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Fabrication of Ni-doped TiO_2 thin film photoelectrode for solar cells

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Abstract

TiO_2 and Ni-doped TiO_2 thin films have been prepared by sol–gel dip coating method. X-ray diffraction studies show that TiO_2 and Ni-doped nanocrystalline TiO_2 thin films are of anatase phase. The surface morphology of CdS quantum dot sensitized TiO_2 thin film and CdS quantum dot sensitized Ni-doped TiO_2 thin film were analysed by scanning electron microscopy. The absorption edge of TiO_2 thin films shift towards longer wavelengths (i.e. red shifted) with Ni doping, which greatly enhances the light absorption of TiO_2 in the visible region. The power conversion efficiency of CdS quantum dot sensitized Ni-doped TiO_2 (CdS QDS-NT) based solar cell exhibited an efficiency of 1.33%, which is higher than that of CdS quantum dot sensitized TiO_2 (CdS QDS-T) (0.98%) solar cells.

Keywords: Sol–gel method; Nanocrystalline materials; Quantum dot sensitized solar cell; Photovoltaic

1. Introduction

Titanium dioxide has received extensive attention for solar energy applications during the past decades due to its superior physical and chemical properties (Ding et al., 2011; Lu et al., 2010; Sauvage et al., 2010). Although TiO_2 is one of the most important material widely investigated for use in photocatalysis, photoelectrodes, and solar cells, the wide bandgap (3.2 eV) of TiO_2 limits its usage in the UV region. To extend the activity of a photoelectrode into the visible light region, various approaches have been employed like doping TiO_2 with impurities (Mohapatra et al., 2007; Khan et al., 2002; Ranjitha et al., 2013) and sensitization of TiO_2 with semiconductors which absorb light in the visible region. Considering that metal ion doping (such as Mn, Co, Fe and Ni) (Kim et al., 2007; Chandramohan et al., 2010; Li et al., 2009; Dong et al., 2010) are able to control the band gap and absorption properties, especially Ni^{2+} doping, (Dong et al., 2010; Kudo and Sekizawa, 2000) is able to improve the photoactivity. Also, narrow-band gap semiconductor materials have been used to act as light-harvesting sensitizers to enhance the photoelectric properties of TiO_2. Especially, metal chalcogenide semiconductors CdS (Sun et al., 2008; Peter et al., 2002), CdSe (Lee et al., 2008; Diguna et al., 2007), PbS (Ratanatawanate et al., 2008), Bi_2S_3 (Bessekhouad et al., 2004), In_2S_3 (Gan et al., 2011), $CuInS_2$ (Nanu et al., 2005)) have received much more attention because of their appropriate direct energy band gap values

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(Tsukigase et al., 2011; Ghows and Entezari, 2011; Zhu et al., 2010) and their ability to transfer electrons to large band gap semiconductors such as TiO_2 or ZnO. Among these, cadmium sulfide (CdS) and cadmium selenide (CdSe) are more promising materials reported to have better performance. Comparing CdS and CdSe, CdS has a higher conduction band edge with respect to that of TiO_2 (Gratzel, 2001) which is advantageous to the injection of excited electrons from CdS.

Some researchers have reported that the photo-response in the visible region can be obtained when nickel is doped into TiO_2, which could be ascribed to the narrower band gap of nickel doped TiO_2 (Zhang and Reller, 2002; Hong and Kang, 2006). The photocatalytic and magnetic properties have been studied by Zhang et al. (2006) and Xu et al. (2006) in metal doped TiO_2. The result of such investigations, have shown that the photoreactivity, charge carrier recombination rate, and interfacial electron transfer rate are affected by metal ion doping (Choi et al., 1994). Doped TiO_2 is widely used in solar cell applications and in one of the works, it has been reported that power conversion efficiency of 8% was achieved in dye-based solar cells fabricated using nitrogen-doped TiO_2 while 6% efficiency with pure TiO_2 (Wang et al., 1999). Tomata et al. (1998) used organic alkoxide of Ti and inorganic salts of Ni as raw materials, hexane as solvent, to prepare Ni^{2+}-doped TiO_2. Wu et al., 2003 have synthesized Ni/TiO_2 nanocomposite by sol–gel process.

In the present work, Ni-doped TiO_2 was synthesized by sol–gel dip coating method. The effect of Ni doping on the performance of CdS quantum dot sensitized TiO_2 based solar cells has been investigated.

2. Experiment

Ni-doped TiO_2 nanocrystalline thin films have been synthesized by sol–gel method. Titanium (IV) iso-propoxide (0.3 M), nickel nitrate, acetic acid (0.1 M) and polyethylene glycol 400 (1%) were dissolved in 20 ml of ethanol. The solution was stirred for 1 h to yield a homogeneous, clear, and transparent solution using magnetic stirrer. The Ni-doped TiO_2 thin films were deposited on ITO-coated glass substrates by dip-coating method. The Ni-doped TiO_2 films were annealed at 500 °C for one hour to remove organic residues and for film densification.

CdS quantum dots have been deposited onto Ni-doped TiO_2 thin film by successive ionic layer adsorption and reaction (SILAR) method. 0.15 M of cadmium nitrate in ethanol was taken as cationic pre-cursor solution and 0.15 M of sodium sulfide in ethanol was taken as anionic pre-cursor. The undoped nanocrystalline TiO_2 thin film was dipped in cationic solution for 10 s for adsorption of cadmium ions and rinsed in deionised water to remove loosely bounded Cd-species. Then it was dipped in anionic solution for 10 s and rinsed with deionised water. The sulfide ions react with adsorbed cadmium ions forming CdS in undoped nanocrystalline TiO_2 thin film. The SILAR process was repeated to get a uniform coating. The obtained film was then dried at 100 °C. The same procedure was repeated to prepare CdS quantum dot sensitized Ni-doped TiO_2 thin films. The thickness of the Ni-doped TiO_2 film and CdS layer has been determined using surface profilometer and was found to be 0.35 μm and 0.2 μm for Ni-doped TiO_2 thin film and CdS layer.

The X-ray diffraction studies has been carried out using X-ray diffractometer XPERT-PRO diffractometer system operating with Cu Kα radiation: surface morphology of the samples has been studied using JEOL-6390 scanning electron microscope (SEM): high resolution transmission electron microscope (HRTEM) images and elemental analysis of the prepared samples have been recorded using a JEOL JEM 2100 electron microscope and the optical properties has been studied using the absorbance spectra recorded using JASCO–UV–VIS–NIR spectrophotometer (JASCO V570). The thickness of the samples has been determined using surface profilometer. The sandwich type photoelectrochemical solar cell has been fabricated by using the CdS quantum dot sensitized Ni-doped TiO_2 electrode, as photoelectrode with Pt coated ITO as the counter electrode, 0.1 M lithium iodide and 0.03 M iodine dissolved in acetonitrile was used as the electrolyte solution. The *J–V* characteristics of the cell was recorded using a Keithley 4200-SCS meter. A xenon lamp source (Oriel, USA) with an irradiance of 100 mW/cm^2 was used to illuminate the solar cell (equivalent to AM1.5 irradiation). The schematic diagram of the fabricated solar cell is shown in (Fig. 1).

3. Results and discussion

Fig. 2 shows the X-ray diffraction pattern of TiO_2 and Ni doped TiO_2 thin films. The X-ray diffraction pattern has been collected in symmetric configuration by powder X-ray diffraction method. The obtained X-ray diffraction pattern shows (1 0 1) as predominant peak. The peak identified as (1 0 1) crystal direction of TiO_2 is observed at $2\theta = 25.3°$. The crystal phase of undoped and Ni-doped TiO_2 thin films was observed to be anatase phase. These results are in good agreement with the report, that is to

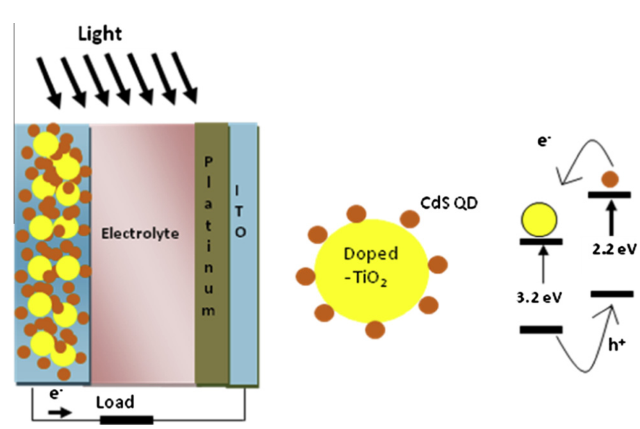

Fig. 1. Schematic representation of solar cell structure.