Electronic Supplementary Information (ESI†)

Multidimensional Self-Assembly of Peanut Shaped PbS Nanostructures

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Precursor injection temperature effect on the shape of the PbS nanostructure:

To investigate the precursor injection temperature effect on the shape of the PbS nanostructure we carried out a control reactions by injecting sulphur precursor (within hot HDA) into TOPO and lead nitrate mixture at 160°C. The same amount of precursors was used as used for the PbS peanut synthesis. First, lead precursor was prepared by adding lead nitrate into TOPO at 160°C and mixing the reaction solution for 10 minutes. At the same time we also prepared a sulphur precursor by adding thioura into HDA at 160°C. After then the sulphur precursor was injected into the lead precursor in one shot and annealing was carried out for 60 minutes. The color of the reaction mixture turned to deep red then reddish black.

The SEM images of the resultant PbS nanostructures obtained from the above reaction are shows a different shape from the peanuts (Figure S1).

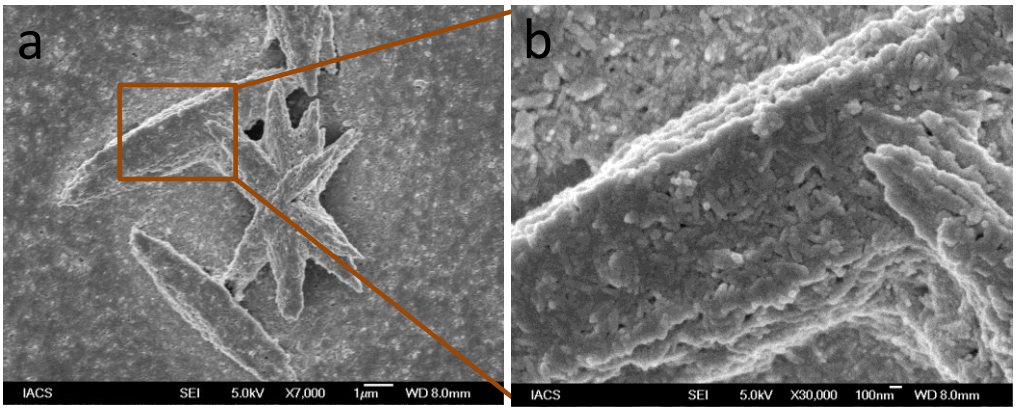

Fig. S1 SEM images of PbS nanostructures obtained by injecting hot (160^{o}C) thiourea (0.035g) containing HDA (0.4g) into a mixture of TOPO (2g) and lead nitrate (0.144g) heated at 160°C with continuous stirring under a nitrogen flow and annealing was carried out for 60 minutes.

Effect of evaporation rate on the assembled structure:

The morphology of drop-casted nanoparticle films was controlled by the evaporation kinetics of the solvent and the particle interactions in the liquid phase. Toluene has a boiling point (B.P.) of 110.6^{o}C, so the evaporation rate of toluene is slow compare to other volatile solvents like chloroform (B.P. = 61.2^{o}C), dichloromethane (B.P. = 40^{o}C) etc. So during the evaporation of a toluene droplet, the nanoparticles get enough time to orient themselves in a definite pattern (Figure S2a) and form an assembled structure for 2.5 mM nanoparticles solution by van der Waals attraction. But for low boiling solvent they cannot orient themselves in that way due to greater evaporation rates (Figure S2b and S2c for chloroform and dichloromethane respectively). Hence for tuning the assembly of nanoparticles in a 2D

way, we have to choose definite concentration of nanoparticles and a suitable assembling solvent as the evaporation rate can affect the dimensionality of the assembled structure.

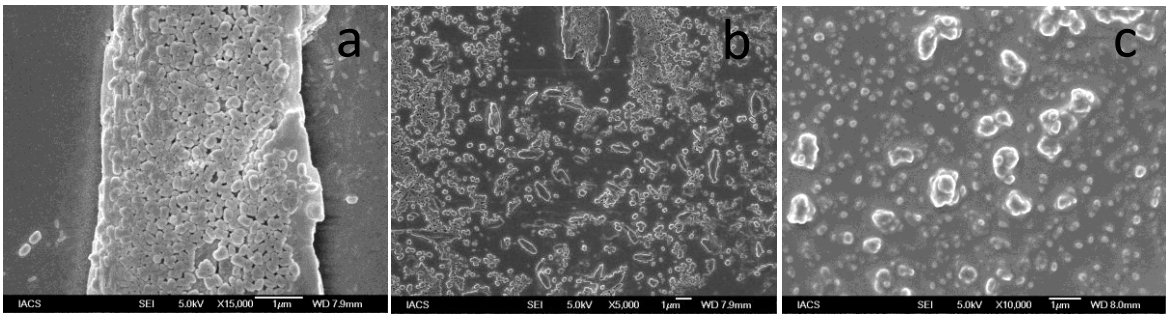

Fig. S2 SEM images of PbS peanuts film formed after solvent evaporation from (a) toluene, (b) chloroform and (c) dichloromethane respectively. The SEM pictures suggest that the nature of assembly and compactness of the peanuts within the film are highly dependent on solvent evaporation rate and the nature of compactness reduces with the faster evaporation rates.

Origin of the additional peaks observed in the XRD patterns:

The XRD pattern of the PbS peanuts shows that major peaks match well with Bragg reflection conditions of the standard face-centred cubic (fcc) structure of bulk PbS (JCPDS #05-0592). However, additional peaks are also observed in the XRD patterns which are not matching with the cubic PbS phase. Notably, the peanut shaped PbS nanostructures have been prepared by using 0.144g lead nitrate, 0.035g thiourea, 2g TOPO and 0.4g HDA at 160°C. Presumably both the ligands, TOPO and HAD, passivate the PbS nanocrystal surfaces and may contribute to the XRD pattern. In order to find the origin of these additional peaks, we have done control experiments using only the ligands. We have taken 2 g TOPO and 0.4 g HDA and heated at 160°C to form a homogeneous solution. This condition resembles the

actual PbS peanut synthesis condition, however, without the reactants for lead sulfide. The solution is then cooled down to room temperature, where it forms solid again. The powder solid of mixed surfactant was taken for XRD measurements. The XRD pattern of this mixed surfactant shows peaks at 23.16°, 24.4°, 25.5°, 26°, 26.9°, 28.5°, 29.8°, 31.6°, 33°, 34.8°, 35.7°, 37°, 38°, 39.4°, 41.14°, 42.12°, 43°, 44.65°, 48°, 53.4°, 55°, 59.9°, 61.6° and 64.2° respectively (Fig. S3). Most of these peaks are weak in intensity. Some of these peaks are overlapped with the XRD peaks of face-centred cubic (fcc) structure of bulk PbS (JCPDS #05-0592). Rest of the peaks are separated from the PbS cubic structures. This control experiment suggests that the additional peaks observed in the XRD patterns of the PbS peanuts are the contributions from the unremoved mixed surfactants.

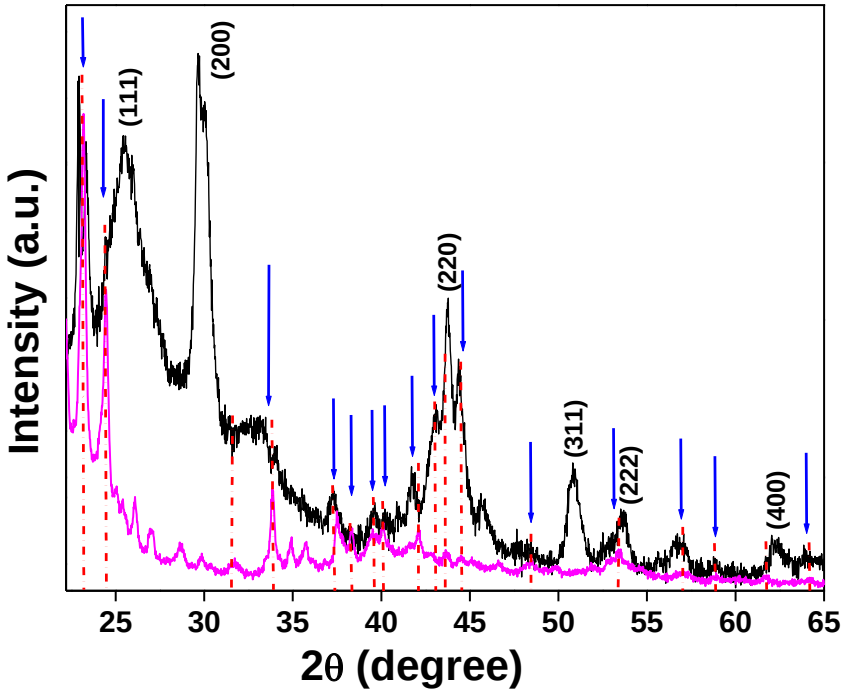

Fig. S3 XRD patterns of the drop casted films of the PbS peanut (black curve). The peak positions are designated with the Miller indices of bulk rock-salt cubic PbS (JCPDS #05-0592). The XRD pattern of the mixed surfactants (2 g TOPO and 0.4 g HAD) is shown by the magenta curve. The blue arrows show the additional peaks in the XRD patterns of the PbS

peanuts which are not matching with the cubic PbS phase. The red dotted vertical lines indicate the surfactant peaks which contribute to the XRD pattern of the PbS peanuts.

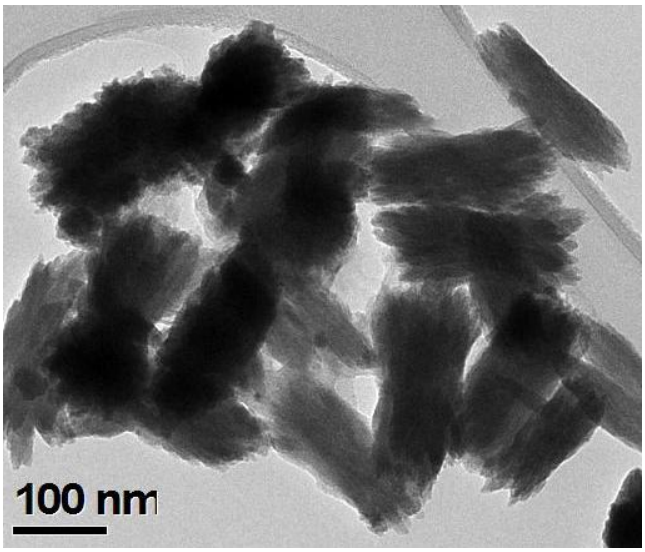

Fig. S4 TEM images of flat bundle like aggregated whiskers of PbS prepared at 130^{o}C without injecting HDA. We have carried out the reaction for 10 minutes at 110°C by injecting lead nitrate (0.144g) and thiourea (0.035g) into melted TOPO (2g) only. The temperature was then increased to 130°C, where the reaction was stopped immediately when the reaction mixture turned to milky-gray color.

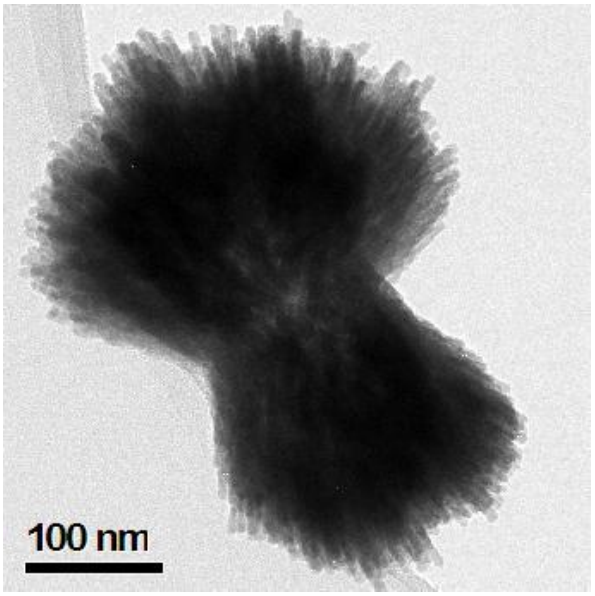

Fig. S5 TEM images of bundles of tightly bounded rods of PbS prepared by follow the same procedure for the preparation of PbS peanuts only HDA was not used in this reaction. We have carried out the reaction for 10 minutes at 110°C by injecting lead nitrate (0.144g) and thiourea (0.035g) into melted TOPO (2g) only. The temperature was then increased to 160°C and annealing was carried out for 60 minutes, a dark black color solution results as the end product.