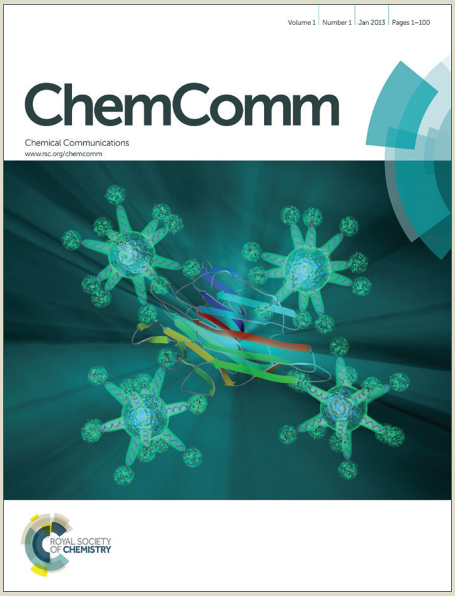
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Ag_2S-$AgInS_2$: p-n junction heteronanostructures with quasi type-II band alignment

Riya Bose*, Goutam Manna, Santanu Jana and Narayan Pradhan*

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X

We report here the fabrication of p-n junction diode in a single nanostructure by synthesizing a heterostructure involving n-type $AgInS_2$ and p-type Ag_2S. The quasi type-II band alignment between these ternary-binary semiconductors in the p-n junction heterostructures also slows down carrier recombination rate and the heterostructures show rectification behavior. Hence, they can be used as an active material for fabrication of bulk heterojunction photovoltaic device without any additional semiconductor material or dye required for charge separation or formation of p-n junction.

Current research in materials science has been propelled to synthesize new functional materials which can be readily applied for different technological applications. Among these, for electronic semiconductor devices, a p-n junction diode comes first which is the elementary building block for most of the devices such as photodiodes, transistors, solar cells, LEDs, and integrated circuits, and they are the active sites where the electronic action of the device takes place.[1] So far, a semiconductor p-n junction diode is constructed by doping two different layers of a single semiconductor with different types of impurity ions in order to introduce electron or hole excess in the different parts by electrochemical/ thermal vapor/ chemical vapor/ pulsed laser deposition method (p-n homojunction),[1c, 2] or by making a bilayer with sequential deposition of two different semiconductors, one p-type and one n-type (p-n heterojunction).[1a, 1b, 3] In addition, formation of a semiconductor p-n junction has been reported by co-deposition/mixing of a p-type and an n-type semiconductor together (bulk heterojunction) which further improves the charge separation as well as carrier transport, and hence increases the carrier lifetime by preventing excitonic recombination, which is highly desirable for device applications.[4]

To enhance the applicability of semiconductor nanomaterials, different synthetic methodologies have been developed to integrate two different material components in a single building block.[5] Apart from the advantage of assembling and tuning the optical/electrical properties of individual components in the nanoscale, the performance of these heterostructured materials often outperforms that of the individual components due to generation of new synergetic properties. With an eye on the importance of the semiconductor p-n junction and ability of heterostructures to combine properties of two different semiconductor materials, we designed here nanocrystalline heterostructures involving $AgInS_2$ (AIS) and Ag_2S. Both $AgInS_2$ and Ag_2S are important low bandgap semiconductors with high absorption coefficient which is highly desirable for photovoltaic device construction.[6,7] Besides, both of these are free from toxic heavy elements like Pb and Cd. But most importantly, apart from containing all those advantageous individual properties, Scanning tunneling spectroscopy (STS) analysis of these heterostructures reveals that $AgInS_2$ part behaves as an n-type semiconductor and Ag_2S part behaves as a p-type semiconductor. Hence a single heterostructure serves the purpose of a p-n junction. Moreover, $AgInS_2$ and Ag_2S having a quasi type-II band alignment among themselves, carrier recombination rate is also slowed down. Accordingly, these heterostructures show rectification behavior without any additional semiconductor or organic dye which is essentially required for charge separation or formation of a p-n junction.[8] Detailed synthesis, characterization, elucidation of p-n heterojunction by STS analysis and rectification properties of the $AgInS_2$-Ag_2S heterostructures have been studied and reported here.

We employ here a simple one-pot approach to synthesize the binary-ternary Ag_2S-$AgInS_2$ heterostructures where S-injection to a mixture of In and Ag precursors in oleylamine and octadecene leads to the formation of the heterostructures (Detailed synthetic procedure has been provided in Electronic Supplementary Information, ESI). Figure 1(a-c) show the high-angle annular dark-field imaging-scanning transmission electron microscope (HAADF-STEM) image and high resolution transmission electron microscope (HRTEM) images obtained from a typical reaction after 10 min annealing at 210 °C after S injection. These nanostructures clearly consist of two parts- the larger part is 20-30 nm long and has lighter contrast in bright field TEM images and there is a smaller part with darker contrast of size 10-15 nm (Figure 1(b-c)). X-ray diffraction (XRD) of the heterostructures also shows coexistence of two sets of peaks which correspond to orthorhombic $AgInS_2$ and monoclinic Ag_2S (Figure S1). This confirms that the heterostructures consist of $AgInS_2$ and Ag_2S, the lighter contrast part in bright field TEM images being $AgInS_2$ and the darker one Ag_2S, as Ag_2S has a higher electron density than $AgInS_2$. The small lattice mismatch between orthorhombic $AgInS_2$ and monoclinic Ag_2S eases growth of one over another. HRTEM analysis of the heterostructures has been provided in Figure S2. Detailed structural characterizations of the $AgInS_2$-Ag_2S heterostructures and their interface have also been reported in literature.[9]

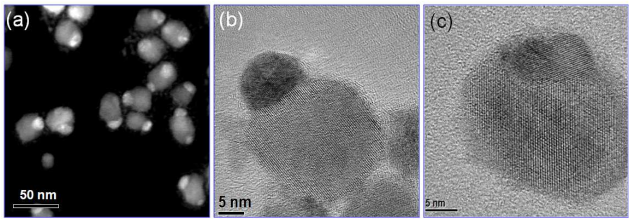


Fig. 1 (a) HAADF-STEM image of $AgInS_2$-Ag_2S heterostructures. The bright part signifies Ag_2S and the dark part signifies $AgInS_2$. (b-c) HRTEM images of single heterostructures. Here the dark contrast part corresponds to Ag_2S and the other part to $AgInS_2$.

Analysis of the intermediate samples shows that initially In_2O_3 agglomerated nanostructures are formed followed by formation of Ag(0) nanoparticles after addition of Ag(OAc). S injection to this solution leads to the formation of Ag_2S, as formation of In_2S_3 is not feasible at ~180 °C-210 °C temperature. Ag_2S being a super ion conductor with a lot of Ag+ vacancies,[9-10] In^{3+} ions diffuse into it to form $AgInS_2$ species, which in turn is pushed out from Ag_2S and locates on a suitable lattice plane of Ag_2S with minimized lattice mismatch. So Ag_2S acts here as catalyst to form $AgInS_2$ by acting as a host for In^{3+} ions as well as serves as the source material for formation of $AgInS_2$.[9] This mechanism has been confirmed by analysis of TEM, XRD and absorbance of the stepwise collected samples during the reaction (Detailed formation mechanism has been provided in ESI (Figure S3-S4)).

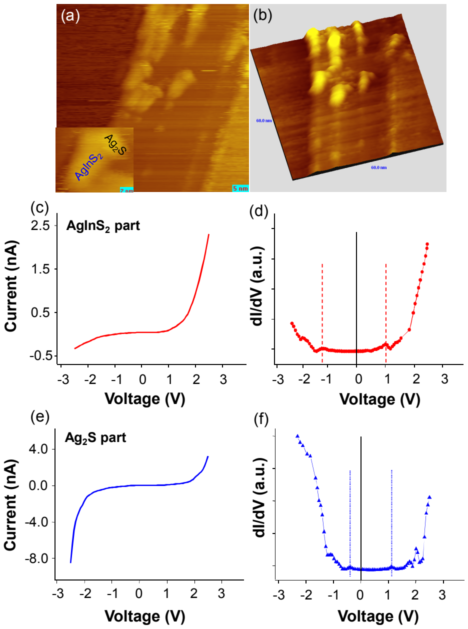


Fig. 2 (a) STM image of $AgInS_2$-Ag_2S heterostructures. Inset shows the STM image for a single heterostructure where $AgInS_2$ and Ag_2S parts have been marked. (b) STM image of the heterostructures in 3-D imaging mode (60 nm x 60 nm). (c-d) Current vs Voltage (I-V) plot and dI/dV vs V plot, obtained by numerical differentiation of the I-V curve for the $AgInS_2$ part respectively. The band positions are marked by the red dotted line and the Fermi level position is marked by the black line. (e-f) I-V plot and dI/dV vs V plot respectively for the Ag_2S part. The band positions are marked by the blue dotted line and the Fermi level position is marked by the black line.

To further characterize these nanostructures and to understand the band alignment with respect to Fermi level for the two counterparts $AgInS_2$ and Ag_2S, we performed STM (scanning tunnelling microscope) and STS analysis. Figure 2a shows the STM image of the heterostructures and Figure 2b shows the same in 3-D imaging mode. Inset of Figure 2a shows the enlarged view of a single heterostructure. In accordance with the TEM image, it can be concluded that the smaller part is Ag_2S and the larger part is $AgInS_2$. Current-Voltage (I-V) characteristics of the two counterparts were measured by placing the STM tip on the corresponding positions. Bias was applied on the sample and I-V characteristics were recorded for both directions of the voltage sweep. It is found that when the tip is placed over the $AgInS_2$ part, current increases steadily in the +ve voltage region than in the –ve voltage region (Figure 2c), whereas for Ag_2S part, current increases more when –ve voltage is applied (compared to the +ve voltage region) (Figure 2e). A set of current-voltage plots obtained by the STS measurement of 10 different particles has been provided in ESI (Figure S5). A plot of dI/dV vs V shows that, for $AgInS_2$ part, the conduction band position (right side peak marked by red dotted line) is at 1.0 eV and the valence band position (left side peak marked by red dotted line) is at -1.2 eV with respect to the Fermi level which implies that Fermi level is slightly closer to the conduction band (Figure 2d). But for Ag_2S part, the conduction band (right side peak marked by blue dotted line) is at 1.1 eV whereas valence band position (left side peak marked by blue dotted line) is at 0.4 eV with respect to the Fermi level (Figure 2f). So, in this case, Fermi level is much closer to the valence band than the conduction band. This implies that in these heterostructures, $AgInS_2$ part behaves as an n-type semiconductor whereas the Ag_2S part behaves as a p-type semiconductor. So, it can be concluded here that each of these heterostructures behaves as a p-n junction diode. A band gap of 2.2 eV for $AgInS_2$ and ~1.5 eV for Ag_2S was obtained. Small difference in the band gap values compared to that obtained from the spectroscopic data can be attributed to the electron-hole excitonic coulomb interaction which is absent in tunnelling data.[11]

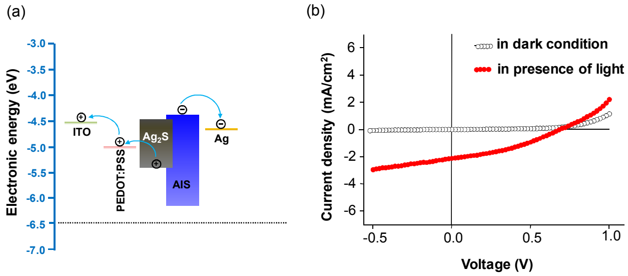


Fig. 3 (a) Band alignments of an ITO/PEDOT:PSS/Ag_2S-$AgInS_2$/Ag device. (b) Current density-Voltage (J-V) characteristics of the device under dark and illumination conditions.

As $AgInS_2$ and Ag_2S have a quasi type-II band alignment where conduction band of both the semiconductors have a negligible energy offset and there is a high energy offset between the valence bands,[8c, 12] the electron is delocalized over the entire structure and the hole is confined to Ag_2S. This leads to a reduced overlap between electron and hole wave function which slows down charge recombination and is highly desirable for light harvesting applications.[13] Along with that, these p-n junction heterostructures should show rectification behavior. To confirm this, we fabricated a device using $AgInS_2$-Ag_2S heterostructures as active material, PEDOT-PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) as the hole transporting material, Ag as top electrode and ITO (Indium Tin Oxide) as bottom electrode. Figure 3a shows the band alignments of the components of the device. Positions of the different layers shows that photogenerated excitons will break into electrons and holes in the $Ag_2S/AgInS_2$ interfaces and the holes will move easily to the bottom electrode through PEDOT:PSS whereas the electrons will be collected at the Ag electrode. Figure 3b shows the typical current density-voltage (*J-V*) characteristics of our device under white light illuminations as well as in dark. The dark *J-V* characteristics confirm non-linear rectification behavior and the *J-V* characteristics under illumination confirm the photovoltaic properties. Our device shows a fill factor (FF) of 36% with an open circuit voltage (V_{OC}) of 0.68 volt and short circuit current density (J_{SC}) of 2.13 mA/cm^2. Photon conversion efficiency of our device is 0.52% and its performance is found to be consistent for measurement over a week which demonstrates the stability of the device. Spectral response of the device has been provided in ESI (Figure S6). So, it can be confirmed that $AgInS_2$-Ag_2S heterostructures can be used as active material in a bulk heterojunction photovoltaic device for generation as well as dissociation of the photo-exciton into electrons and holes. This is even more beneficiary than mixing of p- and n-type semiconductors as charge separation and carrier transport are even easier with every nanostructure having a p-n junction. However, a more detailed experimentation is needed for further optimization of the device performance incorporating these heterostructures.

To summarize, we report here fabrication of p-n heterojunction in a single nanostructure with integration of n-type $AgInS_2$ and p-type Ag_2S in a single building block. Even there are reports of single nanostructure p-n junctions; the procedures are hectic and expensive.[1c, 2d] On the contrary, these nanostructures are synthesized by a simple colloidal approach where Ag_2S, being a superion conductor, serves as the host for catalyzing the growth of $AgInS_2$ as well as serves as the source material. The p- and n-type behavior of the semiconductors is confirmed by STS analysis. Further, quasi type-II band alignment of $AgInS_2$ and Ag_2S slows down carrier recombination and hence these heterostructures with p-n junction show rectification properties and can be used as an active material for fabrication of bulk heterojunction photovoltaic devices without any additional material which is usually required for charge separation or formation of p-n junction. The controlled ability to synthesize such structures having a p-n junction and with suitable band offsets promoting charge separation provides a better insight into fundamental synthetic chemistry as well as opens avenues for diverse optoelectronic applications.

Notes and references

Centre for Advanced Materials and Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032 India. Email:camnp@iacs.res.in, camrb@iacs.res.in

† Electronic Supplementary Information (ESI) available: Experimental procedure, supporting figures

1 (a) B. N. Pal, I. Robel, A. Mohite, R. Laocharoensuk, D. J. Werder, V. I. Klimov, *Adv. Func. Mater.* 2012, **22**, 1741-1748; (b) M. G. Panthani, C. J. Stolle, D. K. Reid, D. J. Rhee, T. B. Harvey, V. A. Akhavan, Y. Yu, B. A. Korgel, *J. Phys. Chem. Lett.* 2013, **4**, 2030-2034; (c) M.-T. Chen, M.-P. Lu, Y.-J. Wu, J. Song, C.-Y. Lee, M.-Y. Lu, Y.-C. Chang, L.-J. Chou, Z. L. Wang, L.-J. Chen, *Nano Lett.* 2010, **10**, 4387-4393; (d) W. Shockley, M. Sparks, G. K. Teal, *Phys. Rev.* 1951, **83**, 151-162.

2 (a) J. Huang, S. Chu, J. Kong, L. Zhang, C. M. Schwarz, G. Wang, L. Chernyak, Z. Chen, J. Liu, *Adv. Opt. Mater.* 2013, **1**, 179-185; (b) H. Yanagi, K. Ueda, H. Ohta, M. Orita, M. Hirano, H. Hosono, *Solid State Commun.* 2001, **121**, 15-17; (c) K. Han, M. Tao, *Sol. Energ. Mater. Sol. Cells* 2009, **93**, 153-157; (d) C. Hak Dong, S. Z. Anvar, U. Y. Shavkat, A. Chi Won, Y. Yung Kee, K. Tae Won, *Nanotechnology* **2012**, *23*, 115401/1-115401/6.

3 (a) P. Maraghechi, A. J. Labelle, A. R. Kirmani, X. Lan, M. M. Adachi, S. M. Thon, S. Hoogland, A. Lee, Z. Ning, A. Fischer, A. Amassian, E. H. Sargent, *ACS Nano* 2013, **7**, 6111-6116; (b) J. Gao, J. M. Luther, O. E. Semonin, R. J. Ellingson, A. J. Nozik, M. C. Beard, *Nano Lett.* 2011, **11**, 1002-1008; (c) L. Etgar, T. Moehl, S. Gabriel, S. G. Hickey, A. Eychmüller, M. Grätzel, *ACS Nano* 2012, **6**, 3092-3099.

4 (a) A. K. Rath, M. Bernechea, L. Martinez, F. P. G. de Arquer, J. Osmond, G. Konstantatos, *Nat Photon* 2012, **6**, 529-534; (b) M. Shanmugam, C. A. Durcan, R. Jacobs-Gedrim, B. Yu, *Nano Energy* 2013, **2**, 419-424.

5 (a) S. Shen, Y. Zhang, L. Peng, Y. Du, Q. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 7115-7118; (b) D. J. Milliron, S. M. Hughes, Y. Cui, L. Manna, J. Li, L.-W. Wang, A. P. Alivisatos, *Nature* 2004, **430**, 190-195; (c) P. D. Cozzoli, T. Pellegrino, L. Manna, *Chem. Soc. Rev.* 2006, **35**, 1195-1208; (d) P. D. Cozzoli, L. Manna, *Nat. Mater.* 2005, **4**, 801-802; (e) W. Shi, H. Zeng, Y. Sahoo, T. Y. Ohulchanskyy, Y. Ding, Z. L. Wang, M. Swihart, P. N. Prasad, *Nano Lett.* 2006, **6**, 875-881; (f) C. Wang, H. Yin, S. Dai, S. Sun, *Chem. Mater.* **22**, 3277-3280; (g) B. P. Khanal, A. Pandey, L. Li, Q. Lin, W. K. Bae, H. Luo, V. I. Klimov, J. M. Pietryga, *ACS Nano* 2012, **6**, 3832-3840; (h) C. d. M. Donega, *Chem. Soc. Rev.* 2011, **40,** 1512-1546; (i) S. Shen, Y. Zhang, Y. Liu, L. Peng, X. Chen, Q. Wang, *Chem. Mater.* **2012**, *24*, 2407-2413.

6 (a) H. Xiao, J. Tahir-Kheli, W. A. Goddard, *J. Phys. Chem. Lett.* 2011, **2**, 212-217; (b) B. Mao, C.-H. Chuang, J. Wang, C. Burda, *J. Phys. Chem. C* 2011, **115**, 8945-8954; (c) M. Deng, S. Shen, X. Wang, Y. Zhang, H. Xu, T. Zhang, Q. Wang, *CrystEngComm* **2013**, *15*, 6443-6447.

7 (a) P. Jiang, Z.-Q. Tian, C.-N. Zhu, Z.-L. Zhang, D.-W. Pang, *Chem. Mater.* 2011, **24**, 3-5; (b) Y. Du, B. Xu, T. Fu, M. Cai, F. Li, Y. Zhang, Q. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 1470-1471; (c) S. Shen, Q. Wang, *Chem. Mater.* **2013**, *25*, 1166-1178.

8 (a) T. Sasamura, K.-i. Okazaki, A. Kudo, S. Kuwabata, T. Torimoto, *RSC Adv.* 2012, **2**, 552-559; (b) K. C. Cheng, W. C. Law, K. T. Yong, J. S. Nevins, D. F. Watson, H. P. Ho, P. N. Prasad, *Chem. Phys. Lett.* 2011, **515**, 254-257; (c) Y. Lei, H. Jia, W. He, Y. Zhang, L. Mi, H. Hou, G. Zhu, Z. Zheng, *J. Am. Chem. Soc.* 2012, **134**, 17392-17395; (d) I. Hwang, M. Seol, H. Kim, K. Yong, *Appl. Phys. Lett.* 2013, **103**, 023902-4.

9 G. Zhu, Z. Xu, *J. Am. Chem. Soc.* 2011, **133**, 148-157.

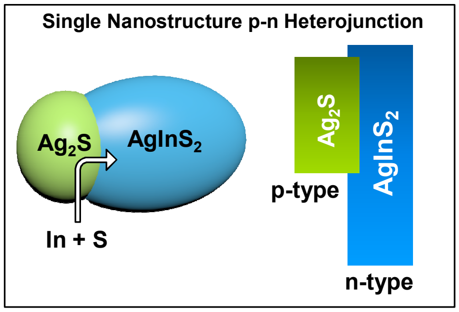
10 J. Wang, K. Chen, M. Gong, B. Xu, Q. Yang, *Nano Lett.* 2013, **13,** 3996-4000.

11 (a) U. Banin, Y. Cao, D. Katz, O. Millo, *Nature* 1999, **400**, 542-544; (b) D. Katz, T. Wizansky, O. Millo, E. Rothenberg, T. Mokari, U. Banin, *Phys. Rev. Lett.* 2002, **89**, 086801/1-086801/4.

12 J. S. Jang, P. H. Borse, J. S. Lee, S. H. Choi, H. G. Kim, *J. Chem. Phys.* 2008, **128**, 154717-6.

13 (a) K. Wu, N. Song, Z. Liu, H. Zhu, W. Rodríguez-Córdoba, T. Lian, *J. Phys. Chem. A* 2013, **117**, 7561-7570; (b) M. Saba, S. Minniberger, F. Quochi, J. Roither, M. Marceddu, A. Gocalinska, M. V. Kovalenko, D. V. Talapin, W. Heiss, A. Mura, G. Bongiovanni, *Adv. Mater.* 2009, **21**, 4942-4946; (c) A. Sugunan, Y. Zhao, S. Mitra, L. Dong, S. Li, S. Popov, S. Marcinkevicius, M. S. Toprak, M. Muhammed, *Nanotechnology* 2011, **22**, 425202/1-425202/7.

TOC:



A single nanostructure p-n junction diode has been fabricated colloidally by synthesizing a heterostructure comprising of p-type Ag_2S and n-type $AgInS_2$, where the quasi type-II band alignment of the constituents further improve charge separation.