

Photoelectrocatalytic Degradation of Methylene Blue using Nanocrystalline Al-doped CdSe/TiO₂ Thin Film under Visible Light

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Abstract

Aluminium doped CdSe/TiO₂ nanocrystalline thin film was synthesized through the spray pyrolysis method at the optimized temperature on fluorine-doped tin oxide (F.T.O.) glass substrate. The synthesized thin film was characterized by Atomic Force microscopy (AFM), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and UV-visible spectroscopy techniques. The thin film's photoelectrocatalysis (PEC) performance was investigated via methylene blue (MB) dye degradation from an aqueous solution under visible light. AFM investigation confirms that Al-doped CdSe/TiO₂ thin film has a non-uniform grain size. The grain size and surface roughness increase with the doping concentration. SEM analysis confirmed uniform film deposition with regularly arrayed crystal grains and indicated a flower-type crystal structure presence of TiO₂ on the thin film. The particle size was determined by using SEM and found to be 119.3 nm, and due to the doping, the size was increased. The EDAX analysis confirms the elements Cd, Se, Al, Ti and O present on the thin film. The direct band gap was determined by UV-VIS spectroscopy and by Tauc's relation is found to be 2.1 eV. The direct band gap of TiO₂ is 3.2 eV and due to Al doping in CdSe is reduced to activate in the Visible region. The maximum photodegradation percentage was obtained for 5 % Al-doped CdSe/TiO₂ thin film for Xenon lamp (500W) is 75.48% and in visible light (sunlight) is 94.42% for 300 min

Set up



Fig.1. Spray System



Fig.2 Al- doped CdSe/TiO2 Thin Film

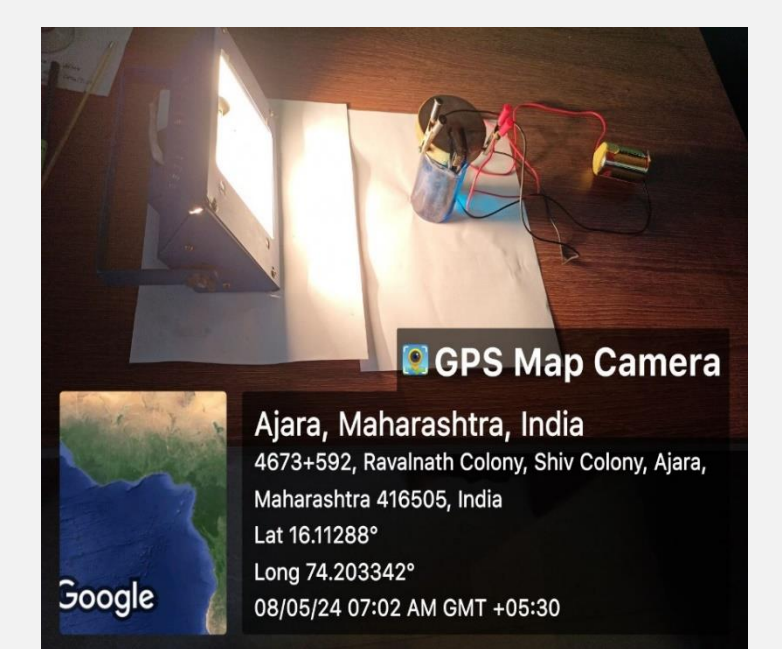


Fig.3 Photoelectrocatalytic Degradation



Fig. 4 Decolouration of MB

Introduction

Cadmium Selenide is an n-type of direct band gap II-VI semiconductor[1]. It has a high absorption coefficient and high resistivity due to this it has a variety of applications in the field of optoelectronics devices such as light emitting diode, laser diode, solar cells, and photocatalysis[2]. Cadmium Selenide can act as a photosensitizer because it has a narrow band gap(1.7eV). This property has sensitized the wide band gap semiconductors such as TiO₂(3.2eV)[3]. Titanium dioxide (TiO₂) is a promising semiconductor material used for photoelectrochemical cells for energy conversion and photocatalytic degradation of hazardous or organic pollutants in wastewater. It also has superior photoreactivity, non-toxicity, long-term stability and low price.[4] The photocatalysis process is mainly based on electron-hole pair generation of semiconductor material. If the TiO₂ semiconductor is coupled with another semiconductor like CdSe the photodegradation efficiency and functionality can be further increased.[4] The semiconductor photocatalysts act as a photosensitizer, which absorbs the energy of incident photons equal to or greater than its band gap and hits the electron from the occupied valence band to the unoccupied conduction band to create electron-hole pairs which are used for photodegradation. Several approaches have been taken to achieve photodegradation efficiency, like the coupling of semiconductors, doping of metal, non-metal, dual semiconductor, and nanocrystalline semiconductors.[5] Various thin film deposition methods has been extensively used such as chemical bath deposition (CBD), thermal evaporation, pulsed laser deposition, electrodeposition and spray pyrolysis.[6] Among all deposition techniques spray pyrolysis is used for thin film deposition because it has numerous advantages like non-vacuum equipment, non-toxic gas usage, quality thin film formation and cost effectiveness

Results

The AFM analysis gives the surface morphology and grain size of Al doped CdSe/ TiO₂ thin film . Grain size increases due to Al doping. The optical band gap is determined by Tauc relation from the UV- Vis. data and is obtained 2.2 eV . Due to Al doping in CdSe /TiO₂ the band gap of TiO₂ is reduced and is activated in visible region



Fig. 5 SEM image of Al doped CdSe/TiO2

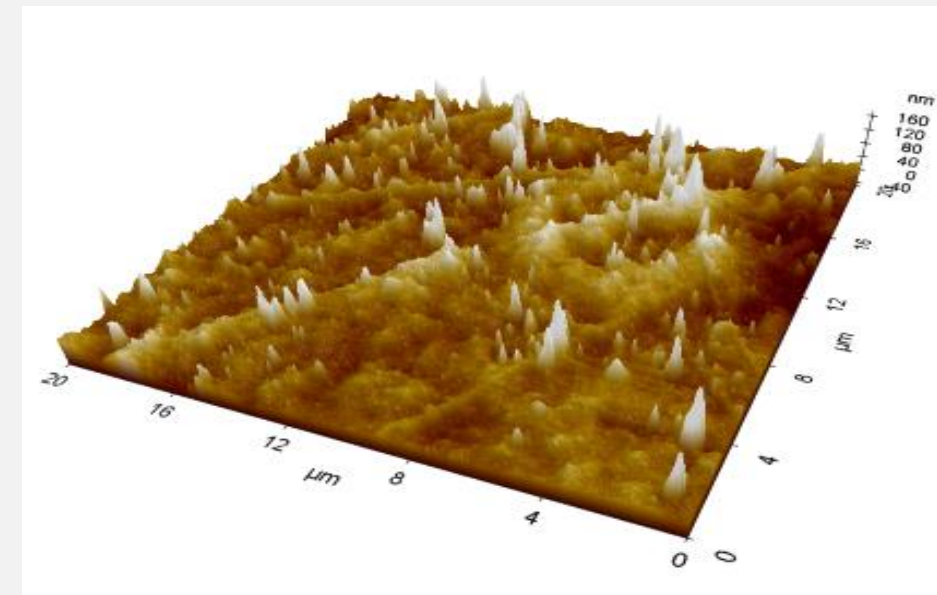


Fig. 6 CdSe/TiO2

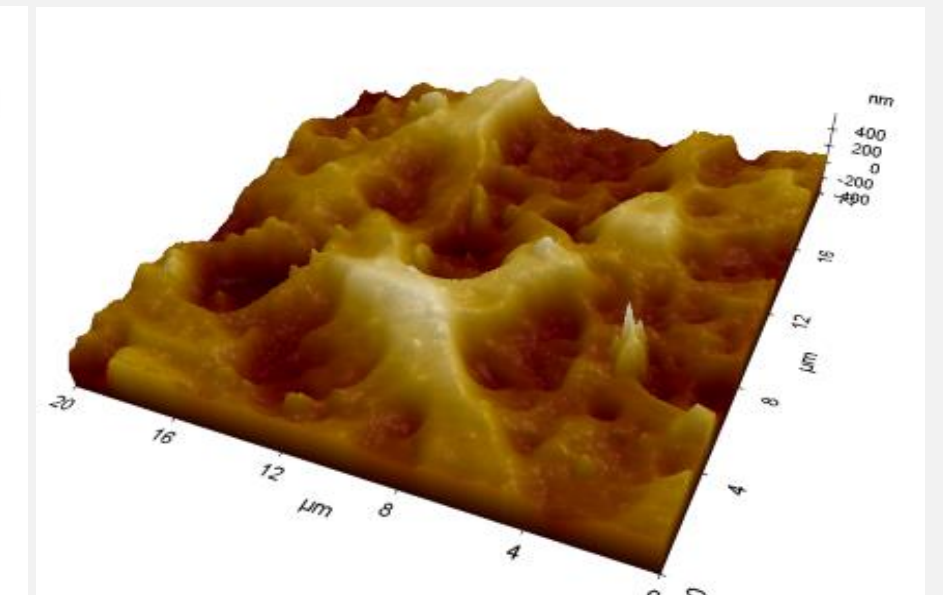


Fig. 7 Al-doped CdSe/TiO2

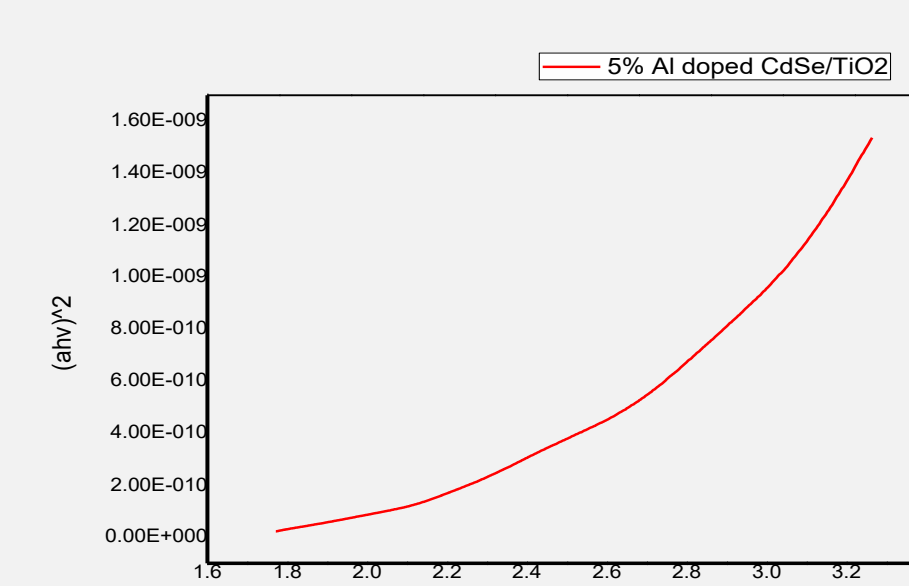


Fig. 8 Optical Band Gap of 5 % Al-doped CdSe/TiO2

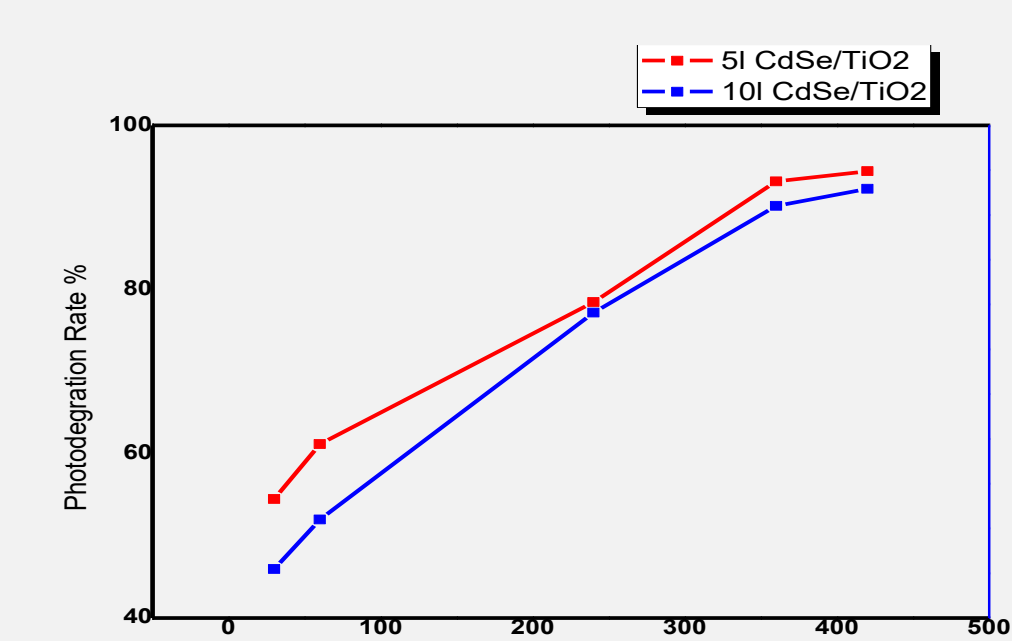


Fig. 9 Photoelectrocatalytic degradation of MB

Design/Other information

Materials and Methods :

The thin films of cadmium selenide CdSe and Al-doped CdSe have been deposited on Fluorine-doped tin oxide (F.T.O.) substrates at optimized temperature by spray pyrolysis at 400°C. The substrates underwent thorough cleaning to remove any contaminants that could affect the film deposition process. Initially, they were washed with a laboline solution to eliminate sticky particles of oil, grease, and lint. Subsequently, they were rinsed with water and boiled in chromic acid for 5 minutes. Chromic acid solution was prepared by dissolving 1 gram of chromium tetrachloride in 100 cc of double distilled water, resulting in a total of 3.5 grams of chromium tetrachloride dissolved in 350 cc of double distilled water. After this step, the substrates were cleaned once again in double distilled water and subjected to ultrasonic cleaning. Cadmium acetate [Cd (CH₃COO)₂], selenourea [N₂H₄CSe], aluminium chloride [AlCl₃], Titanium acetylacetonate [C₁₇H₃₀O₈Ti] were used as precursors for and cadmium, Selenium, aluminium, and titanium dioxide. Sodium sulfide, [Na₂S], Sulphur [S], Sodium hydroxide, Methanol, Ethanol, and Glass substrate, etc. All chemicals are A.R. grade and purchased from Sigma Aldrich.

Preparation of Al-doped CdSe/TiO₂ Thin Film:

The preparation of aluminum-doped cadmium selenide (CdSe) thin film involved the creation of precursor solutions for both cadmium (Cd) and selenium (Se). The Cd precursor was obtained by dissolving 0.076 grams of cadmium acetate in 19 ml of double distilled water to achieve a concentration of 0.015 M. Similarly, the Se precursor was prepared by dissolving 0.035 grams of titanium acetylacetonate in 19 ml of double distilled water, and Al precursor was obtained by dissolving 0.006 grams of aluminium chloride is dissolved in double distilled water also resulting in a concentration of 0.015 M. The combined precursor solution totalling 40 ml was then sprayed onto fluorine-doped tin oxide substrates to deposit the aluminium-doped CdSe thin film. The deposition process was conducted at optimized temperatures 400°C. Now 1.048 gm powder of Titanium acetylacetonate was dissolved in 40 ml solution of methanol as a precursor of TiO₂ and is sprayed on to the Al doped thin film to form a thin film of Al doped CdSe/TiO₂

Conclusions

The nanocrystalline Al doped CdSe thin film shows n-type conductivity. The particle size was determined by using SEM found to be 119.3 nm, and due to the doping, the size was increased. The EDAX analysis confirms the elements Cd, Se, Al, Ti and O present on the thin film. The direct band gap was determined by UV-VIS spectroscopy and by Tauc's relation is found to be 2.1 eV. The direct band gap of TiO₂ is 3.2 eV and due to Al doping in CdSe is reduced to activate in the Visible region. The maximum photodegradation percentage was obtained for 5 % Al-doped CdSe/TiO₂ thin film for Xenon lamp (500W) is 75.48% and in visible light (sunlight) is 94.42% for 300 min

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