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Solution-growth-synthesized $Cu(In,Ga)Se_2$ nanoparticles in ethanol bath for the applications of dye-sensitized solar cell and photoelectrochemical reaction

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ABSTRACT

In this study, ternary $CuInSe_2$ and quaternary $CuIn_{1-x}Ga_xSe_2$ (CIGSe) nanoparticles (NPs) are grown in the ethanol bath using the one step solution growth method. The influence of Ga content in samples on the optical and electronic properties of the samples is investigated. Average particle sizes of samples are less than 66 nm after a 10-min. reaction in the solution. The NPs are prepared as the ink for the deposition of CIGSe samples on substrates. X-ray diffraction patterns of samples reveal that samples are the chalcopyrite CIGSe phase when the [Ga]/[In+Ga] molar ratio in solution bath of less than 0.5. The carrier concentration and mobility of samples are in the ranges of 1.2×10^{13}–9.1×10^{15} cm^{-3} and 1.4–205 $cm^2/V/s$, respectively. The results show that the maximum photo-conversion efficiency of 7.02% for the dye-sensitized solar cells using CIGSe as the counter electrodes and the maximum photoelectrochemical performances of 0.96 mA/cm^2 at an external bias of −0.8 V vs. an Ag/AgCl electrode using the CIGSe as the photoelectrodes in salt–water solution, respectively.

1. Introduction

The development of renewable energy has become increasingly important due to the emergence global warming and associated climate change. Among these renewable energy technologies, photovoltaics (PV), which converts solar energy into electrical power, has received a lot of attentions as a solution to future clean energy demands. Dye-sensitized solar cells (DSSCs) are third-generation PV with the good solar-to-electrical power conversion efficiency, low cost, and easy fabrication procedures [1–3]. Commercial DSSCs consist of a mesoporous TiO_2/dye photoelectrode, I^-/I_3^- electrolyte, and a counter electrode (CE). Platinum (Pt) nanoparticles (NPs) deposited onto a transparent conducting oxide (TCO), such as indium-doped tin oxide (ITO)-coated glass substrates, have shown excellent electrocatalytic ability, high chemical stability, and good electrical conductivity in an I^-/I_3^- electrolyte [3–5]. However, DSSCs using Pt NPs on a TCO layer as the CE have limited industrial applications due to the scarcity and high cost of Pt. Several possible candidates with good electrocatalytic ability in the electrolyte, such as metal alloys [6,7], carbon-based materials [1,8,9], conducting polymers [8,9] and transition metal sulphides/selenides [10–13], have been investigated. Binary metal selenides/sulphides such as $NiSe_2$ [13], $CoSe_2$ [13], CoS [4,14], NiS [15,16], MoS_2 [17,18], WS_2 [19], and $RuSe_2$ [20] on TCO layer have been tested as CEs in DSSCs due to their excellent stability and good electrocatalytic activity for the reaction of I_3^- ions in an electrolyte [9,12]. Recently, multi-component metal sulphides such as $CuInS_2$ [21,22], $CuInS_2$–ZnS [23], $Cu_2In_2ZnS_5$ [24], $CuSbS_2$ [11], and Cu_2ZnSnS_4 [10,25] as CEs in DSSCs have received a lot of attentions. Compared with binary metal sulphides, the physical properties of these multi-component metal sulphides such as electrical conductivity, carrier mobility, catalytic activity in an electrolyte, and the position of the conduction band for these metal sulphides can be adjusted by the small changes of compositions in the samples [9,22,26,27]. Liu et al. [21] prepared sponge-like $CuInS_2$ microspheres using a one-step solvothermal method. The photo-conversion efficiency (PCE) of their DSSC using $CuInS_2$ as the CE was around 3.31%, which increased to 6.18% when a mixture of $CuInS_2$/graphene oxide was used as the CE in their DSSC. Both open-circuit voltages (V_{oc}) and short circuit densities (J_{sc}) for their DSSCs using the $CuInS_2$ + graphene oxides (0, 3%, 6%) as CEs increased due to the increase in the electrical conductivity and

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electrical carrier mobility in samples compared with that just using $CuInS_2$ as the CE in the DSSC. Chen et al. [22] prepared $CuInS_2$ nanoparticles by incorporation of Cu^+ ions into In_2S_3 nanoplates at room temperature and had a maximum of PCE of 6.83% for their DSSCs using $CuInS_2$ as the CE. The major contribution for PCE of their DSSC using $CuInS_2$ as the CE is due to the high crystalline $CuInS_2$ samples formed under an annealed temperature of 480 °C. It can improve the charge transfer rate and electrical properties of $CuInS_2$ CEs in DSSCs. Yi et al. [23] prepared wurtzite $CuInS_2$–ZnS heterostructured nanorods using a seed-assisted synthetic route. The maximum PCE of their DSSCs using wurtzite $CuInS_2$–ZnS nanorods as the CEs was 7.5%. Their results also show that the V_{oc} and J_{sc} of their DSSCs using the $CuInS_2$–ZnS nanorod as the CE ($V_{oc} = 0.77$ V, $J_{sc} = 15.3$ mA/cm^2) are higher than that of DSSC using Pt as the CE ($V_{oc} = 0.72$ V, $J_{sc} = 13.8$ mA/cm^2). The increase in the V_{oc} of DSSCs using the $CuInS_2$–ZnS nanorods as the CEs is due to relatively lower series resistances of samples than that of Pt electrodes. With doping ZnS into the $CuInS_2$ samples, the charge transfer resistance at CE/electrolyte interface decreased compared with that for pure $CuInS_2$, which made the higher J_{sc} of DSSCs using $CuInS_2$–ZnS nanorods as CEs. Fan et al. [25] prepared copper–zinc-tin sulphide (CZTS) thin film electrodes using the sulfurization of direct current magnetron sputtered Cu–Zn–Sn metal alloys on ITO-coated glass substrates. The maximum PCE value of their DSSCs using CZTS samples as the CE was 7.94%, which indicates that the CZTS samples has a potential to replace the Pt as the CE in a DSSC. However, major problem of their CZTS CEs for the possible industrial applications is the vacuum apparatus that has to be used for the preparation of CZTS samples. Xin et al. [10] also prepared CZTS nanocrystals using a solution-based synthesis approach with the reaction temperature and time of 225 °C for 1 h and obtained the CZTSSe samples under Se vapor thermal treatment. The PCEs of their DSSCs using CZTS and CZTSSe nanocrystals on substrates as the CEs were 3.62% and 7.37%, respectively. Their results showed that by incorporation of Se ions into CZTS samples would improve the PCE of the DSSC. These studies showed that by incorporation of metal ions into the metal seleindes may enhance the PCEs of DSSCs using these multicomponent metal seleindes as the CEs because of the decrease and increase in the electrical resistance and electrocatalytic ability of CEs in electrolyte, respectively. The goal of this study is to try to develop a simple, low-cost, non-vacuum and time saving method for the preparation of ternary $CuInSe_2$ and the quaternary $Cu(In,Ga)Se_2$ (CIGSe) NPs with similar performances of CZTS CEs in DSSCs because the prices of In and Ga elements would increase the cost of DSSC modules. The CIGSe inks were then prepared from the obtained NPs and directly deposited onto substrates using a spin-coating process. The electrical properties, electrocatalytic activities, charge transfer resistances and cell performance of DSSCs using various CIGSe and Pt as CEs are studies using cyclic voltammetry, Tafel plots, electrochemical impedance spectroscopy (EIS) and current density–voltage (J–V) curves obtained under 100-mW/cm^2 light illumination from a class A solar simulator, respectively. The possible application for solar salt–water splitting using these CIGSe photoelectrodes in a photoelectrochemical cell was also tested in this study.

2. Experimental details

2.1. Synthesis of CIGSe NPs

The preparation of CIGSe NPs was carried out using a one-pot synthesis method. The [Ga]/[In+Ga] molar ratio in the precursor solution bath was varied to study its effect on the preparation of CIGSe NPs. Analytical-grade copper nitrate [$Cu(NO_3)_2$•2•$5H_2O$], indium nitrate [$In(NO_3)_3$•$5H_2O$], gallium nitrate [$Ga(NO_3)_3$], sodium borohydride [$NaBH_4$], Se powders, and absolute ethanol were obtained from Merck and Simga-Aldrich Co. and used as received. The cationic and anodic precursors were prepared in the ethanol bath separately. 24 ml of ethanol bath, which was well stirred, contained 9.6 mmol Se powders and 14.4 mmol $NaBH_4$ in order to form Se^{2-} ions in the anodic solution at room temperature. In the organic solution containing $NaBH_4$, the Se powders were first reduced into Se^{2-} ions, which can be dissolved in an organic solution that becomes a colorless solution in 5 min. 18 ml of ethanol bath, which was well stirred, containing 0.8 mmol $Cu(NO_3)_2$, 0.8–0.32 mmol $In(NO_3)_3$ and 0–0.48 mmol $Ga(NO_3)_3$ was used as the cationic solution. The cationic solution was injected into the anionic solution and reacted under ultrasonic irradiation (UC-DC150H, DELTA) operating at a frequency of 40 kHz and a power of 200 W. The reaction was carried out in a nitrogen environment at a temperature of 70 °C. The NPs were obtained at 10 min. after the cationic solution was injected into the anionic solution bath. The detail [Ga]/[In+Ga] molar ratios in the reaction bath for the preparation of NPs are shown in Table 1. After the reaction in the solution bath, the NPs were rinsed with ethanol and acetone several times and dried in an oven at 70 °C for 2 h.

2.2. Deposition of CIGSe thin films and fabrication of DSSCs

Terpineol ($C_{10}H_{18}O$, purity > 96%, viscosity = 25.66 mPa s) was used for the preparation of CIGSe NPs ink. 0.1 g of NPs was mixed with 0.9 g of terpineol at a water bath under ultrasonic irradiation (UC-DC150H, DELTA) operating at a frequency of 40 kHz and a power of 200 W for one day. The inks were directly deposited onto the surfaces of soda-lime glass substrates or fluorine-doped tin oxide (FTO)-coated glass substrates (FTO, 7 Ω/sq, transmittance ≧ 80%, NSG America, Inc., New Jersey, USA) using the spin-coating process. The as-deposited films on substrates were placed in an oven and kept at 80 °C for 24 h. Then, the films on substrates were put into a quartz tube under a nitrogen environment and annealed at 550 °C for 30 min in order to obtain high-crystallinity samples. The thickness of films on substrates measured using a surface profiler (Surfcorder ET3000, Kosaka Laboratory Co.) was kept at 3 μm. The process for the fabrication of DSSCs with various CIGSe films on FTO-coated glass substrates is the same with our previous study [12].

2.3. Characterization of performances of CIGSe electrodes in DSSCs and salt water

The microstructures and particle size distributions of NPs were investigated using transmission electron microscopy (TEM, Hitachi H-7500). The crystallographic study of samples was conducted using an X-ray diffractometer (Siemems D5005) with CuKα ($\lambda = 1.5405$ Å) irradiation and a Raman spectroscopy (Protrustech, UniRaman, 523-nm YAG laser), respectively. X-ray diffraction (XRD) patterns were recorded in the 2θ range of 20°–80°. The surface microstructures and compositions of the samples on glass substrates were studied using field-emission scanning electron microscopy (FE-SEM, JEOL JSM 5410) with energy-dispersive analysis of X-ray (EDAX, OXFOED 6587). The mobility and carrier concentration of the samples on glass substrates were measured using room-temperature Hall measurement (Ecopia Model HMS-3000) with a magnetic flux of 0.57 T. Electrocatalytic abilities and electrochemical properties of the CIGSe films on FTO-coated glass substrates in the electrolyte were investigate using cyclic voltammetry (CV), Tafel polarization curve and EIS. The CV curves of CIGSe electrodes in the electrolyte were recorded using a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, Netherlands). The test procedures are similar with those reported in our previous study [12]. Tafel plots and EIS spectra of various CIGSe samples were measured by using the potentiostat/galvanostat (PGSTAT 30, Autolab,

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