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$CuInGaSe_2$ nanoparticles by pulsed laser ablation in liquid medium

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ABSTRACT

Pulsed laser ablation in liquid medium (PLALM) is a nanofabrication technique to produce complex nanostructures. $CuInGaSe_2$ (CIGS) is an alloy with applications in photovoltaic industry. In this work, we studied the effects of laser ablation wavelength, energy fluence and liquid medium on the properties of the CIGS nanoparticles synthesized by PLALM. The nanoparticles obtained were analyzed by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), selected area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS) and UV–vis absorption spectroscopy. XPS results confirmed the chemical states and composition of the ablated products. TEM analysis showed different morphologies for the nanomaterials obtained in different liquid media and ablation wavelengths. The optical properties for these CIGS nanocolloids were analyzed using UV–vis absorption spectroscopy. The results demonstrated the use of PLALM as a useful synthesis technique for nanoparticles of quaternary photovoltaic materials.

1. Introduction

Nanomaterials with potential applications in solar energy conversion and optoelectronics such as visible and near infrared photodetectors, light emitters, data storage etc. is an emerging research area. The size, shape, composition, monodispersity and surface properties of these nanomaterials are important to explore their novel properties in various applications. Colloidal nanomaterials have attained much interest because they can be synthesized at relatively low temperature on a large scale and further processed using low cost techniques like spin coating, mechanical spray or printing techniques. Nanomaterials of chalcopyrites such as $CuInSe_2$ (CIS), $CuInGaSe_2$ (CIGS) and $Cu_2ZnSn(S,Se)_4$ (CZTS) are of considerable importance because these are promising absorber materials in solar cells and efficient photodetectors of UV–vis and near infrared. They have high optical absorption coefficients as well as high internal quantum efficiencies [1]. These are eco-friendly and band-gap engineerable nanomaterials due to the following points (i) nanomaterials having both large surface to volume ratios and quantum confinement effects (ii) materials more eco-friendly having less toxicity and environmental hazard (iii) good visible and NIR spectral response that could be useful in imaging applications such as biomedical imaging, conventional imaging as well as industrial applications like sensors, communications and environmental monitoring (iv) band gap engineering for nanomaterials to explore applications in solar cells and design of new and efficient photodetectors.

Among solar cells made up of CIGS, thin film solar cells have achieved 20% efficiency which was developed using vacuum co-evaporation [2–4]. Other solution based techniques for CIGS synthesis include electrodeposition [5] and coating of metal salt [6] or organometallic precursor [7]. Another interesting alternative is to use particles as precursors in the form of an ink or colloid. Quaternary and ternary chalcogenide nanomaterials were synthesized by several colloidal methods and solar cell efficiencies up 12% were achieved [8]. Liu and Chuang [9] fabricated CIGS thin films using nanoparticle precursor inks of different compositions (Cu, In, Ga and Se) prepared by a rotary ball milling technique followed by subsequent annealing of the precursor films. The sintering was carried out in a non-vacuum environment with selenization and the crystalline structure, morphology, stoichiometry and photovoltaic propertied were described. A laser (6 kW fiber coupled diode laser) post treatment of CIGS ink nanoparticles as well as an ink mixture of CIG (Cu–In–Ga) alloy and Se nanoparticles led to formation of chalcopyrite structures [10]. Nanoparticles (NPs) of

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CIGS were also obtained by a wet chemical synthesis without selenization process [11]. CIGS nanoparticles synthesized by a modified polyol route were characterized for their morphology, structure and elemental composition [12].

Pulsed laser ablation in liquid medium (PLALM) is a well-known, simple and effective conventional method to synthesize nanoparticle colloids. It is a one pot, one step, green method that has a number of advantages like wide range of applicable materials, many choices of solvents, rapid, easy, lack of toxic reagents as well as stabilizing agents and biocompatibility. In this physical method, output of a pulsed laser is focused on a target that is submerged in a liquid. Ablation process leads to generation of nanomaterials in the colloidal form having good crystallinity and stability. PLALM has emerged as a reliable physical method to obtain various kinds of nanoparticles (NPs), like pure noble metal nanoparticles, alloys, oxides, semiconductors and ceramics [13,14]. The products obtained by laser ablation in liquid depend on many parameters of the input laser pulses as well as the nature of the surrounding media. The laser wavelength, pulse duration, fluence, beam waist, repetition rate and number of pulses incident per unit area are the laser parameters that affects the nanomaterial products of ablation.

Guo and Liu [15] obtained colloidal metallic nanoparticles of Cu–In, Cu–Ga and Cu–In–Ga alloys with different compositions using a femtosecond laser ablation in liquid phase and fabricated $CuInGaSe_2$ (CIGS) solar cells using electrophoretic deposition of these nanoparticles. The CIGS solar cell fabricated demonstrated a solar energy conversion efficiency of 7.37%. Nanocolloids synthesis was completely free of any ligands and was highly stable. Other materials having applications in solar cells and optoelectronics synthesized by PLALM include ZnS [16], PbS [16], SnS [17], CdS [18], Sb_2S_3[19], CdTe [20,21], CdSe [21,22] and ZnTe [21]. Here we report synthesis, morphology and properties of CIGS nanoparticles using pulsed laser ablation of a CIGS alloy target in different liquid media by varying the laser fluence and ablation wavelengths.

2. Experimental

Pulsed laser ablation in liquid technique was employed to fabricate CIGS nanoparticle suspensions. The CIGS target (1/0.3/0.7/2 at.%, ACI alloys, USA) was in the shape of a disc of about 25 mm diameter and 3 mm thickness. Nanoparticle colloids of CIGS ($CuInGaSe_2$) were synthesized in distilled water, acetone and ethanol. The target was kept at the bottom of a glass vessel filled with 10 ml liquid. The height of the liquid medium was 3 cm from the top surface of the target. The ablation experiment was carried out using the fundamental (1064 nm) and second harmonic (532 nm) outputs from a q-switched Nd:YAG laser (Model LQ 929, Solar Laser System) operated at 10 Hz with a pulse width of 10 ns. A laser energy meter (Model PM100D, Thorlabs Inc.) was used to monitor the output energies of the laser. The laser beam was focused on the alloy target using a lens with a focal length of 20 cm. In these experiments, the target was kept at three different distances above the focal point and the energy fluence for 1064 nm was estimated at 30, 20 and 9 J/cm^2 and for 532 nm the energies were 27.6, 19.4 and 6 J/cm^2. The ablation time was 5 min for all these experiments at room temperature. The glass vessel containing the alloy target and liquid was kept on a linear translation stage and a translational speed of 100 micrometer/second was applied to avoid continuous irradiation of the target at same point during the ablation.

Drops of all of the colloidal solutions obtained in different liquids, under different fluence and ablation wavelengths were dried separately on carbon-copper grids to characterize their morphology, size and structure using Transmission Electron Microscopy (TEM, Model FEI Titan G2 80-300). All the samples were dried on conducting carbon tapes to do X-ray photoelectron spectroscopy (XPS) analysis (Thermo Scientific Inc. Model K-Alpha). The analysis was done with monochromatized Al Kα radiation (E = 1486.68 eV). The X-ray diffraction patterns were recorded by an Empyrean PANalytical diffractometer using CuKα radiation of wavelength 1.5406 Å operated at 45 kV and 40 mA, at

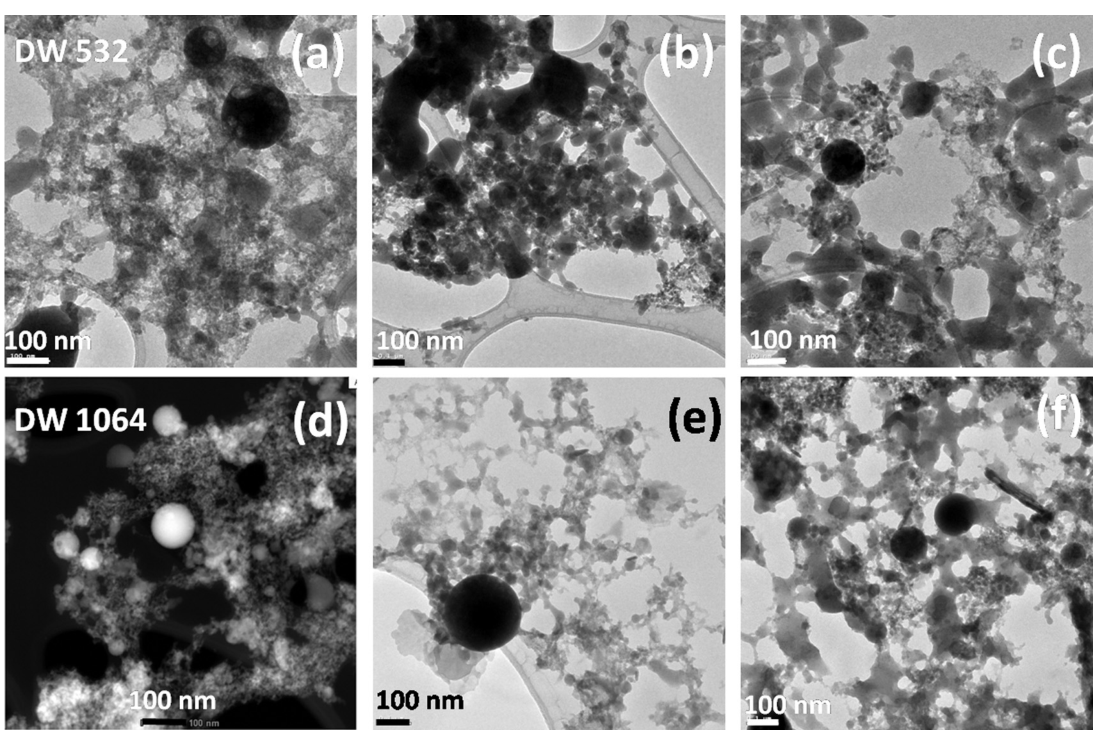

Fig. 1. TEM micrographs of CIGS nanoparticles obtained by pulsed laser ablation of CIGS target in distilled water using (a–c) 532 nm wavelength, 27.6, 19.4 and 6 J/cm^2 energy fluence (d–f) 1064 nm wavelength, 30, 20 and 9 J/cm^2 energy fluence respectively (ablation time 5 min, room temperature).