



Thiocyanate functionalized ionic liquid electrolyte for photoelectrochemical study of cadmium selenide pebbles



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ABSTRACT

A thiocyanate functionalized ionic liquid based electrolyte is developed for the application in CdSe thin film solar cell. An aqueous solvent consisting of polysulfide and thiocyanate functionalized IL has been found as the optimum solvent for preparing the liquid electrolytes. This solvent ratio appears to give higher cell efficiency compared to pure aqueous polysulfide electrolyte. Polysulfide and thiocyanate functionalized IL give rise to a good redox couple in the electrolyte for photoelectrochemical performance. The CdSe photoanode used for solar cell study has been synthesized by a simple and cost-effective one-step, one-pot chemical bath deposition method onto the F: SnO₂ substrates. The as-deposited films were annealed at temperatures 100, 200, 300 and 400 °C, respectively for 1 h in ambient air. The maximum current density of 3.55 mA/cm² for the sample annealed at 300 °C is observed in the polysulfide electrolyte with the power conversion efficiency 0.76%. Addition of thiocyanate functionalized IL in polysulfide produced the highest current density of 4.93 mA/cm² with the two fold increase in the power conversion efficiency up to 1.32%.

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1. Introduction

Electrolyte is an important factor as like the electrode material for the efficient solar cell. As per the green context, Ionic Liquids (ILs) successfully replaces the conventional organic solvents in photoelectrochemical solar cells. Due to the unique physico-chemical properties they can be employed as an electrolyte in electrochemical systems. IL electrolytes have great affect on energy conversion efficiency and stability of solar cells. Graetzel proposed IL based dye sensitized solar cells (DSSCs) which are potentially the ideal basis of a liquid or gel electrolyte. It is now possible to depart completely from the classical solid-state junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photoelectrochemical cell. The phenomenal progress realized recently in the

fabrication and characterization of nanocrystalline materials has opened up vast new opportunities for these systems [1].

ILs are room temperature molten salts that entirely consist of ions and are liquid at or close to room temperature. ILs can exhibit advantageous properties like high thermal and chemical stability, negligible volatility, flame retardancy, moderate viscosity, high polarity, low melting point, high ionic conductivity, solubility (affinity) with many compounds [2,3]. Their physical and chemical properties can be tailored by tuning the pairing and structure of the cations and anions, so that they are also known as “designer solvents”. Many ILs offer a range of properties that make them attractive to the field of electrochemistry. A variety of electrochemical devices including solar cells, high energy density batteries, fuel cells and supercapacitors have become of intense interest as part of various proposed solutions to improve sustainability of energy supply in our societies [4]. Thus, they pertain to a new class of electrolytes that, in contrast to ordinary electrolytes, contain no molecular solvent. The keen attention to IL was due to their properties such as the wide liquid state interval, incombustibility and explosion safety, non-volatility (very low vapor pressure); certain ILs are characterized by relatively high ion

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conductivity and a wide interval of decomposition voltage, most of ILs are nontoxic. It is for the latter reason that they are called “green liquids” [5,6].

For the successful operation of a photoelectrochemical solar cell, a good electrolyte with a redox mediator is required. The redox mediator regenerates the oxidized sensitizer by donating an electron. There are not many electrolyte/redox mediator systems which can function in all kinds of solar cells like photoelectrochemical solar cell, DSSCs and Quantum Dot Sensitized Solar Cells (QDSSCs). The iodide-based electrolyte systems best suits for DSSCs [7]. However, in chalcogenide based photoelectrochemical solar cells and QDSSCs, iodide-based electrolytes produce very poor results [8–11]. This problem can be resolved by coating the surface of a photoanode, resulting in a good efficiency with I^-/I_3^- redox electrolyte [10]. Hence, the electrolyte chosen plays a major role in determining the performance of aforementioned liquid junction solar cells. Polysulfide electrolytes have been used by many researchers as an electrolyte of choice for chalcogenide based photoanodes and QDSSCs [12,13]. An optimized polysulfide electrolyte system has been reported for use in CdS QDSSCs by Lee and Chang [14]. The effect of polysulfide electrolyte composition for higher performance of Si QDSSCs is studied by Seo et al. [15]. Chen et al. [16] have demonstrated dextran based highly conductive hydrogel polysulfide electrolyte for efficient solar cells. Cobalt complex based electrolytes are used by Chae et al. [17] for cobalt sulfide thin films. Yang and co-workers [18] used Na_2S based electrolyte for CdS solar cells. A new terpyridine cobalt complex redox shuttle electrolyte is used for DSSCs [19]. We have used the polysulfide and thiocyanate IL based electrolytes to study photoelectrochemical performance of CdSe pebbles. There are varieties of polysulfide compositions reported in the literature which give reasonable efficiencies for CdSe based solar cells. The compositions contain various amounts of KCl, NaOH, or KOH as additives. Lee et al. [20] reported an efficiency of 2.9% in a CdSe QDSSC by using an electrolyte consisting of Na_2S , S and KCl in water/methanol mixture. Meanwhile, Diguna et al. [21] obtained an efficiency of 2.7% with just Na_2S and S in the liquid electrolyte. However, a lower efficiency of 1.83% has been reported with an electrolyte composition of Na_2S , S and NaOH [22]. A somewhat lower efficiency was obtained by Salant et al. [23] with an electrolyte composition of Na_2S , S, and KOH.

CdSe is of special interest because of its direct optical band gap energy of 1.74 eV. Varieties of physical and chemical techniques are available for the growth of CdSe thin films [24–26].

In the present work, we first time report on the thiocyanate functionalized IL based electrolyte for photoelectrochemical study of CdSe thin films synthesized by a facile and low cost chemical bath deposition (CBD) method with novel pebble-like microstructures. The as-deposited films were annealed at temperatures 100, 200, 300 and 400 °C respectively for 1 h in ambient air. The maximum current density of 3.55 mA/cm² for the sample annealed at 300 °C is observed in the polysulfide electrolyte with the power conversion efficiency 0.76%. Addition of thiocyanate functionalized IL in polysulfide produced the highest current density of 4.93 mA/cm² with the two fold increase in the power conversion efficiency up to 1.32%.

2. Experimental

2.1. Thin film deposition

Thin films of CdSe are deposited on glass and F: SnO₂ (FTO) substrates by CBD using cadmium sulfate ($CdSO_4 \cdot xH_2O$) as a precursor for Cd, 25 vol% NH_4OH as a complexing agent and freshly prepared sodium selenosulphate (Na_2SeSO_3) for Se source. All

chemicals used were of analytical grade and used without further purification.

Initially, Na_2SeSO_3 is prepared by a standard procedure [27]. In a typical experiment, Se powder was dissolved in an aqueous solution containing sodium sulphite and this solution is refluxed for 12 h at 70 °C. Unreacted Se was removed by filtration. For the deposition of CdSe by CBD, an aqueous solution of 0.1 M cadmium sulfate in 30 ml was taken in a 100 ml beaker, followed by slow addition of 30 ml 25 vol% NH_4OH with constant stirring, to maintain pH of the solution at ~ 11 . The solution became milky and turbid after addition of ammoniacal solution in cadmium precursor at room temperature due to the formation of $Cd(OH)_2$. Excess addition of ammonia leads to a clear and transparent solution. Finally, 30 ml freshly prepared 0.1 M Na_2SeSO_3 is added to the solution which undergo a colour change from transparent to light yellow. The temperature of the bath is kept constant at 70 °C and a deposition is carried out for 8 h. The substrates (glass/FTO) were removed from bath and rinsed thoroughly using double distilled water and kept at room temperature for air drying, this as-deposited sample is represented as CdSe₈. Further, the as-deposited samples are air annealed at temperatures 100, 200, 300 and 400 °C for 1 h and are represented as CdSe₈-100, CdSe₈-200, CdSe₈-300 and CdSe₈-400, respectively.

2.2. Characterization of CdSe thin films

Surface morphology was examined using FESEM (JEOL JSM-6500F). The elemental information of the films was analyzed using an XPS Thermo K-Alpha with multi-channel detector, which has high photonic energies from 0.1 to 3 keV. The XRD spectra of the films were recorded using X-ray diffractometer (Bruker AXS D8 model). For photoelectrochemical study the CdSe thin films (average area 1 cm²) and graphite rod (average area 1 cm²) were employed as the working and counter electrodes, respectively. The distance between the photoelectrode and counter electrode was kept constant at 0.5 cm. An aqueous polysulfide + thiocyanate functionalized IL electrolyte solution was used as the redox electrolyte. Measurements for the power output characteristics and J–V plots were made at fixed intervals after waiting a sufficient amount of time for the system to reach equilibrium (both in the dark and under illumination).

2.3. Synthesis of thiocyanate functionalized ionic liquid

IL is synthesized according to a simple modified literature method [2,28]. Briefly, the procedure is- a mixture of 1-methylimidazole and slightly excess molar quantity of 1-chlorobutane was refluxed at 70 °C for 48 h in acetone. Two layers were formed, upper solvent layer was decanted. The IL, [BMIm][Cl] (1-butyl-3-methyl imidazolium chloride) thus formed was purified by washing with ethyl acetate (10 ml × 3) followed by *n*-hexane. It was then dried in vacuum under reduced pressure. In further step a metathesis reaction of [BMIm][Cl] and potassium thiocyanate was carried out. A stoichiometric mixture of [BMIm][Cl] and KSCN in dichloromethane was stirred vigorously for 48 h at room temperature. Synthesized IL, [BMIm][SCN] (1-butyl-3-methyl imidazolium thiocyanate) was then dried in vacuum under reduced pressure (Scheme 1). It was then characterized by ¹HNMR spectroscopy (Fig. 5).

2.4. ¹HNMR Data for [BMIm][SCN]

Structure of the synthesized ionic liquid is confirmed by ¹HNMR. The obtained ¹HNMR data is as follows,

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