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Development of copper doped titania based photoanode and its performance for dye sensitized solar cell applications

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ABSTRACT

Photoanode is one of the most important components in dye-sensitized solar cells (DSSCs) for which oxide ceramics are among the top choices. It has been established that the metal doping can introduce structural defects in oxide ceramics such as in titania lattice which can result in increase in photo-absorption of solar cells. Metals such as Cu being inexpensive and readily available, have potential to cause phase transformation in titania at lower temperature supportive to cell performance. However, there is not enough data available in the literature on performance of DSSCs based on Cu-doped titania photoanode. In this work, we have synthesized undoped and doped titania nanoparticles by wet-chemistry routes. Various process routes such as effects of annealing temperature, Cu concentration, pore former, etc. were employed to investigate the structural, thermal and electrical performance of doped and undoped materials and thin films for DSSCs. For qualitative and quantitative analyses, techniques such as X-ray diffraction, scanning electron microscopy, thermal analyses, molecular spectroscopy and potentiostat were employed. Studies have revealed that dopant existed in the form of CuO in nanoparticles and thin films. Cu doping assisted in reduction in particle size and band gap, which was further verified by red absorption shift. IV measurements of the cells fabricated with Cu-doped titania photoanode, N3 dye, I^-/I_3^- electrolyte and gold coated FTO counter electrode, revealed an 11% increase in V_{oc}, compared to V_{oc} of cell made with similar components but using undoped titania photoanode. The inclusion of carbon microspheres caused formation of cavities into the photoanode made with titania and Cu:Titania and increased the porosity and surface area for greater dye adsorption. It was found that porosity increased from 31% to 42% by adding in-house fabricated 2.5 wt% carbon microspheres into 3 wt % Cu-doped titania thin films.

1. Introduction

The efficiency of Dye Sensitized Solar Cells (DSSC's) depends on various factors. The efficiency is very much related to the properties of semiconductor photoanode. Few other relevant factors are properties of dye, nature of redox couple, catalytic properties of counter electrode, etc. In other words each and every layer of a DSSC affects the efficiency of the cell. Focusing on semiconductor photoanode, titania is one of the most usable and attractive semiconductor materials for DSSCs because of its chemical stability and easy availability. The main downside of titania is that it only absorbs UV radiation from solar spectrum which makes only 4% of the electromagnetic radiations coming from sun [1,2]. In order to enhance the absorption of solar radiation by titania, we need to create oxygen deficiencies or structural defects in its structure to decrease the band gap. The reduction in band gap of titania which is 3.2 eV for Anatase, can lead to make it active in visible light. Moreover, forming pores in titania layer of photoanode can lead to enhanced adsorption of dye and hence greater absorption of incident light. Homogenous thin films of titania formed by using a low cost solution based technique such as sol–gel can further offer price control as well as better films could lead to better performance of the cells. The Sol-Gel process is a versatile method for preparing bulk materials of controlled porosity, either crystalline or amorphous, as well as fibers, films, catalysts, adsorbents and nanoparticles, nanocomposites etc. [3]. Sol gel process is widely being used to synthesize metal oxides owing to the fact that it allows formation of metastable materials with compositional homogeneity and high purity requiring simple laboratory apparatus [4]. Sol gel process has been employed to synthesize ultra-fine-

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stoichiometric controlled nickel ferrite nanoparticles [5], silica nanoparticles [6], etc. Zang et al. [7] reported the synthesis of ZnO particles by a facile Sol–gel method. Sol–gel synthesis of doped nanoparticles and films like Pr doped ZnO nanoparticles [8], Bi doped CdO thin films [9] etc. has also been reported in literature.

Previous studies with titania based photoanode have shown that doping titania with various metals could enhance some of the photovoltaic properties of the cell. Doping the titania semiconductor renders three main advantages in DSSCs, namely, reduction in band gap resulting in enhanced efficiency, reduction in photocatalytic activity of DSSCs and moreover, reduction in recombination. For example, Feng et al. [10] reported negative shifting of conduction band of titania as a result of Ta doping, due to which increase in open circuit voltage (V_{oc}) was observed. Geetha et al. [11] reported improvements in photoelectric performance of DSSCs by using chromium doped titania semiconductor as photoanode. Zalas et al. [12] studied the influence of rare earth metal doping on performance of DSSCs. These modified electrodes prevented back transfer of electrons and enhanced dye absorption ability. Lu et al. [13] and Lee et al. [14] studied niobium doped titania semiconductor based DSSC and reported an improvement in cell performance due to doping.

Copper is readily available in earth's crust and is a cheap metal with high electronic conductivity [15], which make it an attractive metal for doping titania semiconductor photoanode of DSSCs. Doping copper in titania can create structural defects in titania lattice hence reducing its wide band gap. In this research, we have studied the doping effects of copper on structure, crystallinity and morphology of titania based photoanode and discussed how doping with copper shifts the absorption edge of titania to visible region and improves the open circuit voltage. Meanwhile, thermal stability of Cu doped titania based photoanode is also reported along with result on performance of photoanode with enhanced micro porosity that accompanies higher dye absorption.

2. Experimentation

2.1. Syntheses of undoped and doped titania NPs

Undoped titania nanoparticles (NPs) and doped with 1wt% and 3wt% Cu were prepared by sol–gel method. For fabrication of titania NPs, appropriate amount of titanium isopropoxide (Sigma–Aldrich) was stirred for a few hours in a suitable volume of ethanol. Isopropoxide chain was hydrolyzed by addition of suitable volumes of water and HCl and was stirred continuously for several hours. The sol was kept for a full day, dried and then annealed at 450 °C and 650 °C for 4 h each. To prepare Cu-doped titania another solution was made containing $CuCl_2 \cdot 5H_2O$, water and ethanol. This solution was added while hydrolyzing TTIP solution. The sol was kept for 24 h, dried and annealed at similar conditions as for undoped titania.

Sol gel method employed in our paper allowed us to gain control on the concentration of copper dopant in TiO_2 nanoparticles. The dopant concentration is controlled by the weight of the dopant added relative to the volume and density of the precursor (TTIP).

$$m = \rho * V$$

where, m = mass of dopant in grams, ρ is density of the liquid TTIP in g/cm^3, V is volume of TTIP in cm^3.

2.2. Synthesis of carbon microspheres

Glucose and distilled water were stirred together magnetically for 2 h at room temperature. The resulting mixture was filled in a Teflon lined stainless steel autoclave. The autoclave was maintained at 200 °C in oven for 14 h. After cooling, autoclave was taken out of the oven and dark precipitate was collected. These precipitate was washed with distilled water, collected on a filter paper and then dried in oven at 110 °C for 14 h. The obtained product was ground using pestle and mortar and a fine powder was obtained. The powder was subsequently annealed at 325 °C for 10 h to obtain carbon microspheres. Carbon microspheres (2.5 wt%) were incorporated into the photoanodes followed by annealing at temperature above 400 °C to ensure the pore formation.

2.3. Thin film deposition and cell fabrication

Paste formation for doctor blade coating was carried out by stirring appropriate amounts of ethanol, distilled water, HNO_3, and PEG with doped and undoped powders. These pastes were coated on the conductive side of FTO coated glass substrates. The coated films were dried at room temperature for several hours and then annealed at 450 °C and 650 °C. After annealing we got porous photoanodes made with doped and undoped titania. Photoanode with coated surface facing upwards was put in 0.0001 M solution of N3 dye in ethanol for 24 h in dark. After the dye got adsorbed on to the surface, the photoanodes were washed with ethanol, dried and clipped with gold coated FTO counter electrode. The I_3/I_3^- electrolyte was prepared by stirring together potassium iodide and iodine crystals in ethylene glycol solvent and a few drops were added between the two electrodes.

2.4. Characterization

The X-ray diffraction (XRD) pattern of the samples was obtained using a θ-θ STOE Germany X Ray diffractometer at room temperature irradiating X Rays from Cu-Kα for structure and phase analysis. XRD was operated at 40 kV and 30 mA. The measurements were recorded in step of 0.04° and scan angle range of 10–80°. SEM-EDS of the samples were carried out using a JEOL 2300 scanning electron microscope at an operating voltage of 20 kV with an EDS detector. UV–VIS spectra of the samples were obtained using a BMS 2800 UV–Vis spectrophotometer with $BaSO_4$ powder as the standard reference sample and data was taken in the range of 300–900 nm. TG–DT analyses of the samples were performed using Perkin Elmer diamond TG/DTA version 2.0 with a 2 g sample each. Temperature range was set from room temperature to 500 °C. Optical Microscopic Images of coatings were obtained using Optika B-600 MET with camera Optika 40. IV characteristics of the DSSCs were obtained using Biological VSP (potentiostat system).

3. Results and discussion

3.1. Effect of annealing temperature and Cu concentration on nanoparticles

The similarity in ionic radius of Cu^{2+} (0.73 Å) to that of Ti^{4+} (0.64 Å) enables copper to substitute titanium in titania lattice. Titania doped with Cu^{2+} initiates the formation of rutile phase along with anatase. As shown in Fig. 1 (a), when annealed at 450 °C, titania changes from amorphous to crystalline phase. At 450 °C pure anatase phase is formed corresponding to JCPDS card# 78-2486. Anatase is metastable phase of titania and is usually formed at low temperature during solution-phase synthesis [16]. During polymerization of TiO_6 octahedral units as crystal nucleation, phase of TiO_2 depends on which of the phases grows faster during polymerization [17]. It has been reported that during synthesis of TiO_2 nanoparticles by various methods, the initial crystalline TiO_2 phase formed is anatase. Structurally, the reason can be attributed to the