CrystEngComm

www.rsc.org/crystengcomm

Volume 15 | Number 33 | 7 September 2013 | Pages 6433-6626



RSCPublishing

COVER ARTICLE Xu, Zhang, Wang *et al*. Controlled synthesis of AgInS₂ nanocrystals and their application in organic–inorganic hybrid photodetectors

CrystEngComm

COMMUNICATION

View Article Online View Journal | View Issue

Cite this: CrystEngComm, 2013, 15, 6443

Received 27th January 2013, Accepted 16th March 2013

DOI: 10.1039/c3ce40173a

www.rsc.org/crystengcomm

Controlled synthesis of AgInS₂ nanocrystals and their application in organic–inorganic hybrid photodetectors[†]

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High quality AgInS₂ nanocrystals (NCs) are synthesized using a simple single-source precursor method, in which the size and morphology of the products can be precisely controlled from heliotrope seed-like NCs of 6 \times 12 nm to heliotrope seed-like dimer NCs of 8 \times 16 nm by tuning the composition of the coordinating solvents of oleic acid and 1-dodecanethiol. The results show that 1-dodecanethiol plays a dominant role in determining the morphology of AgInS₂ NCs due to its strong absorption onto the {001} crystal plane of AgInS₂ NCs. The photoelectric properties of the as-prepared AgInS₂ NCs have been characterized using AgInS₂-poly(3-hexylthiophene) hybrid nanodevices. The results illustrate that the AgInS₂ NCs present very high photosensitivity and photostability to outside illumination. The high sensitivity and stability of the hybrid nanodevice indicate a broad spectrum of applications in the photoelectric nanodevices.

1. Introduction

I-III-VI ternary semiconductors have attracted tremendous attention in flexible photovoltaic device studies due to their appropriate band-gap energies, high absorption coefficients, high radiation stability and nonlinear optical properties.¹⁻⁴ Among these semiconductors, AgInS₂ nanocrystals (NCs) have suitable band gap energy, high radiation stability, high absorption coefficients, and low toxicity, which endow them a promising candidate for fabricating optoelectronic devices.^{5,6} Up to date, different strategies have been developed for the synthesis of AgInS₂ NCs and preliminary studies on the photoluminescence properties of AgInS₂ have been carried out.⁷⁻¹⁰ However, it still remains a

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challenge to achieve the controlled synthesis of high quality AgInS₂ NCs with uniform shape and narrow size distribution by a simple synthetic route. Moreover, less attention has been paid to the photoelectric applications of AgInS₂ NCs.

Herein, we report the successful synthesis of high quality AgInS₂ NCs with narrow size distribution and well-defined morphology using a single-source precursor method, in which heliotrope seedlike AgInS₂ NCs (single-AgInS₂) of 6 \times 12 nm and heliotrope seedlike AgInS₂ dimer NCs (dimer-AgInS₂) of 8×16 nm were obtained, respectively, by tuning the composition of the coordinating solvents of oleic acid (OA) and 1-dodecanethiol (DT). Furthermore, the photoelectric properties of the as-prepared AgInS₂ NCs have been characterized using AgInS2-poly (3-hexylthiophene) (P3HT) hybrid nanodevices with high photosensitivity and photostability to outside illumination. Hybrid photoelectric devices based on organic-inorganic materials have been popular due to the combination of advantages of both the polymers (large-scale production at a low cost, the tunable functionality and high flexibility) and inorganic NCs (superior intrinsic carrier mobilities and broad band absorption).¹¹⁻¹⁴ To our best knowledge, this is the first report of a facile synthesis of high quality AgInS₂ NCs and their photoelectric properties. We expect that the high sensitivity and stability of the hybrid nanodevice will hold a broad spectrum of applications in photoelectric nanodevices.

2. Experimental details

2.1. Chemicals

Silver nitrate (AgNO₃, AR, Sinopharm Chemical Reagent Co., Ltd), indium nitrate (In(NO₃)₃, 99.99%, Aladdin), sodium diethyldithiocarbamate trihydrate (Na(DDTC)·3H₂O, 99%, Sinopharm Chemical Reagent Co., Ltd.), oleic acid (OA, 90%, Aldrich), 1-dodecanethiol (DT, 98%, Aladdin), 1,2-dichlorobenzene, poly(3hexylthiophene) (P3HT). All the chemicals were analytical grade and used as received without further purification.

2.2. Synthesis of Ag(DDTC) and In(DDTC)₃ precursors

For synthesizing Ag(DDTC), 10 mmol of $AgNO_3$ was dissolved in 80 mL of water. Then 80 mL aqueous solution of $Na(DDTC)\cdot 3H_2O$

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(10 mmol) was dropped into the AgNO₃ solution under continuous magnetic stirring. After stirring for 30 min, the yellow precipitate was kept stationary under the ambient condition for 4 h. The resulting precipitate was filtered and washed four times with pure water and dried in an oven at 60 °C. In(DDTC)₃ was also prepared by the same procedure described as above, except that the molar ratio of indium nitrate to Na(DDTC) was 1 to 3.

2.3. Synthesis of AgInS₂ NCs

In a typical procedure, Ag(DDTC) (0.05 mmol, 0.013 g), $In(DDTC)_3$ (0.05 mmol, 0.028 g), OA (21.15 g) and DT (5 g) with a molar ratio of 3 : 1 were added into a 100 mL three-neck flask. The flask was sealed and heated to 200 °C after degassed under magnetic stirring. After reaction for 2 h in N₂, the crude solution was cooled down to room temperature naturally and then precipitated with excess absolute ethanol. Finally, the purified product was dispersed in cyclohexane (with mass concentration of 0.19%). AgInS₂ dimer structures were synthesized when the ratio of OA (7.05 g) to DT (15 g) was 1 : 3, and the other condition remained unchanged.

2.4. Fabrication of photodetector devices

A standard lithographic patterning method was employed to fabricate the electrodes for photodetector devices on a thermally oxidized (500 nm) Si (100) substrate. After the electrode area was defined by photo-lithography, a Cr adhesion layer and ~200 nm Au layer were deposited on the Si substrate by sputtering. Then, the electrodes were written using lift-off techniques. The electrodes are of interdigital with area about ~200 × 200 μ m², and the gaps distance between the electrodes was fixed at 10 μ m. The photodetector was fabricated by dropping 2.5 μ L of 0.19 wt% AgInS₂ NCs solution onto the Au electrodes. P3HT (19 mg) was dissolved in 9.981 g of 1,2-dichlorobenzene to form an auxiliary component. In order to improve the absorption efficiency and conductivity of devices, a 5 μ L of P3HT solution was deposited onto the top surface of the aforementioned device and was dried naturally.

2.5. Characterization

The powder X-ray diffraction patterns (XRD) were recorded on an X'Pert-Pro MPD diffractometer (Holland) with a slit of $1/2^{\circ}$ at a scanning rate of 4° min⁻¹, using Cu K α radiation ($\lambda = 1.5406$ Å) in the range of 20–80°. The UV-vis spectra were measured by a Perkin Elmer/Lambda 25 UV-Vis spectrometer (USA). Fourier transform infrared spectroscopy (FTIR) spectra were obtained by a Thermo Scientific Nicolet 6700 spectrameter. The transmission electron microscopy (TEM), high-resolution TEM (HRTEM), energy-dispersive spectroscopy (EDS), and selected area electron diffraction (SAED) were presented by a Tecnai G2 F20 S-Twin, FEI (operated at 200 kV) for characterizing the morphology of AgInS₂ nanocrystals. Dynamic laser scattering measurement was executed by Zetasizer (Malvern).

3. Results and discussions

The typical transmission electron microscope (TEM) images of the as-prepared AgInS₂ NCs are shown in Fig. 1. Fig. 1a and b



Fig. 1 Characterization of the as-obtained $AgInS_2\,NCs.\,TEM$ and HRTEM images of single-AgInS_ (a, b) and dimer-AgInS_2 (c, d); X-ray diffraction patterns (e).

represent TEM and high resolution TEM (HR-TEM) images of the single-AgInS₂ at the mole ratio of OA and DT as 3 : 1. It is observed that the obtained AgInS2 NCs are in heliotrope seed-like shape and are highly monodisperse in diameter of 6 nm and length of 12 nm with a standard deviation less than 5% by counting 100 particles. With the molar ratio of OA to DT changing to 1 : 3, highly uniform and well-crystallined heliotrope seed-like AgInS2 dimer nanostructures with size of 8 \times 16 nm are obtained for the first time by coupling the (002) planes of two identical quasi-semicircular shaped AgInS₂ NCs (Fig. 1c and d). We attribute the assembling of two quasi-semicircular shaped AgInS₂ NCs into a dimer-AgInS₂ to the well developed facet of the basal plane which results the strong tendency to pack into pairs. The dynamic light scattering (DLS) measurement of the products evidence that the single- and dimer-AgInS₂ NCs are formed in the reaction, instead of the resultants from the drying process during TEM sampling (Fig. S1 in ESI[†]). XRD patterns of the as-synthesized AgInS2 NCs are presented in Fig. 1e, which illustrates that both the single-AgInS₂ and dimer-AgInS₂ possess the same orthorhombic phase (JCPDS Card. No.

25-1328, with cell constants a = 6.990 Å, b = 8.319 Å, c = 6.706 Å), instead of the formation of separated silver sulfide and indium sulfide. Energy-dispersive spectroscopy (EDS) line-scanning and selected area electron diffraction (SAED) results further confirm the composition and the crystalline phase of the products (Fig. S2 and S3 in ESI†).

It is interesting to observe that the morphology of AgInS₂ NCs can be easily tuned by adjusting the composition of the coordinating solvent. The composition of the coordinating solvent in the NCs preparation has been shown to play a vital role in determining the size and morphology of the products.^{15–22} In the current study, OA and DT are used together as both solvents and capping ligands for the synthesis of AgInS₂ NCs. When OA was used alone in the reaction system, no product was obtained which indicates that DT determines the decomposition of the singlesource precursors and the formation of AgInS₂ nucleus. Regarding the reaction with OA to DT as coordinating solvent, OA is considered non-selectively adsorbed on the crystal facets resulting in the isotropic growth of nanocrystals,¹⁶⁻¹⁹ while DT is usually selectively adsorbed on certain crystal facets leading to the anisotropic growth of nanocrystals.²⁰⁻²² Therefore, in the case of the reaction with the mole ratio of OA to DT as 3:1, the lower amount of DT is selectively absorbed onto the {001} crystal plane of AgInS₂ NCs, which slows down the growth along <001> direction and leads to the formation of heliotrope seed-like AgInS₂ NCs. By decreasing the molar ratio of OA to DT to 1 : 3, more DT molecules are absorbed onto the {001} crystal plane which further deters the growth along <001> direction and facilitates the growth along <010> direction, resulting in the formation of quasi-semicircular-AgInS₂ NCs (Fig. 1d). The well-developed (002) basal planes in the quasi-semicircular-AgInS₂ NCs induce the pairing of the quasi-semicircular-AgInS₂ NCs into dimer-AgInS₂ nanostructures through van der Waals force interactions of aliphatic hydrocarbon chains of DT molecules, which is entropy favoring due to the least geometric restrictions. The gap between two adjacent AgInS₂ NCs in the dimer nanostructure is about 2 nm (Fig. 1d), which is smaller than twice of the length of alkyl chain in DT (1.77 nm),²³ suggesting that the DT chains are interdigitated during the formation of dimer-AgInS₂ nanostructures.

More evidence of the ligand coordination can be derived from Fourier transform infrared spectroscopy (FTIR) spectra of the AgInS₂ NCs as shown in Fig. 2. The AgInS₂ NCs obtained from the reaction in the presence of both OA and DT are merely capped with DT. In detail, in the FTIR spectra of single- and dimer-AgInS₂ NCs, the characteristic peaks at 668 cm⁻¹, 2858 cm⁻¹ and 2931 cm⁻¹ can be assigned to the stretching vibration of C-S, and the symmetric and asymmetric stretching vibration of peaks at C-H of DT, respectively. The methylene scissoring vibration at 1470 cm⁻¹ and 1380 cm⁻¹ are found in the FTIR spectra of single- and dimer-AgInS₂, as well as the methylene rocking at 721 cm⁻¹. Moreover, the disappearance of the S-H stretching vibrations at 2570 cm⁻¹ indicates the S atom is anchored on the surface of AgInS2 NCs with strong interaction. Additionally, the absence of the C=O stretching vibration at 1710 cm⁻¹ and C=C stretching vibration at 1411 cm⁻¹ depicts that no OA caps on the surface of AgInS₂ NCs.



Fig. 2 FTIR spectra of OA, DT, single-AgInS₂ NCs, and dimer-AgInS₂ NCs.

The band-gap energies of the as-obtained AgInS₂ NCs are subsequently determined. Fig. 3a depicts the UV-vis absorption spectra of the obtained single-AgInS2 and dimer-AgInS2 at the same concentration. From Fig. 3a, it is observed that the dimer-AgInS₂ presents a stronger absorbance below 600 nm wavelength in comparison with single-AgInS2. The band-gap energy is determined by plotting the squared absorbance versus energy and extrapolating to zero (Fig. 3b). The band-gap energies of the obtained single-AgInS2 and dimer-AgInS2 are calculated to be 2.07 and 2.08 eV, respectively. Due to the appropriate band-gap energy, high absorption coefficient and high radiation stability, the photoelectric performance of the obtained AgInS₂ NCs is further executed by mixing the AgInS2 NCs with P3HT as the hybrid inorganic-organic sensing materials. Since, as it is well documented, P3HT is a classical π -electron-conjugated polymer with strong absorption in the visible range and high electrical conductivity,²⁴ the combination of AgInS2 NCs with P3HT film significantly broadens the absorption spectrum (Fig. 3a) and improves the electrical conductivity of the organic-inorganic hybrid photodetector.

A schematic illustration of a device based on the hybrid material is shown in Fig. 4a. Fig. 4b and c depict the typical current-voltage (I-V) characteristics of the single-AgInS₂/P3HT and dimer-AgInS₂/P3HT based photodetectors under dark condition and different wavelength illumination of 365 nm, 420 nm, 500 nm, and 600 nm, respectively, which clearly represent the action of the hybrid device to the various irradiations. When the intensity of the incident light is changed, the photocurrent of the device remarkably changes accordingly (Fig. 4b and c), which can be attributed to the change in the photon density of the incident light at different light densities. This photocurrent measurement on the hybrid device at different incident light densities indicates its high photosensitivity of the hybrid AgInS₂/P3HT device. It is also observed the nonlinear I-V behaviors for both single- and dimer-AgInS₂/P3HT based devices in the OFF/ON state, indicating that the Schottky contact is formed between Au electrodes and the hybrid photo-sensing AgInS2 NCs. It has been reported that the



Fig. 3 (a) UV-Vis spectra of single-, dimer-AgInS₂, P3HT, single-AgInS₂/P3HT, and dimer-AgInS₂/P3HT. (b) The band-gaps of single- and dimer-AgInS₂ are determined by plotting the squared absorbance *versus* energy and extrapolating to zero.

Schottky contact in a photodetector can dramatically increase photosensitivity and response/recovery time.^{25,26} After switching to the ON state, the current of both photodetectors markedly increases due to the generation of electrons and holes under outside illumination. A possible process for generating the electrons and holes is described in the inset of Fig. 4a. Upon outside illumination, a great number of electrons and holes are generated from the interface of P3HT and AgInS₂ NCs. Electrons are transferred to the AgInS₂ layer due to its high electron affinity, while the holes are accepted by the P3HT layer which is perfect for acting as a hole acceptor due to its high field effect hole mobility (up to 0.1 cm² V⁻¹ s⁻¹).^{13,27,28}

The hybrid device is further demonstrated to exhibit excellent photoresponse characteristics (Fig. 4d). The photocurrents of pure P3HT, single-AgInS₂/P3HT, and dimer-AgInS₂/P3HT based devices are measured under a 365 nm UV lamp with an incident light density of 2.11 mW cm⁻² as the irradiation source. With the light irradiation ON and OFF, the device based on pure P3HT shows a long response time of 7 s and weak photoresponse as shown in Fig. 4d. The feature of irreversible and low ON/OFF switching demonstrates the inefficient charge separation in the device



Fig. 4 (a) Schematic illustration of the hybrid device. (b) *I–V* curves of the single-AgInS₂/P3HT based photodetectors in the dark and under different wavelength illumination. (c) *I–V* curves of the dimer-AgInS₂/P3HT based photodetectors in the dark and under different wavelength illumination. (d) The photoresponse of pure P3HT (black curve), single-AgInS₂/P3HT (red curve), and dimer-AgInS₂/P3HT (blue curve) based devices under identical 365 nm illumination with incident light density of 2.11 mW cm⁻² at 2 V DC bias.

without AgInS₂ NCs as the electron acceptors.²⁹ For the single-AgInS₂/P3HT and dimer-AgInS₂/P3HT hybrid devices, the current in the devices showed two distinct states, a "low" current in the dark and a "high" current under illumination. The switch in these two states was quick and reversible, allowing the device to perform as a high-quality photosensitive switcher. The very fast response/ recovery time can be attributed to the excellent photoresponse of the highly crystalline AgInS₂ NCs. Since the trap density induced by defects is markedly reduced, the photoresponse can rapidly reach a steady state in the rise and decay stages. It is notable that the hybrid device made of dimer-AgInS₂/P3HT has a higher ON/ OFF ratio than that of the single-AgInS₂/P3HT device, when the same amount of AgInS₂/P3HT is used, as shown in Fig. 4d. We attribute the higher electron-hole generation capability and the photosensitivity of dimer-AgInS₂/P3HT based photodetector to the higher absorbance of dimer-AgInS₂ in comparison with single-AgInS₂ NCs, and also to the fact of the nanogaps ($\sim 2 \text{ nm}$) existed in dimer-AgInS₂ nanostructures (Fig. 1d), in which the nanogap facilitates the electron transport in two AgInS₂ NCs caused by quantum tunneling effect.30-32

4. Conclusions

In summary, high quality $AgInS_2 NCs$ with well-defined size and morphology have been successfully prepared *via* a facile cothermal decomposition of Ag(DDTC) and $In(DDTC)_3$ in a mixture of OA and DT. The heliotrope seed-like $AgInS_2 NCs$ of 6×12 nm and heliotrope seed-like $AgInS_2$ dimer NCs of 8×16 nm are obtained by tuning the mole ratio of the coordinating solvents of OA and DT from 3:1 to 1:3, in which the DT plays a dominant role in determining the morphology of $AgInS_2 NCs$ due to its strong absorption onto the {001} crystal plane of $AgInS_2 NCs$. Furthermore, $AgInS_2 NC$ has been demonstrated to be a promising candidate for photoelectric applications with high sensitivity, quick response, and stable reversibility when hybrided with P3HT. We expect that the high sensitivity and stability of the hybrid nanodevice will hold a broad spectrum of applications in the photoelectric nanodevices.

Acknowledgements

Q. Wang acknowledges funding by CAS "Bairen Ji Hua" program, MOST (2011CB965004), NSFC (21073225, 21101166), NSF of Jiangsu province (BK2012007), Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology (1210908-02-K), and the CAS/SAFEA International Partnership Program for Creative Research Teams.

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