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Synthesis and Characterization of Ag Doped CuS Powders Modified with Anionic surfactant

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Abstract: Nanocrystalline Ag doped CuS powders were synthesized directly from coppernitratetrihydrate, thiourea and silver nitrate in the presence of SDBS in ethylene glycol at 125°C. The physical properties of prepared nanoparticles were characterized by X-ray diffraction (XRD), UV-Vis spectroscopy, SEM/EDS, Thermal analysis (TG/DTA) and Atomic force microscopy (AFM). The CuS powders had sphere – like shape without any dopant and this turned to a porous sphere like structure, when the Ag loading was from 0.05 and up to 0.15mM. If the Ag content was further increased, the sphere-shape reappeared (0.2 mM). The optical band gap was calculated for these samples and it is 4.2, 4.25, 4.4, and 4.9eV for the addition of Ag 0.05, 0.1, 0.15 and 0.2mM respectively. The particle sizes were calculated and it regimes from 8 to 23nm.
Keywords: Nanocrystalline, dopant and poroussphere.

Introduction

CuS nanomaterials have been studied extensively due to their unique characteristics, modifying CuS with noble metals, such as Pt, Au and Ag, which work as electron traps, can improve its photo catalytic property by aiding electron – hole separation via the formation of a schottky barrier at metal– semiconductor interfaces. Numerous efforts have been undertaken to prepare low cost co-catalysts. One of the widely used strategies to extend the photo response of a wide band gap semi conductor towards the visible spectral region is combining wide band gap semiconductors with those with narrow band gaps.

Compared with a single semiconductor, composite semiconductors can extend the absorption range and enhance the absorption of the solar spectrum[1,2]. However, the toxicity and harmful effects of cadmium, lead and their compounds to the environment and to human beings have caused them to be regulated by several regulatory control agencies. Hence, it is imperative to replace highly toxic cadmium or lead – based materials with other environment friendly ones. For this reason, various no-toxic materials have been investigated. Among them, copper sulfide has become one of the alternative candidates in modifying wide band gap semiconductors because it is eco – friendly and economic[3, 4]. Very recently,[5]reported the fabrication of CuS/ZnS porous nanosheets and their visible – light driven photocatalytic H_2 production activity without having platinum as a cocatalyst[6], synthesized monodisperseCuS/ ZnS hollow spheres and evaluated photocatalytic decolorization of a methyl orange(MO) aqueous solution under UV-visible light irradiation. Both materials were proven to be efficient UV- Visible light driven photo catalysts. So to the best of our knowledge, however, there is no report regarding CuS/Ag nano structure as an efficient UV- visible light activated photo catalyst. In this work Silver doped CuSNanomaterials were synthesized by solvothermal method.

Experimental Procedures

Materials

Copper nitrate tri hydrate, Ethylene glycol, Thiourea, SDBS and silver nitrate are purchased from Sd. Fine chemicals (AR) grade and used without further purification.

Preparation

1mM of copper nitrate tri hydrate and 2mM of thiourea as a copper and sulfur sources were dissolved in 40 ml of ethylene glycol as a solvent. Then 0.05 mM of SDBS with various concentrations of silver nitrate such as 0.05, 0.1, 0.15 and 0.2 mM was separately added with the above solutions under the vigorous stirring of 45 mins. Then the solution was transferred to stainless steel auto clave at 125°C for 10 hrs. The black color precipitation appeared and it was washed with ethanol and deionized water several times to remove impurities present in the sample. The final product was dried at 60° for 6 hrs.

Characterization

The powder X-ray diffraction analysis is carried out using XPERT- PRO diffractometer into CuK_α radiation, λ= 1.5406Å over the range 10˚ – 80° at the scan rate of 0.02°/sec. The optical absorption spectrum of the synthesized nanoCuS recorded 200 –600nm using SHIMADZU-UV 1800 spectrophotometer covering the entire near UV- visible region. The surface morphology of the prepared CuS was examined by SEM with EDS using JEOL-JSM – 5610 LV with INCA EDS and Atomic Force Molecular (AFM) spectroscopy images of the samples were performed using AGILENT–NP410A series 5500. The thermal characteristics were determined by thermo Gravimetric analysis and differential thermal analysis using NETZSCH – STA 449F3 JUPITER in a nitrogen Atmosphere.

Results and Discussion

Structural Analysis (XRD)

To examine the structural properties and crystal phase identifications, powder X-ray diffraction (XRD) was used with CuK□ radiation (λ = 1.5406 Å) in the range of 10° – 80° with 2°/min scanning speed. The observed XRD pattern (Fig.1(a-e)) exhibits well crystalline nature and mixed phases of Ag and CuS for as – synthesized nanostructure. Several well defined diffraction reflections related to CuS were observed in the obtained pattern. The observed diffraction reflections for CuS(101), (102), (103), (110) and (116) are similar to bulk CuS and correspond to hexagonal phase of CuS. The obtained results are in good agreement with standard JCPDS data card no.78-0877. In addition to the CuSmajor reflection with d-spacing (Å) at 3.074 (108), a small peak corresponding to Ag (200) also appeared at 44.15. Except CuS and Ag, no other reflections related to impurities such as Cu and Ag_2O were found in the pattern.

The calculated grainsize of the silver doped CuSnanocrytallites with the increasing amount of silver ions dosages were 8, 20, 23 and 18nm for 0.05, 0.1, 0.15 and 0.2 mM dosage of silver ions, respectively. The low dosage of Silver ions CuS makes the sphere shaped CuS. But the uniform porous spheres were observed at the addition concentration of silver from 0.1 and 0.15mM. Further addition of Ag made the sphere shape reappear.

This may occur because the Ag aggregates at the grain boundary. The change of surface properties of metal ions doped semiconductor, such as oxygen vacancies, crystal deficiencies and increased specific surface area increasing the amount of silver ions resulted in increased lattice deficiency.To verify further the change of structures of samples on the addition of Ag, the lattice constant was changed from a = 3.80Å, c = 16.378Å, (CuS) to a = 3.785 Å and c = 16.355 Å (CuS:Ag). The results revealed that crystal phase of products was not affected by the dopant but the degree of crystallization was different. That was to say that the combined action of SDBS and Ag prevented fine particles from aggregating and helped to form structure with porosityat the addition of lower amount of Ag on CuS.

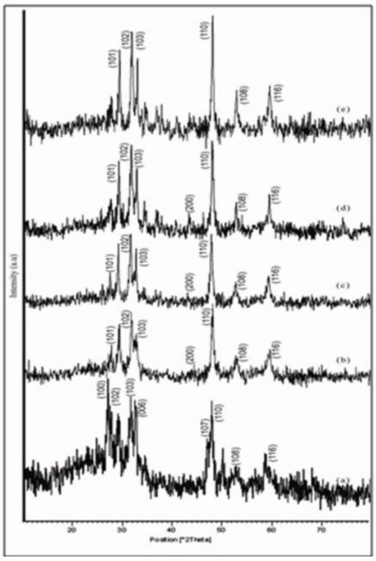


Fig 1. XRD patterns of (0.05mM) SDBS assisted CuS doped with Ag: (a) 0.0, (b) 0.05 mM, (c) 0.1 mM, (d) 0.15 mM and (e) 0.2 mM

Optical Absorption Analysis(UV- Vis)

UV – Vis spectroscopy was performed to examine the optical property of synthesized Ag doped CuS and the results are reported in Fig. 2(a-e). The as – synthesized Ag – doped absorption band at 496 nm is the characteristic band for the hexagonal structure of CuS[7]. The obtained UV – Vis spectrum for Ag doped CuSnano structures shows significant change in the absorption spectrum due to the doping of Ag ions into CuS lattice. The observed results are almost similar to the already reported literature[8]. The average optical transmission in the visible region decreased substantially at shoot wavelengths mean the ultraviolet range. With increasing silver contents, the absorption edge shifted slightly to a longer wavelength region and the band gap also narrowed with increasing Ag contents. The increase of crystallinity with increase of Ag concentration may be the reason for more transmittance. The doping of Ag in the CuS changes the properties of Cu Ssignificantly. At this moment, it is appropriate to mention here that desirable amount of conductivity and transparency can be achieved with appropriate amount of silver dopant[9].Detailed study on the doping amount of Ag on the properties of Ag doped CuS is in progress, which may shed some light to understand further the samples exhibiting newer properties depending upon the temperature. The band gap energy of the prepared sample is around 4.25- 4.9eV (Fig. 3).

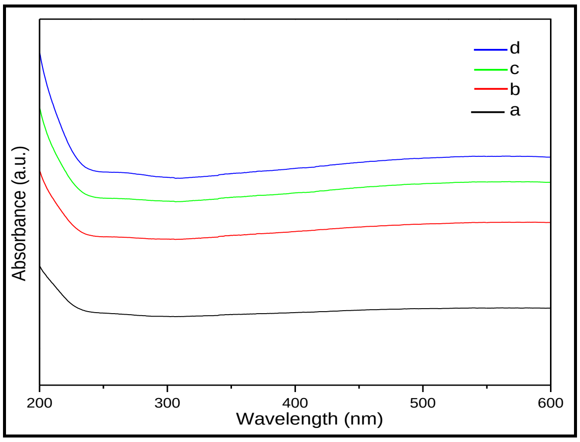


Fig.2 UV- Visible absorption spectra of Ag doped SDBS assisted CuS (a) 0.05 mM, (b) 0.1 mM, (c) 0.15 mM and (d) 0.2 mM

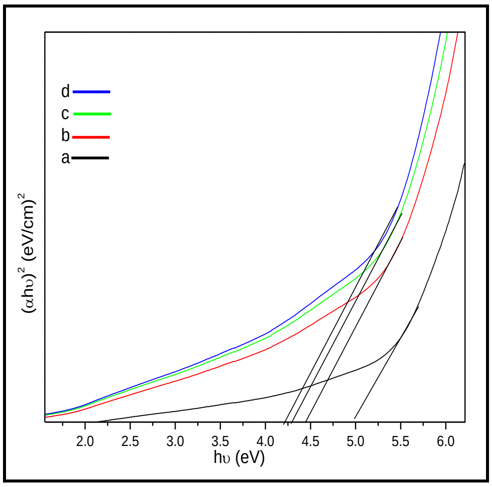


Fig. 3 Plots of variation of $(\alpha h\nu)^2$ *Vs.hν*

Surface Morphological Analysis

SEM/EDS studies

The general morphologies of as – synthesized Ag-doped CuS nano structures were investigated by using SEM and the results are shown in Fig. 4 (a-e). The figure exhibits the typical low–magnification SEM image, which confirms that the as–synthesized nanomaterials are sphere shaped and in very high density. The porous sphere ike structures are formed when Ag concentration increased from 0.1mM to0.15mM. This porous spheres disappears at 0.2mM of Ag. The typical diameters are in the range from 8–23 nm. To check the composition and purity of the Ag doped CuS nanostructures, the nanostructures were investigated using energy dispersive spectroscopy (EDS) and elemental mapping, and both attached to SEM. The EDS spectrum shows various well defined peaks of Cu, S and Ag (fig.5 (a-e)). No peak related to any other impurity was detected in the spectrum.

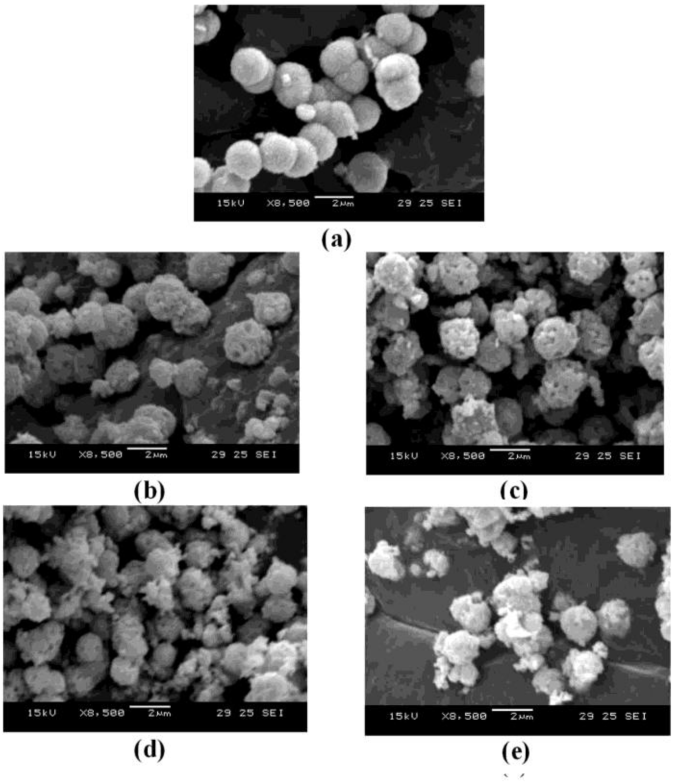


Fig.4 SEM Photographs of (0.05mM) SDBS assisted CuS doped with Ag: (a) 0.0 (b) 0.05 mM, (c) 0.1 mM, (d) 0.15 mM and (e) 0.2 mM

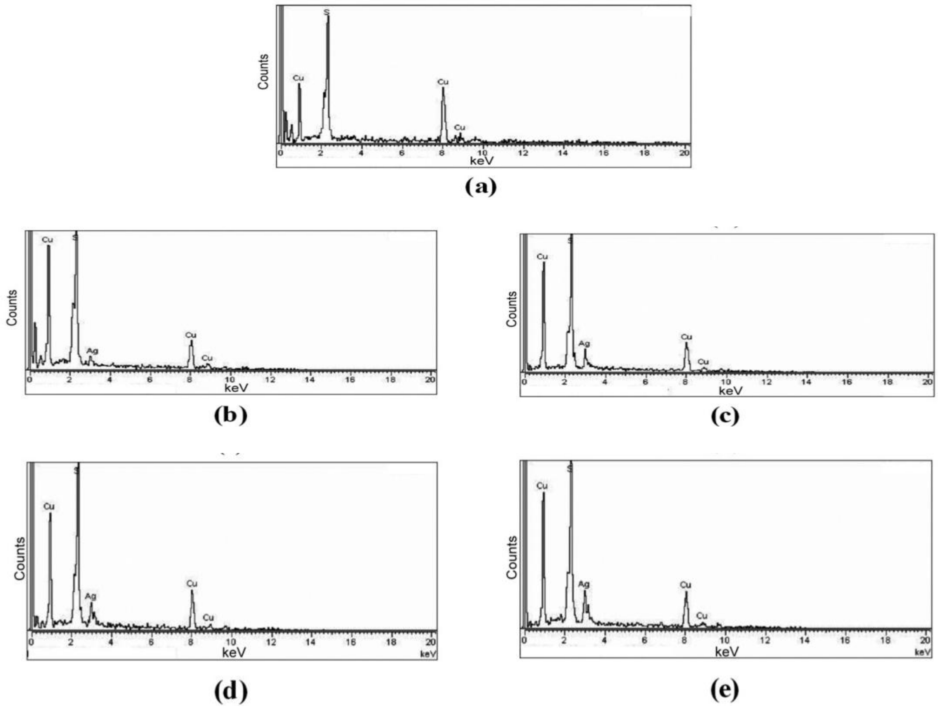
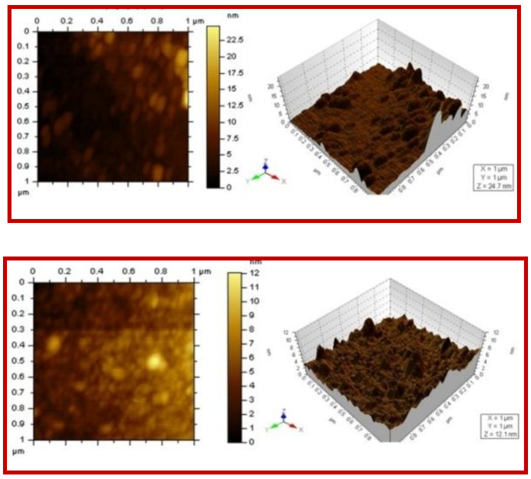


Fig.5 EDS spectra of (0.05mM) SDBS assisted CuS doped with Ag: (a) 0.0 (b) 0.05 mM, (c) 0.1 mM, (d) 0.15 mM and (e) 0.2 mM

AFM Studies

A surface plot of an image obtained by the AFM in contact mode is given in Fig.6 (a, b) which shows three dimensional AFM surface heights morphologies of the CuS: Ag nanospheres (with Ag 0.05 and 0.1mM), the scanning area is 1 x 1 μm^2. The CuS: Ag has smooth surface and compact grains size particles. Ag doped CuS samples were examined by a section analysis to obtain the vertical dimensions of the particles. A mean particle size of 12nm was obtained. The particle diameter measured by AFM is correlated well with optical absorbance measurements of the particles[10] that were roughly spherical with porous. Compared to undoped CuS, Ag doped CuS is quite monodisperse and mean diameter decreases considerably.

(a)

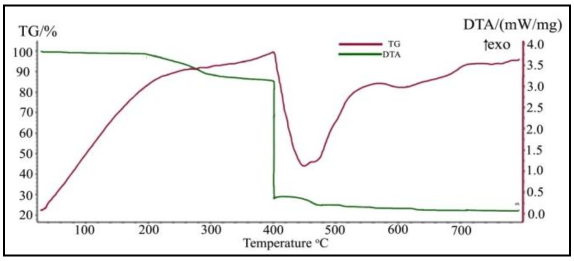


(b)

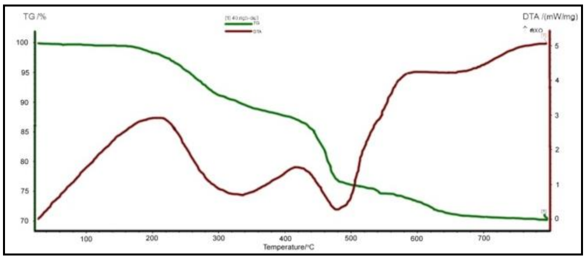
Fig.6 AFM images of of Ag doped SDBS assisted CuS 0.05 and (b) 0.10 mM

Thermal Analysis (TG/DTA)

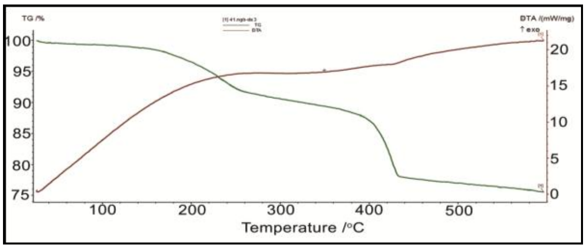
Thermal behavior of the SDBS assisted CuS and Ag doped samples was studied in the temperature range of 100˚C – 700°C. With temperature rise of 20°C min^{-1} under insert Nitrogen atmosphere – TG/DTA thermo grams are shown in Fig.7 (a- c) respectively. According to DTA curves, water is lost at 150° C and 420°C in the SDBS assisted CuS which is in accordance with the presence of different water sites in the SDBS structure due to the presence of Na, K, Ca and Mg cat ions. According to DTA curves weight loss extents of 19.1 and 15.70% are obtained for CuS:Ag (0.05mM) and CuS:Ag(1mM) respectively. Generally, the samples undergo endothermic changes between 150° and 480°˙C , due to desorption of sample. According to DTA curves, maximum weight loss extents take place at 73 and 76% respectively.



(a)



(b)



(c)

Fig. 7 TG/DTA curves of (0.05mM) SDBS assisted CuS doped with Ag: (a) 0.0 (b) 0.05 mM and (c) 0.1 mM

Conclusion

Ag doped CuSnano spheres with porous structure were synthesized by solvothermal method at 125°C temperature. The synthesized nanostructures were characterized in terms of their structural and optical properties which revealed the well – crystalline nature and good optical properties. A small amount of Ag (<0.1 mM) in CuS made the nano spheres in to porous sphere. Further addition of Ag on CuS will not make any change Ag plays an importance role in the formation of nanoparticles with different shapes and sizes. The UV – Vis spectra of two morphologies (sphere and porous sphere) exhibit an obvious difference on their absorption peak positions. Corresponding calculation results exhibit the optical band gap of 4.9 and 4.4 eV. The results indicate the obtained CuS particles. Optical performance is easily controlled by changing the dopant concentration under solvothermal route, which is considered to be a facile approach to prepare other sulfide materials that involve well – defined shapes and precisely controlled morphologies.

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