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Facile synthesis and characterization of $Ti_{(1-x)}Cu_xO_2$ nanoparticles for high efficiency dye sensitized solar cell applications

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ABSTRACT

In this study, we demonstrate the facile synthesis of $Ti_{(1-x)}Cu_xO_2$ (x = 0.0, 0.03, 0.06 and 0.09) nanoparticles through solvothermal microwave irradiation (SMI) technique and explored their photocatalytic applications. A combined analysis of XRD, FESEM and TEM studies indicate that doping of Cu^{2+} in TiO_2 lattice do not affect the microstructure of the particles. The UV–Vis. absorption study indicates that the introduction of Cu element lead to decrease in optical bandgap of TiO_2 from 3.450 eV to 3.155 eV (for x = 0.0 to 0.09). By using $Ti_{(1-x)}Cu_xO_2$ nanoparticles photoanodes were prepared on transparent conductive fluorine doped tin oxide substrates by doctor-blade technique. The dye-sensitized solar cells (DSSCs) were assembled and an analysis was made to evaluate the variations in open-circuit voltage depending on the concentration of Cu in $Ti_{(1-x)}Cu_xO_2$. The optimum efficiency of 6.51% was found at $Ti_{0.94}Cu_{0.06}O_2$ based DSSCs, which gives an efficiency improved by 4% compared with that of the cells based on pure TiO_2 (6.26%). This work demonstrates that $Ti_{(1-x)}Cu_xO_2$ is a most fascinating material and has great potential for application in photoenergy conversion devices.

1. Introduction

Titania (TiO_2) is an essential material that has wide applications as a white shade in paints [1], electro clay materials [2], impetus bolsters [3], photocatalysis [4], hydrogen storage [5] and to form efficient dye sensitized solar cells (DSSCs) [6]. Dye-sensitized solar cells (DSSCs) have pulled in critical consideration as a promising renewable energy source on account of their high proficiency, basic manufacture handle what's more, ease [7–10]. Many semiconductor nanomaterials have been studied as photoanode materials to develop high performance DSSCs, such as TiO_2, ZnO, SnO_2, CdS, CdTe, ZnTe, Nb_2O_5, and $SrTiO_3$. Among the wide range of reported materials, TiO_2 is considered as the best semiconductor anode material, because of its chemical stability and good charge transport capacity. As such, photovoltaic performance of more than 11% for a DSSC was accomplished by utilizing TiO_2 nanoparticle as photoanode. The morphology and crystallite (grain) size of TiO_2 assume basic parts in the photoelectric change proficiency of DSSCs [6,11–13]. In the previous two decades, many research endeavors have been made to upgrade the power transformation efficiencies of TiO_2 nanoparticles with the end goal of commercialization, for example, the change of the semiconductor nanocrystal anode, dye, cathode and electrolyte [14–16] For example, Paulose et al. prepared highly-ordered TiO_2 nanotube arrays by potentiostatic anodization of a titanium film in a fluoride containing electrolyte and achieved a solar conversion efficiency of 4.4% [17].

In the process of the photocurrent generation in DSSCs, energized states dye atoms infuse electrons into the conduction band of TiO_2, from which the electrons are transported into the back contact and after that streams in the outer circuit. In the meantime, there are some recombination's and traps brought about by a few electrons with tri-iodide of the electrolyte or oxidized dye molecules. The two contradicting electron ways are in contention and it affects the electron transport process and accumulation proficiency in the nanostructure TiO_2 material. A productive course to improve the photovoltaic execution of DSSCs is to expand the electron-transport rate. Moreover, the improvement of charge-transfer ability is helpful to increase the short circuit current density (J_{sc}) that could offer opportunity to enhance the photoelectric conversion efficiency of DSSCs. Singh et al. synthesized the PbS-TiO_2 nanocomposite for working electrode in DSSCs and this composite serves as surface state depressors, which reduces recombination rate and increases the conversion efficiency of DSSCs [18]. In recent

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years, researchers observed that doping the TiO_2 with metal or nonmetal ions could be a promising approach to improve the electron-transport rate and other properties of TiO_2 photoanode. Notwithstanding, DSSCs based on such photoanode, to date, have experienced low internal surface area and thus insufficient dye loading, bringing about low efficiencies.

Recently, Yao et al. have prepared nearly monodisperse Nd-doped TiO_2 nanorods and found that the Nd doping leads to a significant increase of solar conversion efficiency from 3.3% to 4.4% [19]. Lee et al. prepared Nb-doped TiO_2 thin film was deposited on a fluorine-doped tin oxide (FTO) electrode by pulsed laser deposition and found that the doping significantly enhances the cell efficiency by the order of 1.2 [20]. Similar results were also found by Lu et al. when 5 mol% Nb-doped TiO_2 was applied as the photoanodes of DSSCs [21]. Zhang et al. reported the synthesis of various concentration of Zn doped TiO_2 nanoparticles and its use as photoanodes of DSSCs. The photovoltaic parameters of DSSCs based on Zn-doped TiO_2 are significantly better, compared to that of a cell based on undoped TiO_2 [22]. In order to improve the performance of DSSCs, few researchers have recently explored a chemical/structural modification strategy for titania containing electrodes [12–14,23,24]. Be that as it may, the absence cost effective synthesis methods for a scaled up production these structures is a setback in this area. To the best of our understanding solvothermal microwave irradiation (SMI) synthesis method is a straightforward, practical and mechanically versatile technique for the production of good quality nanoparticles [25–27].

In the literature, tiny spherical titania having high surface-to-volume has been shown to adequately adsorb dye molecules. Nanostructured photoanode with smaller grain size was observed to offer brilliant dye-loading, light-harvesting and electron-transport properties [28–30]. Copper (Cu) doped TiO_2 nanoparticles or nano films have been used as photocatalysts and dilute magnetic semiconductors (DMS) [31,32]. However, limited studies have so far been reported regarding the Cu-doped TiO_2 nanoparticles, particularly as a photoanode for DSSCs. In a recent work, Cu doped TiO_2 nanostructured photoanode sensitized with Ru535 dye was shown to improve the photovoltaic efficiency of DSSC. The results showed that the open circuit voltage (V_{oc}) of Cu doped TiO_2 electrode enhances significantly. However, in that case, the cell efficiency of doped TiO_2 was shown to be lesser than that of pure TiO_2 [33]. Keeping these in view, in the present work, we report convenient preparation strategy for $Ti_{(1-x)}Cu_xO_2$ ($x = 0.00$. 0.03, 0.06 and 0.09) nanoparticles through solvothermal microwave irradiation (SMI) technique. A detailed discussion regarding the structural properties, size, morphology and optical properties of the as-synthesized $Ti_{(1-x)}Cu_xO_2$ has been made. Furthermore, the $Ti_{(1-x)}Cu_xO_2$ ($x = 0.0$, 0.03, 0.06 and 0.09) nanoparticles were successfully applied as the photoanode material in a DSSC using low cost molecular dye N3 {*cis*-Ru(H_2dcbpy)$_2$(NCS)$_2$ (H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridyl)} as sensitizer and their photovoltaic performance has been verified.

2. Experimental details

2.1. Materials

Analytical reagent (AR) grade titanium tetra chloride ($TiCl_4$), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) and urea ($CO(NH_2)_2$) were purchased from Sigma Aldrich Missouri, USA. Ethylene glycol ($C_2H_6O_2$), acetone ($(CH_3)_2CO$) and double distilled water were purchased from Central Drug House (P) Ltd. These chemicals were used without additional purification for the preparation of $Ti_{(1-x)}Cu_xO_2$ ($x = 0.00$, 0.03, 0.06 and 0.09) nanoparticles.

2.2. Synthesis of $Ti_{(1-x)}Cu_xO_2$ nanoparticles

In a typical synthesis procedure for the preparation of $Ti_{(1-x)}Cu_xO_2$ (where $x = 0.00$) nanocrystals, 0.1 M $CO(NH_2)_2$ was dissolved in 100 ml ethylene glycol under vigorous stirring condition for 1 h at 30 °C. Subsequently 0.1 M $TiCl_4$ solutions were added in 100 ml ethylene glycol and stirred well at room temperature. Both the solutions were slowly mixed and stirred for another 2 h at 50 °C temperature to get a clear and deep blue coloured solution. The resulting dissolved mixture solution was called as stack solution. This stack solution was transferred into a microwave safe container (porcelain bowl) and kept in a domestic microwave oven IFB 23BC4 23 L operated with frequency 2.45 GHz and output power 900 W. The microwave output power and temperature of this unit can be controlled from 0 to 900 W (10 levels, in steps of 100 W) and 110 to 220 °C (10 levels). In our experiment, microwave irradiation was carried out at 300 W power in the air medium for 5 min. The resultant product obtained in the form of colloidal precipitate was cooled to room temperature naturally and then centrifuged at 10000 rpm for 30 min. The resultant precipitate was collected and washed several times with double distilled water and acetone to remove the un-reacted precursors. The final washed precipitate was dried in a heating oven at 60 °C for 10 h. The final product was weighed accurately and collected as the yield. In order to prepare $Ti_{0.97}Cu_{0.03}O_2$ ($x = 0.03$), $Ti_{0.94}Cu_{0.06}O_2$ ($x = 0.06$) and $Ti_{0.91}Cu_{0.09}O_2$ ($x = 0.09$) nanoparticles the corresponding mole% of $TiCl_4$ reactant was replaced by the $CuCl_2 \cdot 2H_2O$ precursor and the above procedure was followed. The prepared powders were used to characterize and to fabricate DSSCs. The quantity of precursors used and the obtained yield percentage of product are given in the Supplementary Material (Table S1).

2.3. Preparation of electrodes and cell fabrication

$Ti_{(1-x)}Cu_xO_2$ ($x = 0.00$. 0.03, 0.06 and 0.09) nanocrystalline films were prepared on the FTO substrates (fluorine-doped SnO_2, 15–20 Ω/sq) using a doctor-blade method [34] with adhesive tape to control the thickness. Before forming the electrode, the FTO has been rinsed with distilled water and immersed in isopropanol for 2 h to increase its hydrophilicity. The electrodes were then heated at 450 °C for 30 min in air with a temperature ramping rate of 2 °C/min. After the sintering, when the temperature got cooled to about 90 °C, the electrodes were immersed in a dye bath containing 0.5 mM N3 {*cis*-Ru(H_2dcbpy)$_2$(NCS)$_2$(H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridyl)} in ethanol for 24 h. The thicknesses of the films were measured at different places by using thickness measuring unit model US M probe Vis. spectroscopic reflectometer. The average thickness of the dye sensitized photoanode film was about 10 μm. The Pt-coated FTO was used as the counter electrode. The counter electrode and the dye sensitized photoanode films were placed facing each other. Then, the two plates were detained together using the binder clips. The redox electrolyte solution was prepared by a mixture of 0.5 M LiI, 0.05 M I_2, 0.6 M 4-*tert*-butylpyridine (TBP) in acetonitrile, and 0.6 M 1-hexyl-3-methylimidazolium iodide (HMII) in 3-methoxypropionitrile (MPN). Finally the electrolyte solution was injected between the dye sensitized photoanode and counter electrode.

2.4. Characterization

The crystalline structures of the synthesized $Ti_{(1-x)}Cu_xO_2$ nanoparticles were characterized through X-ray diffraction (XRD) analysis, which was performed using an automated PANalytical X-ray powder diffractometer operating at 40 kV and 30 mA with monochromated CuK_α radiation ($\lambda = 1.541$ Å) and the scanning 2θ