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Recycled polycrystalline CdS film electrodes with enhanced photo-electrochemical characteristics

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ABSTRACT

Waste cadmium sulfide (CdS) film electrodes, originally deposited onto glass/fluorine doped tin oxide (glass/FTO) substrates, were used to prepare recycled CdS film electrodes. The waste glass/FTO/CdS were processed in acidic media to recover the glass/FTO substrates, the Cd^{2+} ions (in the acidic solutions) and the gaseous H_2S (recaptured in basic media). All components of the waste electrodes were thus recovered. The recovered glass/FTO and the Cd^{2+} ions were then reused to produce new recycled glass/FTO/CdS electrodes by chemical bath deposition. The produced films were then characterized by X-ray diffractometry, scanning electron microscopy, electronic absorption spectroscopy and other techniques. The Cd^{2+} ions were recovered with efficiency higher than 90% from the waste films, as observed from atomic absorption spectrometry. The recycled films were assessed in photo-electrochemical conversion of light to electricity, and exhibited comparable efficiency to those freshly prepared from authentic starting materials and other literature values. Photoelectrochemical characteristics for the recovered films were further enhanced by avoiding stirring of the chemical deposition bath during preparation. The results manifest the feasibility of recycling CdS electrodes and enhancing their photo-electrochemical characteristics by simple low cost methods. Both environmental protection and economic goals can thus be potentially achieved.

1. Introduction

As photo-voltaic PV systems involve advanced preparation techniques, and demand huge amounts of starting materials to prepare relatively thick wafers (mm scale thickness), attention is now paid to other less demanding alternative photo-electrochemical (PEC) processes. Currently research is active on PEC processes which use thin film electrodes, for light-to-electricity conversion. The film electrodes typically involve nano-size polycrystalline materials, most commonly metal chalcogenides (MX: M = Cu, Zn, In, Cd, Sn; X = S, Se, Te). Basic and applied research involves preparation methods, composite materials, efficiency & stability enhancement, characterization, and other optimization study. Both theoretical, modeling and experimental studies are active in these areas.

Due to the wide application of PV systems which involve homo- and hetero-junctions of Si, GaAs, InP, in addition to many other elements (such as Ge, Se, Te, Cd), such materials are now becoming a cause of concern to the environment. Many elements involved in PV systems are considered to be environmentally hazardous. Efforts are now being made to recover different elements from waste PV grids [1,2].

Film PEC systems have not yet reached the wide application of PV systems, and are still more at the research level. Naturally research is focused on their efficiency more than on their environmental impact and recycling. Therefore, less attention has been paid to recycle hazardous elements commonly used in PEC film electrodes. Malinowska et al. reported how CBD deposited CdS electrodes can be recovered in terms of Cd^{2+} ions and how the reclaimed ions can be reused to deposit new CdS films by a number of methods [3]. Other methods have been proposed to make benefit from waste CdS and other photovoltaic materials [4].

CdS electrodes are intentionally chosen here for more than one reason. CdS films are being widely studied in PEC research. PV systems using p-n junctions of Cu_2S/CdS were reported as early as 1954 [5]. CdS is used commercially in yellow dyes [6,7], solid state lasers [8] and

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other applications [9]. Moreover, Cd ions are highly hazardous and are believed to be carcinogenic. They are slowly absorbed by the body, but once absorbed they cause troubles to the kidneys and the lungs [10]. The US EPA recommended maximum concentration limit for Cd^{2+} ions in drinking water is 0.005 mg/L (5 ppm) [11–13]. For these reasons, it is necessary to find simple and practical strategies to prevent dumping Cd ions to the environment and to reclaim any traces present in the environment. Recycling waste CdS electrodes commonly used in PEC processes could be a viable method to achieve these strategies.

Different techniques have been used for this purpose, including ion exchange, coagulation, chemical precipitation and others. Precipitation has been widely used for Cd recovery [14]. In precipitation, the Cd^{2+} ions are allowed to react with an anion to precipitate. Carbonate [15], hydroxide [16] and other ions are useful for this purpose. Depending on the used pH value, Cd^{2+} ions can be lowered from ~ 7000 mg/L to as low as 0.3 mg/L using precipitation with carbonate [15]. Hydroxide precipitation studies showed that up to ~ 99% removal can be achieved with hydroxide, starting with 100 mg/L going down to less than 0.3 mg/L at pH 9 [17]. The sulfide precipitation has been reported to lower the Cd^{2+} ion concentrations in aqueous solutions [18]. Each of these methods has its own advantages and disadvantages, while the sulfide precipitation seems to have the upper hand due to many reasons [14].

In this work, more than one objective is targeted. Recovering residual Cd^{2+} ions from waste CdS film electrodes will be assessed. The glass/FTO substrates will be recovered, and the sulfide ions will also be recovered. Preparing new recycled CdS film electrodes will then be deposited onto the recovered substrates. The recycled CdS film electrodes will then be assessed in PEC processes. Unlike earlier reports, the recycled CdS electrodes will be characterized and tested for real light-to-electricity conversion, in comparison with other authentic CdS electrodes. Enhancing the recycled electrode conversion efficiency will also be assessed.

2. Experimental

2.1. Materials

Common solvents and chemicals were purchased from Aldrich, Frutarom and Merck. CdS films prepared and used in earlier research activities were used for recycling purposes here. The deposition procedure for the original waste films is described in earlier reports [19,20]. The films were earlier deposited onto glass/fluorine doped tin oxide (glass/FTO) substrates (Aldrich, with surface resistivity ~ 7 Ω/sq).

2.2. Equipment

Solid state electronic absorption spectra were measured for CdS films on a Shimadzu UV-1601spectrometer. Glass/FTO substrates were used for baseline correction. A Perkin-Elmer LS 50 Luminescence Spectrometer was used to measure the film photoluminescence spectra using 390 nm wavelength for excitation, and a cut-off filter (removing 450 nm and shorter).

X-ray diffraction (XRD) patterns were measured on an XRD-7000, SHIMADZU X-ray diffractometer, with a CuKα (λ = 1.5406 Å) source at ISAA Environment Consulting Co. Ltd, Chungju City, S. Korea. Scanning electronic microscopic (SEM) micrographs and energy dispersive X-ray spectroscopy (EDX) were measured on a Field Emission Scanning Electron Microscope FE-SEM, JEOL JSM-6700F at same place. Additional XRD and SEM measurements were made, for confirmation, at Pukyong National University, 365 Sinseonro, Namgu, 608739 Busan, South Korea.

Cd^{2+} ion concentrations were measured using atomic absorption spectroscopy (AAS). A Thermo 50–60 Hz Type ICE 3500 atomic absorption spectrometer was used for this purpose. Pre-calibration was made using known Cd^{2+} ion concentrations. Illumination was performed using a 50 W halogen spot lamp, with wide spectral range 450–800 nm and high stability. A Lutron-LX 102 lightmeter and a Zonen CM11 Pyranometer were used to measure light intensity.

2.3. CdS film recycling

Waste CdS film electrodes used in earlier studies were immersed in minimal amounts of HCl solutions with different concentrations (0.6, 0.8 and 1.0 M) for 5 min. The 1.0 M concentration was more suitable and was used unless otherwise stated. The acidic solution was then taken with the Cd^{2+} ions for further use. AAS was used to measure Cd^{2+} ion concentrations in recovered solutions. The resulting H_2S gas was channeled through tubes and traps and captured separately inside NaOH (1.0 M) solution. Depending on number of waste CdS film electrodes added and amount of HCl used, different Cd^{2+} concentrations were recovered. For practical purposes, enough waste electrodes were added so as to reclaim a solution with 0.2 M, for recycled electrode purposes. Higher than 90% of Cd^{2+} ions could be recovered from the waste.

The waste glass/FTO substrates (originally purchased from Aldrich as highly transparent conducting slides) were then taken from the acidic media and washed with distilled water. The substrates were cleaned by standard methods for re-deposition purposes, by treatment with concentrated HCl (1.0 M) for 60 min followed by methanol for 30 min in a sonicator. The substrates were then immersed again in dilute HCl (10% v/v) for 5 s, rinsed with distilled water, immersed in methanol and rinsed with distilled water. The cleaned glass/FTO substrates were used for recycled CdS electrode preparations, while fresh substrates were used to prepare fresh glass/FTO electrode after precleaning as described above.

The recovered Cd^{2+} solutions were then used to deposit recycled CdS films onto the recovered Glass/FTO substrates by chemical bath deposition (CBD) method as described earlier [21–24]. Distilled water (25 mL) was added to 2.5 mL of recycled Cd^{2+} solution (0.20). To the solution were added solutions of NH_4Cl (10 mL, 0.20 M) and NH_4OH (15.0 mL, 2.0 M), to make the overall solution basic. Preparation batches were made with or without stirring, for further enhancement as described below. This was to check effect of stirring on recycled CdS electrodes. The temperature was kept at 80 °C during the deposition process. The glass/FTO substrates (4 × 1 cm^2), were partly dipped (3 cm) vertically inside the solution. The system was then rubber stoppered. A solution of thiourea (2.5 mL, 0.6 M) was added to the solution with a syringe. The final pH value of the solution was ~ 10.3. The deposition process was continued for different times 30, 45 and 60 min. The 60 min time showed electrodes with preferred characteristics and was therefore used unless otherwise stated.

The CdS films were then taken, washed with distilled water and dried by washing with ethanol and stored in a dry box. Annealing was performed in a horizontal tube furnace under nitrogen for 60 min at 250 °C. This temperature was chosen based on earlier studies as being the suitable annealing temperature for CdS films [25]. The annealed films were slowly cooled back to room temperature with a ramp rate of −1.5 °C/min. Film thickness was calculated gravimetrically by calculating amount of CdS deposited onto each electrode. Thicknesses were 400–600 nm for the freshly prepared film, 300–500 nm for the recycled film with stirring and 200–500 nm for the recycled film with no stirring.

For comparison purposes, fresh CdS electrodes were prepared by CBD using authentic starting materials using literature methods as described above [19,20]. The electrodes were prepared using stirring during deposition as described earlier and annealed at the desired temperature 250 °C.

2.4. The photo-electrochemical (PEC) experiment

PEC study was performed in a three-electrode cell. A PAR 263A