Electrodeposited Heterojunction CIS Semiconductor Alloys for Photocatalytic Degradation of Textile Dyes

N. Karthikeyan, T. Sivaranjani, A. Stephen

Abstract—Nanocrystalline Copper Indium Selenide (CIS) semiconductor photocatalysts establishing heterojunction with modified band gap energies were synthesized by pulsed electrodeposition method, and successfully employed in the degradation of two representative textile dyes, methylene blue and methyl orange, under visible light irradiation. Prepared photocatalysts were characterized by XRD, SEM, EDX, AFM, CL and UV-Vis DRS. The degradations of the dyes were estimated by UV-Vis spectrometry. Suitably positioned bandgap edges and formation of heterojunction enhance photo generation of electron-hole pairs, reduce their recombination by acting as sink for photo-generated charge carriers, and thus enhances the redox reactions which effectively enhance the degradation of the textile dyes.

Index Terms—CIS semiconductor alloys, Copper Indium Selenide, electrodeposition, heterojunction,nanocrystals,photocatalytic degradation, textile dyes.

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1 INTRODUCTION

MANY researches in several laboratories throughout the world have been actively focusing on mitigating world's two major challenges, viz. scarcity of clean water and energy. Among the two, water is the most vital natural resource for life. One of the reasons for the scarcity of clean water is pollution of existing freshwater resources by industrial activities. Contamination of freshwater resources by the industrial effluents increases with the ever increasing industrialization and globalization.

Textile industries are one of the strong economic strengths of many developing countries. Effluents generated from the dyeing, bleaching, and washing processes involving many organic chemicals in these industries are one of the key pollutants of the fresh water systems[1, 2]. Already several methods, such as adsorption, coagulation, and membrane separation, have been employed to treat these effluents but they are proved to be very expensive and even generate secondary pollutants.Certain situations, such as low concentration and toxicity of the pollutants, have greatly limited the conventional decontaminating applications[3, 4].

In the recent years, photocatalysis has become a hot topic among the environmental researchers for the purpose of purifying wastewater, especiallyfor the treatment of organic compounds at low levels. Many semiconductor photocatalysts such as TiO_2, ZnO, SnO_2, Fe_2O_3, and multinary composites based on such semiconductors havealready demonstrated their high potential in degrading a wide range of organic pollutants into biodegradable or less toxic organic compounds or even innocuous products, such as H_2O and CO_2[5, 6]. Efforts are continuously made to improve the photocatalytic degrading efficiency of the semiconductor photocatalysts to make them more economical by harvesting the freely available solar energy and also to employ them in large scale applications, by many techniques such as tuning their bandgaps, increasing specific surface area, forming heterojunctions or multinary composites or multiphase compounds and preventing recombination of the photogenerated electron-hole pairs. Therefore semiconductor photocatalysts have the advantage of not only generating harmless products but also reducingoperating costs in the most efficient way[7, 8].

Cu-based chalcopyrite compounds, and in particular Copper Indium Selenide (CIS) semiconductorsare very successful in solar energy trapping applications due to its high optical absorption in the visible spectrum, wide compositional tolerance, compositionally tunable band gaps, low toxicity and their earth abundance [9-13]. Though these materials have been extensively employed in photovoltaic applications, there are hardly any research reports of using them, particularly CIS semiconductor alloys forming heterojunction and exhibiting different crystallographic structures with two different band gap energies, for photocatalytic degradation of textile dyes triggered by photon-induced redox reactions.

Therefore, in this study nanocrystalline Copper Indium Selenide (CIS) semiconductor alloys formingheterojunction were synthesized through pulsed-current electrodeposition (PED) technique, which could reduce or completely avoid compositional gradients by regenerating the initial ion concentrations at the cathode / solution interface at the beginning of each pulse period. By tailoring pulse shape and duration, this technique enables close control of the nucleation and growth processes and allows modification of film microstructure.

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The physical and chemical properties of the prepared semiconductor photocatalytic sample were studied with various characterization techniques. And its visible light driven photocatalytic degradation efficiency was investigated by the photodegradation of methylene blue (MB) and methyl orange (MO) dyes under visible light irradiation.

2 EXPERIMENTAL

2.1 Preparation of materials

The Copper Indium Selenide (CIS) alloy deposits were obtained by pulsed current electrodeposition (PED) onto Indium Tin Oxide (ITO) coated glass substrates of dimensions 4 cm x 2.5 cm. The ITO glass substrateand bagged a graphite sheet were kept parallel to each other as working and counter electrodes respectively. Initially the ITO glasses were cleaned by sonicating for 10 min, first in acetone, then in isopropyl alcohol and finally in de-ionized distilled water.

The electrolyte bath contains the aqueous solutions of$CuCl_2$, $InCl_3$ and SeO_2prepared in various relative concentrations. In the beginning, three stock solutions were prepared separately,

(A) By dissolving 20 mg of SeO_2 in 50 m1 de-ionized double distilled water,

(B) By dissolving 25 mg of $CuCl_2$ in 50 m1 de-ionized double distilled water, and

(C) $InC1_3$ by the reaction of 130 mg of Indium with 2 m1 of concentrated HCl diluted with de-ionized double water to give a total of 50 m1 solution.

The electrolytic solutions were obtained by mixing the stock solutions A, B, and C in the volume ratio of 10:6:5. The CIS deposits were prepared at different deposition current densities of 1 mA cm^{-2}, 3 mA cm^{-2} and 10 mA cm^{-2}. During pulsed electrodepositions, the current was applied for 1 millisecond (T_{ON} - pulse-on-period) and cut-off for 9 milliseconds (T_{OFF} - pulse-off-period). The duty cycle, defined as $T_{ON}/(T_{ON}+T_{OFF})$, was 10% and the frequency was 100 Hz.

The sample was deposited for 30 minutes at the room temperature. The electrolytic bath was stirred continuously using a magnetic stirrer. Application of pulsed current ensures uniform dispersal of ions before every pulse during T_{ON}, and also enables fresh nucleation during the ON time and formation of nanoscale structures. At the end of the deposition, the CIS deposits were rinsed a few times with de-ionized double distilled water and dried.

Then the deposits / films were mechanically removed from the substrate. This is a slightly modified method of what has been reported elsewhere[14-16]. A portion of the prepared samples were then annealed at 300^0C in argon atmosphere for 3 hours.The representative textile dye solutionswere prepared by dissolving 9.6 mg of Methylene Blue (MB) and 9.82 mg of Methyl Orange (MO) separately in two beakers containing 1000 ml of distilled water.

2.2 Characterization of materials

The as deposited film samples, the prepared powder samples and the annealed powder samples were characterized by various techniques. The surface morphologies of the samples were visualized on atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). Diffused reflectance spectrawere taken in the wavelength ranging from 200 nm to 1200 nm using UV-Vis DRS spectrophotometer and cathodoluminescence (CL) spectrum taken at 77K were used to study the optical responses and the optical band gaps of the prepared semiconductor photocatalysts.

X-rays generated by an applied voltage of 40 kV, 30 mA in Rich Seifertdiffractometer with $CuK_{\alpha 1}$ ($\lambda = 0.15406$ nm) from a copper target and selected using a quartz curved crystal primary monochromater was used determine the crystallographic structures and the phases. Double beam UV-Vis spectrophotometer was used to determine the decolouration of the dyes.

2.3 Photocatalytic degradation experiment

The photocatalytic degradation activity was studied with an indigenously designed photocatalytic reactor fitted with three projection lamps (7748XHP 250 W, Philips, full spectrum) as visible light source. Reaction suspensions were prepared by adding required amount of CIS photocatalysts into 1000 ml of MB solution, under continuous stirring. Then photocatalytic decolouration study of the MB was carried out under visible light irradiation. Same procedure is repeated for the MO as well.

The analytical samples from the suspensions were collected at equal intervals of time, centrifuged and filtered.The decolouration of methylene blue and methyl orange were analyzed by UV-Vis spectrophotometer at their respective peak wavelengths of 664 nm and 464 nm. Decolouration was estimated using the formula, C_t/C_0, where C_0 is the initial concentration and C_t is the concentration of irradiated suspension at time t, taken at regular intervals.

3 RESULTS AND DISCUSSION

3.1 Structural analysis

The X-ray diffraction patterns of the CIS deposits prepared at the deposition current densities of 1 mA cm^{-2}, 3 mA cm^{-2} and 10 mA cm^{-2} are shown in figures 1(a), 1(b) and 1(c) respectively. All the three XRD patterns of the as deposited samples reveal formation of stoichiometric and non-stoichiometricchalcopyrite phases. The compositions of both the samples deposited at 1 mA cm^{-2} and 3 mA cm^{-2} have mixture of two phases and they were fitted to tetragonal phase $CuInSe_2$ (JCPDS 081-1936) and hexagonal phase $(Cu_2Se)_x(In_2Se_3)_{1-x}$ (JCPDS 038-0957) crystallographic structures. However, it is evident that growth of stoichiometric$CuInSe_2$ along (112) plane was prominent when deposited at the current density of 1 mA cm^{-2} and non-stoichiometric$(Cu_2Se)_x(In_2Se_3)_{1-x}$ along (0016) plane was prominent when deposited at the current density of 3 mA cm^{-2}.

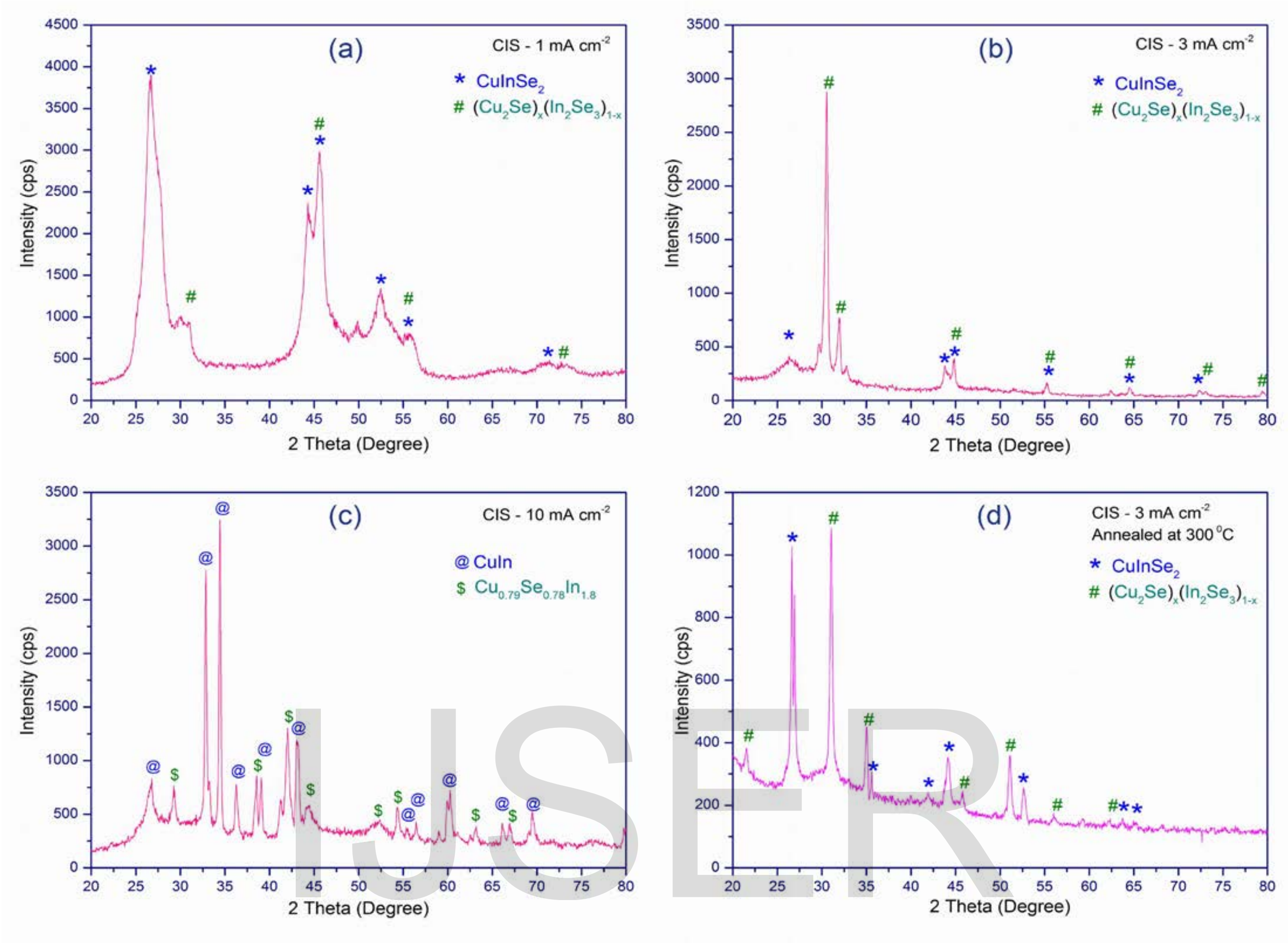


Fig. 1:XRD patterns of the CIS deposits prepared at (a) 1 mA cm^{-2}, (b) 3 mA cm^{-2}, (c) 10 mA cm^{-2} and (d) 3 mA cm^{-2} and annealed at 300 ^{0}C for 3 hrs. in argon atmosphere.

Formation of less commonmonoclinic CuIn intermetallic compound (JCPDS 035-1150)along with the non-stoichiometric tetragonal $Cu_{0.79}In_{0.78}Se_{1.8}$ (JCPDS 079-2208) crystallographic structure was revealed by the fittings of the XRD pattern recorded for the sample deposited at the current density of 10 mA cm^{-2}. The pattern was shown in figure 1 (c). Similar formation of CuIn intermetallic compound at room temperature was reported by a few researchers [17, 18]. Based on the results of the XRD studies and literature reviews, the sample deposited at the current density of 3 mA cm^{-2} was chosen to be employed

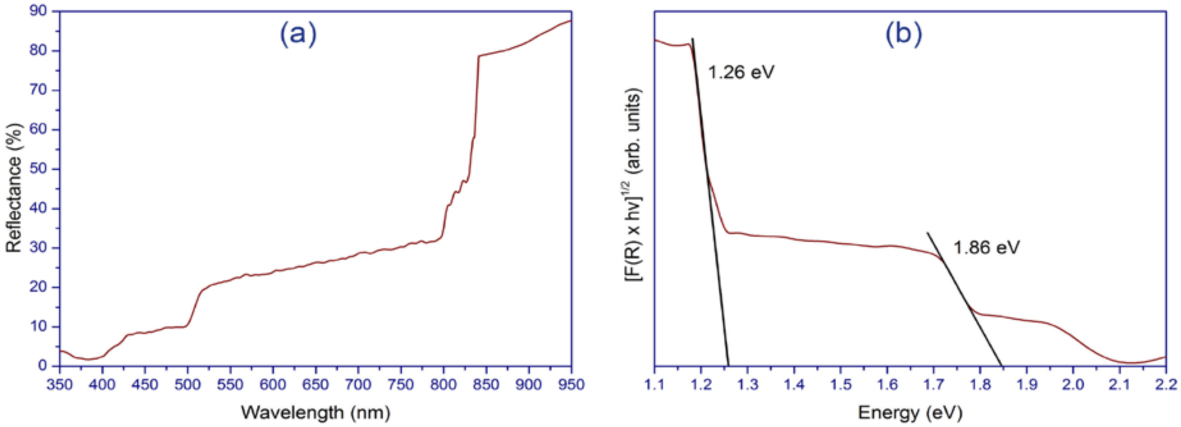


Fig. 2: (a) UV-Vis DRS spectrum and (b) Kubelka-Munk plot for the annealed CIS.

in photocatalytic degradation studies, and hence subjected to annealing at 300^0C in argon atmosphere for 3 hours to refine the structures and other physical properties. Figure 1(d) shows the XRD pattern of the sample annealed at 300^0C and reveals further refinement of the structure of the $CuInSe_2$ along (112) plane. Both the stoichiometric and the non-stoichiometric phases retain the respective crystallographic structures.

3.2 Optical properties of the photocatalysts

The UV-Vis DRS of the prepared CIS deposits was taken in the wavelength ranging from 200 nm to 1200 nm and the relevant portion is shown in figure 2(a). The spectrum indicates the presence of two prominent phases of CIS semiconductor with different band gap energies. Figure 2 (b) shows the Kubelka-Munk plotand the estimated bandgap energies for the prepared sample are 1.26 eV and 1.86 eV. These results indicate that the sample at the current densityof 3 mA cm^{-2} and annealed at 300 ^{0}C has strong capabilities to generate electron-hole pairs under the irradiation of visible light and hence its suitability for photocatalytic degradation.

3.3 Surface morphological studies - FESEM

FESEM images in figures 3 (a) and 3 (b) show the typical surface morphology of the as-prepared deposits at the current densities 3 mA cm^{-2} and 10 mA cm^{-2} respectively. The as prepared deposits obtained at 3 mA cm^{-2} exhibit platelet and tree-like morphology and the deposits obtained at 10 mA cm^{-2} exhibit tree-like morphology.

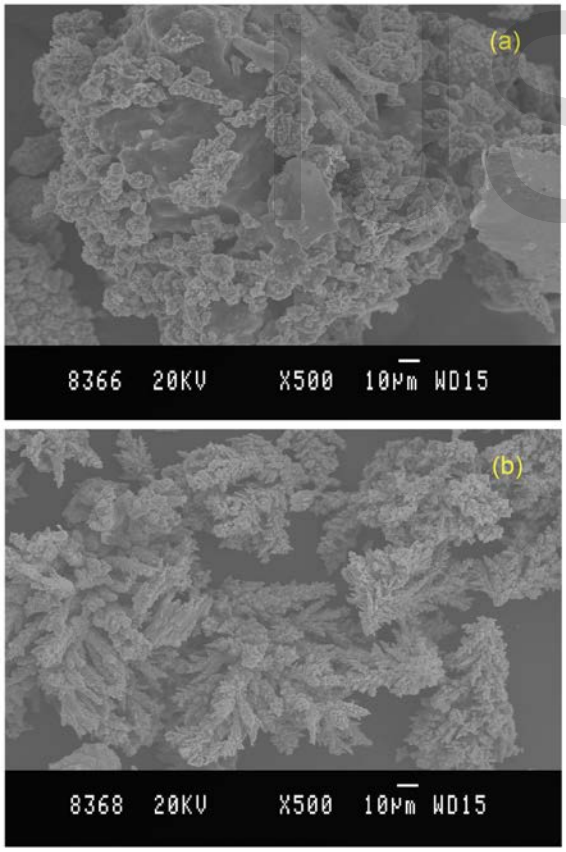


Fig. 3: FESEM images of the deposits at the current densities (a) 3 mA cm^{-2} and (b) 10 mA cm^{-2}.

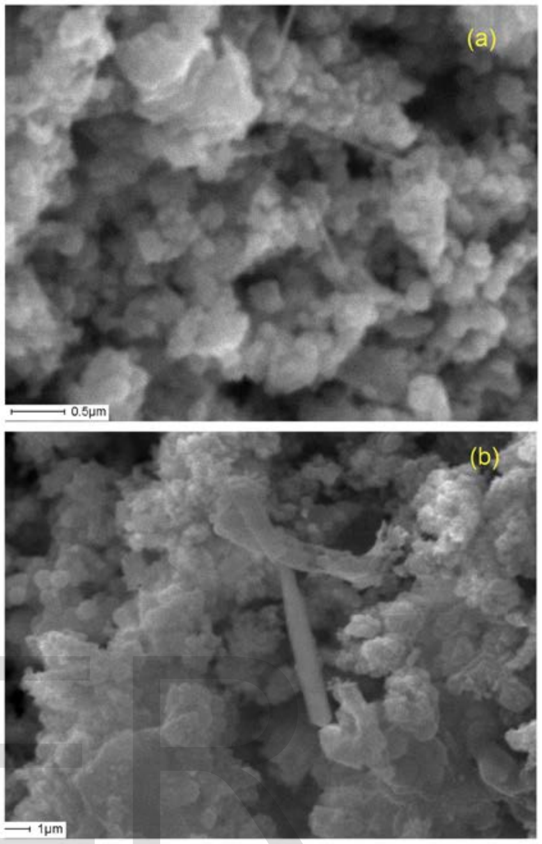


Fig. 4: FESEM images of the CIS deposited at 3 mA cm^{-2} and annealed at 300 ^{0}C at two magnifications.

The FESEM images of the annealed samples at two different magnifications are shown in figures 4(a) and 4(b). Both images show granular structureof densely agglomerated non-uniform sphere like particles mixed with a few nanorods like structures. The sample annealed at 300 ^{0}C in argon atmosphere for 3 hrs develops fairly significant porous nature.

This increases the specific surface area, and which in turn increases the photon-induced electron-hole productions, the adsorption of more redox medium onto the grain surfaces of the photocatalysts and the migration of generated charge carriers across the surface. This is a favourable feature to enhance the photocatalytic activity. The FESEM-EDX measurement confirmed the presence of Copper, Indium and Selenium without any other impurities.

3.4 Surface morphological studies - AFM

The topographies of the prepared nanocrystalline CIS semiconductor films, before removing from the ITO coated glass substrates and before the heat treatment, were examined with the AFM. Figures 5 (a) and 5 (b) respectively show the side and the top views of the CIS films deposited at the current density 3 mA cm^{-2}. Thickness of the film at the edge was around 500 nm.

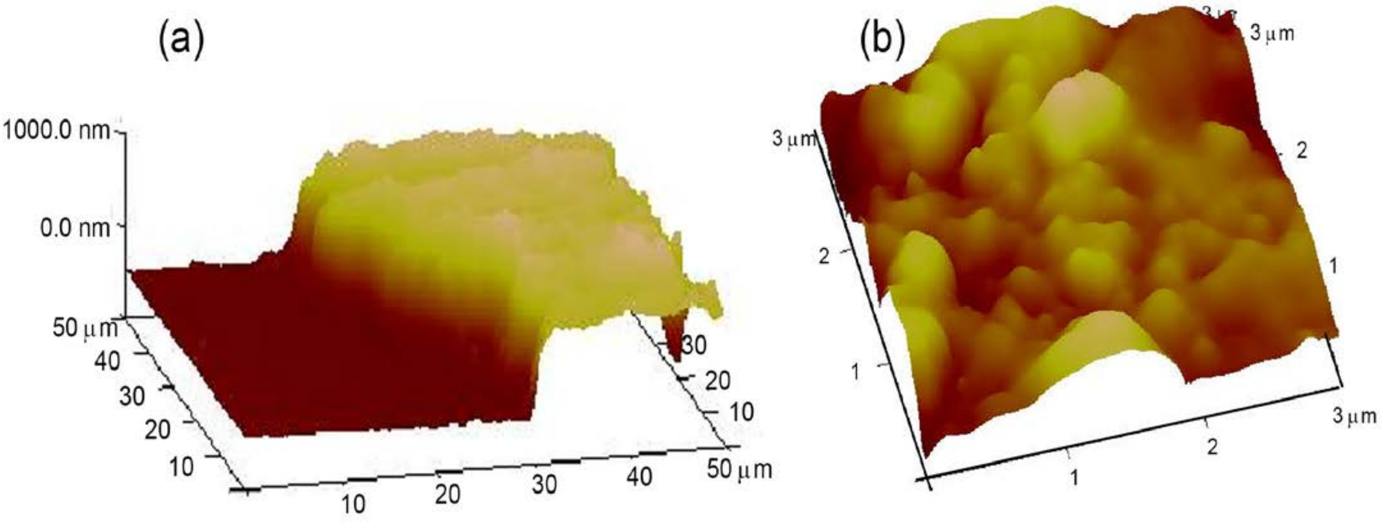
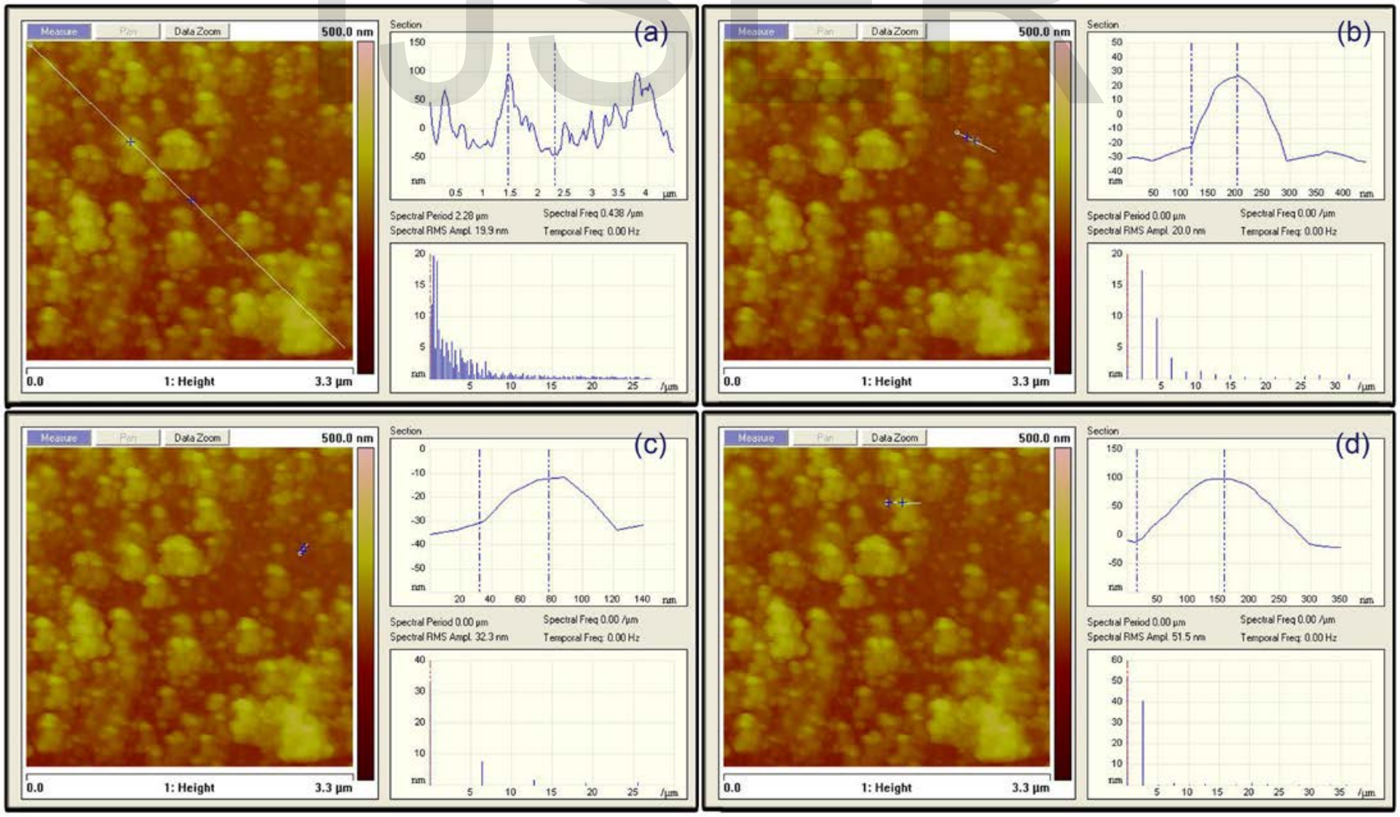


Fig. 5: AFM images at the edges (a) side view and (b) top view of CIS films deposited at the current density 3 mA cm^{-2}.

The roughness analysis of the CIS films,before removing from the ITO coated glass substrates and before the heat treatment, are shown in figures 6 (a), 6 (b), 6 (c) and 6 (d).These AFM explorations reveal non-uniform granular deposits with the grain sizes varying from 10 nm to 65 nm and the surface roughness is varying from (RMS value) 20 nm to 52 nm. In general high roughness value is undesirable; nevertheless here it would be a positive factor as it increases the specific surface area, which is an important factor for enhanced photocatalytic activities.



(a)
Spectral Period 2.28 µm
Spectral RMS Ampl. 19.9 nm
Spectral Freq 0.438 /µm
Temporal Freq: 0.00 Hz

(b)
Spectral Period 0.00 µm
Spectral RMS Ampl. 20.0 nm
Spectral Freq 0.00 /µm
Temporal Freq: 0.00 Hz

(c)
Spectral Period 0.00 µm
Spectral RMS Ampl. 32.3 nm
Spectral Freq 0.00 /µm
Temporal Freq: 0.00 Hz

(d)
Spectral Period 0.00 µm
Spectral RMS Ampl. 51.5 nm
Spectral Freq 0.00 /µm
Temporal Freq: 0.00 Hz

Fig. 6: AFM images on surface roughness analysis at different cross sections (a), (b), (c) and (d) of CIS films deposited at the current density 3 mA cm^{-2}.

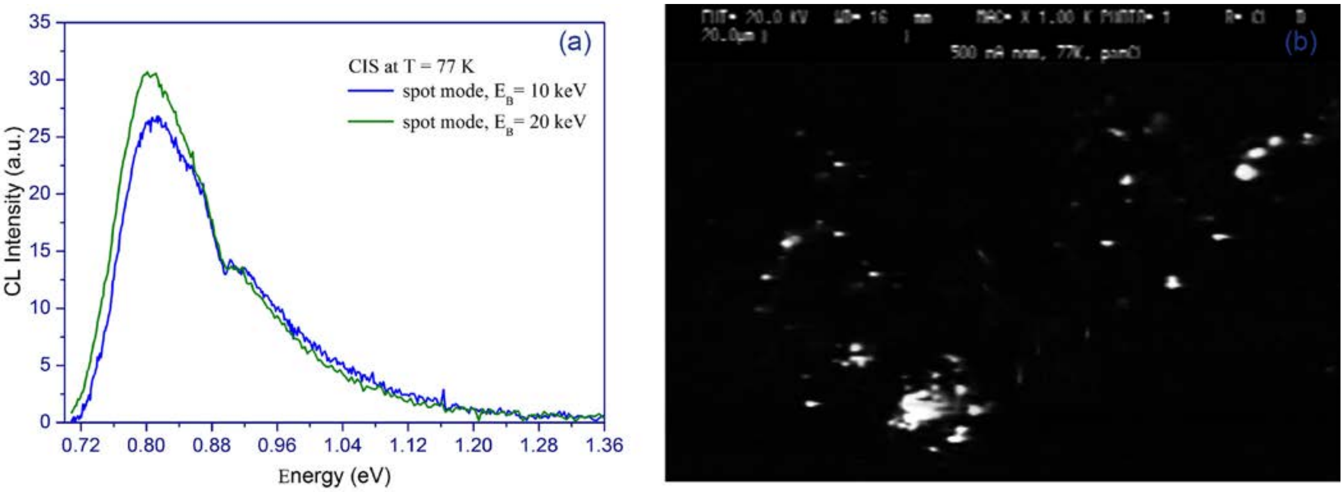


Fig. 7:Cathodoluminescence (a) spectrum and (b) image recorded at 77 K.

3.5 Cathodoluminescence spectrum

The Cathodoluminescence (CL) spectrum,recorded at 77K, of the CIS deposited at the current densities 3 mA cm^{-2}is shown in figure 7 (a). The electronic band gap was determined as 0.83eV and the spectrum reveals a shoulder at 0.92eV. The figure 7 (b) shows the CL image at 77K and reveals the non-uniformity of the CIS phases.

3.6 The degradation profile of MB and MO

The photocatalytic capabilities of the CIS sample deposited at the current density of 3 mA cm^{-2} and annealed at 300 ^{0}C was tested on MB and MO dyes, separately, under the irradiation of visible light.The absorption spectra of the degraded MB dye samples and MO dye samples collected at a regular interval of 30 minutes during the irradiation process of 120 minutes are respectively shown in figures 8(a) and 8(b).

The decolouration profile of both the MB and the MO was constructed by analyzing the relative concentrations of the samples using UV-Visible spectrophotometer at the peak absorption wavelengths (664 nm for MB and 464 nm for MO) and shown in figure 8(c). Decolouration rate (η) was calculated using the equation,

$$\eta\ (\%) = (C_t\ / C_0) \times 100$$

where, C_0 is the initial concentration of the reaction dye solution (at t = 0) and C_t is the concentrations measured at regular intervals of time during the irradiation.Photocatalytic degradation of about 80% and 78% were achieved on the methylene blue and methyl orange dyes respectively by the CIS semiconductor photocatalyst.

The observed results could be explained in terms of formation of a heterojunction of the two nanocrystalline phases of the CIS semiconductor alloy, with two different modified band gap energies of 1.26 eV and 1.86 eV. When this system is alloyed to form a heterojunction with their conduction and valence bands suitably positioned, then one of the phases act as sink for the photogenerated electron-hole pairs in the other phase. This migration across the heterojunction minimizes the recombination of the electron-hole pairs and provides sufficient time for them to further migrate across the surface of the

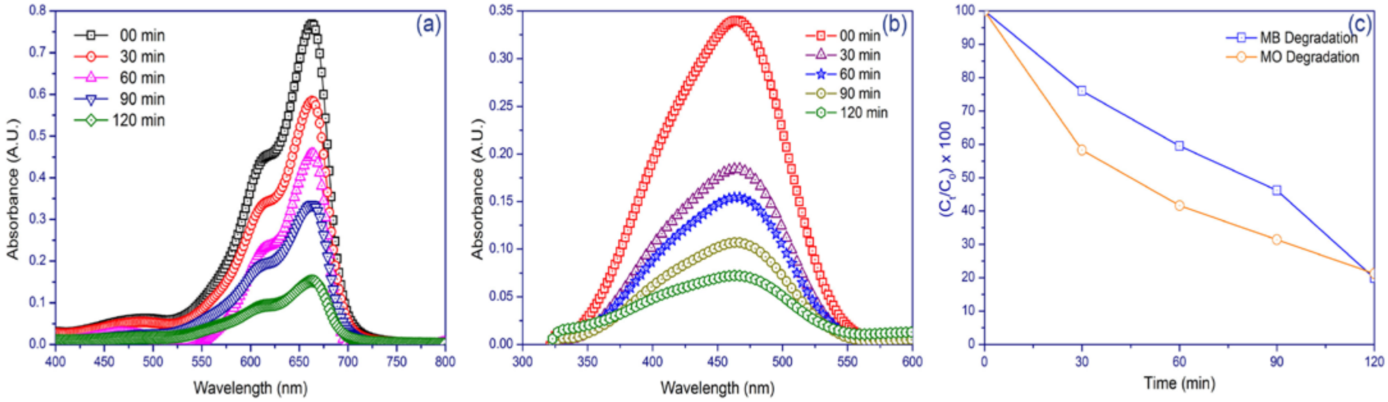


Fig. 8: (a) & (b) Absorption spectra of the degraded MB & MO dyes and (c) Degradation profile of the MB & MO dyes

photocatalysts, where these pairs participate in reduction and oxidation (redox) reactions with the adsorbed H_2O and O_2 molecules respectively. These reactions lead to the production of hydroxyl radicals ($OH^\bullet$) and the highly reactive hydroxyl radicals attack MB or MO dye molecules, which are part of the respective reaction medium, and degrade them.

4 CONCLUSIONS

Threesystems of nanocrystalline Copper Indium Selenide (CIS) alloys were prepared through the pulsed current electrodeposition technique by applying three different deposition current densities. Based on the XRD characterization results, the chosen CIS deposited at the current density3 mA cm^{-2} was annealed at 300 ^{0}C in argon atmosphere for 3 hrs to tune their structural and optical properties. UV-Vis diffused reflectance characterization confirmed the successful tuning of band gap energies of 1.26 eV and 1.86 eV in the two different crystallographic structures of the annealed CIS. The surface morphological studies with FESEM and AFMrevealed irregularly shaped oblique sphere like granular nature with widespread interlaying pores of the prepared deposits. The average grain sizes of the catalysts were varying from about 10 nm to 65 nm.

The photocatalytic degradation capability of the prepared sample wasassessed on the MB and MO dyes under the irradiation of visible light, and about 80% and 78% degradations were achieved on the respective dyes in 120 minutes. The successful degradation abilities of the annealed CIS sample were attributed to the formation of heterojunction with fittingly positioned energy band edges of the two crystallographic structures, which ably facilitated enhanced the generation of electron-hole pairs, the reduction of recombination, the migration of the charge carriers through heterojunction & across the surfaces, the redox reactions and finally the degradations of the textile dyes under the irradiation of visible light.

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