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Electrodeposition of (ZnSe:colloidal HgS) composite and their photoelectrochemical characterization

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ABSTRACT

Present investigation explores the possibilities of surfactant facilitated colloidal HgS particulate inclusion during the electrodeposition of ZnSe semiconductor film. Inclusion of colloidal particles was inferred on the basis of current–voltage, photoaction spectral studies and as well as absorption studies of colloidal HgS suspensions. Tafel plots were constructed for the examination of corrosion behaviour of the electrodeposited composites. The results show that inclusion of colloidal HgS particles improves the photoactivity and electrochemical corrosion of the ZnSe semiconductor films.

1. Introduction

Photoelectrochemical processes at the semiconductor (SC)–electrolyte interface have received much attention because of their possible applications in the conversion of solar energy into electrical energy and especially in case of water splitting to generate environment friendly fuels [1–4]. Choice of materials plays an important role for the fabrication of any photoelectrochemical cell. For the occurrence of effective charge transfer processes at the SC–electrolyte interface, the SC material (i) must have a band gap between 1–3 eV so that it can utilize the maximum part of the solar spectrum and (ii) material must be stable against corrosion when placed in a specific redox system. Zinc selenide is a semiconductor material of considerable current practical interest. Because of its somewhat large band gap (2.7 eV) [5,6], ZnSe exhibits acceptable resistance towards electrochemical corrosion but its photoexcitability is confined only to high frequencies. On the other hand, HgS has a low band gap (0.5 eV) material [7] and can utilize a larger fraction of the incident photons. But the main drawbacks with the low band gap materials are (i) they can only generate a lower photovoltage and (ii) these materials are usually found to be susceptible towards the electrochemical corrosion. Coupling of ZnSe semiconductor material with HgS particulate of colloidal dimensions is expected to provide a multiple band gap system, which, in principle, may be suitable for accomplishing the twin task of increased absorption of solar spectrum, and enhanced resistance towards electrochemical corrosion. In the present investigation, we have explored possibility of inclusion of HgS particles of colloidal dimensions during the electrodeposition of ZnSe semiconductor materials in the presence of a cationic surfactant. The multiple band gap system (ZnSe SC–colloidal HgS) has been characterized to assess its suitability for accomplishing photoelectrochemical conversions. Its ability to withstand impairment in structural and functional intactness as a result of electrochemical corrosion has also been examined.

2. Experimental

Colloidal mercuric sulfide solution was prepared by the reaction between two set of solutions, i.e., solution of 0.01 M $HgCl_2$ (Qualigence, India) and 0.01 M Na_2S (s.d.fine-chem Ltd., India) solution, in the presence of cetylpyridinium chloride (CPC). The presence of the surfactant is essential to avoid coagulation of the dispersed particles [8,9]. Absorption studies of the colloidal solution were carried out with the help of UV/visible spectrophotometer (Specard-200, Germany; least count = 0.001). Refractive index measurements were carried out using Abbe's refractometer.

For electrodeposition, $ZnSO_4$ (CDH, India) and SeO_2 (Flucka Chemika, Switzerland) solution of desired composition (pH $\approx$ 3.5) was prepared. A known volume of colloidal HgS (5, 10 and 20 ml, respectively) was then added to the prepared electroplating solution and electrochemical co-deposition carried out using a three-electrode setup [10,11]. Both the working and counter electrodes were titanium foils (1.0 cm^2); and a saturated calomel

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Table 1
Some physico-chemical properties along with estimated values of particle size for colloidal dispersion of different composition.

Colloidal dispersion	Optical density	HC × 10^4	Molecular weight × 10^{-4} (M)	Aggregation number (AN)	Particle size (nm)	Surface area (m^2/g)
(5 ml 0.01 M $HgCl_2$)+(10 ml 0.01 M Na_2S+5 ml 10 mM CPC)	2.52	0.0254	116.33	8525	5.8	14

Experimental value of $n = 1.339 \pm 0.002$ and $n_0 = 1.330$ were used in calculation of 'HC'.

electrode (SCE) was used as reference electrode. For potential and current measurements, digital multimeters (HIL, 2161) were used. *Passage of constant current* (0.2 mA/cm^2) *for the 30 min deposition time interval was ensured* using constant current power supply (Lake Shore, Model 120, USA). The electrodeposited films were also subjected to thermal treatment for their effective binding at the titanium substrate. After deposition the films were kept in a furnace at 100 °C for 30 min in air and then allowed to approach the laboratory temperature while still being kept in the furnace.

For photoelectrochemical studies, I_2/I^{3-} redox couple was used as testing solution. After equilibration the titanium supported material was illuminated using 500 W tungsten lamp. To obtain photopotential, change in potential of the working electrode was monitored till no further change in potential occurred. For photoaction spectral studies, the working electrode equilibrated with the testing solution containing the redox couple was subjected to illumination using f/3.4 monochromator (Applied Photophysics, London). Photopotentials, E_p, in the wavelength range of 400–800 nm were recorded using titanium counter electrode. E_p^2 vs. λ plots were constructed to obtain threshold wavelength, which was then used to obtain band gap of the electrodeposits. For corrosion studies, current–voltage behaviour of the electrodeposited films was investigated to construct Tafel plots for the estimation of corrosion currents [12,13].

3. Results and discussion

3.1. Particle size calculation of colloidal HgS suspensions

Due to high electrolytic content, preparation of colloidal solution in aqueous medium often possess problems because in such conditions colloidal particles have their natural tendency to undergo coagulate. To overcome this difficulty, preparation of colloidal solution was carried out in the presence of cetylpyridinium chloride (cpc), a cationic surfactant. As we know surfactants have their natural tendency to get adsorbed at the air–water, oil–water or solid–water interfaces and they formed an oriented monolayer wherein the hydrophilic groups point towards the aqueous phase and the hydrocarbon chains point towards the air, oil or solid phase [14]. In our case surfactant ions (positively charged hydrocarbon chains) gets adsorbed at the surface of the colloidal particles and thus generate an overall positive charge on them. Mutual repulsions of these positively charged particles are obviously responsible for the observed stability of the colloidal solution in spite of high electrolytic content.

Before using colloidal solution for deposition process, it is desirable to determine the characteristics of HgS colloidal particles present in the dispersion medium. For the determination of the molecular weight of the colloidal particle we have used the following relationship [15]:

$$(HC/\tau)_{C \to 0} = 1/M \tag{1}$$

where M is the molecular weight of colloidal HgS particle, C is the concentration of the solution in g/cm^3, H is the constant and τ is the turbidity of the colloidal solution.

Refractive index measurements were used for the estimation of 'HC', since [16]

$$HC = 32\pi^3 n_0 (n - n_0)^2 / 3N\lambda^4 C \tag{2}$$

where n_0 is the refractive index of the solvent; n the refractive index of the solution and λ the wavelength of sodium light.

For the determination of 'τ' optical density measurements were carried out since

$$OD = \tau d \tag{3}$$

where d denotes optical path length.

For colloidal HgS dispersions, refractive index and optical density values along with estimated values of HC and M are summarized in Table 1. With the help of these data we have estimated the size of the colloidal HgS particles present in the dispersion medium. The estimated values of particle size along with the aggregation number are also included in Table 1. Aggregation number (AN) were calculated using the relationship

$$AN = \frac{\text{MW of the colloidal particle}}{\text{MW of one molecule of HgS}} \tag{4}$$

We can also define surface area (S_A) of the dispersed colloidal HgS as

$$S_A = \frac{\text{area (of the particulate)}}{\text{mass (of the particulate)}} \tag{5}$$

Assuming dispersed colloidal particle to be spherical with radius 'r' we can write

$$S_A = \frac{\pi r^2}{V\rho} \tag{6}$$

where V and ρ, respectively, denote volume of the particle and density of the material. Particulate surface area values estimated using the above relationship are included in Table 1.

3.2. Current–voltage studies of different electroplating solutions

In principle, colloidal particle inclusion during electrodeposition process is not expected. In view of high electrolytic content of the electroplating solution and low magnitude of the operating electrical field, electrophoretic migration of the colloidal particles towards the electrode surface where electrodeposition occurs, is highly unlikely. For colloidal particles deposition to take place, it is necessary that colloidal particles must approach the electrode surface to undergo adsorption. For such systems, Guglielmi [17] postulated a mechanism based on two successive adsorption steps. The first step consists of a loose adsorption followed by field assisted strong adsorption. In our case, the colloidal HgS particles are stabilized as a result of adsorption of a positively charged cationic surfactant (CPC), which ultimately facilitate the colloidal particles to migrate towards the cathode as a result of the combined effect of diffusion and electrodriven migration and get attached permanently within the growing ZnSe electrodeposits.

With a view to ascertain the inclusion of colloidal HgS particles during electrochemical formation of ZnSe, 0.01 M $ZnSO_4$ and 0.001 M SeO_2 solution containing different concentration of colloidal HgS were subjected to current–voltage studies. Results