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Enhanced photovoltaic performance of dye sensitized solar cell using SnO_2 nanoflowers

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ABSTRACT

The study highlighted enhanced performance of SnO_2 based DSSC using photoanode with nanostructured morphology. The simple organic surfactant free hydrothermal synthesis method was used for preparation of SnO_2 nanoflowers for dye sensitized solar cell (DSSC) application. The hydrothermal reaction time was varied to obtain different SnO_2 nanostructures. The hydrothermal reaction time showed considerable effect on optical and structural properties of the prepared samples. The results indicated that the prepared samples were pure rutile SnO_2. The band gap of prepared samples was greater than bulk SnO_2 and varied from 3.64 to 3.81 eV with increase in hydrothermal reaction time. With increase in reaction time from 4 to 24 h, the microstructure of SnO_2 changed from agglomerated nanoparticles to nanopetals and finally to self-assembled nanoflowers. Flower-like SnO_2 nanostructures showed size around 300–700 nm, and composed of large numbers of 3 dimensional petals connected with each other forming 3D nanoflowers by self-assembly. Consequently, the DSSC with flower-like SnO_2 nanostructures exhibited good photovoltaic performance with Voc, Jsc and η about 0.43 V, 4.36 mA/cm^2 and 1.11%, respectively.

1. Introduction

The nanostructured materials with desired morphologies, crystalline phases, optical and electrical properties is one of the great research interests for their applications in various fields like, optoelectronic devices, photo-catalysts, gas sensors, lithium ion batteries and nanostructured solar cells [1,2]. Now a day it is well proved that, the properties of nanostructured materials are influenced by process parameters and controllable synthesis process. Considerable efforts have been taken to synthesize different photoanodes with various morphologies to enhance rapid collection of generated charges at the metal oxide/dye interface of Dye Sensitized Solar Cells (DSSC) [3,4]. A literature shows that the photoanode of DSSC with network of nanowires or nanorods provides direct conduction paths for injected electrons and hence enhances its photovoltaic performance [5–7]. The study by Jiang et al. [8], showed that the DSSC based on nanoflower like morphology offers high surface area, supports optimum dye loading, and also have good electron transportation due to its oriented branching. Being a suitable alternative to TiO_2 photoanode in DSSC, SnO_2 with different nanostructures has attracted much attention of research community [9]. The recent study on SnO_2 based DSSCs showed four times more photoelectric conversion efficiency for photoanode with flower-like nanostructures than that of photoanode with spherical SnO_2 nanocrystals [10]. According the study the flower-like architecture composed with SnO_2 nanorods offers higher specific surface area and more stable spatial structure.

In the study by *Elumalai* et al. [11], reported synthesis of SnO_2 flowers and fibers developed by the electrospinning technique. According to them, the flower like morphology has lower density of surface traps in the band gap on account of their enhanced crystallinity. Also they have reported that the SnO_2 flowers have higher fermi energy than that of the fibers. The photovoltaic performance of SnO_2 flower-based DSSC shows V_{OC} ~0.7 V, J_{SC} ~7.30 mA/cm^2, and η ~3.0% with N3 dye [11]. Different nanostructures of SnO_2 such as nanorods [12], nanobelts [13], nanotubes [14], nanodiskettes [15], nanowires [16] and hollow microspheres [17] are prepared using various physical and chemical synthesis methods. Among different methods, hydrothermal method is a simple, cost-effective, low temperature and large scale synthesis process. The controllable

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grain sizes, purity, morphology and degree of crystallinity can be easily obtained by optimizing operating conditions in hydrothermal method [18]. Unlike many advanced methods that can prepare a large variety of forms and chemical compounds, such as chemical vapor-based methods, the respective costs for instrumentation, energy and precursors are far less for hydrothermal methods. The low reaction temperatures also avoid other problems encountered with high temperature processes, for example poor stoichiometry control due to volatilization of components. Another important advantage of the hydrothermal synthesis is that the purity of hydrothermally synthesized powders significantly exceeds the purity of the starting materials. It is because the hydrothermal crystallization is a self-purifying process, during which the growing crystals tend to reject impurities present in the growth environment. The impurities are subsequently removed from the system together with the crystallizing solution, which does not take place during other synthesis routes, such as high temperature calcination. Several reports are available on hydrothermal synthesis of SnO_2 usually in aqueous solutions using inorganic or organic tin precursors [19–21]. Most of the workers use organic surfactant to obtain desired morphology of SnO_2 [18,22]. But further processing is required to remove the organic surfactant. On the other hand, it has been well studied that the hydrothermal reaction time has a strong influence on the crystallinity and morphology of nanostructured materials [6,19,21,23].

In the present study, SnO_2 agglomerates, nanopetals and nanoflowers have been successfully synthesized by hydrothermal method without use of any organic surfactant, by optimizing reaction time. The DSSC is fabricated using these Photoanodes and their photovoltaic performance is discussed.

2. Methods

2.1. Synthesis of SnO_2 nanostructures

SnO_2 nanostructures were synthesized by hydrothermal method with Tin(IV) chloride pentahydrate ($SnCl_45H_2O$) and sodium hydroxide (NaOH) as precursor. For synthesis $SnCl_45H_2O$ was purchased from Thermo Fisher Scientific and NaOH from LOBA chemicals. Both chemicals were of analytical grade. In a typical process, 0.1 M $SnCl_45H_2O$ and NaOH were mixed with double distilled water under vigorous stirring. Ethanol was dropped slowly into the solution until the solution turns into white precipitate. The mixture was stirred for 2 h at room temperature. The whole mixture then was transferred into Teflon-lined stainless steel autoclave to react at 180 °C. The reaction was carried out three times with reaction time 4, 12 and 24 h. After the complete reaction, the resulting product was filtered and washed several times and finally dried at 60 °C for 4 h. The photoanodes prepared with 4, 12 and 24 h reaction time were named as HPA-1, HPA-2 and HPA-3, respectively.

2.2. Fabrication of solar cell

The prepared photoanodes were sensitized using Eosin Y (EY) dye as a light harvesting component. All the prepared photoelectrode films were immersed into 0.3 mM EY dye solution for 24 h to adsorb dye molecules. Platinum coated FTO electrode was prepared using sputtering method with platinum target material under moderate vacuum condition. The iodine/iodide (I_3^-/I^-) electrolyte was purchased from Aldrich.

To fabricate the Solar cell, The EY dye sensitized SnO_2 photoanode was clamped with the Pt- FTO counter electrode to form a sandwiched type structure. The electrolyte solution was injected into the inter space between the photoanode and the counter electrode. The solution was allowed to wick up between the electrodes by capillary action. The device is now ready for characterization under illumination from photoanode side. Three different cells were fabricated with prepared photoanodes.

3. Characterization

The crystal structure and morphology of the photoelectrode films were characterized by X-ray diffractometer (XRD, Rigaku "D/B max-2400", $\lambda = 1.54$ Å) and scanning electron microscopy (SEM, JEOL-JSM 6360-A), respectively. The Scherrer's formula is used to estimate the crystallite size of the prepared sample from XRD data using equation

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

Where, D is crystallite size, β is FWHM of the observed peak, λ is wavelength of the X-ray and θ is angle of diffraction.

The optical absorption measurements of dye in solution, unsensitized and dye sensitized SnO_2 photoelectrodes were carried out with UV–Vis spectrometer (JascoV-670) in the range of 200–800 nm. The fabricated devices were characterized by AM 1.5 solar simulator equipped with a 450 W xenon lamp at 1000 W/m^2 (Model Sol 2A, Newsport) to study the performance of cell.

4. Results and discussion

4.1. Structural analysis SnO_2 nanocrystals

Fig. 1 shows the XRD patterns of as-synthesized SnO_2 samples at 180 °C for different reaction times of 4, 12 and 24 h. All the observed peaks in the patterns corresponded to the rutile structure of SnO_2 (space group: $P4_2/mnm$, a = 0.4739 nm, c = 0.3186 nm, JCPDS file No. 41-1445). It is observed that the SnO_2 diffraction peaks appear clearly with increase in hydrothermal reaction time. This confirms the increase of crystallinity in the samples. The diffraction peaks are broadened due to the small crystallite sizes of SnO_2. However, the sample synthesized at 4 and 12 h also shows characteristic peak of SnO along with SnO_2.

Table 1 gives the calculated average crystallite size, of SnO_2 samples prepared at 12 and 24 h, using its (110), (101), (200) and (211) orientations and is in the range of 20 − 40 nm. It is well known that from XRD what we calculate is the crystal size and not

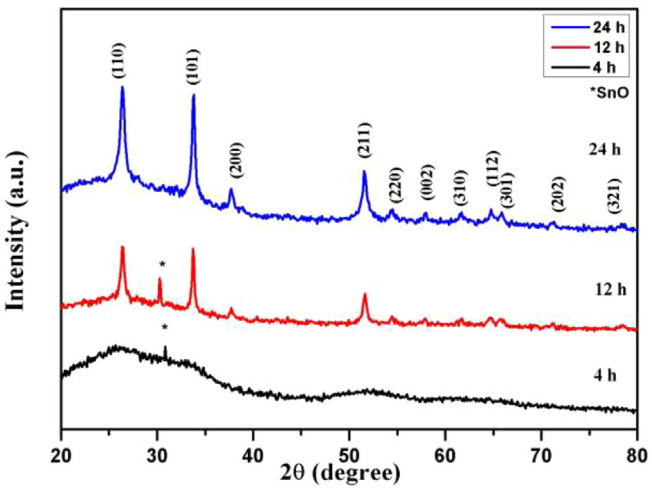

Fig. 1. XRD pattern of hydrothermally synthesized SnO_2 nanostructures.