

SUPPLEMENTARY INFORMATION

A pioneering method for the synthesis of spherical lead monosulfide (PbS) nanoparticles using a surfactant-free microemulsion scheme

Hemant Tarkas¹, Abhilasha Rokade¹, Devashri Upasani², Narendra Pardhi¹, Avinash Rokde¹, Jaydeep Sali², Shashikant P. Patole^{3,*} and Sandesh Jadkar^{1,*}

¹Department of Physics, Savitribai Phule Pune University, Pune 411 007 (India)

²Department of Physics, KBC North Maharashtra University, Jalgaon 425 001 (India)

³Department of Physics, Khalifa University of Science and Technology, Abu Dhabi 127788 (UAE)

*Corresponding authors:

Email: sandesh@physics.unipune.ac.in (Sandesh Jadkar)

Email: Shashikant.Patole@ku.ac.ae (Shashikant P. Patole)

I: Calibration Curve

The calibration curve aids in estimating the amount of IPA required for a particular ratio of dimethyl sulfoxide (DMSO) and cyclohexane (CyHx) components of the CID SFME scheme without hampering the stability of the microemulsion. Empirical equations obtained from the calibration curve are,

$$\text{Part A:} \quad \text{If } \text{DSMO}/\text{CyHx} \leq 1, y = 0.80656 (x) + 1.218 \quad \dots(1)$$

$$\text{Part B:} \quad \text{If } \text{DSMO}/\text{CyHx} \geq 1, y = -0.12903 (x) + 2.113 \quad \dots(2)$$

Equations (1) and (2) were obtained from Part A and B curves, respectively.

The simulated values for the particular ratio of DMSO and CyHx components of the CID SFME scheme of

required IPA for microemulsion stability are shown in **Table S1**.

Table S1: Optimization for CID components for stable microemulsion simulated data

DMSO and CyHx	Part A	DMSO and CyHx	Part B
0	1.218	1	1.98387
0.05	1.25833	1.2	1.95806
0.1	1.29866	1.4	1.93226
0.15	1.33898	1.6	1.90645
0.2	1.37931	1.8	1.88065
0.25	1.41964	2	1.85484
0.3	1.45997	2.2	1.82903
0.35	1.5003	2.4	1.80323
0.4	1.54062	2.6	1.77742
0.45	1.58095	2.8	1.75162
0.5	1.62128	3	1.72581
0.55	1.66161	3.2	1.7
0.6	1.70194	3.4	1.6742
0.65	1.74226	3.6	1.64839
0.7	1.78259	3.8	1.62259
0.75	1.82292	4	1.59678
0.8	1.86325		
0.85	1.90358		
0.9	1.9439		
0.95	1.98423		
1	2.02456		

II: UV-Visible Spectroscopy

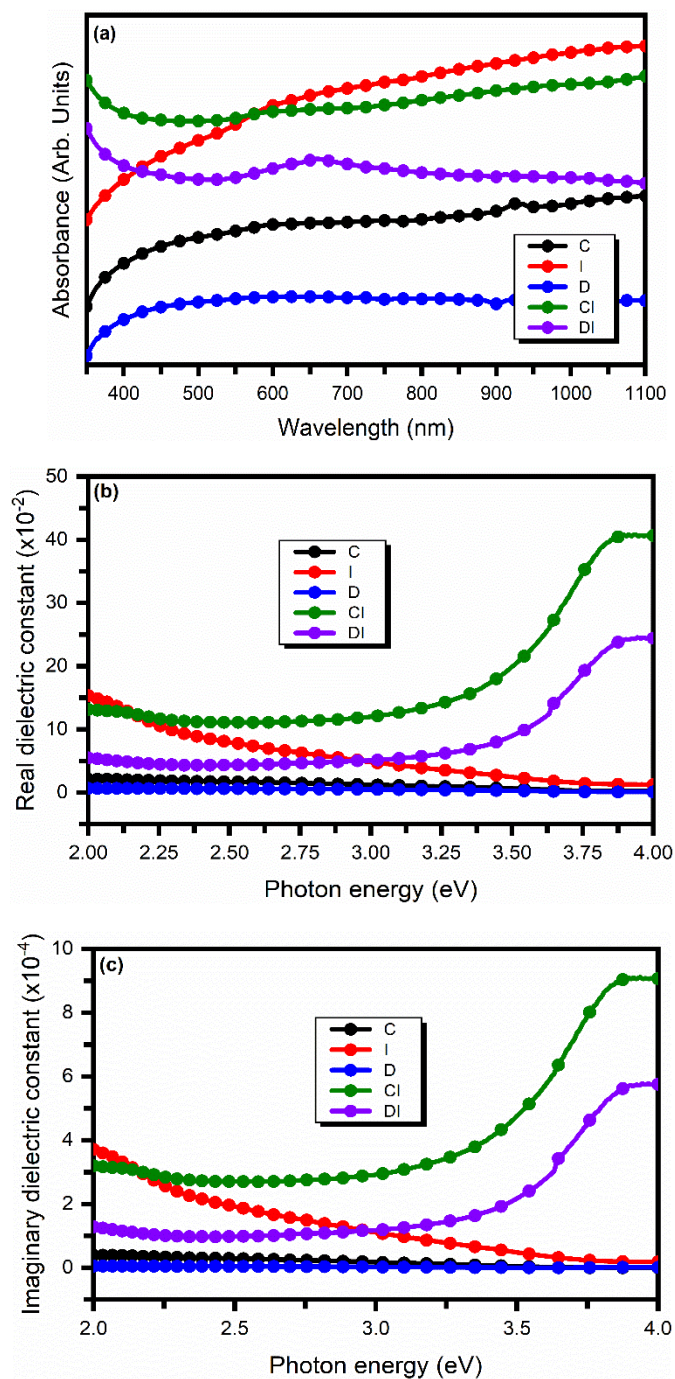


Figure S1: (a) Absorption curve, (b) Real dielectric constant, and (c) Imaginary dielectric constant of PbS nanoparticles in CID components. Here, C = CyHx, I = IPA, D = DMSO, CI = CyHx:IPA pair, and DI = DMSO:IPA pair

III: Fabrication of device

Considering band energy positions, we fabricated the FTO/TiO₂/PbS/PANI/NiS/C device architecture. Firstly, 1.1 g of preheated TiO₂ powder (Degussa P25) for 60 min at 120 °C was dispersed in 8.5 ml ethanol, and then 1.5 ml of acetylacetone was added to form a slurry. This slurry was then kept for 30 min bath sonication. After sonication, 0.25 ml of the slurry was spread over a 1.5 cm² sized FTO-coated pre-cleaned glass substrate and spin-coated at 4000 rpm for 50 s to develop a 500 nm thick, mesoporous TiO₂ electron transporting layer. These films were then dried at 125 °C for 10 min and annealed at 500 °C temperature for 30 min. After cooling, these TiO₂-coated FTO/glass substrates were removed from the muffle furnace. Then 1 ml blend solution of PbS:PANI composite was prepared by dispersing 15 mg PbS (0.0125 M) and 50 mg of PANI in a solution mixture of chlorobenzene (0.5 ml):Isopropanol (0.5 ml). Subsequently, the PbS:PANI composite layer (active layer) was deposited over TiO₂-coated FTO/glass substrate by dropping the prepared composite solution at 50 °C. Afterward, NiS, hole transporting layer (HTL) was deposited over the composite layer by dropping 10 mg/ml ethanolic solution of synthesized NiS at 50 °C. Then, carbon back contact was developed by applying a paste of graphite powder over the HTL layer of the device. Carbon back contact extracts and collects the photogenerated holes. This fabricated device was then characterized under standard conditions.

IV: Synthesis of Polyaniline (PANI)

Polyaniline was synthesized by dissolving 5 gm of (NH₄)₂S₂O₈ in 50 ml of 1 M HCl solution in water at 0 °C maintained by ice bath. A solution of 2 ml aniline was prepared separately in another container containing 50 ml of 1 M HCl. The (NH₄)₂S₂O₈ solution was added slowly into the aniline solution and kept at 0 °C. Then, after complete solution mixing, the product was filtered and washed with 1 M HCl solution and then with water three times and dried at 60 °C in a vacuum oven for 5 hrs. Green powder of PANI was then obtained.

V: Synthesis of Nickel Sulfide (NiS)

NiS was synthesized by a simple chemical two-step ion exchange method. 0.1 M nickel nitrate [Ni(NO₃)] was first dissolved in 50 ml double distilled water. In this solution, ammonia was slowly added to maintain pH between 9 and 10, which gives precipitate, indicating the formation of a nickel hydroxide complex. The sulfur precursor solution was prepared separately by dissolving 0.1 M Na₂S·H₂O in 50 ml double distilled water. The

sulfur precursor solution was slowly added to the nickel precursor with vigorous and continuous stirring. The solution hastily turned blackish brown, indicating the formation of NiS. Then, the product was separated and washed with water and methanol three times using the centrifugation and separation method. Then, the product was dried at 120 °C in a vacuum oven.

VI: Tauc plots for band gap calculations

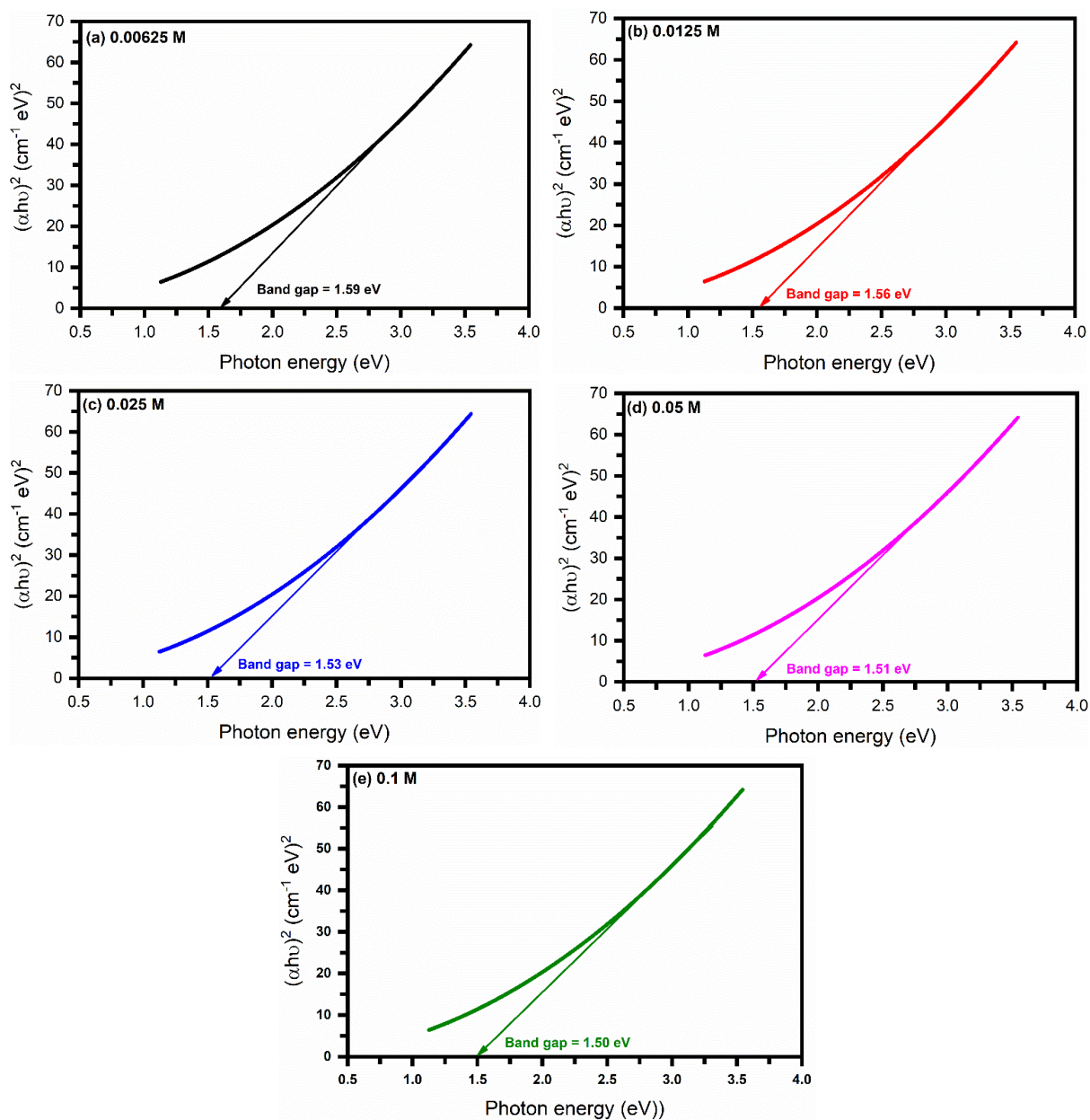


Figure S2: Measurement of band gap using Tauc plots of PbS for (a) 0.00625 M, (b) 0.00125 M, (c) 0.025 M, (d) 0.05 M, and (e) 0.1 M Imaginary under CID-SFME scheme for different solution concentrations

VII: FTIR Spectroscopy

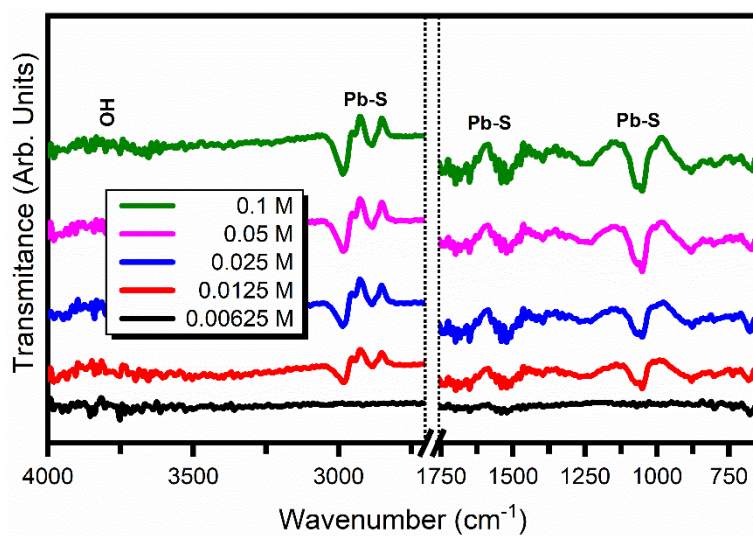


Figure S3: FTIR spectra of PbS thin films synthesized by using CID SFME scheme for different solution concentration