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PHASE SELECTIVE SOLVOTHERMAL SYNTHESIS OF INDIUM SULPHIDE NANOCRYSTAL

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Abstract

At present, photocatalytic based degradation of organic pollutants using semiconducting nanomaterials is drawing considerable attention due to direct disposal of organic pollutants such as domestic wastes, pesticides, hydrocarbons, dyes, phenols, fertilizers into the fresh water bodies like rivers, ponds, lakes and underground water through industries (i.e. textiles, paper manufacturing, food processing etc), agriculture and domestic uses. As a result ,it is very difficult for surviving the aquatic flora and fauna. Earlier, adsorbents such as charcoal, clays, zeolites, and ores were employed for purifying and removing the organic pollutants from the water sources. However, it is noticed that adsorption has significant effect on enhancing the photocatalytic activity of the semiconducting nanomaterials and nanocomposite materials. Adsorption process depends on the many factors including morphology, high surface area, pore volume and intra-particles mesoporosity. Photocatalytic degradation decreases for methylene blue, rhodamine B and methyl orange dyes. Analysis reveals that not only type of dyes (cationic or anionic) but also symmetry, molecular structure and orientation of dye molecule are the important factors for electrostatic interaction dependent adsorption which essentially controls the efficiency of the nanocatalyst. In addition, strong interaction between n-type nanomaterials and cationic dyes results degradation of dyes via adsorption process even in the dark.

Keywords: *photocatalytic, degradation, mesoporosity, nanocomposite materials*

Experimental Section

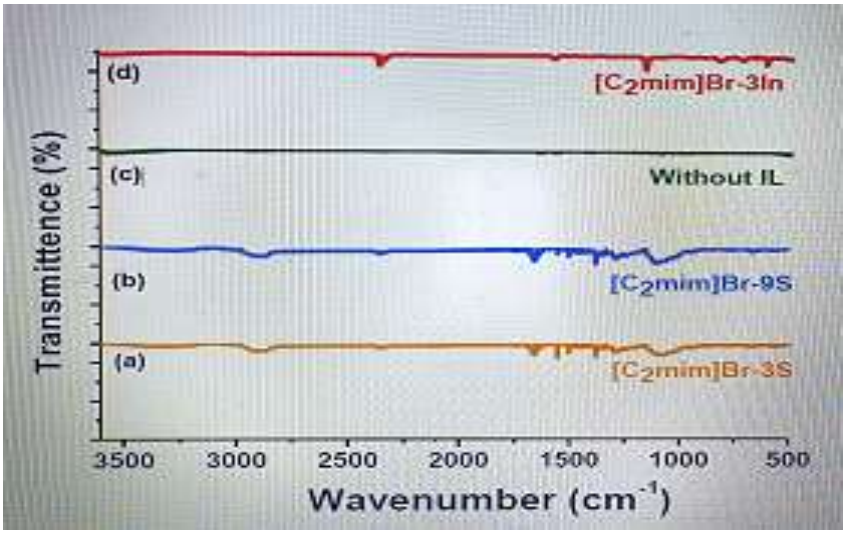
Chemicals: Details and purity of the chemicals used are given as**.** Indium(III) chloride ($InCl_3$) (99.00%), Thiourea (CN_2H_4S) (99.0%), 1-methylimidazole (C4H6N2) (99.0%), Bromoethane (C2H5Br) (99.0%) and n-Butyl Bromide (C4H9Br) (96.0%), n-Hexyl Bromide (C6H13Br), Octyl Bromide (C8H17Br) and Decyl Bromide (C10H21Br) were purchased from Himedia; Thioacetamide (C_2H_5NS) (99.0%) and charcoal from CDH (Central Drug House), Ethanol (C_2H_5OH) (99.9%) from Changshu Yangyuan Chemical; Tetra methyl ammonium bromide $(CH_3)_4N(Br)$ (99.0%), Ethyl Acetate (99.5%), Acetonitrile (99.5%),

Dichloromethane (99.5%) were purchased from Loba Chemie and Silver Nitrate from Fisher scientific, Crystal Violet (CV), Methylene Blue (MB) and Methyl Orange (MO) were purchased from Himedia. Rhodamine B was purchased from Loba Chemie. All the chemicals were of analytical grade and were used without further purification.

Synthesis of Ionic Liquids: For synthesizing the ionic liquids including 1-ethyl-3-methylimidazolium bromide [C2mim]+ Br-, 1-butyl-3-methylimidazolium bromide [C4mim]+ Br-, 1-hexyl-3-methylimidazolium bromide [C6mim]+Br-, 1-octyl-3-methylimidazolium bromide [C8mim]+ Br- and 1-decyl-3-methylimidazolium bromide [C10mim]+ Br-, the following methods were carried out.**65-66** Different instrumentation technique like 13C, 1H NMR and FTIR were used for confirming the purity of products.

Highly phase selective solvothermal synthesis of indium sulphide nanocrystals within band gap in the range 2.01-2.41 eV using task-specific ILs such as [Cnmim]Br (1-alkyl-3-methylimidazolium bromide), concentration and types of sulphur precursors. In fisrt part of this chapter, we have studied the effect of tunable ionic liquids based on varying alkyl chain length, H-bonding and aromatic Π-stacking ability, for tuning the crystal phase, size and morphology of In2S3 nanocrystals. In addition, different other factors like the effect of sulphur precursors, reaction temperature, are also examined. Thereafter, growth mechanism of the nanocrystals is explained from atomistic origin using microscopic studies like SEM, TEM and HRTEM. Adsorption based catalysis and photocatalysis is studied for all the In2S3 samples. Maximum catalytic and photocatalytic efficiency in visible light is observed for the sample prepared in presence of tetramethyl ammonium bromide (TMAB) IL. However, a significant degradation of crystal violet dye is also noticed if the same sample is simply kept in dark for the entire reaction time. On the other hand, in next part of this chapter, we have tried to obtain the pure phase of In2S3 nanocrystal uisng IL ([C2mim]+Br-) by varying the concentration of thiourea and other reaction conditions. Change in morphology, particles size distribution and optical property of of In2S3 particles are further studied using different characterization techniques. Emission spectra of pure In_2S_3 indicates that the as prepared materials is blue emitting in nature. Thereafter, four different dyes crystal violet (CV), methylene blue (MB), rhodamine B (RB) and methyl orange (MO) are used as model organic pollutant to study the photocatalytic degradation in the presence of visible light. It is observed that catalytic/photocatalytic efficiency is dependent on adsorption capacity of dye which again is controlled by molecular structure, orientation and symmetry of the dye molecules.

Synthesis of indium sulphide nanoparticles: In a novel solvothermal approach, indium sulphide nanoparticles are synthesized by varying reaction parameters such as different imidazolium-based ionic liquids (ILs) with varying and tunable alkyl chain length, reaction temperature etc. Here ILs are used as nanosynthetic template. In a typical synthesis, 1% (w/v) IL was dissolved in a mixture of distilled water and ethanol (1:3) and stirred for 5 minutes. 0.00307 moles of InCl3 was dissolved in distilled water and was mixed with IL solution, and stirred for 30 minutes. Now aqueous solution of thiourea/ thioacetamide (0.0046 moles) was added to the IL-containing solution and stirred for a while. Then this solution was poured into a Teflon lined autoclave with a capacity of 100 mL and kept in hot air oven at 120oC, 150°C and 180oC respectively with varying reaction time. The obtained nanocrystals were centrifuged and subsequently washed many times using methanol, ethanol and acetone and then kept in an oven at 80°C for drying. It is seen from the Fourier transformed infrared (FTIR) spectra (**Figure given below**) of the samples prepared with [Cnmim]Br (1-alkyl-3-methylimidazolium bromide) IL, that there is no stretching vibration band of the C(2)–H of imidazole ring or no imidazole ring skeleton stretching vibration bands, which implies the complete removal of IL. Bending or stretching vibrational bands for hydroxyl group (–OH) in the FTIR spectra is also not appearing. It means as-prepared samples are free from hydroxide or impurity of water.



Effect of sulphur precursor

The PXRD patterns of as-prepared indium sulphide nanomaterials prepared in different reaction conditions are analyzed. During the synthesis, once thiourea (TU) is used as precursor while thioacetamide (TA) is used for other case keeping all the reaction parameters

same. The cubic β-In2S3 (JCPDS card no. 32-456) appears for both the cases. However indium hydroxide (JCPDS card no. 85-1338) impurity appears (indexed by *) in addition when thiourea is used. Appearance of indium hydroxide peak can be attributed to slow release of sulphur at 150oC on solvothermal condition. Due to less reactivity and higher decomposition temperature of TU compared to TA, more chances of reaction to be occurred between oxygen and In3+ in the previous. It is known that the reactivity of precursors also governs the nucleation and growth of nanocrystals, so the crystallite size of the nano-size particles is less (ca. 8.17 nm) in case of more reactive precursors. The effect of concentration of precursors (both In3+ and S2-) and reaction time on phase evolution is also studied and there is no formidable change in crystal phase noticed.

Effect of reaction temperature

To understand the effect of reaction temperature on phase evolution, indium sulphide nanoparticles are solvothermally prepared at different temperatures 120oC, 150oC, and 180oC in the presence and absence of ionic liquid ([C2mim] Br) under similar reaction conditions. When no IL is used and reaction temperature is maintained at 120oC for 7 hours (M10), pure cubic phase with high crystallinity is obtained (JCPDS card no. 32-456), however in presence of [C2mim]Br ionic liquid under similar reaction conditions, cubic phase appears with less crystallinity indicating a significant effect played by ionic liquid on size of particles. But there is a drastic change in phase if the simply reaction temperature is increased from 120oC to 150oC without ionic liquid. Despite of phase tuning, ionic liquids played a tremendous role in controlling particle size.

Conclusion: Nanoparticles of ~10 nm size are obtained in presence of IL which are less compared to the synthesis without taking IL, confirms the feasibility of ILs as a templating agent in inorganic synthesis. Except for size control, for the first time, it is noticed that by varying the properties of ILs like alkyl side chain length and aromatic ,-stacking ability, the crystal phase of In2S3 nanocrystals can be tuned. For example, cubic □-In2S3 is observed up to [C4mim]Br IL, however tetragonal -In2S3 polymorph is obtained when ILs of higher chain length (n, 6) is used. Judicious choice of reaction temperature and reaction precursors aside from the ILs is also mandatory, as it not only controls the size and morphology of the nanoparticle but also tunes the crystal phase, which is essential for band gap engineering. Unlike thioacetamide, indium hydroxide is appearing as an impurity along with In2S3 when thiourea is used as a sulphur source due to slow release of sulphur and hard soft acid base

(HSAB) interaction; however, pure In2S3 is achieved at 18 times of stoichiometric sulphur concentration. In addition, photoluminescence spectra show that In2S3 nanocrystals are emitting in blue region on exciting under 379 nm at room temperature. Very good catalytic and photocatalytic performance was obtained from TMAB mediated In2S3 samples using crystal violet (CV) as a model dye. However, photocatalytic degradation decreases for methylene blue, rhodamine B and methyl orange dyes. Analysis reveals that not only type of dyes (cationic or anionic) but also symmetry, molecular structure and orientation of dye molecule are the important factors for electrostatic interaction dependent adsorption which essentially controls the efficiency of the nanocatalyst. In addition, strong interaction between n-type nanomaterials and cationic dyes results degradation of dyes via adsorption process even in the dark.

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