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Silver–copper nanoalloys-an efficient sensitizer for metal-cluster-sensitized solar cells delivering stable current and high open circuit voltage

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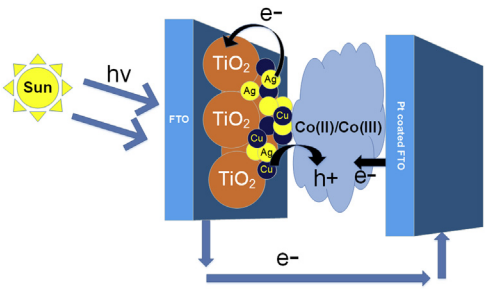
HIGHLIGHTS

- Synthesis of monometallic and alloyed Ag–Cu clusters through salt reduction method.
- Synthesis of mesoporous TiO_2 through sol-hydrothermal technique.
- Spray-coating technique to deposit clusters on TiO_2 photoanodes.
- Cu-rich alloyed clusters exhibit J_{sc} of 2.87 $mAcm^{-2}$ and V_{oc} of 691 mV with PCE 1.1%.
- Ag sensitizers demonstrate high J_{sc} whereas Cu sensitizers exhibit high V_{oc}.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal clusters (CLs) are recognized as a new class of sensitizers in a metal-cluster-sensitized solar cell (MCSC) which is an extension to well-recognized dye-sensitized solar cells (DSSCs). The function performed by dyes in DSSCs has predominately been executed by metal CLs in MCSCs. The distinct behavior of CLs at nano-scaled level can enhance their significance in photovoltaic applications. Recently, metal CLs have been explored as sensitizers in a solar cell, and the efficiency of the cell has been reported to be more than 2%. Herein, we present glutathione-protected Ag–Cu bimetallic CLs (alloyed CLs or nanoalloys) as sensitizer in MCSCs. Spray-coating technique has been employed to deposit CLs on photoanodes. The TiO_2 modified with Cu rich alloyed CLs exhibit the short circuit photocurrent (J_{sc}) of 2.87 $mAcm^{-2}$ with V_{oc} of 691 mV. EIS and Mott–Schottky analysis have been performed to explicate the processes occurring inside MCSCs. Comparative study has been conducted to elucidate the effect of alloying on photo-electrochemical (PEC) response. Our results lay the foundations for exploring other nanoalloys as sensitizers in solar cells because nanoalloys present a greater degree of flexibility in properties, structure, size, and the composition of the constituent elements.

1. Introduction

The promising field of using plasmonic metals such as Ag, Au and Cu into photovoltaic applications has become one of the most widely researched areas. The mechanisms unique to plasmonic metals direct and localize solar light at nano-scaled level much

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below the wavelength of light [1]. The search of new materials, their synthesis and applications have ever been remained forefront in the technological advancement. Utilization of metal nanoparticles (NPs) and CLs in emerging technologies are evident that the human quest for searching and employing nanomaterials is growing with the passage of time. From practical viewpoints, several strategies have been proposed and put forwarded to incorporate metal NPs into solar cells for their performance enhancement. In this respect, one strategy to enhance the performance of solar cells is the use of plasmonic metal NPs for improving light absorption through surface plasmon excitation phenomena [2,3]. Increasing the optical path length of light through scattering process from the plasmonic NPs has been considered another effective approach to improve the absorption in solar cells [4]. The most interesting approach for employing NPs into solar cells is their distinct use as sensitizers without additional use of dyes [5]. The frequent use of metal NPs and clusters in energy applications calls for the stability of NPs. Coalescence and oxidation of metal NPs are the associated issues. In this regards, some sort of ligands or protecting agents have been recommended such as thiolates [6–8], dendrimers [9] and selenolates [10]. These ligands stabilize and protect the NPs especially oxidizing metals (e.g Cu). The change of ligands has no or little effect on the optical properties of metal NPs and CLs [11,12]. Thiolate and di-thiolate protected Ag and Au nanocluster molecules have also been synthesized [13]. Excited state dynamics of glutathione-protected metal CLs have been thoroughly studied [14]. Keeping in view the growing trend in the use of metal NPs, Tatsuma et al. synthesized metal CLs (Ag, Au, Cu etc) in powder forms so as to enhance the stability of NPs [15]. Both experimental and theoretical techniques have been employed to characterize metal NPs and CLs. In addition to monometallic metal NPs, bimetallic CLs and NPs have also received much attention of researchers around the world. Theoretical study of Ag and Au bimetallic CLs has been executed using different set of ligands [11]. Among the nanoalloys, Ag–Cu nanoalloys represent one of the most widely researched bi- and multi-metallic systems and have largely been explored with reference to their applicability in energy applications. Electronic structures and chemical ordering of promising Ag–Cu bimetallic CLs have also been investigated theoretically [16–19]. Optical absorption properties and symmetries adopted by Ag–Cu bimetallic CLs have theoretically been investigated by one of our groups [20]. Size and shape dependencies of optical spectra of monometallic Ag and Cu CLs have also been investigated [21].

Aforementioned discussion reveals that Ag, Au and Cu CLs and NPs are optically attractive materials. Some researchers have made efforts to explore distinct properties of metal CLs as photosensitizers in solar cells. In this regard, Ag CLs have been investigated with reference to their ability to function as photo-sensitizers coupled with TiO_2 semiconductor [22]. The breakthrough in the use of metal CLs as sensitizers was the research put forwarded by Kamat P.V et al. when they achieved power conversion efficiency (PCE) greater than 2% with glutathione-protected Au CLs [23]. Monometallic metal CLs have already been studied from photosensitization viewpoint but alloyed CLs have not been investigated so far as photo-sensitizers. Herein, we demonstrate Ag–Cu alloyed CLs as photo-sensitizers in MCSCs because optical properties are greatly influenced not only by size and shapes of CLs but the composition of the constituting elements as well [24].

We synthesize glutathione-protected Ag–Cu alloyed CLs and disperse into polymer-based Nafion dispersions (DuPont D520). Soaking or immersion techniques are normally used to deposit sensitizers on photoanodes, where photoanodes are dipped into dye solutions. In the case of metal CLs to be deposited on TiO_2 photoanodes, these soaking techniques do not provide proper control on the density of CLs. Herein, unlike common soaking techniques, we make use of spray-coating technique, for the first time, to deposit Ag–Cu alloyed CLs on the mesoporous TiO_2. Nafion has been employed to disperse and stabilize metal CLs since it is mostly used as catalyst dispersions and stabilizing agent for NPs [25,26]. We investigate PEC response of resultant MCSCs. We also demonstrate the effect of alloying of Ag and Cu on PEC response. We synthesize separately monometallic Ag and Cu CLs followed by the synthesis of alloyed CLs as Ag_1Cu_3, Ag_3Cu_1 and Ag_1Cu_1. The subscripts in alloyed CLs indicate the proportion of Ag and Cu. Through investigation, it has been found that the TiO_2 modified with Cu rich alloyed CLs exhibit PCE greater than 1% with stable J_{sc} of 2.87 mA/cm^2 and V_{oc} of 691 mV. Throughout the research paper, the efforts have been made on comparative study to demonstrate the effect of alloying of Ag and Cu on PEC response. Further investigation encompasses EIS and Mott–Schottky analysis to explicate the processes occurring in MCSCs. Our investigation reveals that Cu rich alloyed CLs show high V_{oc} owing to Cu and high J_{sc} is due to the presence of Ag.

Throughout the paper, for convenience, the term 'bare TiO_2' or TiO_2 is used for un-modified TiO_2 photoanode. The terms Cu rich and Ag rich are used for Ag_1Cu_3 and Ag_3Cu_1 alloyed CLs, respectively. Moreover, fabricated MCSCs have been named according to the type of CLs used to modify TiO_2. For example, the J_{sc} of Ag_1Cu_3 means that the J_{sc} of MCSCs (devices) constructed from TiO_2 photoanodes modified with Ag_1Cu_3 CLs.

2. Experimental

All chemicals and salts were used as analytical grades without any further purification. We synthesized TiO_2 colloids, Ag, Cu and Ag–Cu alloyed CLs followed by the fabrication of the MCSCs. TiO_2 colloidal solution was synthesized by a sol-hydrothermal method reported elsewhere with a little modification [27]. The method has briefly been mentioned in the supporting information. Synthesis of Ag, Cu and Ag–Cu bimetallic CLs have been carried out according to the literature [8]. Briefly, for the synthesis of Ag_1Cu_3 bimetallic CLs, 0.25 mM $AgNO_3$ and 0.75 mM $CuSO_4{:}5H_2O$ were mixed together thoroughly and added to 90 ml DI water. Later on, 0.25 mM L-Glutathione was added to the mixed solution and aged for 30 min under constant stirring. An ice-cold $NaBH_4$ (0.2 M, 10 ml) was added and the color of the solution turned into dark brown. Vigorous stirring continued for minimum 10 h followed by dropwise addition to 90 ml Methanol. The precipitates thus obtained were collected using centrifugation at 4000 rpm for 30 min. The precipitates then thoroughly washed with methanol and dried in vacuum followed by the addition to Nafion dispersions, and ultrasonically agitated for 20 min. Monometallic Ag and Cu clusters were synthesized similarly and described in the supporting information.

MCSCs have been fabricated according to the literature [23]. Spin-coating technique was employed to deposit TiO_2 paste on transparent conducting glass i.e FTO glass. All TiO_2 coated photoanodes were prepared under similar spin-coating parameters. Supporting information can be viewed for detailed synthesis and device-fabrication procedures. Metal CLs were spray-coated onto photoanodes using TiO_2 coated FTO as substrate. Spraying technique was carried out at room temperature using nitrogen as a carrier gas under mild pressure.

The surface morphologies of photoanodes were characterized by scanning electron microscopy (JSM, 6390A) with energy dispersive X-ray spectroscopy (SEM-EDS). The crystallite size of TiO_2 and its crystal phase were determined through the X-ray diffraction (XRD) technique. The XRD data were acquired with a scanning speed of $10^\circ min^{-1}$ in the 2Θ range between 20 and 80°