Controllable Growth of Semiconductor Heterostructures Mediated by Bifunctional Ag_2S Nanocrystals as Catalyst or Source-Host

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Introduction

- A great deal of research over the past decade has enabled us to get precise control over size and morphology of several single component nanocrystals.
- Fabrication of heterostructures with two or more single crystalline semiconductor components has been a major challenge and yet considerable amount of research has been carried out in this direction as new properties (originating from heterointerfaces) are very likely to generate.
- Till-date two solution based synthetic routes are extensively used for creating nano-heterostructures:
  - Seeded growth method
  - Catalyst-assisted growth method.

Seeded growth

Second material grows on the selective crystallographic facets of the seeds (of first material) and results in heterostructured material.

Difficulties

- Proper lattice mismatch between growing facets of two materials is required .
- Difficulty in controlling the surface structure of the seeds.
- Self-nucleation of the second material.

Catalyst-assisted growth

- This process generally works at an elevated temperature.
- The catalyst particle, in liquid or quasi-liquid state at the reaction temperature dissociates the precursor of the second material and absorbs the species that can be dissolved in it.
- Nano-heterostructure emerges from the supersaturation of the second material maintaining minimum interface energy.

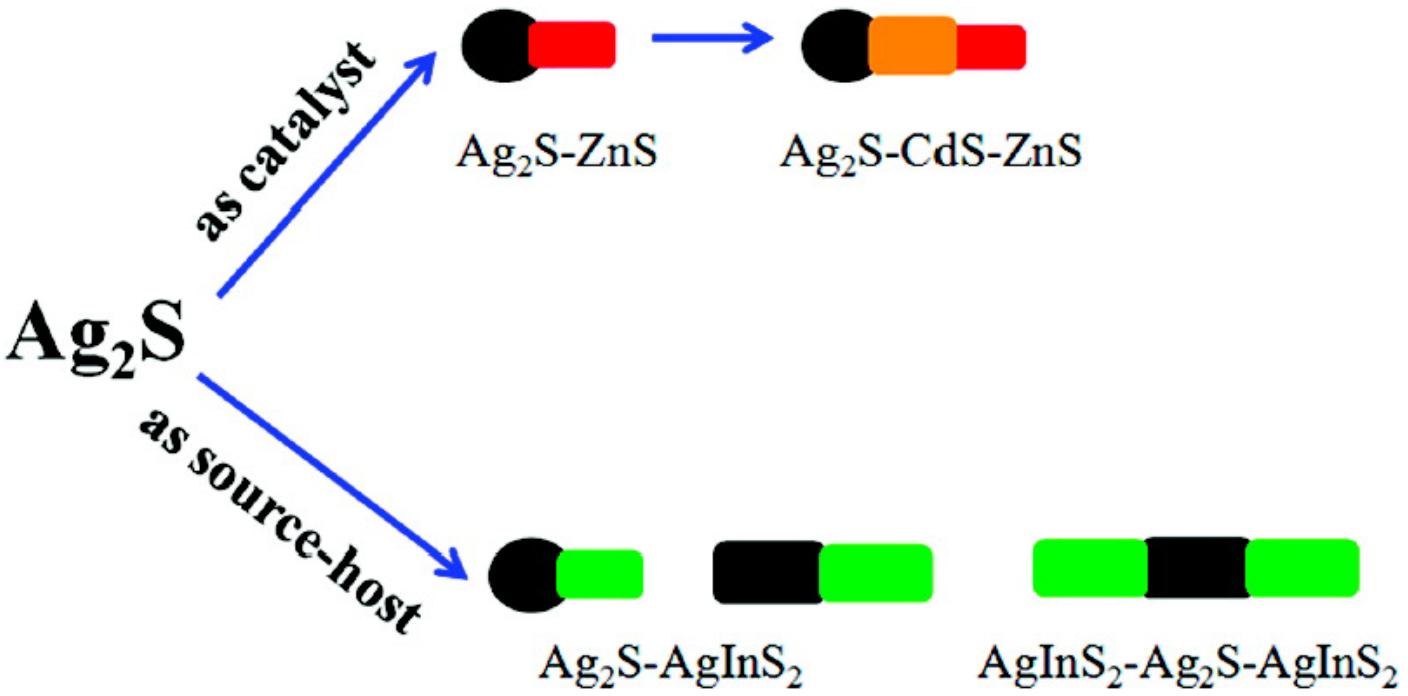
Prerequisites:

- Limited solubility of aim materials in the catalyst.
- No possibility of formation of solid solution between catalyst and the aim material.

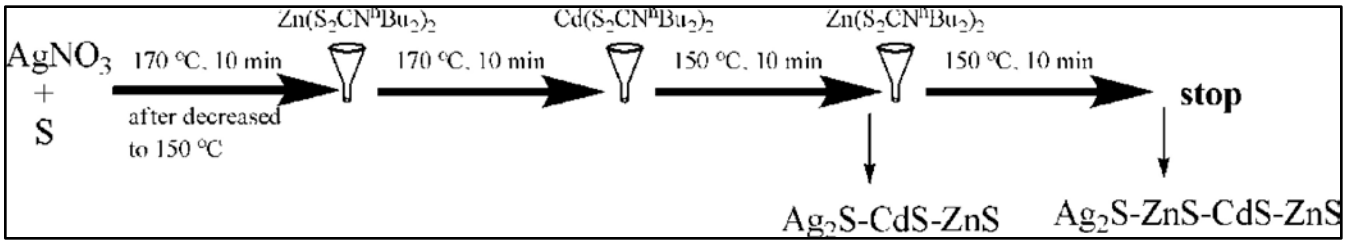
Inputs from recent literature…..

- Recently, Cu_2S-In_2S_3 heterostructure was synthesized using $Cu_{1.94}S$ NCs as catalyst. During this synthesis copper sulphide underwent structural transformation (monoclinic to hexagonal).
- Same heterostructure was previous synthesized using Cu_2S as seed.
- Fabrication of Cu_2S-$CuInS_2$ heterostructure using the same precursors is also reported in the literature using Cu_2S as seed.
- Copper sulphide can act as both seed and catalyst in similar reaction system.
- In^{3+} doesn't dissolve in hexagonal phase but does in monoclinic phase of copper sulphide. Yet no $CuInS_2$ species formed when $Cu_{1.94}S$ was used in the reaction.

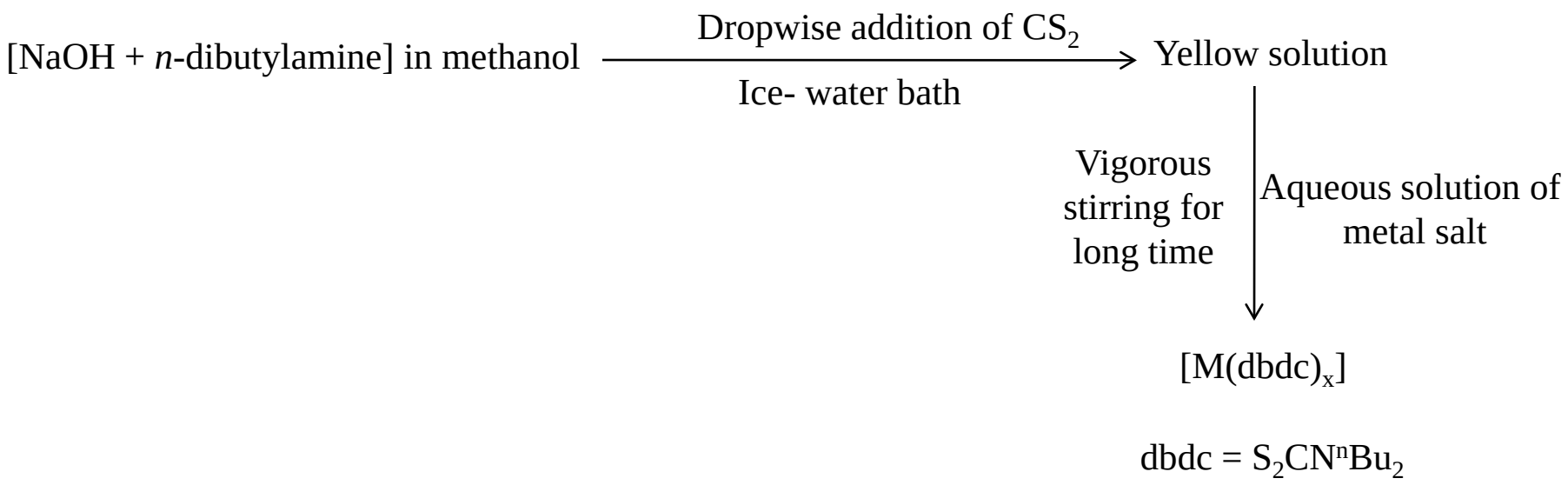
In this paper.....



Reaction scheme



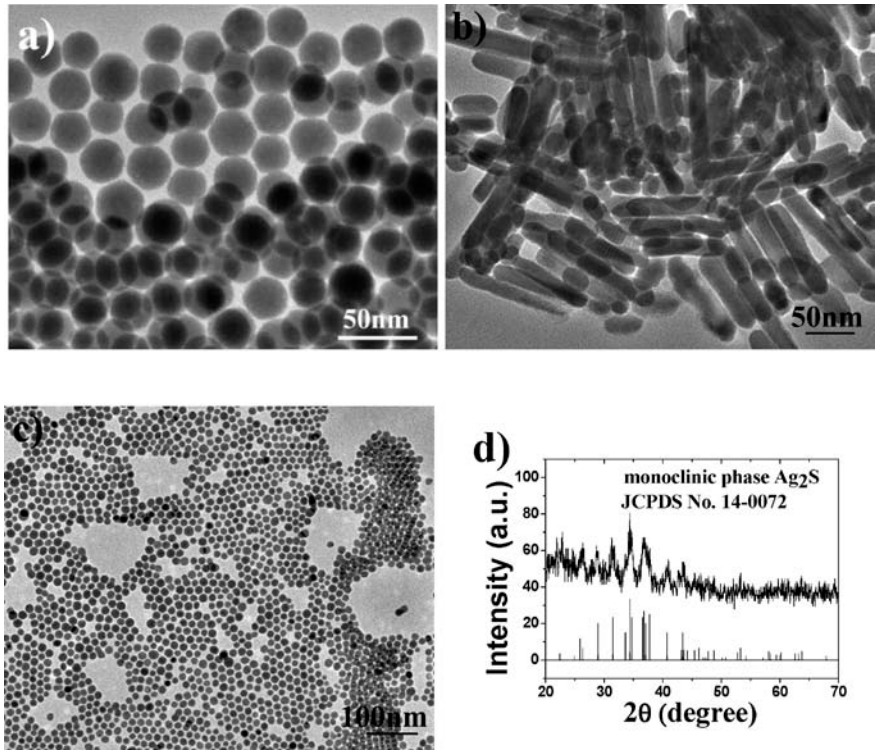
Synthesis of metal sulfide precursor $[M(dbdc)_x]$



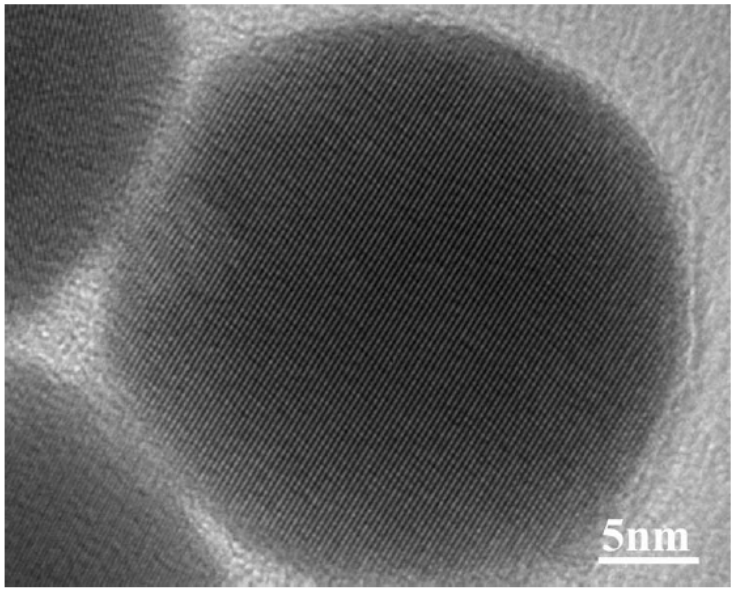
dbdc = $S_2CN^nBu_2$

Synthesis and characterization of Ag_2S nanocrystals

- Ag_2S nanocrystals were synthesized by direct reaction between $AgNO_3$ and S powder in octadecylamine in N_2 atmosphere.



TEM images of Ag_2S samples obtained by the reaction between AgNO3 and S in octadecylamine. (a) 170°C, (b) 130°C, and (c) 85°C. (d) XRD pattern of Ag_2S nanocrystals with standard value for comparison.

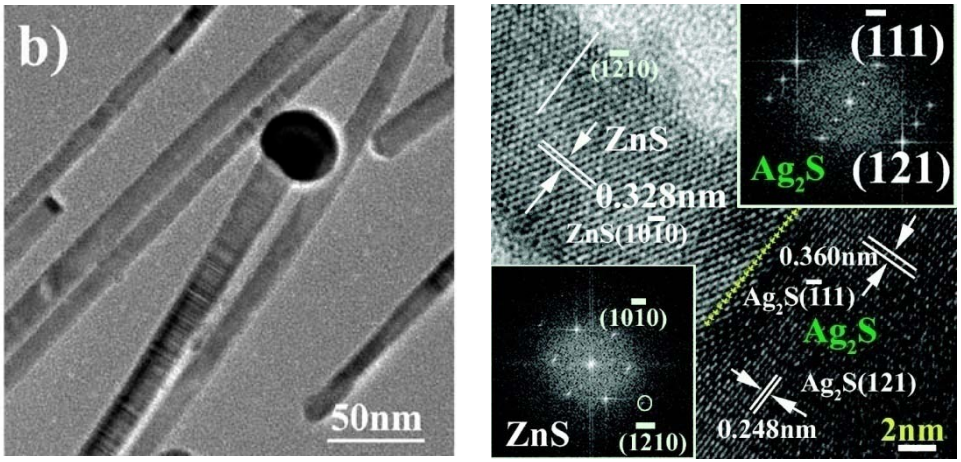


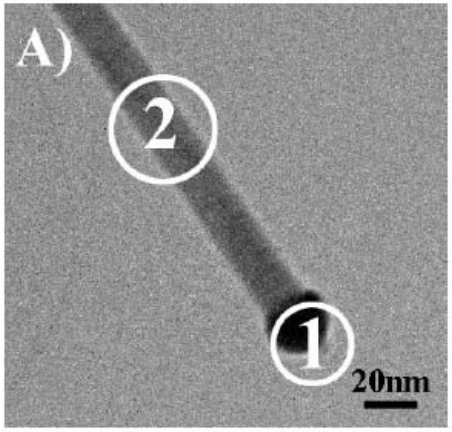
HRTEM image of Ag_2S nanocrystals

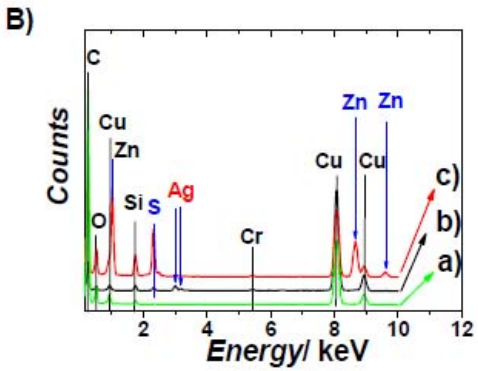
Ag_2S as catalyst

Ag_2S –ZnS NW heterostructure formation

$$AgNO_3 + Zn(dbdc)_2 \xrightarrow[\text{dodecaylamine}]{\Delta} Ag_2S\text{ –ZnS NW}$$

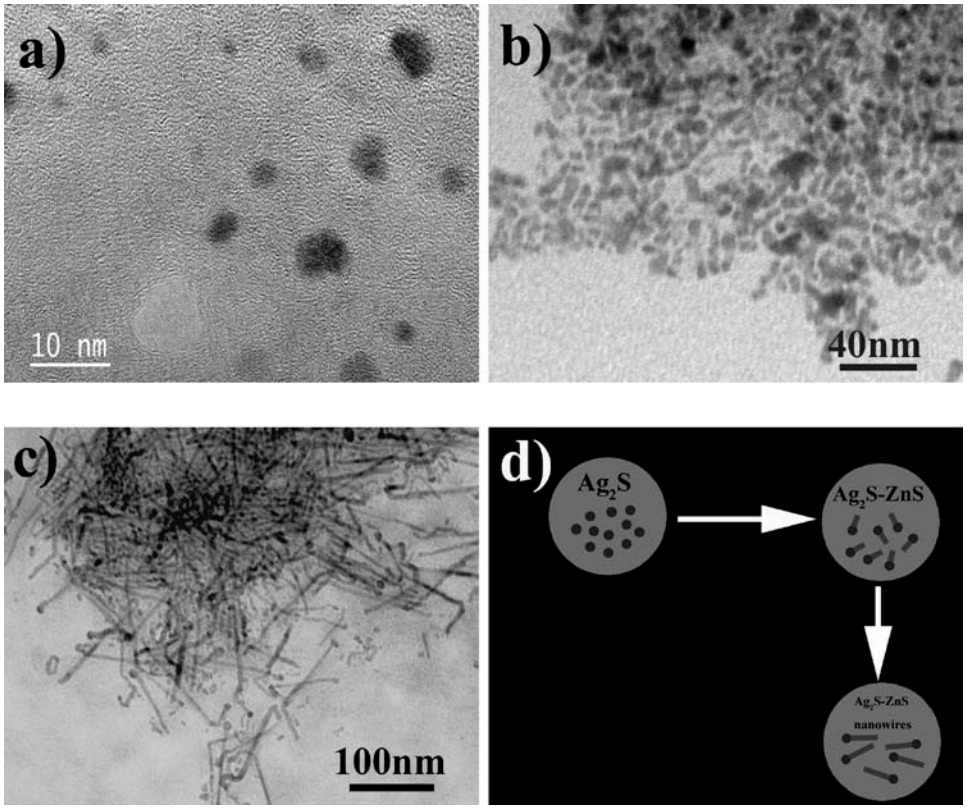




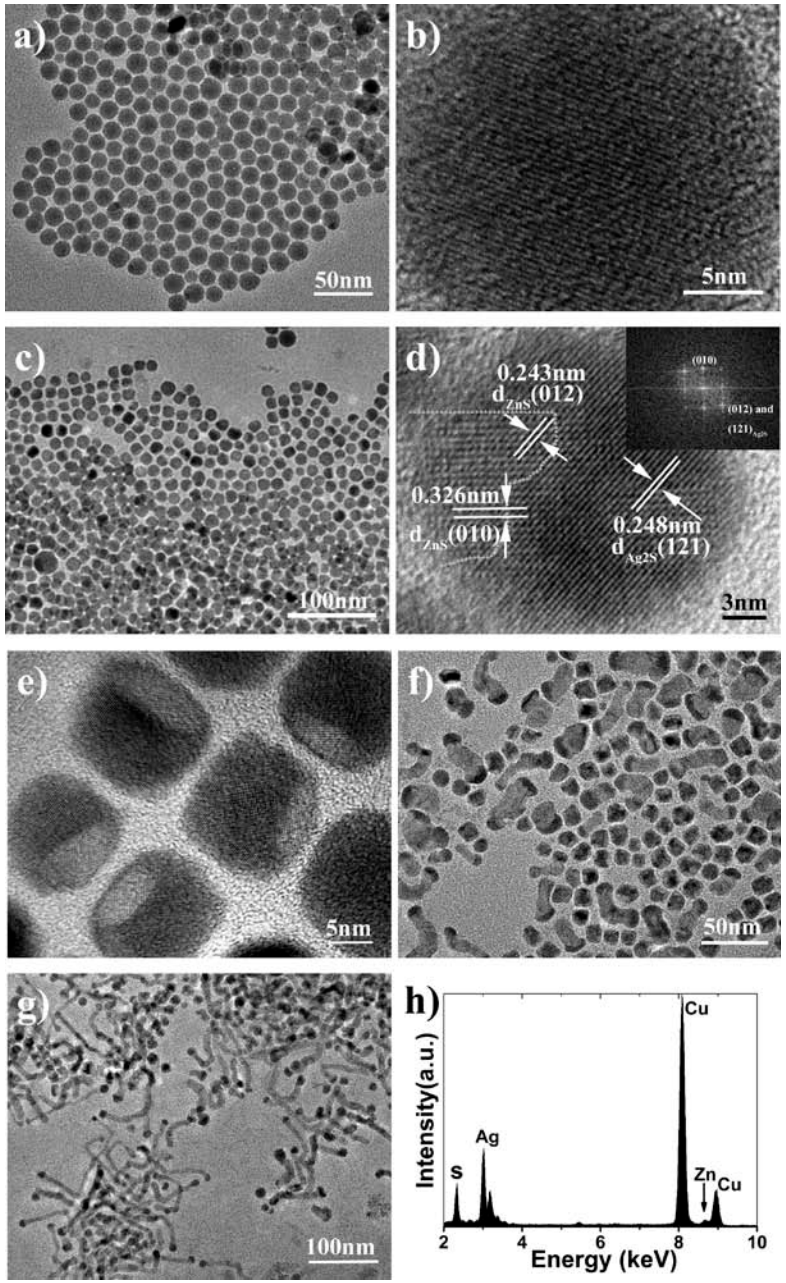


TEM image and EDS spectra of typical synthesized Ag_2S-ZnS NWs heterostructures

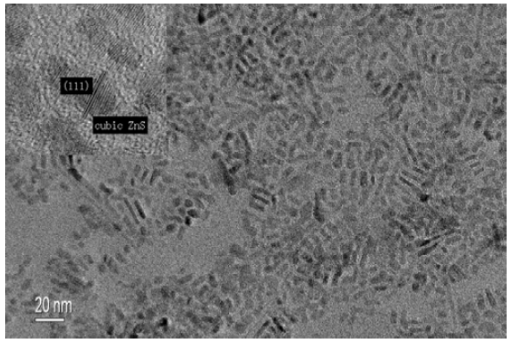
Growth process for the Ag_2S-ZnS NWs



The growth process for the Ag_2S-ZnS NWs heterostructures at various stages as the temperature increases. TEM images of (a) the Ag_2S NCs formed when the system was heated to 130 ºC, (b) the shorter ZnS nanorods grown on the Ag_2S NCs when heated to 150 ºC, (c) the elongated ZnS NWs with Ag_2S NCs “head” were formed when further heated to 170 ºC. (d) A schematic diagram of the heteroepitaxial growth process of ZnS NWs on Ag_2S NCs.



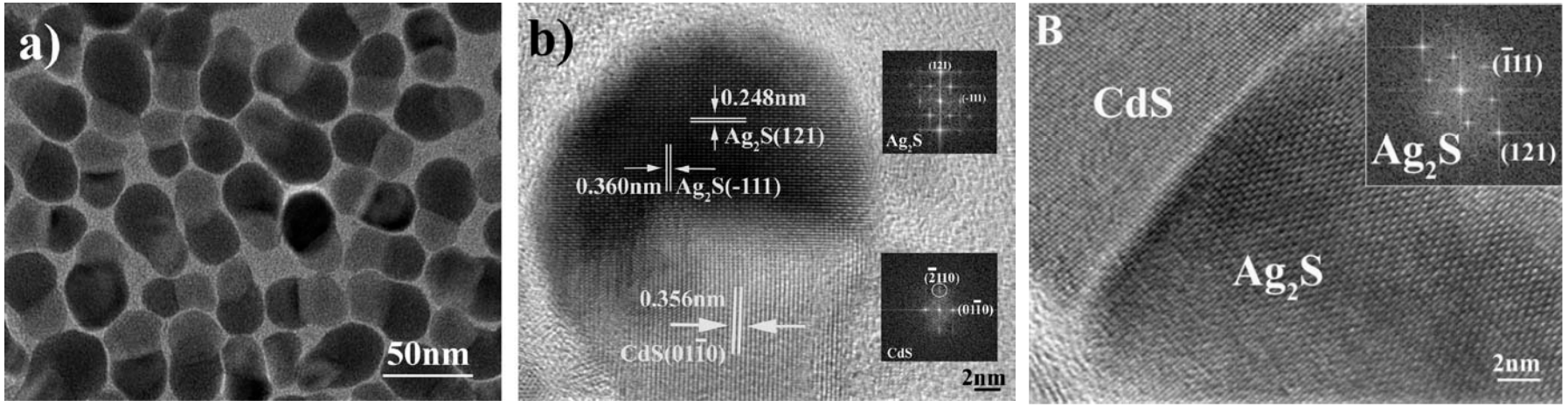
- When Ag_2S was not added cubic ZnS NCs formed instead of hexagonal NWs.



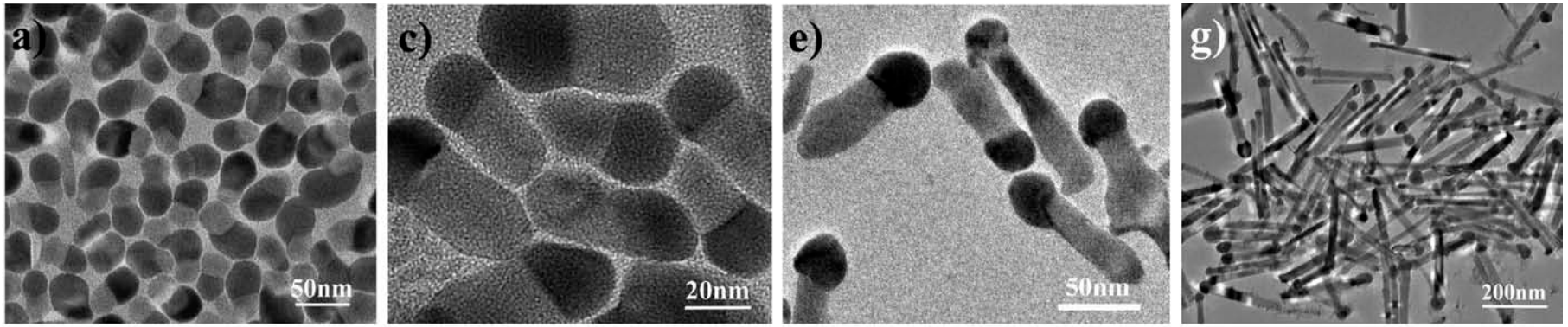
- Use of other metal sulphide like CuS, CdS, Bi_2S_3, In_2S_3 didn't give heterostructure. Instead ZnS NCs formed.
- Ag_2S NCs were prepared separately, added to $Zn(dbdc)_2$ and heated to higher temperature

The growth process of ZnS nanowires on Ag_2S nanocrystals. (a, b) TEM images of samples extracted at 110 ºC, (c−e) at 130 ºC, (f) at 150 ºC, and (g) at 170 ºC. (h) EDS spectrum of the cubic nanoparticles extracted at 130 ºC showing the existence of Ag, Zn, and S.

Ag_2S –CdS NW heterostructure formation

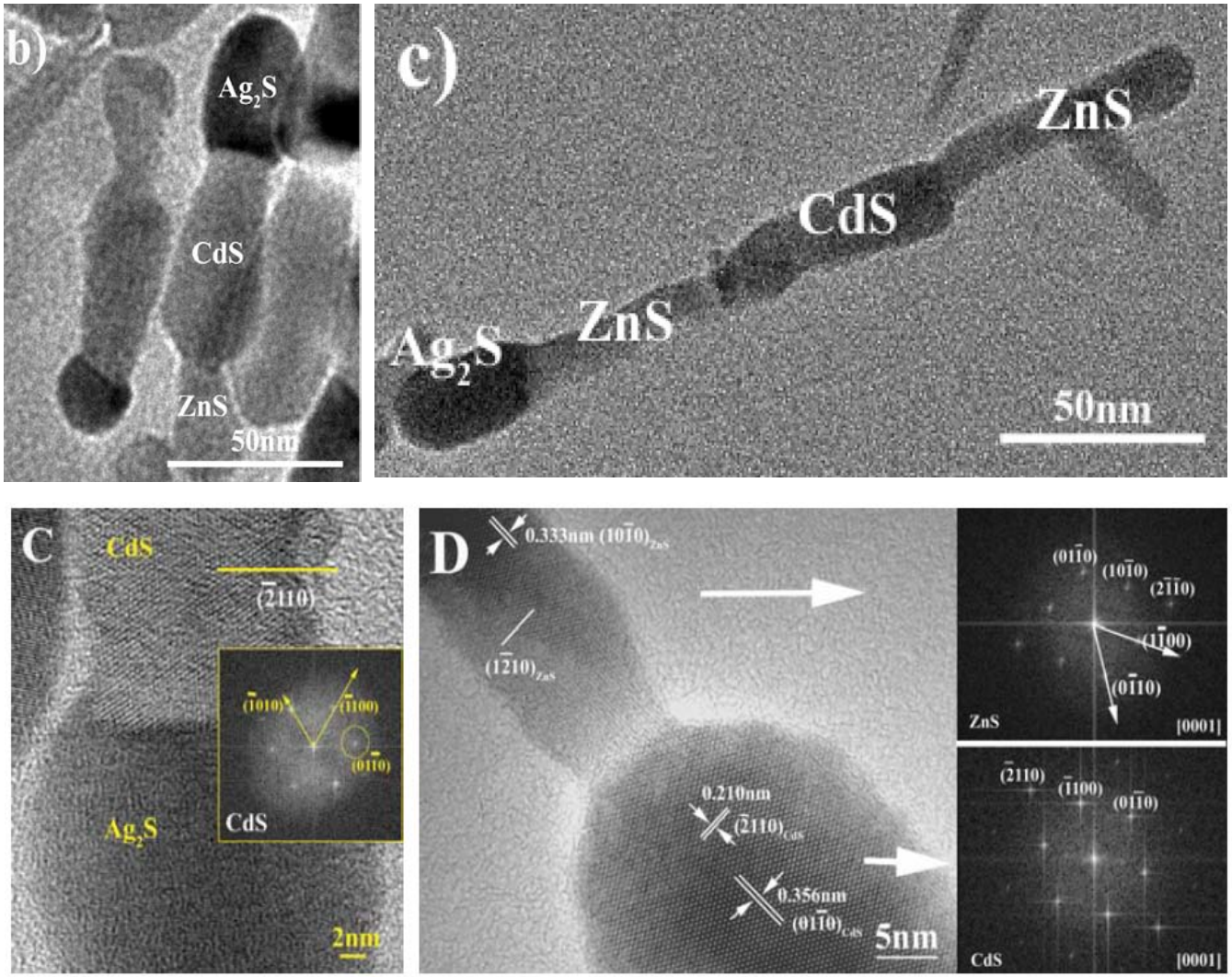


TEM images of Ag_2S-CdS NW.



TEM images of Ag_2S-CdS heterostructures, which show that the length of CdS segment increases with the amount of $Cd(dbdc)_2$

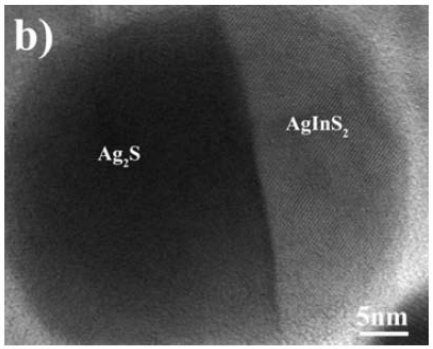
Formation of trimer and tetramer semiconductor heterostructure

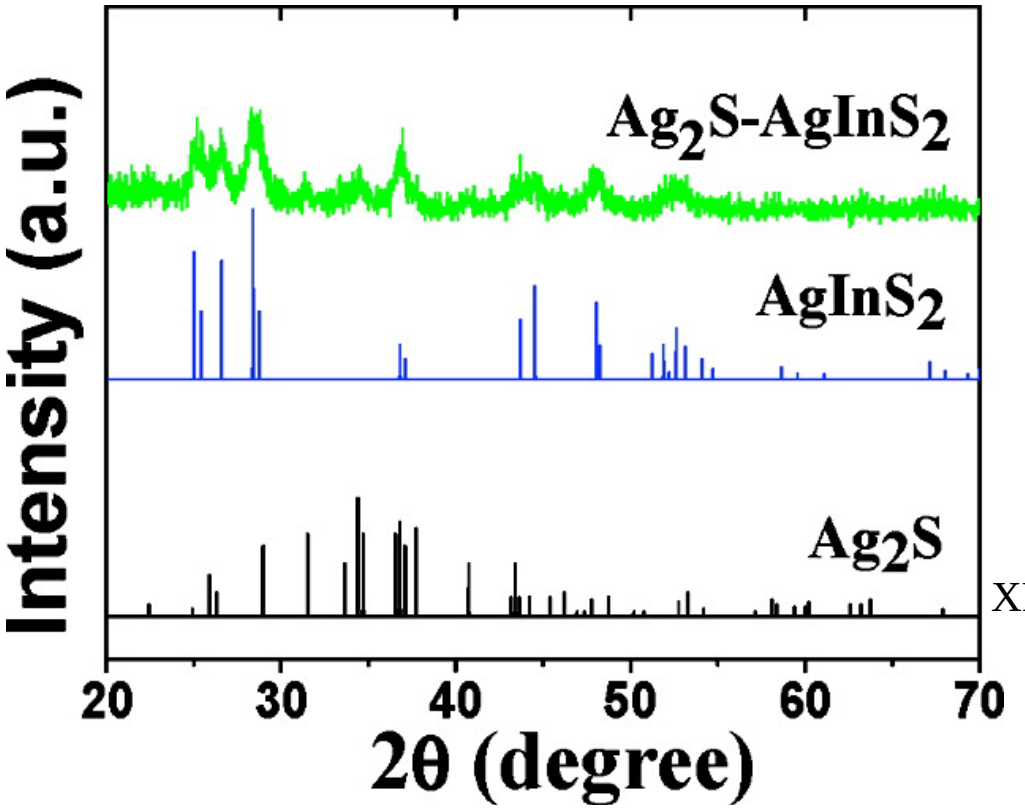


Ag_2S NC as source-host

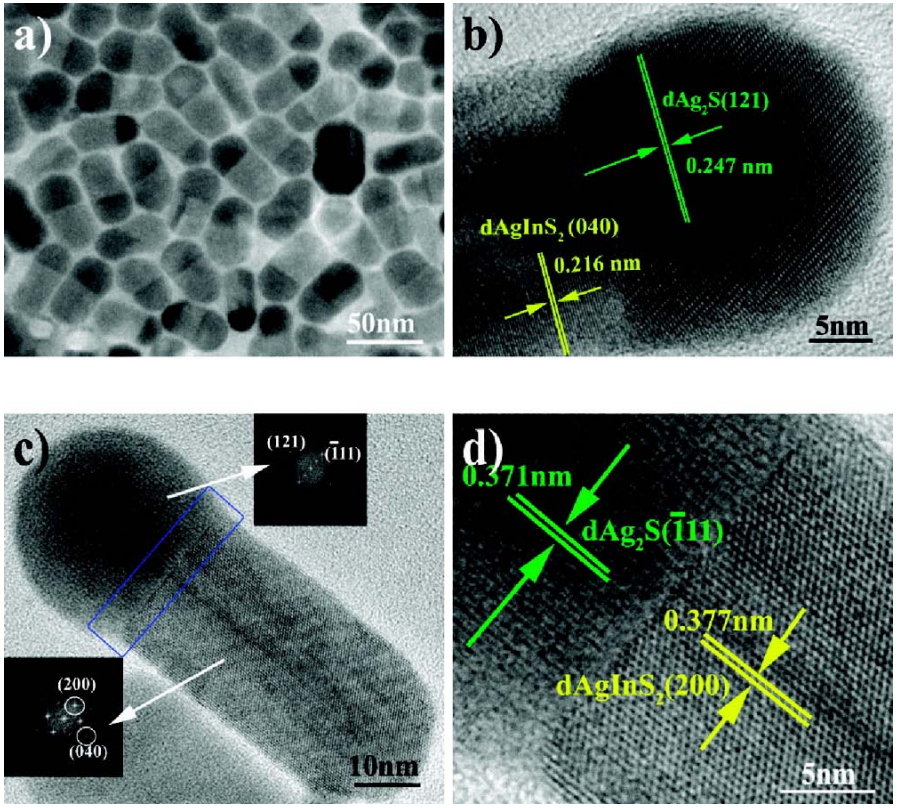
Formation of Ag_2S –$AgInS_2$ *heterostructure*

Ag_2S NCs + $In(dbdc)_3$ $\xrightarrow[10\text{ minute}]{150^{o}\text{ C}}$ Ag_2S –$AgInS_2$ heterostructure

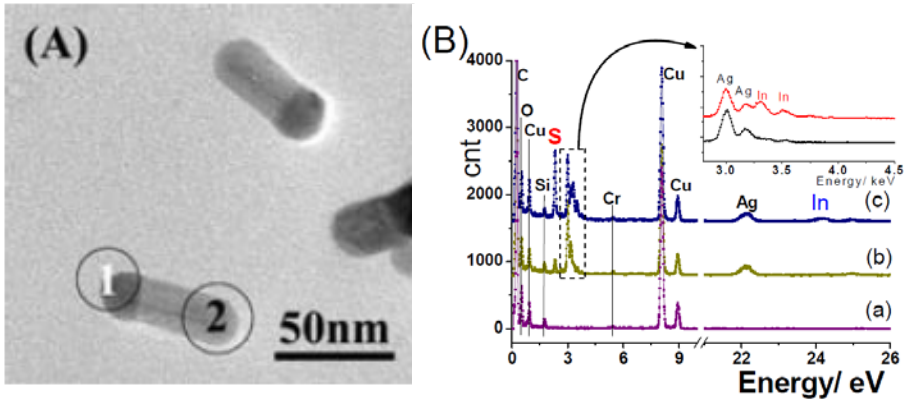




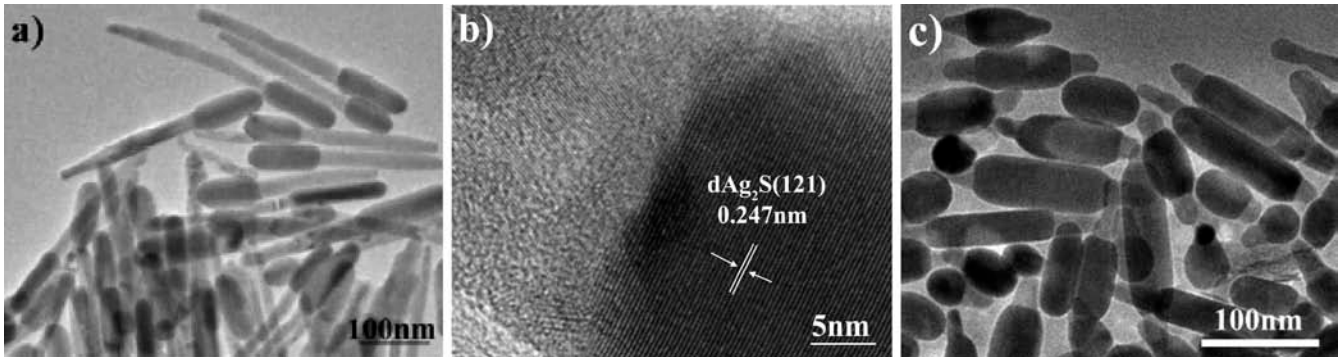
XRD pattern of Ag_2S –$AgInS_2$ heterostructure



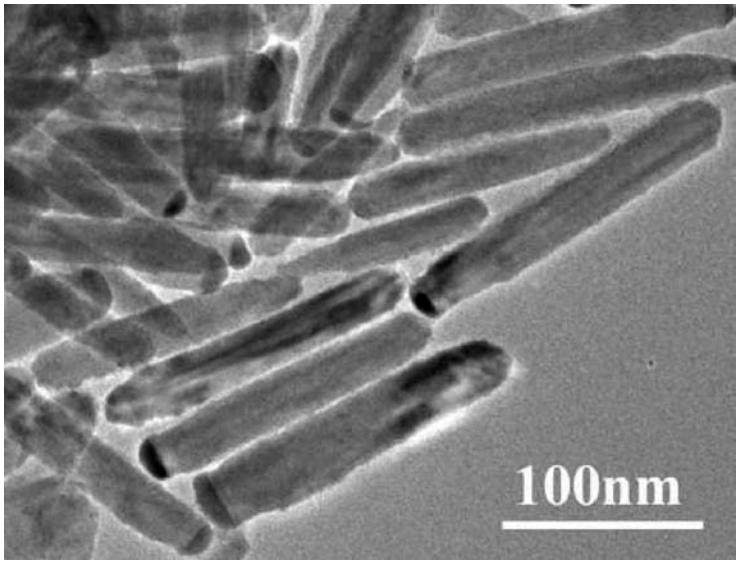
(a) Typical TEM image of the obtained Ag_2S-$AgInS_2$ heterostructure nanocrystals (b) HRTEM image shows the lattice planes of grain boundary. (c) TEM image of a typical Ag_2S-$AgInS_2$ heterostructure nanocrystal. The insets show the corresponding FFT, which further gives the detailed structure of the heterojunction. (d) HRTEM image from the area circled by a blue line in (c).



(A) TEM image of Ag2S-AgInS2 heterostructured nanocrystals. (B) The EDS spectra recorded (a) on the carbon film for comparison, (b) on the area 1 marked by a circle in A, which shows the existence of Ag and S, and (c) on the area 2 marked by a circle in A, which shows the existence of Ag, In, and S. The EDS spectra recorded on several different heterostructure NC show the same element composition.



(a) TEM image of rodlike Ag_2S-$AgInS_2$ heterostructures with rodlike Ag_2S as source-host reacted at (a) 150 ºC and (c) 170 ºC, (b) HRTEM of the interface showing $AgInS_2$ grown on the (121) plane of Ag_2S.



TEM image of the $AgInS_2$ nanorods with a small Ag_2S segment

Conclusions

- Ag_2S nanocrystals can act as a bifunctional semiconductor mediator for the growth of semiconductor heterostructors in solution phase.
- Heterostructure morphology, including the length and diameter, can be tuned by adjusting the reaction conditions.
- Interfacial structure can be stable even if the lattice mismatch is quite large.
- Method developed here can also be used to construct multisegmented heterostructure.

My View…..

- High mobility of Ag^+ in Ag_2S create a lot of cation vacancies and other cations which can dissolve in this cation vacancies should lead to heterostructure.
- In Ag_2Te NWs, Ag_2Te exists in single crystalline monoclinic phase. With suitable metal telluride precursors, different metal telluride heterostructure can be synthesized in solution phase.

Happy Pongal

Thank You