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Galvanic synthesis of $Cu_{2-X}Se$ thin films and their photocatalytic and thermoelectric properties

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ABSTRACT

$Cu_{2-X}Se$ thin film with cubic berzelianite phase was prepared by a simple, low-cost two electrode electrochemical technique and the photocatalytic and thermoelectric properties of the thin films were investigated. The results showed that $Cu_{2-X}Se$ crystallized in the cubic berzelianite phase and found to possess both direct and indirect band gaps of 2.9 and 1.05 eV respectively, covering almost the entire range of solar-spectrum. The photocatalytic discoloration of aqueous methylene blue (MB) and rose-bengal (RB) dyes over $Cu_{2-X}Se$ thin films were investigated under visible light irradiation. $Cu_{2-X}Se$ thin films showed higher catalytic activity for MB compared to RB in presence of H_2O_2. The photocatalytic discoloration followed first-order reaction kinetics. Complete removal of aqueous MB was realized after visible light irradiation for 150 min with $Cu_{2-X}Se$ thin film catalyst in presence of H_2O_2. Thermoelectric performances through power factor and figure of merit have been evaluated. Carrier concentration obtained from thermoelectric power was used to evaluate the mobility of carriers from electrical conductivity measurement.

1. Introduction

Recently, transition-metal chalcogenide based nanostructures have attracted wide attention due to their unique shape and size dependent physical and chemical properties that can be tailored by varying their synthesis conditions. Among the transition-metal chalcogenides, copper selenide has received attention due to its unique photoelectrical property and wide applications in electronic and optoelectronic devices, as in absorber layer in solar cells, field-effect transistor, gas-sensing, as anode material for Li-ion batteries, hydrogen storage, photocatalysis and photothermal therapy [1–9]. In the past few years, there have been several reports of copper selenide nanostructure synthesis, including hot-solution injection method [1], solvo-thermal method [2,7,10,11], single source precursor method [5], template-assisted methods [6], sonochemical process [12], microwave irradiation [13], and electro-deposition [14] with different morphologies like nanooctahedra [1,10], nanoparticles [2], nanorods [2,5], nanoplates [2], nanocrystals [12], nanoboxes [6], nanosheets [7,13], nanocubes [11], nanoflakes [12]. It is well known that copper selenides have various stoichiometric (Cu_2Se, CuSe, Cu_3Se_2, $CuSe_2$, Cu_5Se_4) and nonstoichiometric ($Cu_{2-X}Se$) phases. Especially, $Cu_{2-X}Se$, as a face-centred cubic berzelianite phase possesses not only a direct band gap of 2.2 eV but also an indirect band gap of 1.4 eV for $x = 0.2$. This unique property creates its importance towards its application in natural sunlight driven photocatalysis [15].

Photocatalysis has many benefits in terms of the removal of harmful organic compounds and clean up measures of polluted water. Dyes are potentially carcinogenic. The discharge and subsequent accumulation of these toxic compounds in aquatic media cause dreadful risks to the environment. The conventional methods used to remove the dyes like coagulation/flocculation, activated carbon, ozonation, sodium hypochlorite treatment, adsorption and bio-treatment have not been found effective as they give either large amounts of sludge or toxic by-products when the degradation is incomplete. Alternatively, sunlight is the source of illumination to carry out different photocatalytic reactions for discolouring organic pollutants in presence of suitable semiconductors as it offers complete discoloration of toxic chemicals. Visible light is a major component of sunlight as compared to UV light, which is only about 4% of total solar radiation. Transition metal oxides with wide band gap such as TiO_2, ZnO, and SnO_2 have been studied extensively as photocatalysts due to their low cost and high chemical stability [16–19]. However, most of these photocatalysts are only capable of utilizing the ultraviolet light and/or a very small quantity of visible light due to their wide band gaps, which greatly limit their

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photocatalytic performance and hinder their practical applications. To make the most of solar energy utilization, various efforts have been made to explore visible-light driven photocatalysts, and plentiful impressive photocatalysts with good photocatalytic activity have been developed [20–22]. Among them, copper selenide as photocatalyst is an emerging one [8,23]. There is only a handful number of reports on copper selenide based photocatalysts particularly with hexagonal phase stoichiometric CuSe compound and all photocatalysts that have been studied previously were in powder-form, and no thin film based photocatalysts have been reported although they have clear advantages over powder-type catalysts from a practical perspective. Powder form catalyst requires post-reaction separation of solid loose particles from solvent to reuse while thin film based photocatalysts can be recovered just by simple treatments, such as washing with deionized water and acetone, respectively, and then being dried.

Copper selenide can also be used from a different perspective. It has been found to possess thermoelectric property. Since the world is suffering from energy crisis, thermoelectric materials can be one of the options for alternative energy sources, since they are capable of converting waste heat directly into useful electrical energy. Many efforts have been made to increase the figure of merit through nanostructuring of the materials [24]. Among the transition-metal chalcogenides, there are reports on the thermoelectric performance of copper selenide synthesized by ball milling and hot pressing [24], aqueous preparation [25], spark plasma sintering compaction [26–28], melting Cu and Se atoms [29].

In this paper, we report the synthesis of thin film of berzelianite ($Cu_{2-X}Se$) by a simple, low-cost two electrode galvanic electrodeposition process at room temperature. The beauty of the technique is that, it involves no external energy source, like a potentiostat or galvanostat, which is essential for conventional three-electrode electrochemical deposition. We have previously employed this method to deposit several other semiconductor thin films such as CuO, Cu_7S_4 etc. [30,31]. UV–vis–NIR absorption spectroscopy reveals that the nanocrytals have strong absorption bands covering almost the entire range of the solar spectrum making it suitable for natural sunlight driven photocatalysis. We have studied the photo-catalytic behaviour of the deposited $Cu_{2-X}Se$ films for the first time against Methylene Blue (MB) and Rose Bengal (RB) dyes. Photocatalytic discoloration of MB using CuSe with hexagonal phase as powder form has been reported earlier [8,23]. There is no report of photo discoloration of RB dye using copper selenide group compounds. To the best of our knowledge, we report the photo discoloration of organic pollutants for the first time using $Cu_{2-X}Se$ film as catalyst. Thermoelectric property of $Cu_{2-X}Se$ film has also been investigated. Power factor ($P = S^2\sigma$), figure of merit (ZT), carrier concentration (n) and mobility (μ) have been evaluated from the thermoelectric measurement.

2. Experimental details

2.1. Chemicals

$(CH_3COO)_2Cu{\cdot}H_2O$, SeO_2 and $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$ were purchased from MERCK. $AgNO_3$, p-benzoquinone (BQ) and Sodium oxalate (AO) were obtained from Fisher Scientific and tert-butanol (TBA) from SDFCL. All the chemicals were used without further purification. Millipore water was used in all the experiments.

2.2. Preparation of working solution for the deposition of $Cu_{2-X}Se$ thin film

To an aqueous 10 ml of 0.1 (M) $(CH_3COO)_2Cu{\cdot}H_2O$ solution, a 10 ml 0.01 (M) solution of di-sodium salt of EDTA ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) was added as a complexing agent. The solution was stirred for about 5 min. To the resulting solution, 10 ml 0.04 (M) solution of SeO_2 was added and the total volume was adjusted to 100 ml with Millipore water. The pH of the working solution was adjusted to 2.5. This condition was found to be optimum for producing good films of $Cu_{2-X}Se$.

2.3. Cell set up for the galvanic deposition of $Cu_{2-X}Se$ thin film

ITO (Indium Tin Oxide) coated glass substrates were cleaned with detergent and dipped into chromic acid solution for about 10 min and washed thoroughly with water. They were then boiled in water and finally in methanol for proper degreasing of surface and fast drying. A Sn strip (99.99% purity) and a cleaned ITO coated glass substrate were dipped into the working solution and short-circuited externally through a Cu wire. Here, Sn strip (easily oxidizable) acts as a self-decaying anode and the ITO coated glass substrate as cathode. The deposition was carried out at room temperature under continuous stirring, using a magnetic stirrer.

2.4. Characterization

The deposited films were characterized by optical, structural and morphological studies. X-ray diffraction pattern was recorded by an X-ray diffractometer (Seifert P3000, Cu Kα radiation λ = 1.54 Å). The film composition was determined using energy dispersive X-ray analysis (EDX, BRUKER). The morphology of the thin films was observed under field-emission scanning electron microscope (FESEM) (Carl-Zeiss-SIGMA) and atomic force microscope (AFM) (SOLVER Next-NT-MDT). The UV–vis–NIR spectrum of the thin film was taken by a 'JASCO V-570' UV-VIS-NIR spectrophotometer and photocatalytic measurements were done by a 'JASCO V-530' UV-VIS spectrophotometer. The thicknesses of the films were determined using a profilometer (BRUKER, DEKTAK-XT).

2.5. Photocatalytic properties

Considering strong absorption in the visible region, dyes like Methylene Blue (MB) and Rose Bengal (RB) were chosen to examine their photo discoloration in presence of $Cu_{2-X}Se$ thin films. The high photocatalytic activity of $Cu_{2-X}Se$ was evaluated individually for each dye keeping all the experimental conditions unaltered. All measurements were carried out under visible-light and at ambient temperature with the assistance of H_2O_2. The dye solutions were prepared by dissolving the required amount of dyes in 100 ml Millipore water to obtain a concentration of 1×10^{-4} (M). The working solution was prepared by taking 10 ml 10^{-4} (M) dye solution, 1 ml H_2O_2 (30%, w/w) and DI water in a beaker to make the total volume 60 ml. Four thin films of $Cu_{2-X}Se$ with thicknesses around 200 nm each (surface area of 10 cm^2 each) were placed inside this beaker in an inclined position. Irradiation of light was carried out using a 200 W tungsten lamp (≥410 nm) and a 1 M solution of $NaNO_2$ was used as the UV cutoff filter [32]. The lamp was placed vertically over the reaction vessel at a distance of 10 cm. The optical irradiance at the surface of dye solution was kept at 70 mW cm^{-2}. Before illumination, the solution set-up was magnetically stirred for 30 min to establish adsorption–desorption equilibrium of dye with the catalyst. Later, the set-up was irradiated and at given time intervals UV–vis absorption spectra of an aliquot of the dyes were recorded using a UV-VIS spectrophotometer.

2.6. Thermoelectric properties

For measurement of thermoelectric power (S), a temperature difference (5–10 K) was created through one end of the sample by means of an auxiliary heater and the corresponding potential drop