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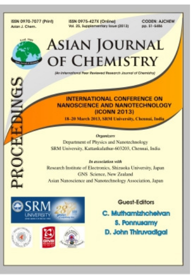

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Synthesis of Silver Nanoparticles Doped Bismuth Sulphide Using Single Source Precursor and its Electrocatalytic Activity on Oxidation of Hydrazine†

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A methodology is developed on synthesis of silver doped bismuth sulphide ($AgBiS_2$) nanoparticles *via* a single source approach using bismuth diethyldithiocarbamate as the sulfur precursor under reflux condition in presence of hexadecylamine. Here the long chain acted as both capping agent as well as shape directing agent. The resulting nanoparticles were characterized by analytical methods such as DRS UV-Visible spectroscopy, powder X-ray diffraction and field emission scanning electron microscopy. A flower like shaped $AgBiS_2$ was observed from field emission scanning electron microscopy studies and the cubic shape crystalline structure was confirmed from XRD analysis. The electrochemical behaviour of the system was investigated using cyclic voltammetry and differential pulse voltammetry method on electrochemical oxidation of hydrazine at different pH ranges and concentrations. An enhanced oxidation current was obtained in neutral pH ranges. A linear calibration graph was constructed by plotting the increasing peak current against the concentration of hydrazine. From the calibration graph, unknown concentration of hydrazine present in various water sources can be calculated. The proposed method can be employed for the routine determination of hydrazine at trace level using $AgBiS_2$ as electron transfer mediator.

Key Words: Single source precursor, $AgBiS_2$, Electrocatalytic activity, Detection of hydrazine.

INTRODUCTION

Due to their importance in scientific research and potential technology applications, I-V-VI ternary chalcogenide semiconducting compounds have been found to be an attractive material because of its linear, nonlinear, optoelectronics, thermoelectric and optical recording properties[1]. Among these compounds, there has been much interest in $AgBiS_2$ due to its unusual electronic and magnetic properties. These types of noble metal doped semiconductor are the focus of catalytic applications because these nanoparticles can be hybridized with other substrates for enhanced catalytic functions. $AgBiS_2$ has been prepared through a solid-state reaction, a solid solution technique and a flux technique. By contrast, the Tang and Xie groups have synthesized cubic phase $AgBiS_2$ nanorods by a direct low temperature polyol route[2] and a solvothermal route[3], dendritic $AgBiS_2$ crystals are synthesized under microwave irradiation[4]. Nanorods and coral-shaped $AgBiS_2$ crystals were prepared by a polyol route[5,6]. The flower and hexapod $AgBiS_2$ crystals were obtained by cyclic microwave-assisted synthesis[7]. The flowers and nano whiskers were studied *via* solvothermal methods[8] and 3D arrays of close-packed $AgBiS_2$ crystals were synthesized by sonochemical approach[9], flower-like $AgBiS_2$ crystals obtained by biomolecule assisted route[10]. To the best of our knowledge, there have been no reports on the similar preparation of Ag doped Bi_2S_3 nanostructures employing sodium dithiocarbamate (NaDTC) as single source precursor in presence of Ag nanoparticles and hexadecylamine as the capping agents. A long chain amine, hexadecylamine was used as a coordinating solvent because it has been shown to control the growth rate and particle size when used as a capping agent[11]. This also plays a major role in stabilizing the nanocrystalline colloidal dispersions and passivates the particle size. The nanostructured $AgBiS_2$ was isolated and characterized with FE-SEM and XRD studies to study its crystalline nature and morphology. The electrochemical behaviour of the system was investigated using cyclic voltammetry method. The electrocatalytic behaviour of $AgBiS_2$ system was tested against the electrochemical oxidation of hydrazine, which is considered to be highly toxic even though they find wide spread usage in areas such as fuel cells, herbicides, emulsifier, corrosion inhibitor,catalysts, rocket propellants and so on, acute exposure to high levels of hydrazine may cause drastic effects in humans and animals[12,13]. For the oxidation of hydrazine require large over potential at various electrode substrates. Therefore we have attempted to use $AgBiS_2$ as electron transfer

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mediator to operate at lower oxidation potential[14]. Thus the electrocatalytic oxidations of hydrazine were carried out at different pHs as its behaviour was dependent on the pH of the solution and an enhanced oxidation current was obtained in neutral pH range, so the pH of the medium was adjusted by using 0.1 M HCl or NaOH. A linear calibration graph was constructed by plotting the increasing peak current against the concentration of hydrazine.

EXPERIMENTAL

All chemical reagents such as bismuth nitrate, silver nitrate, hexadecylamine and sodium diethyldithiocarbamate were of A.R. grade purchased from SRL Chemicals, Pvt. Ltd., India and were used as received, without further purification. Further experiments were carried out using double distilled water.

The DRS UV-Visible spectrum was recorded using Bruins DRS UV-Visible spectrometer equipped with an integrated sphere. $BaSO_4$ was used as a reference to measure all samples. The FT-IR spectra were recorded using Perkin-Elmer 360 model FT-IR double beam spectrophotometer. XRD patterns of the samples were recorded with a JSO DEBYE FLEX 2002 Seifert difractometer. FE-SEM images were obtained with a field emission JEOL-JSM-6360 instrument, USA. The CV experiment was carried out using CHI 660A electrochemical instrument, USA. A three-electrode system with a single compartment cell system was used for the electrochemical studies. A platinum and Ag wire were used as counter electrode and reference electrode respectively. All potentials were measured against the Ag wire as reference electrode. A GCE was used as working electrode wherein the samples were deposited by drop casting method on GCE using Nafion® as dispersing agent.

Synthesis of silver bismuth sulphide: In a typical procedure, 2 mM of diethyldithiocarbamate dissolved in 50 mL of DI water added drop wise into a clean RB flask containing 100 mL methonalic suspension of 2 mM $Bi(NO_3)_2$ and the reaction mixtures were stirred continuously at room temperature for 6 h. The resulting solution was further aged for 12 h without stirring. The yellow precipitate so formed indicates the formation of bismuth diethyldithiocarbamate (BiDTC) complex, filtered, washed with DI water and dried in a hot air oven at 80 ºC. 1 mM of the dried BiDTC was added to 1 mM of $AgNO_3$ and 5 mM of hexadecylamine and then allowed to reflux at 180 ºC for 2 h. The blackish solid products so obtained were cooled, washed with methanol followed by toluene several times to remove the excess of amines and other impurities, filtered and then dried in vacuum oven at 60 ºC for about 1 h.

RESULTS AND DISCUSSION

The DRS UV-visible spectra of pure and loaded $AgBiS_2$ semiconductors were recorded and the resulting spectrum is shown in Fig. 1. The optical band gap (E_g) was calculated from the energy intercept of a plot of $[\alpha(h\nu)]^2$ *versus* $h\nu$ for a direct transition where α is the absorbance. The direct band gap of as-prepared sample was found to be 2.5 eV from the DRS UV-visible absorption spectrum, which is much similar to the reported value for bulk $AgBiS_2$[15]. A slight difference is due to the energy difference between the position of the conduction band and a free electron, which leads to a quantization of their energy levels.

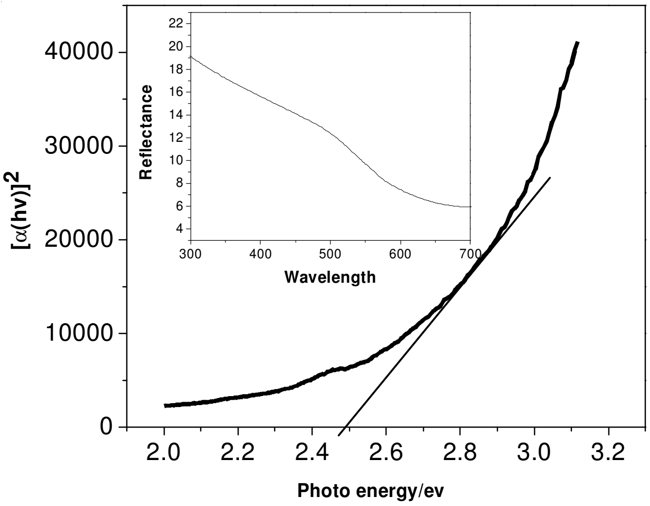

Fig. 1. DRS UV-Vis spectroscopy of $AgBiS_2$

The structure and phase purity of the product were examined by powder X-ray diffraction. All the diffraction Peaks of the XRD patterns taken from the as prepared samples can be indexed and interpreted as cubic $AgBiS_2$ (JCPDS No.04-0699) (Fig. 2) with cell constant a = 5.646Å. No impurities were detected in these products. Moreover, peak shapes are revealing that well-crystallized sulphide nanoparticles which can be easily synthesized through the thermal decomposition process. The broadening of the peaks indicates that the grain sizes of the samples are of nanometer scale. The size and morphology of the sample were examined by field emission scanning electron microscopy. Fig. 3 showed that the as-prepared $AgBiS_2$ consist of flower-like structures in nanometer scale.

The electrochemical behaviours of hydrazine at the $AgBiS_2$ modified glassy carbon electrode (GCE) were investigated in a phosphate buffer solution (PBS) by scanning from -0.2 to

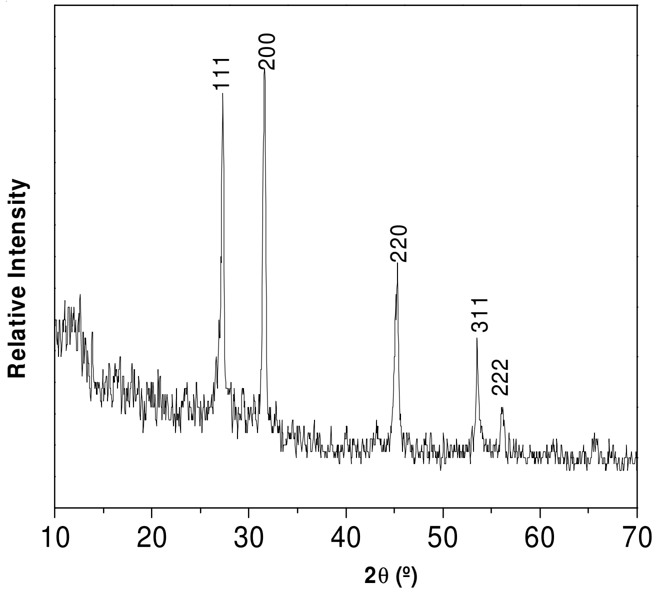

Fig. 2. X-Ray diffraction of $AgBiS_2$

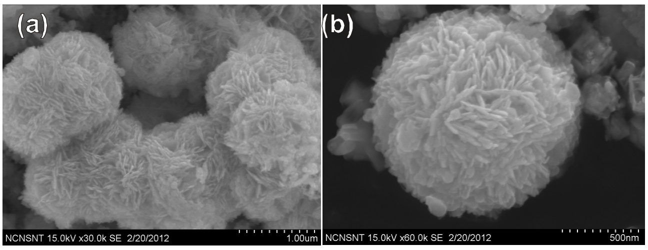

Fig. 3. FE-SEM images of $AgBiS_2$

1.0 V *vs*. Ag wire. When the working electrode was replaced with $AgBiS_2$/GCE, it could be clearly seen that well defined oxidation peak occurred at -0.51 V *vs*. Ag wire corresponding to the hydrazine oxidation. On the other hand no obvious hydrazine oxidation peak was observed at the bare GCE, which implies that $AgBiS_2$ exhibit, an enhanced electrocatalytic activity on oxidation of hydrazine. It is concluded that the peak was assigned due to the oxidation of hydrazine and the peak current (I_p) is found to be higher in the case of $AgBiS_2$/GCE. The influence of variables like scan rate, pH and concentration of hydrazine on peak current was also studied. The effect of scan rate on the anodic peak current of hydrazine was studied and is shown in Fig. 4. A slight shift in peak potential was noted while increasing of potential scan rate and the linear increase of peak current with respect to the scan rate (10-100 mVs^{-1}) was also observed which is due to adsorption controlled electrochemical oxidation of hydrazine. The influence of pH on electrochemical oxidation of hydrazine and is dependent on the pH solution of the medium. Therefore it is necessary to find the optimum pH on oxidation peak current of hydrazine. The cyclic voltammogram of 1.0 mM hydrazine were recorded in the presence of 0.1 M phosphate buffer at the scan rate of 50 mVs^{-1} at different pH (4-11). It can be seen from the Fig. 5 the peak potential (E_p) values of hydrazine were dependent on pH and the anodic peak current of hydrazine found to increase at pH 7 and found to decrease slowly at higher pH value. It is inferred that pK_α value of hydrazine is known to be 7.9[16] that most hydrazine was protonated at pH < 8.0. Thus the maximum catalytic current with better shaped voltammograms was obtained at pH 7 and this buffer medium has an important effect on the efficiency of the electrocatalytic oxidation of hydrazine. So this pH medium was chosen as the optimal pH value. Electrochemical oxidation of hydrazine was carried out at different concentration in presence of $AgBiS_2$/GCE under optimal pH by using DPV method and found that the oxidation peak current increased linearly with increase in the concentration of hydrazine (Fig. 6). Thus the nanoscale $AgBiS_2$ exhibits a promising electrocatalytic activity towards the determination of hydrazine at trace level.

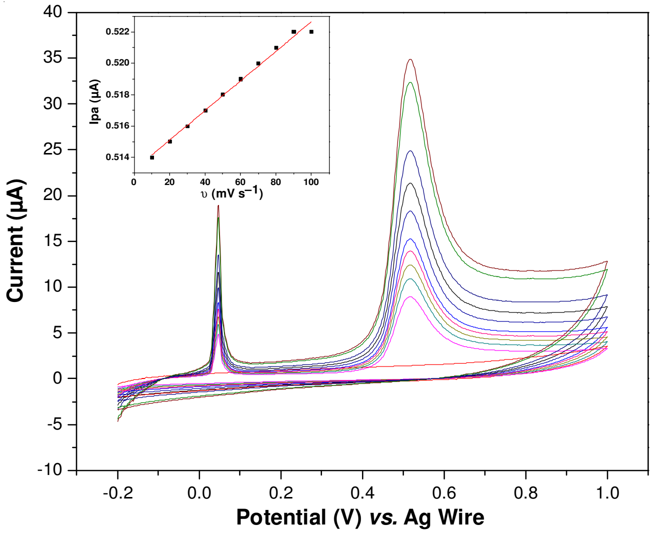

Fig. 4. Cyclic Voltammograms of $AgBiS_2$/GC electrode in 0.1 M PBS (pH7) containing 1.0 mM hydrazine at scan rate 10 to 100 mVs^{-1}. Inset linear plot of I_p Vs scan rate

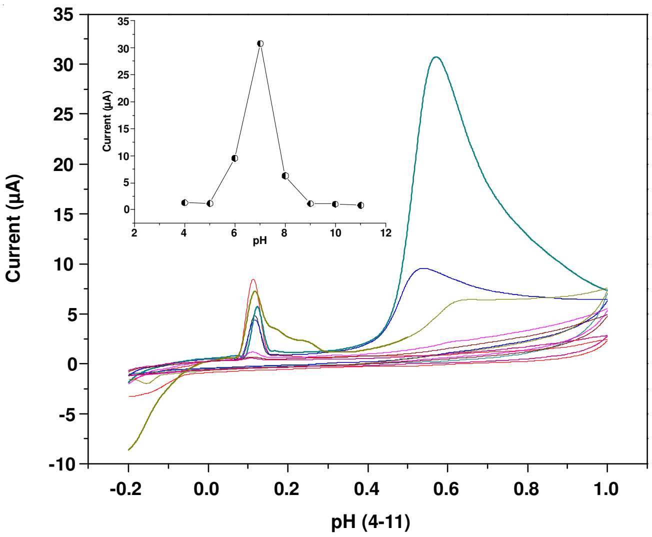

Fig. 5. Shows the effect of pH on the electrocatalytic oxidation of hydrazine at $AgBiS_2$ modified glassy carbon electrode. Inset Ip *vs*. different pH ranges 4-11

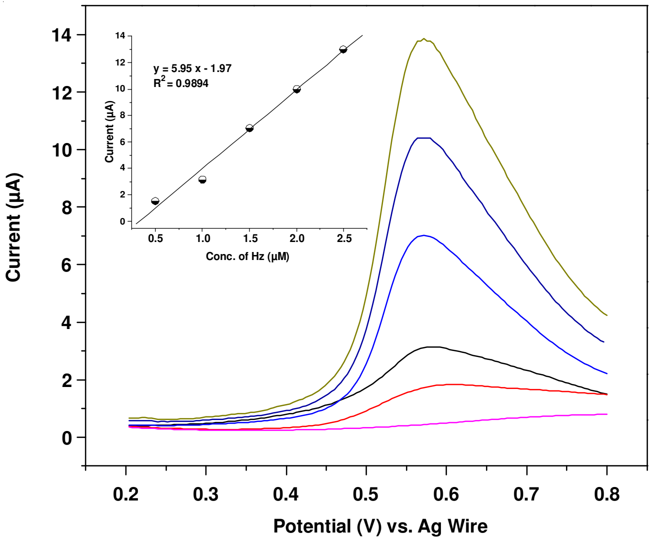

Fig. 6. Differential pulse voltammetry of $AgBiS_2$/GC modified electrode in 0.1 PBS (pH 7) containing hydrazine of different concentrations of (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.0, (5) 2.5 mM. Inset linear graph of Ip *vs*. different concentration

Conclusion

$AgBiS_2$ nanoparticles with flower like shapes were synthesized *via* single source approach. The direct band gap of 2.5 eV was observed for $AgBiS_2$ nanoparticles displayed a strong blue shift caused by quantum confinement effect. The XRD indicated the formation of pure cubic phase $AgBiS_2$. The electrochemical behaviour of the system was investigated using cyclic voltammetry. The $AgBiS_2$ modified GCE showed excellent electrocatalytic oxidation peak current of hydrazine at pH 7 in 0.1 M PBS. Hence the system can be effectively utilized for the electrochemical detection of hydrazine at trace level.

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