607855a

Good quality colloidal nanocrystals of metastable orthorhombic phase of AgInS<sub>2</sub> obtained by decomposing the single-precursor [(Ph<sub>3</sub>P)<sub>2</sub>AgIn(SCOPh)<sub>4</sub>] in a mixture of dodecanethiol and oleic acid at 125–200 °C, exhibit significant third order non-linear optical properties.

Materials with large third-order optical nonlinearity and fast response time are essential for future optical device applications in optical computing, real time holography, optical correlators and phase conjugators.<sup>1</sup> Nanometer-sized semiconductor materials have been demonstrated to be potential candidates for this purpose since they exhibit large third-order optical nonlinearity due to quantum size and interfacial effects. Our interest in the nonlinear optical properties of AgInS<sub>2</sub> nanocrystals (NCs) have been triggered by the fact that functional I–III–VI<sub>2</sub> chalcopyrite semiconducting compounds such as AgGaS<sub>2</sub>, have been shown to be useful linear and non-linear optical materials.<sup>2,3</sup> AgInS<sub>2</sub> exists in two ordered phases:<sup>4–6</sup> tetragonal (chalcopyrite structure) and orthorhombic, and it is potentially suitable material for optoelectronic devices due to its wide band gap in the visible region.<sup>7,8</sup>

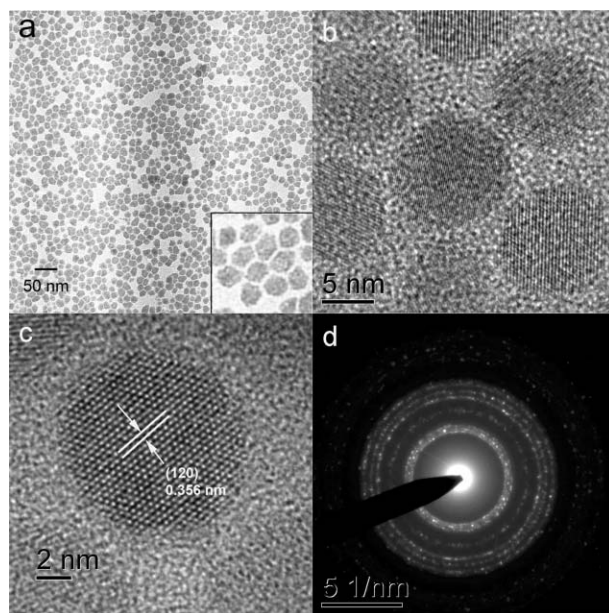
Recently colloidal nanoparticles of different II–VI binary compounds have been studied extensively.<sup>9–11</sup> More complex semiconductor materials such as ternary sulfides, in contrast, are usually produced by means of high temperature syntheses when elements react to attain the thermodynamic equilibrium.<sup>12,13</sup> Low-temperature solution synthesis may be more attractive as it provides opportunity to trap the kinetic products.

For the colloidal NCs, chemists have developed the unique synthesis called injection method. This method has led to successful synthesis of a variety of high-quality NCs ranging from II–VI (e.g., CdS and CdSe) and III–V (e.g., InP and InAs) to IV–VI (e.g., PbS and PbSe) materials.<sup>14–17</sup> However the synthesis of ternary sulfide NCs has seldom been studied.<sup>18,19</sup>

Although the synthesis of AgInS<sub>2</sub> NCs has been reported in the literature,<sup>20–23</sup> good quality monodispersed NCs have never been achieved. Herein, we report for the first time a successful one-pot colloidal synthesis of high-quality NCs of AgInS<sub>2</sub> by direct thermal decomposition of the single-source precursor [(Ph<sub>3</sub>P)<sub>2</sub>Ag(μ-SC{O}Ph-S)<sub>2</sub>In(SC{O}Ph)<sub>2</sub>], **1** in bisurfactants system. The separation between nucleation and growth can be automatically accomplished in a homogeneous reaction system by adding two surfactants, such as dodecanethiol (DT, C<sub>12</sub>H<sub>25</sub>SH) and oleic acid (OA, C<sub>17</sub>H<sub>33</sub>COOH).<sup>24</sup>

The precursor **1** was synthesized according to a known literature method.<sup>25</sup> TG data reveal that the precursor decomposes in the temperature range 175–328 °C to the orthorhombic phase AgInS<sub>2</sub>. The precursor was added to a mixture of DT and OA at room temperature (the molar ratio of precursor : DT = 1 : 50 and the volume ratio of DT : OA = 1 : 3). Then the reaction mixture was heated at 200 °C for 2 h with gentle stirring under inert atmosphere. It is noted that the reaction solution has changed to a clear light yellow solution at *ca* 50 °C, indicating that the precursor could be easily dissolved in warm DT–OA solvents. Soon a red-brown turbidity appeared as the temperature was further elevated to 70 °C or higher, suggesting that the nucleation of AgInS<sub>2</sub> had occurred. This has been proved by X-ray powder diffraction of the product isolated at 70 °C. The precursor decomposed in solution at such low temperature as compared to solid-state due to the reaction with the surfactants.<sup>26</sup> After the reaction, a dark red homogenous solution was obtained which was allowed to cool to room temperature and then an excess ethanol was added to remove the by-products and the excess surfactants. Finally dark red solid was collected by centrifugation.

A typical TEM image of AgInS<sub>2</sub> in Fig. 1a shows polyhedral shapes and narrow size distribution. A high-magnification TEM image of the NCs (see Fig. 1b) clearly shows that the colloidal NCs



**Fig. 1** a) Representative TEM images of AgInS<sub>2</sub> NCs produced at 200 °C; b) and c) HRTEM images of the polyhedral NCs; d) SAED pattern of the NCs.

<sup>a</sup>Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. E-mail: chmjiv@nus.edu.sg

<sup>b</sup>Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117543. E-mail: phyjiwei@nus.edu.sg

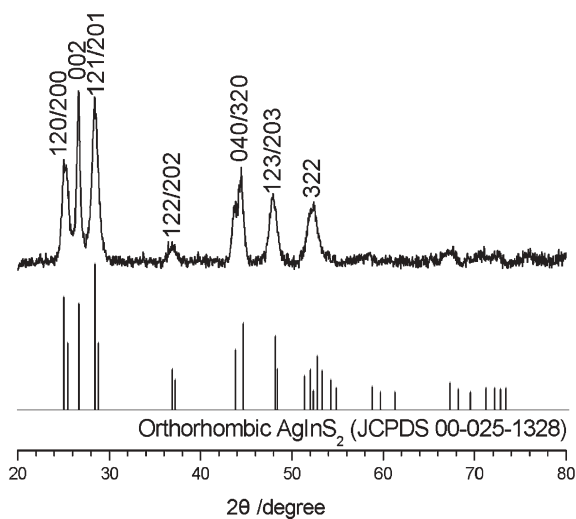
† Electronic supplementary information (ESI) available: experimental details, XRPD, and Z-scans results (3 pages). See DOI: 10.1039/b607855a

have rather uniform size and are nanosized single crystals. The mean diameter of the individual NCs is measured to be  $13.9 \pm 1.8$  nm (based on 300 particles from the TEM image). The lattice fringes visible in the HRTEM images are indicative of the high crystallinity of these particles (Fig. 1c) and the interplanar distance of 0.356 nm can be indexed to plane (120). The indexing of the lattice parameters of the selected area electron diffraction (SAED, shown in Fig. 1d) was consistent with the (200), (002), (121), (122), (040), (123) and (322) lattice planes of orthorhombic  $\text{AgInS}_2$  (JCPDS 00-025-1328). EDAX analysis of NCs in the electron microscope showed the ratio of Ag, In and S is 1 : 1.05 : 2.13. A slightly higher ratio of sulfur may be attributed to the capping of DT.

When the ratio of DT to OA was decreased to 1 : 6, smaller NCs (*ca*  $8.5 \pm 0.9$  nm) were formed together with larger NCs (*ca*  $33.2 \pm 5.2$  nm). When the ratio was increased to 2 : 1, NCs with wide size distribution were formed. When DT alone was used as capping agent, the resulting product was mainly in agglomeration. The use of OA only, however, resulted in micrometer sized  $\text{AgInS}_2$ . Thus a synergistic effect resulting from the combination of DT and OA must be responsible for the NCs growth. A range of temperature of 125–200 °C was found to be suitable for the synthesis of nanoparticles with narrow size distribution. When the temperature was increased to 215 °C or even higher (250 °C), much bigger particles without monodispersity were formed. When the time duration increased from 2 h to 16 h, the wider size distribution proved that Ostwald ripening occurred. In summary, the preferred conditions for forming monodispersed  $\text{AgInS}_2$  NCs were a short time period in a temperature range 125–200 °C with a certain ratio of bisurfactants.

In the presence of other surfactant system such as DT + trioctylphosphine oxide (TOPO), oleylamine + TOPO, oleylamine + DT, oleylamine + OA and only oleylamine, the final particles have the similar polyhedral shape, as we observe in separate experiments.

A representative XRD pattern of the product is shown in Fig. 2. It was synthesized by adding the precursor into a mixed solvent of



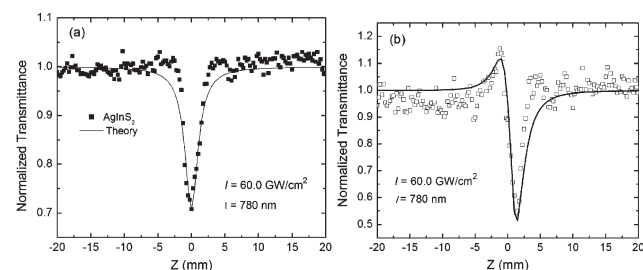
**Fig. 2** Representative X-ray diffraction patterns of  $\text{AgInS}_2$  NCs formed at 200 °C (top) and the simulated diffraction patterns from the JCPDS database (bottom).

DT and OA (the molar ratio of precursor : DT = 1 : 50 and the volume ratio of DT : OA = 1 : 3) and then the reaction mixture was heated at 200 °C for 2 h. All the diffraction peaks can be assigned to the orthorhombic-phase  $\text{AgInS}_2$  reported in the literature (JCPDS 00-025-1328). It is known that the orthorhombic form is stable at high temperature ( $>620$  °C) while the tetragonal form (chalcopyrite type) is stable below 620 °C.<sup>4–7,27</sup> Here the metastable orthorhombic  $\text{AgInS}_2$  NCs were obtained even when the temperature was lowered to 125 °C. It is believed that the surfactants adjust the chemical environment in such a way that the relative stability of one phase over another can be reversed. Such metastable phases of hexagonal wurtzite ZnS and  $\epsilon$ -Co NCs have been trapped in this way.<sup>28</sup>

The formation of high temperature phase of  $\text{AgInS}_2$  has also been noted by us in the pyrolytic decomposition of the precursors  $[(\text{Ph}_3\text{P})_2\text{AgIn}(\text{SCOR})_4]$  ( $\text{R} = \text{Me}, \text{Ph}$ ) below 350 °C.<sup>25</sup> Further evidence for the formation of  $\text{AgInS}_2$  can also be derived from the X-ray Photoelectron Spectroscopy (XPS). Three strong peaks for  $\text{AgInS}_2$  NCs at 367.4, 444.4 and 161.3 eV corresponding to Ag (3d), In (3d) and S (2p) binding energies, respectively, are in agreement with previously published data.<sup>22</sup> The quantification of the peak ratio of Ag, In and S is 1 : 1.1 : 1.82.

The nonlinear optical properties of the  $\text{AgInS}_2$  NCs dispersed in toluene were investigated by femtosecond Z-scans at wavelengths of 780 nm. To minimize average power and reduce accumulative thermal effects, 220 fs laser pulses at a 1 kHz repetition rate were employed. The laser pulses were generated by a mode-locked Ti: Sapphire laser (Quantronix, IMRA), which seeded a Ti: Sapphire regenerative amplifier (Quantronix, Titan). The laser pulses were focused onto a 1 mm-thick quartz cuvette which contained the  $\text{AgInS}_2$  solution with a minimum beam waist of  $\sim 12$   $\mu\text{m}$ . By adding toluene to the  $\text{AgInS}_2$  NCs solution, the linear transmittance of the solution was adjusted to be 50% at 780 nm. The incident and transmitted laser powers were monitored as the cuvette was moved (or Z-scanned) along the propagation direction of the laser pulses.

Fig. 3 (a) and (b) display typical open- and closed-aperture Z-scans carried out with the same irradiance of  $60.0 \text{ GW}\cdot\text{cm}^{-2}$  at the same wavelength of 780 nm, showing positive and negative signs for the absorptive and refractive nonlinearities, respectively. We attribute this negativity to a nonlinear refractive index as self-defocusing effect while the positive sign of nonlinear absorption coefficient is due to two photons absorption. The intensity independence of the Z-scans show pure third-order nonlinear



**Fig. 3** (a) Open- and (b) closed-aperture Z-scan results of  $\text{AgInS}_2$  NCs performed at the same wavelength of 780 nm and irradiance of  $60.0 \text{ GW}\cdot\text{cm}^{-2}$ . The volume fraction of  $\text{AgInS}_2$  NCs in toluene is  $1.81 \times 10^{-4}$ . The solid lines are the best fits using the Z-scan theory (Ref. 29).

processes for the observed nonlinearities. Therefore, the nonlinear absorption and refraction can be described by  $\Delta\alpha = \beta I$ , and  $\Delta n = n_2 I$ , where  $\beta$  and  $n_2$  are the nonlinear absorption coefficient and nonlinear refractive index, respectively, and  $I$  is the light intensity. Both  $\beta$  and  $n_2$  values can be extracted from the best fitting between the Z-scan theory and the data.<sup>29</sup> The  $\beta^{\text{NC}}$  and  $n_2^{\text{NC}}$  values are assumed as  $\beta^{\text{NC}} \approx \beta/(fI^4 V_f)$  and  $n_2^{\text{NC}} \approx (n_2 - (1 - V_f)n_2^{\text{sol}})/(fI^4 V_f)$  where  $\beta^{\text{NC}}$  is the nonlinear absorption coefficient of NCs,  $n_2^{\text{NC}}$  is the nonlinear refractive index of NCs,  $n_2^{\text{sol}}$  is the nonlinear refractive index of toluene,  $f$  is the local field factor, and  $V_f$  is the volume fraction of NCs relative to toluene.

The AgInS<sub>2</sub> NCs possess the highest nonlinear absorption, with  $\beta^{\text{NC}} = 3867 \text{ cm}^2 \cdot \text{GW}^{-1}$ , or  $\text{Im}(\chi^{(3)}) = 8.2 \times 10^{-9} \text{ esu}$ , which is about the same order as that for a Ag nanocomposite silica thin film, measured at 532 nm using a pulsed Nd:YAG laser with 5 ns pulse duration and a repetition rate of 10 Hz.<sup>30</sup> We attribute this nonlinear absorption to the resonance with the two-photon energy of the laser pulses of 3.18 eV. Unfortunately, theoretical values of the two photon absorption for AgInS<sub>2</sub> NCs are not available from the literature. However, the two-photon absorption cross sections of  $\sim 10^{-46} \text{ cm}^3 \text{ s}$  have been calculated for two-photon-allowed transitions in CdSe NCs of 2.9 nm diameter.<sup>31</sup> For comparison, our data show that the two-photon absorption cross sections are in the range from  $10^{-46} \text{ cm}^3 \text{ s}$  for the AgInS<sub>2</sub> NCs.

Similarly, the  $n_2^{\text{NC}}$  ( $= -6.6 \times 10^{-2} \text{ cm}^2 \cdot \text{GW}^{-1}$ , or  $\text{Re}(\chi^{(3)}) = -7.3 \times 10^{-9} \text{ esu}$ ) calculated by eliminating the  $n_2$  value of toluene ( $= 1.1 \times 10^{-6} \text{ cm}^2 \cdot \text{GW}^{-1}$  or  $\text{Re}(\chi^{(3)}) = 8 \times 10^{-13} \text{ esu}$ ) is also found in the the AgInS<sub>2</sub> NCs, about three times larger than that measured by Zhou *et al.* on the silver NCs–bismuth oxide (Ag:Bi<sub>2</sub>O<sub>3</sub>) composite thin films at 800  $\mu\text{m}$ .<sup>32</sup> Such a difference is anticipated due to the following reasons: (1) the dispersion of the nonlinear refraction, in particular, our measured value is due to a self-defocusing effect; (2) different size and volume fraction, in particular, Zhou's result was obtained from Ag:Bi<sub>2</sub>O<sub>3</sub> nanocomposites of larger sizes (50 nm), in which  $\chi^{(3)}$  should be expected to approach to the bulk value; and (3) different composite materials.

In conclusion, we have successfully employed one-pot synthesis to prepare high quality AgInS<sub>2</sub> NCs. Such colloidal ternary chalcogenide NCs are rare<sup>33</sup> and the majority of one-pot synthetic efforts are directed to binary NCs only. It is worth noting that both the nanocrystals and bulk AgInS<sub>2</sub> obtained using this precursor belong to high temperature orthorhombic phase. Further, a combination of suitable capping agents is probably necessary to obtain high quality monodispersed nanocrystals. Toluene-soluble AgInS<sub>2</sub> nanocrystals have paved the way for the measurement of the optical properties. Large optical nonlinearities in the soluble AgInS<sub>2</sub> NCs have been observed using 780 nm, 220 fs laser pulses. The third-order susceptibility, of AgInS<sub>2</sub> NCs is  $1.1 \times 10^{-8} \text{ esu}$ .

We would like to thank NUS (Grant No. R-143-000-283-112) for their generous financial support. We thank Mr Liu Binghai for the HRTEM images.

## Notes and references

- 1 D. F. Eaton, *Science*, 1991, **253**, 281.
- 2 S. C. Abrahams and J. L. Bernstein, *J. Chem. Phys.*, 1973, **59**, 1625.
- 3 I. Yonenaga, K. Sumino, E. Niwa and K. Masumoto, *J. Cryst. Growth*, 1996, **167**, 616.

- 4 R. S. Roth, H. S. Parker and W. S. Brower, *Mater. Res. Bull.*, 1973, **8**, 333.
- 5 I. V. Bodnar, B. V. Korzun and L. V. Yasyukevich, *Russ. J. Inorg. Chem.*, 1998, **43**, 771.
- 6 I. V. Bodnar, L. V. Yasyukevich, B. V. Korzun and A. G. Karoza, *J. Mater. Sci.*, 1998, **33**, 183.
- 7 J. L. Shay, B. Tell, L. M. Schiavone, H. M. Kasper and F. Thiel, *Phys. Rev. B*, 1974, **9**, 1719.
- 8 C. Paorici, L. Zanotti, N. Romeo, G. Sberveglieri and L. Tarricone, *Mater. Res. Bull.*, 1977, **12**, 1207.
- 9 D. J. Milliron, S. M. Hughes, Y. Cui, L. Manna, J. B. Li, L. W. Wang and A. P. Alivisatos, *Nature*, 2004, **430**, 190.
- 10 T. Hyeon, *Chem. Commun.*, 2003, **8**, 927.
- 11 S. H. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
- 12 L. I. Berger and V. D. Prochukhan, *Ternary Diamond-like Semiconductors*, Consultants Bureau, New York, 1969.
- 13 L. L. Kazmerski and S. Wagner, in *Current Topics in Photovoltaics*, ed. T. J. Coutts and J. D. Meakin, Academic Press, Harcourt Brace, London, 1985.
- 14 (a) C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706; (b) X. Peng, J. Wickham and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1998, **120**, 5343; (c) Y. Cao and U. Banin, *J. Am. Chem. Soc.*, 2000, **122**, 9692; (d) D. Battaglia and X. Peng, *Nano Lett.*, 2002, **2**, 1027.
- 15 (a) M. W. Yu and X. Peng, *Angew. Chem., Int. Ed.*, 2002, **41**, 2368; (b) J. S. Steckel, J. P. Zimmer, S. Coe-Sullivan, N. E. Stott, V. Bulović and M. G. Bawendi, *Angew. Chem., Int. Ed.*, 2004, **43**, 2154; (c) Y. W. Jun, S. M. Lee, N. J. Kang and J. Cheon, *J. Am. Chem. Soc.*, 2001, **123**, 5150; (d) J. Joo, H. B. Na, T. Yu, J. H. Yu, Y. W. Kim, F. X. Wu, J. Z. Zhang and T. Hyeon, *J. Am. Chem. Soc.*, 2003, **125**, 11100.
- 16 (a) S. M. Lee, Y. W. Jun, S. N. Cho and J. Cheon, *J. Am. Chem. Soc.*, 2002, **124**, 11244; (b) B. L. Wehrenberg and P. Guyot-Sionnest, *J. Am. Chem. Soc.*, 2003, **125**, 7806; (c) M. A. Hines and G. D. Scholes, *Adv. Mater.*, 2003, **15**, 1844.
- 17 (a) A. P. Alivisatos, *Nat. Biotechnol.*, 2004, **22**, 47; (b) M. Han, X. Gao, J. Z. Su and S. Nie, *Nat. Biotechnol.*, 2001, **19**, 631; (c) M. Kazes, D. Y. Lewis, Y. Ebenstein, T. Mokari and U. Banin, *Adv. Mater.*, 2002, **14**, 317.
- 18 S. L. Castro, S. G. Bailey, R. P. Raffaele, K. K. Banger and A. F. Hepp, *J. Phys. Chem. B*, 2004, **108**, 12429.
- 19 X. Gou, F. Cheng, Y. Shi, L. Zhang, S. Peng, J. Chen and P. Shen, *J. Am. Chem. Soc.*, 2006, **128**, 7222.
- 20 V. S. Gurin, *Colloids Surf., A*, 1998, **142**, 35.
- 21 J. Hu, Q. Lu, K. Tang, Y. Qian, G. Zhou and X. Liu, *Chem. Commun.*, 1999, 1093.
- 22 J. Q. Hu, B. Deng, K. B. Tang, C. R. Wang and Y. T. Qian, *J. Mater. Res.*, 2001, **16**, 3411.
- 23 Y. Cui, J. Ren, G. Chen, Y. Qian and Y. Xie, *Chem. Lett.*, 2001, **30**, 236.
- 24 Z. Liu, D. Xu, J. Liang, J. Shen, S. Zhang and Y. Qian, *J. Phys. Chem. B*, 2005, **109**, 10699.
- 25 (a) T. C. Deivaraj, J. Park, M. Afzaal, P. O'Brien and J. J. Vittal, *Chem. Mater.*, 2003, **15**, 2383; (b) T. C. Deivaraj, J. Park, M. Afzaal, P. O'Brien and J. J. Vittal, *Chem. Commun.*, 2001, 2304.
- 26 Z. Zhang, S. H. Lee, J. J. Vittal and W. S. Chin, *J. Phys. Chem. B*, 2006, **110**, 6649.
- 27 J. Krustok, J. Raudoja, M. Krunk, H. Mändar and H. Collan, *J. Appl. Phys.*, 2000, **88**, 205.
- 28 (a) X. Chen, H. Xu, N. Xu, F. Zhao, W. Lin, G. Lin, Y. Fu, Z. Huang, H. Wang and M. Wu, *Inorg. Chem.*, 2003, **42**, 3100; (b) Y. Zhao, Y. Zhang, H. Zhu, G. C. Hadjipanayis and J. Q. Xiao, *J. Am. Chem. Soc.*, 2004, **126**, 6874; (c) Y. Li, X. Li, C. Yang and Y. Li, *J. Phys. Chem. B*, 2004, **108**, 16002; (d) V. F. Puentes, K. M. Krishnan and A. P. Alivisatos, *Science*, 2001, **291**, 2115.
- 29 M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760.
- 30 A. A. Scalisi, G. Compagnini, L. D'Urso and O. Puglisi, *Appl. Surf. Sci.*, 2004, **226**, 237.
- 31 M. E. Schmidt, S. A. Blanton, M. A. Hines and P. Guyot-Sionnest, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **53**, 12629.
- 32 P. Zhou, G. You, J. Li, S. Wang, S. Qian and L. Chen, *Opt. Express*, 2005, **13**, 1508.
- 33 M. T. Ng, C. B. Boothroyd and J. J. Vittal, *J. Am. Chem. Soc.*, 2006, **128**, 7118.