Journal of Materials Chemistry A

PAPER

Check for updates

Cite this: J. Mater. Chem. A, 2019, 7, 6387

Received 1st January 2019 Accepted 15th February 2019

DOI: 10.1039/c9ta00003h

rsc.li/materials-a

Introduction

Among the different types of transition metals in the periodic table, copper (Cu) shows a great tendency to form different types of chalcogenides due to its high chalcogenicity.1 Different types of main group metals (In, Ga, and Sn) as well as transition metals (Fe, Zn, and Cr) also form copper chalcogenide-based tertiary as well as multinary crystal structures.²⁻⁴ Among all of these copper based multinary chalcogenides, binary chalcogenides such as Cu_{2-x}S, Cu_{2-x}Se, and Cu_{2-x}Te are an interesting class of compounds due to their different electronic, magnetic and optical properties.5-8 The electronic structure associated with their pervious crystal phase and atomic dislocation within the lattice leads to variable energy bands.9 Visible range optical absorption associated with the energy gap and NIR absorption due to defect-based charge carrier availability make them acquire different electronic properties such as semiconductivity and even metallicity.^{10,11} Owing to their size, shape and composition-dependent tunable band gap and associated optical and plasmonic properties, they are promising

Electrospray deposition-induced ambient phase transition in copper sulphide nanostructures*

Arijit Jana, ២ Sourav Kanti Jana, ២ Depanjan Sarkar, ២ Tripti Ahuja, Pallab Basuri, ២ Biswajit Mondal, Sandeep Bose, 🕩 Jyotirmoy Ghosh ២ and Thalappil Pradeep ២ *

We introduce a new and simple method for synthesizing different phases of copper sulphide nanostructures using electrospray deposition (ESD) of molecular sulphur in the form of droplets on metallic copper surfaces under ambient conditions. Different phases of copper sulphide nanostructures were created by controlling the deposition time. Time dependent electron microscopy reveals conversion of the Cu₂S nanopyramids to Cu_{1.8}S platelets during the course of ESD. In the beginning of deposition, direct interaction between sulphur ions and metallic copper creates Cu₂S nanopyramids followed by subsequent slow diffusion of sulphur leading to the formation of copper deficient Cu18S platelets. A detailed characterization of both the nanostructures was performed by using different microscopic and spectroscopic tools such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS). We have also studied the optical properties of these nanostructures in both UV-Vis and near infrared (NIR) regions. The characteristic broad peaks in the UV-Vis region of Cu₂S nanopyramids indicate the photosensitive nature of the material. A positive photocurrent response was observed from the Cu₂S nanopyramids under electrochemical conditions, while Cu18S nanostructure shows an intense localized surface plasmon (LSPR) peak in the NIR region indicating its metallic nature. Current-voltage (I-V) measurements showed metallic conductivity in them

candidates for different applications such as optical limiting, thermoelectrics, photocatalysis, photoacoustics, metal ion batteries, sensors, photothermal therapies and biomedical applications.¹²⁻¹⁹

Among all of these binary copper chalcogenides, copper sulphide is an interesting one due to its several stoichiometric and nonstoichiometric crystal phases, associated with different properties.²⁰ Copper sulphide, a well-known p-type semiconducting material with a direct band gap ranging from 1.2 to 2.5 eV, exhibits various crystallographic forms, due to facile diffusion of copper and sulphur ions.²¹ They form different stoichiometric copper sulphide phases such as covellite (CuS) and chalcocite (Cu₂S) as well as various nonstoichiometric phases such as djurleite (Cu_{1.94}S), digenite (Cu_{1.8}S), anilite (Cu_{1.75}S), geerite (Cu_{1.6}S), etc.²²⁻²⁶ Thermal annealing and temperature dependent phase transitions among different copper sulphide phases make them prone to form mixed phases.27,28 Therefore, it is important to find new synthetic ways to create different copper sulphide nanostructures under ambient conditions with a suitable morphology, shape and crystal structures.

Over the past few decades, significant progress has been made in the solution phase synthesis such as solvothermal methods, microfluidic synthesis, template directed synthesis, microwave assisted synthesis and colloidal phase hot injection



View Article Online

View Journal | View Issue

DST Unit of Nanoscience (DST UNS), Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India. E-mail: pradeep@iitm.ac.in

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ta00003h

methods for making different copper sulphide nanostructures.²⁹⁻³³ Based on the molecular precursor, solvent and temperature associated with the synthetic conditions, different types of crystal phases and microstructural morphologies such as nanowires, nanosheets, nanocubes, nanowalls and hollow spheres were formed.³⁴⁻³⁸ Since the solution phase synthesis of copper sulphide nanostructures, researchers were trying to make them in the solid state. Chemical vapor deposition (CVD) is the most common synthetic method which was extensively used for making high quality atomic layer thin films of copper sulphide for different applications.^{39,40} Common CVD is a high temperature method which requires a copper plate as the source of copper and solid sulphur or hydrogen sulphide gas as the source of sulphur. High temperature processing is needed for making such materials for electronic applications.⁴¹ Therefore, it is important to develop specific copper sulphide nanostructures under ambient conditions for practically viable applications.

Here, we introduce a completely new synthetic procedure for creating different copper sulphide nanostructures by an electrospray deposition (ESD) process under ambient conditions. ESD is an ionic charge droplet based synthetic tool for making different types of nanostructures under ambient conditions.42 We have already shown that ESD can create metallic nanobrushes and nanoparticle assembled nanosheets which exhibit the highest water harvesting capacity, while being an excellent catalyst.43-45 Previous studies have shown that ESD can produce surface enhanced Raman active nanoparticles.46 In the present paper, we have used an ambient electrospray deposition technique for creating copper sulphide nanostructures under ambient conditions by interacting metallic copper with molecular sulphur ions. During the ESD process, Cu₂S nanopyramids were formed initially on top of the metallic copper surface and after subsequent continuous sulphur spray, Cu_{1.8}S platelets were formed on top of the Cu₂S nanopyramids. After successful synthesis of these two nanostructures at different times of sulphur spray, we further demonstrated the phase-dependent change of optical properties. Based on the optical and charge carrier-based plasmonic properties of the materials, we further demonstrate the change in the electrical properties of the nanostructures. We show that the semiconducting Cu₂S nanopyramids were gradually converted to metallic Cu_{1.8}S platelets during the ESD process.

Experimental section

1. Electrospray deposition technique

A home built electrospray source was used for delivering toluene-solvated charged droplets of sulphur towards the copper surface which was grounded. The electrospray source was made by pulling a borosilicate glass capillary (1.5 mm outer diameter and 0.86 mm inner diameter) by using a micropipette puller (P-97, Sutter Instruments, USA). The inner diameter of the formed glass capillary tip was 20 to 25 μ m. A spray plume was generated from the tip of the glass capillary by applying a DC potential of 1.50 to 1.80 kV between a platinum wire placed inside the capillary and the ground which produced a current of

10–15 nA. The capillary tip was manually placed over the copper plate at a distance of 5 to 8 mm and deposition was done. Although droplet dimensions have not been measured, they have been estimated to be in the range of 100 to 150 nm with a solution flow rate of 8 to 10 nL min⁻¹, from various studies.⁴⁷ Detailed electrospray deposition experiments are described in the ESI.[†]

2. Materials used

The borosilicate glass capillary was purchased from Sutter instruments, USA. Both the copper TEM grid (without carbon coating) and the pure copper plate used as a copper source were purchased from SPI supplies and a local source, respectively. Copper plates were ultrasonically cleaned with acetone and isopropanol sequentially to remove organic contaminants. Platinum electrodes of 0.2 mm diameter were purchased from Sigma Aldrich, India. Sulphur powder (100 mesh, 99.5%) was purchased from Sigma Aldrich, India. Toluene (99.5%) and methanol (99.5%) were purchased from Merck, India and Finar, India, respectively. All the chemicals were commercially available and used without further purification.

3. Preparation of sulphur solution

Sulphur solution was made by refluxing 10 mg sulphur powder in 10 mL toluene at 120 °C under an argon atmosphere. After 10 hours of refluxion, a homogeneous solution was formed. Sulphur solution in toluene was mixed with 2 mL methanol for our electrospray deposition experiments.

Results and discussion

For the synthesis of copper sulphide nanostructures under ambient conditions, ESD was carried out by spraying sulphur solution on a copper plate. The experimental set-up used for electrospray deposition (ESD) is shown in Fig. 1a. Ejection of the spray plume during the electrospray deposition process is shown in the inset of Fig. 1a. To understand the chemical nature of the as-synthesized sulphur solution, a mass spectrum was collected from the solvated spray plume by using a similar ESI source. Fig. 1b shows a feature assigned to $[S_{24}(C_7H_8)]^+$. The isotopic distribution pattern of the spectrum was well matched with the theoretical spectrum. During the preparation of sulphur solution in toluene at 120 °C, a toluene solvated trimer of S8 was formed.48,49 After the spray of sulphur, a black circular spot was formed over the copper surface. Fig. 1c shows an optical image of the copper plate after different times of sulphur deposition. From the optical image, it was observed that in the course of deposition, a dark black circular spot evolved with time on top of the copper plate. Sulphur ions ejected from the capillary tip interact with the copper on the surface and form chalcocite (Cu₂S) nanopyramids initially due to superionic diffusion between copper and charged sulphur microdroplets and further continuous sulphur spray over the Cu₂S nanopyramids creates digenite (Cu_{1.8}S) platelets due to slow ionic diffusion of sulphur ions through the vacancy of the upper surface of Cu₂S nanopyramids.⁵⁰ Fig. 1d shows the time





Fig. 1 (a) Schematic representation of the ESD set-up (inset shows the optical image of the spray plume), (b) ESI-MS spectrum of sulphur solution (inset spectrum in black shows the experimental spectrum and red lines show the theoretical spectrum), (c) time-dependent evolution of a black circular spot during ESD, and (d) schematic representation of the growth mechanism of chalcocite (Cu_2S) nanopyramids and digenite ($Cu_{1.8}S$) platelets during ESD.

dependent growth mechanism of both Cu₂S nanopyramids and Cu_{1.8}S platelets during the electrospray deposition process.

To observe the growth of different copper sulphide nanostructures during the ESD process, we have performed timedependent scanning electron microscopy (SEM) measurements. Fig. 2a–c show SEM micrographs of the nanostructures grown over the copper surface with varying times of sulphur spray. After 2 to 5 min of S spray, a highly dense pyramidal morphology was formed with a 1 to 2 μ m edge length on the copper surface (Fig. 2a and b). More than 5 min of S spray creates randomly oriented platelets and their assembled dendritic structures.

Fig. S3[†] shows the time-dependent evolution of different copper sulphide nanostructures on copper plates as well as copper TEM grids. Both the copper surfaces show similar types of growth. Fig. S4 and S5[†] present the elemental composition of the nanopyramids and platelets through the point EDAX spectrum, which shows a copper to sulphur atomic ratio of 1.93 for nanopyramids and 1.80 for platelet nanostructures, respectively.

For further characterization of the as-prepared nanostructures, transmission electron microscopy (TEM) followed by Raman spectroscopy, powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS) studies were performed. The TEM image shown in Fig. 2d reveals that the as-grown nanopyramids have a smooth surface with sharp edges. The high resolution TEM (HRTEM) image of the pyramidal surface shows a lattice spacing of 0.24 nm, assigned to the (102) plane of the hexagonal chalcocite (Cu_2S) phase (reference code 00-026-01116). A nanopyramid with 0.24 nm lattice spacing was seen along the surface indicating that the growth occurs along the (102) direction. More than 5 min of S spray creates randomly oriented platelets on top of the pyramids. From the TEM image in Fig. 2f, we observed crystalline growth of small particles on the outer surface of the platelets. Well resolved lattice fringes observed in the HRTEM image under these conditions correspond to 0.32, 0.28 and 0.19 nm, attributed to the (111), (200) and (220) planes respectively, of cubic digenite ($Cu_{1.8}S$) (reference code 01-072-1966).

Raman spectroscopic measurements were performed *ex situ* to understand the phase transformation from chalcocite (Cu₂S) to digenite (Cu_{1.8}S) during the electrospray deposition process. Fig. 3a shows the time-dependent Raman spectrum after different times of S spray. The characteristic S–S stretching peak at 474 cm⁻¹ indicates the formation of Cu₂S nanopyramids after 5 min of S spray. Raman imaging using the 474 cm⁻¹ mode in Fig. 3a (inset) clearly indicates Cu₂S growth on the copper surface. After more time (more than 5 min) of S spray, the 474 cm⁻¹ peak vanishes and a new peak at 469 cm⁻¹ arises, which indicates further growth of Cu_{1.8}S nanostructures on top of the nanopyramids. For the electrospray deposited sample, there was no additional impurity peak for copper oxide or excess



Fig. 2 (a–c) Large area SEM images at different times of deposition: (a) 2 min spray, (b) 5 min spray, and (c) 15 min spray (inset shows a higher magnification SEM image), (d) low magnification TEM image of Cu₂S nanopyramids (inset depicts the higher magnification TEM image), (e) HRTEM of Cu₂S nanopyramids, (f) TEM image of Cu_{1.8}S platelets, and (g–i) HRTEM image of Cu_{1.8}S platelets. Lattice parameters are marked and inset images show the corresponding FFT patterns.

sulphur on the copper surface which indicated uniformity in the crystal phase of both Cu_2S nanopyramids and $Cu_{1.8}S$ platelets.



Fig. 3 (a) Raman spectra of copper sulphide nanostructures at different spray times (inset shows the Raman image corresponding to the 474 cm⁻¹ peak), (b) powder XRD pattern of Cu₂S nanopyramids over the copper plate after 5 min of S spray, (c) powder XRD pattern of Cu_{1.8}S platelets, (d) survey XPS spectrum after 5 min of S spray and XPS spectra in the (e) Cu 2p and (f) S 2p regions, (g) survey XPS spectra in the (h) Cu 2p and (i) S 2p regions.

The phase and crystal structure of copper sulphide nanostructures were determined by powder X-ray diffraction (PXRD). To understand the time-dependent phase transformation during the electrospray deposition process, PXRD was performed by extracting the sample after different times of electrospray. Fig. 3b shows the PXRD pattern of blackish copper sulphide after 5 min of sulphur spray. From the PXRD pattern, we observed four prominent diffraction peaks at 2θ values of 37.70° , 46.21° , 48.64° and 54.20° . These four primary peaks were indexed to the (102), (110), (103) and (112) lattice planes, respectively of the chalcocite (Cu_2S) phase with the space group of P6₃/mmc (reference code 00-026-1116). After confirming the chalcocite Cu₂S phase, we performed PXRD of the platelet nanostructures and the corresponding spectrum is shown in Fig. 3c. In Fig. 3c, we observed four prominent diffraction peaks at 27.74°, 32.46°, 46.19° and 54.08°. Upon careful analysis of the data and matching with a previous database, these peaks were indexed to the (111), (002), (022) and (113) planes of cubic digenite (Cu_9S_5 or $Cu_{1,8}S$) with the space group Fm3m (reference code 01-072-1966). According to the previous literature, for digenite Cu_{1.8}S, both cubic and rhombohedral phases are closely related and it is very difficult to separate them.⁵¹ Therefore, there is a chance of coexistence of both these phases.

In order to analyze the chemical binding states of different elements on the as-grown copper sulphide nanostructures, a time-dependent XPS study was performed. Copper plates were electrosprayed at different times and XPS spectra were measured. Fig. 3d shows the total XPS spectrum of the copper plate after 5 min of S spray. The total XPS spectrum shown in Fig. 3d contains Cu and S as well as carbon and oxygen, may be due to the adsorbed oxygen on the copper plate, which was exposed to ambient conditions. Fig. 3e shows the XPS spectrum of Cu 2p regions. Two primary peaks centered at 932.8 and 952.7 eV were assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. After peak fitting, we got two peaks at 932.8 eV and 935.3 eV, due to the existence of Cu(0) as well as Cu(1) species. Similarly, two peaks at 952.7 eV and 955.2 eV were assigned to Cu $2p_{1/2}$ of Cu(0) and Cu(1), respectively. This Cu(1) state represents the Cu(1) species present in the Cu₂S nanopyramids. In the S 2p spectrum in Fig. 3f, we saw two peaks centered at 162.1 and 163.2 eV which were assigned to S $2p_{3/2}$ and S $2p_{1/2}$ of the S⁻² species present in the Cu₂S nanopyramids. Fig. 3g-j show the XPS spectra of Cu_{1.8}S platelets synthesized by 15 min sulphur spray. The survey spectrum shown in Fig. 3g presents the Cu, S, C and O peaks. In the Cu 2p XPS, two main peaks centered at 932.5 eV and 952.3 eV were seen, assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, of the Cu_{1.8}S platelets. Shoulder peaks associated with these two primary peaks appear at 934.8 & 936.7 eV and 954.6 & 956.3 eV, due to the coexistence of Cu(I) and Cu(II) $2p_{3/2}$ and $2p_{1/2}$ doublets, respectively. Thus the formation of both Cu(I) and $Cu(\pi)$ mixed states in $Cu_{1.8}$ S platelets was clearly distinguishable in the XPS spectrum. Fig. 3i shows the XPS spectrum of sulphur showing peaks at 161.9 and 163.2 eV, due to S 2P_{3/2} and S 2P_{1/2} of the sulphide (S^{-2}) in Cu_{1.8}S. Based on the Raman spectra, PXRD and XPS analysis, we can conclude that during electrospray deposition, chalcocite (Cu₂S) nanopyramids were formed first and Cu_{1.8}S platelets were grown subsequently.



Fig. 4 (a) UV-Vis-NIR absorption spectrum of Cu_2S nanopyramids and $Cu_{18}S$ platelets; (b and c) solid state photoluminescence spectrum collected by excitation with a 532 nm laser.

For gaining better insight into the electronic properties as well as band structure of the as-synthesized copper sulphide nanostructures, we studied their time-dependent solid-state UV-Vis NIR and solid-state photoluminescence. After spraying sulphur on the copper plate at different times, we have studied the optical response from the as-grown copper sulphide nanostructures in the solid state in the reflectance mode. For Cu₂S nanopyramids, there was a broad absorption maximum at 540 nm (2.29 eV) in the lower wavelength region, which indicated the indirect band gap of the semiconducting Cu₂S nanopyramids. There was a week absorption offset in the 906 nm (1.36 eV) region, which indicated the direct band gap of the Cu₂S nanopyramids. Both these bandgaps were well matched with the previous literature.^{52,53} Surprisingly, there was no NIR



Fig. 5 (a) I-V characteristics of the as-grown Cu₂S nanopyramids under dark (black trace) and light illumination (red trace) in the presence of 0.01 (M) Na₂SO₄ solution (light power 195 W), (b) chronoamperometric reversible photocurrent response from the as-grown electrode before and after light illumination (applied potential -0.4 V vs. Ag/AgCl), (c) Nyquist plot of Cu₂S nanopyramids recorded at a fixed potential of -0.4 V with respect to Ag/AgCl and (d) oxygen and hydrogen (inset) removal under dark and light conditions.

absorption peak for the Cu₂S nanopyramids due to the unavailability of localized surface plasmons in the near infrared region. Fig. 4b shows the solid-state photoluminescence spectrum of Cu₂S nanopyramids. A 532 nm green laser (5 mW at the sample) was used as the excitation source for measuring solidstate photoluminescence from the nanostructures. A sharp photoluminescence emission peak observed at 890 nm (1.39 eV) due to indirect band to band transition for the nanopyramids. The sharpness of the emission peak is increased due to the well defined crystallinity of the nanopyramids.

After studying the optical properties of Cu_2S nanopyramids, we explored the optical properties of $Cu_{1.8}S$ platelets grown by 15 min sulphur spray on a copper plate. From the UV visible NIR spectrum, we can see a broad absorption maximum at 712 nm (1.74 eV) which clearly indicates the band gap of $Cu_{1.8}S$ platelets. In addition to the visible range absorption, there was a broad absorption maximum at 1134 nm (1.09 eV) in the NIR region. This NIR absorption band was attributed to the localized surface plasmon resonance (LSPR) due to the accumulation of a large number of free charge carriers, *i.e.*, holes within the nonstoichiometric $Cu_{1.8}S$ phase. Copper deficiency in $Cu_{1.8}S$ creates several holes which are responsible for the creation of surface plasmons in the NIR region.^{54,55} $Cu_{1.8}S$ platelets also show a broad photoluminescence peak in the 710 nm (1.74 eV) region due to the emissive band gap of $Cu_{1.8}S$ platelets.

In addition to the detailed characterization of the different copper sulphide nanostructures, we have also investigated the photoelectrochemical properties of the chalcocite (Cu₂S) nanopyramids and I-V characteristics of the digenite (Cu_{1.8}S) platelets. To measure the photoelectrochemical properties of the assynthesized Cu₂S nanopyramids, linear sweep voltammetry (LSV) was performed in 0.01 M Na₂SO₄ solution. Prior to the measurement of the photoelectrochemical response, a copper plate (\sim 1 cm²) was electrosprayed for 5 min with sulphur solution and subsequently, it was used as an electrode material for measuring the electrochemical response. During this electrospray, mostly Cu₂S nanopyramids were formed on the substrate as already shown in the SEM micrographs. Fig. 5a shows the LSV plot of the photocurrent response under dark and light illumination conditions. A sharp increase of the photocurrent in the negative potential window (0 V to -0.55 V) is observed from the above plot. The photocurrent increases sharply up to -0.12 mA after light illumination; however, the current decreases within 1 s after turning off the light source. Fig. 5b shows the time resolved reversible photocurrent response measured by the chronoamperometry technique performed at -0.4 V up to three cycles. The efficient photocurrent response from the Cu₂S nanopyramids results from the photoelectron transfer from the Cu₂S nanopyramids to the working electrode. Furthermore, to investigate the interfacial charge transfer behavior upon light illumination, we performed Electrochemical Impedance Spectroscopy (EIS) at -0.4 V with frequency ranging from 1 MHz to 1 mHz with and without light illumination. From the Nyquist plot, we have found that there is a significant decrease of charge transfer resistance from 170 Ω to 130 Ω which indicates photocurrent generation upon light illumination.



Fig. 6 Solid state electrical measurements of $Cu_{1.8}S$ platelets: metallic behavior is shown by $Cu_{1.8}S$ platelets. (a) Metallic *I–V* characteristics of $Cu_{1.8}S$ films with 124 ohm resistance and (b) resistance of the film measured by using a multimeter.

During the photoelectrochemical measurements, we observed gas evolution from both the working and counter electrodes, which is presumably due to the photoelectrochemical water splitting by the Cu₂S electrode. Photoelectrochemical total water splitting was also confirmed by mass spectrometry (MS) measurements. The mechanism of total water splitting can be realized with the help of an energy level diagram at the electrode electrolyte interface as shown in Fig. S6 of the ESI.† Both the optical band gap and energy level of both the conduction and valence bands are well matched for total water splitting, *i.e.* the conduction band should be above the thermodynamic potential of the H₂ evolution (0 V) reaction (H⁺ + e⁻ \rightarrow 1/2H₂) and the valence band should be below the thermodynamic potential of the oxygen evolution (1.23 V) reaction ($OH^- + h^+ \rightarrow 1/2O_2$). Upon photoexcitation of the working electrode (Cu₂S), the photogenerated electrons flow towards the counter electrode (Pt) and react with H⁺ ions and produce H₂ gas at the Pt electrode. Simultaneously, photogenerated holes react with OH- anions and generate O_2 at the working electrode. Fig. 5d shows the MS ion current data under dark as well as light illumination conditions. There is a sharp increase of ion current for both oxygen and hydrogen under light illumination conditions indicating that during light illumination, more amount of water splitting happens than that in the dark. Photo-induced charge carriers reduce the barrier height of this metal-semiconductor junction which increases the photocatalytic efficiency.

After studying the photoelectrochemical response of the Cu₂S nanopyramids, we measured the *I*–*V* characteristics of Cu_{1.8}S platelets. For that, we used a simple scotch tape technique to peel off the Cu_{1.8}S platelets and a film was prepared. Fig. S7† shows a schematic representation of the peeled off film. The continuity and the surface morphology of the film were confirmed through optical and scanning electron microscopy images. Fig. S8 and S9† show the optical images and SEM images of the platelet assembled film which show that it is continuous. We performed the electrical response measurement of the film by making four probe electrical connection using fine copper wires and silver paste. Fig. 6a shows the *I*–*V* data of the film. During the voltage sweep from -1.5 V to +1.5 V at room temperature, we observed the ohmic conductivity of the

thin film and the linear fitting in the I-V characteristics proved that Cu_{1.8}S platelets are metallic in nature. Reciprocal of the slope calculated from the I-V characteristics shows a resistance of 124 ohm which clearly matches with the resistance measured by using a multimeter as shown in Fig. 6b.

Conclusions

In conclusion, we have synthesized two different copper sulphide nanostructures by using ambient electrospray deposition techniques. Without using any solvent and harsh synthetic conditions, we selectively synthesized stoichiometric chalcocite (Cu₂S) nanopyramids and nonstoichiometric digenite (Cu_{1.8}S) platelet structures, exclusively. The important issue in our experiment is tuning the morphology and proper structural control among a variety of copper sulphide phases (Cu₂S and Cu_{1.8}S) by varying electrospray deposition time under ambient conditions. Gradual decrease of the diffusion rate of sulphur ions as well as surface energy barrier of copper atoms is most probably the reason for this phase transition from Cu₂S to Cu_{1.8}S nanostructures. Complete characterization of both the nanostructures was performed by using several spectroscopic tools. From optical measurements, we observed that due to the phase transition from Cu₂S nanopyramids to $Cu_{1.8}S$ platelets, there is a significant increase of localized surface plasmon absorption in the NIR region due to increase in copper deficiency in the Cu_{1.8}S crystal structure. For gaining better insight into the electrical properties of the nanostructures, we measured the photocurrent response of the Cu₂S nanopyramids electrochemically. We observed that a positive photocurrent response arose from Cu₂S nanopyramids under electrochemical conditions. We studied the electrical response of the Cu_{1.8}S platelets showing a sharp metallic conductance due to the accumulation of free charge carriers.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to thank Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras for solid state UV-Vis-NIR spectroscopic measurements. AJ, TA, PB, BM, and SB acknowledge financial support from IIT Madras. DS and JG thanks UGC, Govt. of India for their research fellowships. TP thanks the Department of Science and Technology, Govt. of India for supporting his research through the grant, SR/ NM/TP-92/2016(G).

References

- 1 P. Lukashev, W. R. L. Lambrecht, T. Kotani and M. Van Schilfgaarde, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 1–14.
- 2 C. Coughlan, M. Ibáñez, O. Dobrozhan, A. Singh, A. Cabot and K. M. Ryan, *Chem. Rev.*, 2017, **117**, 5865–6109.
- 3 Z. Guan, A. Tang, P. Lv, Z. Liu, X. Li, Z. Tan, T. Hayat, A. Alsaedi, C. Yang and F. Teng, *Adv. Opt. Mater.*, 2018, 6, 1–13.
- 4 K. E. Knowles, K. H. Hartstein, T. B. Kilburn, A. Marchioro, H. D. Nelson, P. J. Whitham and D. R. Gamelin, *Chem. Rev.*, 2016, **116**, 10820–10851.
- 5 P. Roy and S. K. Srivastava, *CrystEngComm*, 2015, **17**, 7801–7815.
- 6 G. Gariano, V. Lesnyak, R. Brescia, G. Bertoni, Z. Dang, R. Gaspari, L. De Trizio and L. Manna, *J. Am. Chem. Soc.*, 2017, **139**, 9583–9590.
- 7 C. M. Hessel, V. P. Pattani, M. Rasch, M. G. Panthani, B. Koo, J. W. Tunnell and B. A. Korgel, *Nano Lett.*, 2011, 11, 2560–2566.
- 8 W. Li, R. Zamani, P. Rivera Gil, B. Pelaz, M. Ibáñez, D. Cadavid, A. Shavel, R. A. Alvarez-Puebla, W. J. Parak, J. Arbiol and A. Cabot, *J. Am. Chem. Soc.*, 2013, 135, 7098– 7101.
- 9 Y. Sun, L. Xi, J. Yang, L. Wu, X. Shi, L. Chen, J. Snyder, J. Yang and W. Zhang, *J. Mater. Chem. A*, 2017, 5, 5098–5105.
- 10 Y. Wu, C. Wadia, W. Ma, B. Sadtler, A. P. Alivisatos, M. Science, V. Di and L. Berkeley, *Nano Lett.*, 2008, 8, 2551– 2555.
- 11 S. C. Riha, D. C. Johnson and A. L. Prieto, *J. Am. Chem. Soc.*, 2011, **133**, 1383–1390.
- 12 X. Yu, C. Cao, H. Zhu, Q. Li, C. Liu and Q. Gong, *Adv. Funct. Mater.*, 2007, **17**, 1397–1401.
- 13 Z. H. Ge, B. P. Zhang, Y. X. Chen, Z. X. Yu, Y. Liu and J. F. Li, *Chem. Commun.*, 2011, **47**, 12697–12699.
- 14 (a) W. Fu, M. Liu, F. Xue, X. Wang, Z. Diao and L. Guo, *RSC Adv.*, 2016, 6, 80361–80367; (b) Y. Yu, L. Pan, M. Son, M. T. Mayer and W. Zhang, *ACS Energy Lett.*, 2018, 3, 760–766.
- 15 G. Ku, M. Zhou, S. Song, Q. Huang, J. Hazle and C. Li, *ACS Nano*, 2012, **6**, 7489–7496.
- 16 H. Park, J. Kwon, H. Choi, D. Shin, T. Song, X. Wen and D. Lou, ACS Nano, 2018, 12, 2827–2837.
- 17 (a) X. Zhang, G. Wang, A. Gu, Y. Wei and B. Fang, *Chem. Commun.*, 2008, **45**, 5945–5947; (b) P. Sahatiya, A. Kadu, H. Gupta, P. T. Gomathi and S. Badhulika, *ACS Appl. Mater. Interfaces*, 2018, **10**, 9048–9059.

- 18 (a) M. Zhou, S. Song, J. Zhao, M. Tian and C. Li, *J. Mater. Chem. B*, 2015, 3, 8939–8948; (b) Z. Zhang, H. Suo, X. Zhao, D. Sun, L. Fan and C. Guo, *ACS Appl. Mater. Interfaces*, 2018, 10, 14570–14576.
- 19 S. Goel, F. Chen and W. Cai, Small, 2014, 10, 631-645.
- 20 I. Grozdanov and M. Najdoski, J. Solid State Chem., 1995, 114, 469–475.
- 21 J. M. Luther, P. K. Jain, T. Ewers and A. P. Alivisatos, *Nat. Mater.*, 2011, **10**, 361–366.
- 22 M. Liu, X. Xue, C. Ghosh, X. Liu, Y. Liu, E. P. Furlani, M. T. Swihart and P. N. Prasad, *Chem. Mater.*, 2015, 27, 2584–2590.
- 23 M. Lotfipour, T. MacHani, D. P. Rossi and K. E. Plass, *Chem. Mater.*, 2011, 23, 3032–3038.
- 24 X. Zhang, Y. Xu, C. Pang, Y. Wang, L. Shen, A. Gupta and N. Bao, *CrystEngComm*, 2018, **20**, 2351–2356.
- 25 M. Shahriar Zaman, G. Bernard Grajeda and E. D. Haberer, *J. Appl. Phys.*, 2014, **115**, 144311.
- 26 H. Chen, M. Song, J. Tang, G. Hu, S. Xu, Z. Guo, N. Li, J. Cui, X. Zhang, X. Chen and L. Wang, ACS Nano, 2016, 10, 1355– 1362.
- 27 L. Liu, B. Zhou, L. Deng, W. Fu, J. Zhang, M. Wu, W. Zhang and B. Zou, *J. Phys. Chem. C*, 2014, **118**, 26964–26972.
- 28 P. Leidinger, R. Popescu, D. Gerthsen, H. Lünsdorf and C. Feldmann, *Nanoscale*, 2011, 3, 2544–2551.
- 29 (a) Q. Lu, F. Gao and D. Zhao, *Nano Lett.*, 2002, 2, 725–728; (b)
 F. Wang, Q. Li, L. Lin, H. Peng, Z. Liu and D. Xu, *J. Am. Chem. Soc.*, 2015, 137, 12006–12012; (c) S. Han, C. Gu, S. Zhao, S. Xu, M. Gong, Z. Li and S. Yu, *J. Am. Chem. Soc.*, 2016, 138, 12913–12919; (d) X. Chen, J. Yang, T. Wu, L. Li, W. Luo, W. Jiang and L. Wang, *Nanoscale*, 2018, 10, 15130–15163.
- 30 I. Ortiz De Solorzano, M. Prieto, G. Mendoza, T. Alejo, S. Irusta, V. Sebastian and M. Arruebo, ACS Appl. Mater. Interfaces, 2016, 8, 21545–21554.
- 31 S. Sun, S. Wang, D. Deng and Z. Yang, *New J. Chem.*, 2013, 37, 3679–3684.
- 32 Y. Wang, X. Ai, D. Miller, P. Rice, T. Topuria, L. Krupp, A. Kellock and Q. Song, *CrystEngComm*, 2012, 14, 7560–7562.
- 33 L. Liu, H. Zhong, Z. Bai, T. Zhang, W. Fu, L. Shi, H. Xie, L. Deng and B. Zou, *Chem. Mater.*, 2013, 25, 4828–4834.
- 34 F. Zhang and S. S. Wong, Chem. Mater., 2009, 21, 4541-4554.
- 35 M. Ye, X. Wen, N. Zhang, W. Guo, X. Liu and C. Lin, *J. Mater. Chem. A*, 2015, **3**, 9595–9600.
- 36 W. Jiang, F. Wu, Y. Jiang, M. Sun, K. Zhang, Y. Xia, D. Wang and A. Xie, *Nanoscale*, 2017, **9**, 10961–10965.
- 37 P. Kar, S. Farsinezhad, X. Zhang and K. Shankar, *Nanoscale*, 2014, 6, 14305–14318.
- 38 J. Gao, Q. Li, H. Zhao, L. Li, C. Liu, Q. Gong and L. Qi, *Chem. Mater.*, 2008, **20**, 6263–6269.
- 39 M. Xu, H. Wu, P. Da, D. Zhao and G. Zheng, *Nanoscale*, 2012, 4, 1794.
- 40 L. Reijnen, B. Meester, F. De Lange, J. Schoonman and A. Goossens, *Chem. Mater.*, 2005, **17**, 2724–2728.
- 41 A. Itzhak, E. Teblum, O. Girshevitz, S. Okashy, Y. Turkulets,
 L. Burlaka, G. Cohen-taguri, E. S. Avraham, M. Noked,
 I. Shalish and G. D. Nessim, *Chem. Mater.*, 2018, 30, 2379–2388.

Paper

- 42 A. Li, Q. Luo, S. Park and R. G. Cooks, *Angew. Chem., Int. Ed.*, 2014, 53, 3147–3150.
- 43 D. Sarkar, M. K. Mahitha, A. Som, A. Li, M. Wleklinski, R. G. Cooks and T. Pradeep, *Adv. Mater.*, 2016, 28, 2223– 2228.
- 44 D. Sarkar, R. Singh, A. Som, C. K. Manju, M. A. Ganayee, R. Adhikari and T. Pradeep, *J. Phys. Chem. C*, 2018, 122, 17777–17783.
- 45 D. Sarkar, A. Mahapatra, A. Som, R. Kumar, A. Nagar, A. Baidya and T. Pradeep, *Adv. Mater. Interfaces*, 2018, 5, 1800667.
- 46 A. Li, Z. Baird, S. Bag, D. Sarkar, A. Prabhath, T. Pradeep and R. G. Cooks, *Angew. Chem., Int. Ed.*, 2014, **53**, 12528–12531.
- 47 A. Schmidt, M. Karas and T. Du, *J. Am. Soc. Mass Spectrom.*, 2003, **0305**, 492–500.
- 48 B. Meyer, Chem. Rev., 1976, 76, 367-388.
- 49 T. P. Martin, J. Chem. Phys., 1984, 81, 4426-4432.

- 50 (a) Q. Zhang, Z. Shi, K. Yin, H. Dong, F. Xu, X. Peng, K. Yu,
 H. Zhang, C. Chen, I. Valov, H. Zheng and L. Sun, *Nano Lett.*, 2018, 18, 5070–5077; (b) X. Liu, M. T. Mayer and
 D. Wang, *Angew. Chem., Int. Ed.*, 2010, 49, 3165–3168.
- 51 G. Will, E. Hinze and A. R. M. Abdelrahman, *Eur. J. Mineral.*, 2002, **14**, 591–598.
- 52 S. C. Riha, R. D. Schaller, D. J. Gosztola, G. P. Wiederrecht and A. B. F. Martinson, *J. Phys. Chem. Lett.*, 2014, 5, 4055– 4061.
- 53 P. Lukashev, W. R. L. Lambrecht, T. Kotani and M. van Schilfgaarde, *Phys. Rev. B*, 2007, **76**, 195202.
- 54 Y. Zhao, H. Pan, Y. Lou, X. Qiu, J. Zhu and C. Burda, *J. Am. Chem. Soc.*, 2009, **131**, 4253-4261.
- 55 Y. Liu, M. Liu and M. T. Swihart, J. Phys. Chem. C, 2017, 121, 13435–13447.