Electronic Supplementary Information

Onion slice shaped assembled ZnS quantum wires

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Experimental

Materials:
Zinc nitrate [Zn(NO₃)₂·6H₂O], Potassium ethyl xanthogenate [C₂H₅OCS₂K], Decanoic acid [C₁₀H₁₉CO₂H], Cadmium nitrate [Cd(NO₃)₂], Bismuth nitrate [Bi(NO₃)₃], Copper nitrate [Cu(NO₃)₂], methanol and deionized water. All the chemicals were purchased from s.d.Fine chem., India and Sigma Aldrich, USA, and were used without further purification.

Synthesis:
General synthesis of ZnS dot and wire:
In a typical synthetic procedure, aqueous solution of 1.68 mmol (0.5 g) of zinc nitrate was added dropwise to the aqueous saturated ammonium carbonate solution to make a clear solution of 10 ml zinc ammonium carbonate complex solution. Then, in a hot (~60°C) biphasic mixture of water (20 ml) and decanoic acid (33.48 mmol, 5.76 g to 11.6 mmol, 2 g), the prepared zinc ammonium carbonate complex solution was added drop wise with constant stirring which resulted in a homogeneous and transparent solution with the effervescence of carbon dioxide and ammonia. Then, 10 ml aqueous solution of xanthate (potassium ethyl xanthogenate, 1.62 mmol, 0.26 g to 3.56 mmol, 0.57 g, Zn²⁺:Xanthate = 1:1 to 1:2.5) was added to the above solution with constant stirring. After the addition of xanthate, the resulted yellowish solution remains transparent. Immediately after the addition of xanthate, 33 ml of the resulting mixture was transferred into a teflon-lined stainless autoclave (40 ml capacity). The autoclave was sealed and transferred to a pre-heated oven and hydrothermally treated for 30 min to 2 h at 110-180°C. The system was then cooled to ambient temperature naturally. The final product was collected and washed with methanol for several times and air-dried.

Different synthesis condition of the evolution of different shapes:
  a) Variation of zinc to decanoic acid ratio (Zn:decanoic acid= 1:5-20) with Zn: xanthate =1:1 at 150°C for 2 h.
  
In every case bent nanowires assembly with onion shaped was observed.

  b) Variation of reaction time 30 min to 4 h with Zn: xanthate:decanoic acid =1:1:10 at 150°C

A milky white suspension was observed after 30 min, showing the formation of ZnS spherical particles (TEM image). When the reaction time was prolong to >45 min, a copious amount of white precipitate were generated at the bottom of autoclave and TEM image showed the presence of mixture of ZnS spherical and bent nanowire.

  c) Variation of reaction temperature form 110-200°C with Zn: xanthate:decanoic acid =1:1:10 for 2 h

In the temperature range 110-160°C bent nanowires assembly with onion shaped was observed and with the increase in the temperature formation of nanowire become more crystalline. At 180°C, mixture of assembled wires and clustered spherical particles were obtained and at 200°C, triangular particles were obtained.
d) Variation of xanthate concentration (Zn\(^{2+}\) : Xanthate= 1:1 to 1:2.4):
Spherical ZnS particles were obtained.

**Experimental procedure for the synthesis of Cu\(^{2+}\) dopped ZnS:**
In the typical synthetic procedure for the synthesis of Cu\(^{2+}\) doped ZnS nanoparticle, mixed aqueous solution of cuper nitrate (1 to 10 mole% with respect to zinc nitrate ) and zinc nitrate was drop wise added to the water solution saturated ammonium carbonate to prepare a clear solution of zinc ammonium carbonate complex. Then, in a hot biphasic mixture of water and decanoic acid, the zinc and copper carbonate complex solution was added drop wise with constant stirring. This results in a homogeneous transparent solution with the effervescence of carbon dioxide and ammonia. Then, aqueous solution of xanthate (Zn: xanthate=1:1) was added to the above solution with constant stirring. The mixed solution was transferred into a teflon-lined stainless autoclave (40 ml capacity). The autoclave was sealed and transferred to a pre heated oven and heated for 2 h at 110-180°C. The system was then cooled to ambient temperature naturally. The final product was collected and washed with methanol for several times and air-dried.

**Experimental procedure for the synthesis other metal sulphides:**

**Synthesis of CdS :**
In the typical synthesis of CdS, water solution of cadmium nitrate (1.88 mmol, 0.5 gm) was added to a concentrated solution of ammonium hydroxide to prepare a clear solution. After that, all the procedures are identical as for the synthesis of ZnS nano wire.

**Synthesis of Bi\(_2\)S\(_3\) :**
In case of Bi\(_2\)S\(_3\), weighted amount of bismuth nitrate (1.03 mmol, 0.5 g) was added to a water solution of small amount of EDTA to reduce the slow decomposition of bismuth nitrate in water. Then the clear solution was added to a saturated solution of ammonium carbonate. After that, all the procedures are identical as for the synthesis of ZnS nano wire.

**Characterizations:**
Powder X-ray diffraction patterns were collected in the range of 20–80° with a Philips X’pert X-ray powder diffractometer using Cu K\(\alpha\) (\(\lambda = 1.54178\) Å) radiation.

Transmission electronic microscope (TEM) images were collected using a JEOL JEM 2100 microscope operated at 200 kV. Samples were prepared by mounting dichloromethane dispersed samples on lacey carbon formvar coated Cu grids.

The FT-IR spectroscopic measurements were carried out using a PerkinElmer GX spectrophotometer. The spectra were recorded in the range 400–4000 cm\(^{-1}\) as KBr pellet.

UV-vis absorption spectra and photoluminescencce spectra of toluene dispersed nanoparticles were recorded with a Shimadzu UV-2550 spectrophotometer and Fluorolog, Horiba Jobin Yvon fluorometer respectively.
Supporting Figures:

**Fig. S1** A large scale TEM image of the synthesized Onion slice shaped assembled ZnS quantum wires.

**Fig. S2** EDX result of the synthesized ZnS wires.

The EDX spectrum suggests that the wires are composed of zinc and sulphur atoms. The ratio of Zn : S is 1:1, confirms the composition of the synthesized wires as ZnS.
Fig. S3  FT-IR spectra decanoic acid (DA) and decanoic acid stabilized ZnS (DA-ZnS).

A series of sharp bands in the region 2700-3100 cm\(^{-1}\) attributed to the symmetric and asymmetric stretching of methylene and terminal methyl groups.\(^1\) The broad band ~3500 cm\(^{-1}\) corresponds to the OH group of adsorbed water on metal centres. Moreover, there was a decrease in the intensity of a strong band around 1712 cm\(^{-1}\) of localized carbonyl group in decanoic acid stabilized ZnS wire, and concurrent appearance of symmetric and asymmetric stretching vibrations of the carboxylate group (COO\(^-\)) around 1549 cm\(^{-1}\) and 1407 cm\(^{-1}\), with a splitting of \(\Delta \gamma = \gamma_{as} - \gamma_{s} = 142\) cm\(^{-1}\).\(^1\) It suggested that the chemisorbed carboxyl group of decanoic acid is co-ordinated to the surface of the synthesized wires in a bidentate fashion which resulted in high colloidal dispersion of the synthesized ZnS wires in nonpolar solvent.

Fig. S4  Photoluminescence spectrum of the ZnS wires synthesized at 150 °C for 2 h using Zn : xanthate = 1 : 1.

Multi peak Gaussian fitting gives three Gaussian bands at 360 nm, 391 nm and 447 nm. Perfect fitting of the Gaussian curve with experimental curve, confirms the presence of 3 peaks in the PL spectrum. The peaks at 360 nm and 391 nm are assigned to corresponding shallow-donor and acceptor emission peaks.\(^8c,14\) The peak at 447 nm assigned to the surface state emission. Interestingly, area of the surface state emission is much higher than the others, most probably due to the low diameter of the synthesized wires, which leads to the larger increase in surface to volume ratio as well as surface state.
Fig. S5  FTIR spectra of Potassium ethyl-xanthate and ethyl-xanthate xanthate stabilized ZnS particles.

The FTIR spectrum of potassium ethyl-xanthate gave peaks at 1143 cm\(^{-1}\) for C-S bond and at 1055 cm\(^{-1}\) for C-O bond. In case of ZnS particles stabilized by ethyl-xanthate C-S peak shifted to 1212 cm\(^{-1}\) and C-O peak shifted to 1035 cm\(^{-1}\). Thermodynamic stability and the stereochemistry of the metal xanthates may be contributory factors in determining the shifts.\(^2\) The binding force of XA with zinc is much higher than that of DA. As a result when we have used excess amount of XA (1:2), it resulted in the low temperature stable less polar zincblend phase (Cubic) with spherical particle. During the synthesis, half of XA (1 equivalent) utilised to form zinc xanthate and finally resulted in ZnS and the excess XA with soft head group (-CS\(_2\)) acts as stabilizer and co-ordinates with soft zinc (d10) strongly with ZnS nuclei and resulted in the less polar zinc blend structure. In the FT-IR of these particles, the corresponding peak of DA was not observed, only the peak of bonded (surface modified) XA was indentified.

Figure S6  TEM images of very small spherical ZnS nanoparticles cluster synthesized at 150°C for 30 min (a), mixed spherical particles and bend wires synthesized at 150°C for 45 min (b), mixed spherical particles and bend wires synthesized at 180°C for 2 h (c), and triangular nanoparticles synthesized at 200°C for 2 h (d).
Fig. S7. X-ray diffraction patterns of synthesized ZnS particles obtained in varying conditions: i) spherical particles and ii) mixture of spherical particles and wires synthesized using Zn: xanthate =1:1 at 150 °C for 30 min and 45 min respectively; iii) triangle shaped ZnS nanoparticles synthesized using Zn: xanthate =1:1 at 200 °C for 2 h; iv) spherical ZnS nanoparticles synthesized using Zn: xanthate =1:2 at 150 °C for 2 h.

Fig. S8. d) TEM and corresponding HR-TEM (inset) image of ZnS spherical nanoparticles synthesized using Zn: xanthate =1:2 at 150 °C for 2 h.
Decanoic acid with hard acid group force to form the more polar \(^3\) kinetically controlled wurtzite phase for easy co-ordination with soft zinc (d10) of ZnS.\(^4\) In confirmation, when the same experiment was repeated in the presence of excess amount of xanthate (Zn: xanthic acid=1:2), it resulted in the low temperature stable less polar zinc-blend phase (Cubic). During the process, xanthic acid (1:1) form zinc xanthate and finally resulted in ZnS. The excess xanthic acid with soft head group (-CS\(_2\)) acts as stabilizer and co-ordinates with soft zinc (d10) of ZnS nuclei and resulted in the less polar zinc blend structure.\(^3\) The formed wurtzite spherical particles contain chemical bipolarity towards c axis, with one side terminated by S and the other by Zn ions. The decanoic acid selectively co-ordinates on the prismatic mixed plains and zinc terminated side of the particle, keeping the sulphur terminated side free. Then the dot (spherical) to wire transition took place by oriented attachment mechanism \(^5,6\) through the open sulphur sides, i.e., through c axis.

**Step wise formation mechanism**
Fig. S10  Schematic representation with corresponding TEM images of the stepwise formation of the synthesized onion slice shaped ZnS quantum wires.

From the above progressive TEM micrographs depicting the progress of reaction, it is evident that in the initial state of synthesis three dimensionally assembled decanoic acid modified very small (~1 nm) wurtzite spherical particles was formed (Step 1). Then, due to the hydrophobic interaction (repulsion) between the aliphatic chains and the polar solvent (water), the aliphatic chains tried to assemble together and concurrently, oriented attachment between the spherical particles through open sulphur end (<001> direction) takes place (Step 2 and Step 3). Both the effect resulted in a circular wire in an onion slice shape (Step 4). During synthesis, outer ring was formed first followed by inner rings (Step 3), most probably due to the reduced crystal strain for outer rings, which increased gradually towards inner circle.

Fig. S11.  Schematic representation of the effect of temperature on shape of the ZnS.

At higher temperature or longer hydrothermal time (200°C for 2 h, 150°C for 8 h), it resulted in cubic triangular nanoparticles due to the phase transformation of the wurtzite to
zinc blend; and during the phase transformation the wires are transformed to triangle. In the atmospheric pressure, the lower Gibbs free energy (10.25 \text{kJ mol}^{-1}) of zinc blend gives greater stability compared to wurtzite structure of bulk ZnS. As the particle size decreases, the surface energy determines the structural stability.\(^7\) In the present case, the meta-stable wurtzite phase of very small (~1 nm) particles/wires is stabilised by the firmly bonded decanoic acid. At higher temperature or longer time, the stabilization effect of decanoic acid reduced due to the increased mobility of the coordinated acid group which resulted in the phase transformation. On phase transformation from wurtzite to zinc blend, the (001) plane of wurtzite converts directly to the (111) plane of zinc blend.\(^8\) Both the Zn and S atoms in wurtzite and sphalerite are four-coordinated, so the phase transformation only requires a partial atomic rearrangement.\(^9\) During atomic re-arrangement the morphology of wire changed to triangle.

**Fig. S12** TEM images of different metal sulfide nanoparticles synthesized using the developed procedure at 150°C for 2 h.
Fig. S13. X-ray diffraction pattern of different metal sulfide nanoparticles synthesized using the developed procedure at 150°C for 2 h.

Fig. S14. UV-Absorption (a) and Photoluminescence (b) spectra of copper doped ZnS wires with varying ratio.

The UV-Vis absorption spectra of Cu-ZnS showed a considerable red shift compared to un-doped ZnS and increased with amount of copper. The results indicate that doping of Cu$^{2+}$ alter the energy states in the quantum confinement region.

The room temperature PL spectra of ZnS-Cu nano wires are broad and asymmetric. It consists of two prominent peaks. The peak position of 1$^{st}$ peak is same in all cases, where as the 2$^{nd}$ peak showed a considerable red shift, which also increased with amount of copper. The 1$^{st}$ peak is responsible for the recombination between the sulphur vacancy related donor and valence band. The concentration of copper does not change the sulphur vacant site. The 2$^{nd}$ peak is responsible for the transition between the conduction band of ZnS and the t$_2$
energy level of excited Cu$^{2+}$ ($d^9$) which situated between the conduction and valence band of ZnS. The reasonable shift occurs with respect to concentration of copper reveals that the copper concentration alters the energy level in the quantum confinement region.

The origin of the emission of Cu$^{2+}$ doped ZnS is from the involvement of Cu d-state which lies between the valence and conducton band of ZnS nano particles and take part in the recombination process. According to the most acceptable proposed mechanism, Cu $t_2$ state involve in the process. The $t_2$ state stay above the valence band and after excitation the valence hole transfer to this $t_2$ state. The emission band observed due to the recombination of the electron in the conduction band and $t_2$ state hole. The type of doped metal ion and their concentration plays a crucial role in luminescence efficiency and position of emission band.8-9

Table S1. Comparison of the optical properties (UV-vis adsorption peak position) synthesized by different synthetic procedures.

<table>
<thead>
<tr>
<th>Synthetic procedure of ZnS wire</th>
<th>Peak position of UV-vis adsorption spectra (nm)</th>
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<tbody>
<tr>
<td>(a) Hydrothermal (present work)</td>
<td>290</td>
</tr>
<tr>
<td>(b) Solvothermal Technique</td>
<td>312</td>
</tr>
<tr>
<td>(c) Low temperature organic solvent based synthesis</td>
<td>300</td>
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<tr>
<td>(d) Tharmolysis of zinc precursor in organic surfactant</td>
<td>300</td>
</tr>
<tr>
<td>(e) pyrolysis of a single-source precursor</td>
<td>310</td>
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<td>(f) CVD</td>
<td>339</td>
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<tr>
<td>(g) Bulk ZnS</td>
<td>340</td>
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References.