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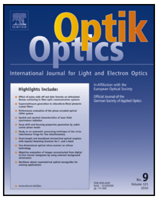

Full length article

Improved electron transfer of TiO_2 based dye sensitized solar cells using Ge as sintering aid

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ABSTRACT

Low electron mobility of TiO_2 semi-conductor and inferior inter-particle contact facilitate recombination reactions that leads to low performance of dye sensitized solar cells (DSSCs). To improve electron mobility at relatively low sintering temperatures, doping of germanium (Ge) nanoparticles with TiO_2 have been trailed due to its excellent optoelectronic and low temperature sintering properties. Anatase TiO_2-Ge nanocomposites have been prepared by using colloidal suspension process and deposited on conducting glass using doctor blade technique. Four types of nanocomposites i.e. (1) TiO_2–0.5 wt%Ge, (2) TiO_2–2 wt%Ge, (3) TiO_2–5 wt%Ge and (4) TiO_2–10 wt%Ge have been prepared and sintered at 400 °C with a control specimen fabricated using pure TiO_2 nanoparticles (sintered at 450 °C) for comparison purpose. To investigate the morphological and structural characteristics, SEM and XRD have been employed. The UV-vis and impedance spectroscopy have been performed to observe light absorption and electron transfer characteristics respectively. Finally, specimens were tested for their photo conversion efficiency. An increase in electron transfer ability and conversion efficiency have been recorded with increase in Ge nanoparticles even at 400 °C sinter temperature compared to reference TiO_2 photoanodessintered at 450 °C.

1. Introduction

Electron recombination reactions and light scattering ability along with dye pick up capacity are the main parameters to improve the performance of electrochemical dye sensitized solar cells (DSSCs) [1,2]. Efficient charge carrier transport (electrons) from the semiconductor nanostructure to the external load through transparent conducting oxide layer without recombining with electrolyte or dye guarantee the suppression of recombination reactions which is still one of the main reasons of less efficiency of DSSC device [3]. For efficient electron transfer, it is of utmost importance that the semiconductor nanoparticles should be sintered to coble initial sintering stage where inter-particle contact area increases by neck growth from 0 to ~0.2%. Sintering temperatures which are restricted to 400 and 450 °C cannot provide this much vibrational energy to increase the thermal entropy (ST) to the extent necessary to lower the surface/boundary energy (γ_{gb}) of nanoparticles by 2/3 compared to solid/vapor surface energy (γ_{sv}) of the system. Without enough heat energy the Gibbs free energy of surfaces will not allow the formation of necks and diffusion of surfaces for proper inter-particle contact [4].

Various approaches have been trialled to improve the incident photon conversion efficiency (IPCE) of DSSCs, such as size quantization [5–7], development of different nano-architectures [8–11] and doping with different cations and anions

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[12–14]. With improvement in light absorption capacity, reduction in recombination reactions and dye loading characteristics, the maximum claimed IPCE reached to 12–14% [15,16]. Recently, hetero-junction photoanodes have been investigated for the efficient transport of the charge carriers from semiconductor oxide to the external load [17]. The idea is to use the so called step approach to facilitate charge transfer using low energy band gap materials such as SnO_2 [18], CdS [19] etc, coupled with wide band gap semiconductors such as TiO_2 and ZnO. Several groups have claimed improved IPCE through hetero-junctions such as ZnO/TiO_2 [20], poly(phenylenevinylene)/C_{60} [21] and $CdTe/TiO_2$ [22]. It is believed that the hetero-junction facilitates the movement of charge carriers and suppresses the recombination reactions at the interface, resulting in high efficiency of the hetero-structured photoanodes.

Novel TiO_2-Ge nanocomposites and sandwich structures have been developed recently for high performance thin film photovoltaic devices [23–25]. Bulk Ge has direct band gap of 0.8 eV (band gap of TiO2 is 3.2ev). And an indirect band gap of 0.66 eV [23] at room temperature with light absorption characteristics in near infrared spectrum. These characteristics make it a potential candidate in the field of DSSCs. The effect of Ge quantum dots (QDs) has been studied on TiO_2 layer to improve the optical performance of TiO_2 layer. In another related study [26], the effect of functionalized Ge (QDs) has been studied on the performance of TiO_2 based, N719 sensitized DSSC. The study was focused more on the dye loading ability of surface functionalized Ge QDs. A 12% increase in IPCE compared to reference specimen has been reported which was attributed to high dye loading and more negative conduction band edge of Ge compared to TiO_2. In this study, the Ge nanoparticles have been employed as sintering aid in DSSCs and its ability to sinter at lower temperatures has been emphasized. Also the effect of second phase sintering mechanism has been discussed to increase inter-particle contact between nanoparticle to impede recombination reactions. The TiO_2-Ge nanocomposite with different wt% of Ge using colloidal suspension method has been prepared and appliedon conducting glass substrate using doctor blade technique.

2. Experimental

2.1. Material preparation

Fluorine doped tin oxide (FTO) conducting glass substrates were washed with deionized (DI) water and sonicated (model: Elmasonic PH350EL) for 30 min followed by rinsing with DI water. TiO_2(supplier by Sigma Aldrich, size range 100–150 nm) and Ge (supplied by sigma aldrich, size range: 100–150 nm) nanoparticles were weighed using digital weight balance (model: FA2104J) and stirred using magnetic stirring (model: C-MAG HS 7) in acetone separately for two hrs with subsequent sonication for 1hr and then stirred over night. The two suspensions were mixed together and again sonicated for 1hr followed by stirring for 12 h. The mixture was then filtered using filter paper and dried at 80 °C for 4 h. The process was repeated for the rest of the specimens. Four series of specimens i.e. (1) TiO_2–0.5 wt%Ge, (2) TiO_2–2 wt%Ge, (3) TiO_2–5 wt%Ge and (4) TiO_2–10 wt%Ge have been prepared with a control specimen fabricated using pure TiO_2 nanoparticles for comparison purpose. It is worth mentioning here that Ge nanoparticles have been heated to 400 °C at ultra-high vacuum condition to remove oxide layer. Furthermore, all the procedures were performed in vacuum glove box.

2.2. DSSC assembly

Doctor blade method has been employed to fabricate photoanode. Nanocomposite paste has been made using ethylene glycol and coated on to the FTO coated glass. The coated specimens were heated to 80 °C for 30 min and sintered at 400 °Cfor 30 min in vacuum glove box. Pure TiO_2photoanode was sinteredat 450 °C for comparison. The sinteredsubstrates were immersed in Ru(dcbpy)2(NCS)2 (dcbpy 1/4 2,2-bipyridyl-4,4-dicarboxylato) dye solution (535-bisTBA (N719), Solaronix) with acetonitrileover night and rinsed with ethanol. Counter electrodes were prepared using Ptsputtercoating on FTO glass. Counter electrodes were drilled and joined with photoanode separated by a thin plastic sheet. Iodide/triiodide redox electrolyte was introduced through drilled holes and then the holes were sealed using hot melt sealant. At least five specimens for each wt% have been fabricated for high reproducibility.

2.3. Characterization

Scanning electcron microscope (SEM model = Quanta FEG 450) was performed to examine surface morphology and homogeneity of nanoparticles. Secondary electron imaging (SEI) mode was used with an accelerating voltage of 1–5 kV. X-ray diffraction (XRD) has been performed for compositional and phase analysis. UV–vis-Nir spectroscopy (model uv2600) has been performed to investigate light absorption characteristics. Electron impedance spectroscopy (EIS) (model: PGSTAT101)has been employed to measure charge transfer ability. Finally auto-lab solar simulator (IVT 300) has been utilized to measure I–V curves, open voltage potential (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and IPCE at AM1.5 sun (1000 W/m^2 irradiation) condition.

3. Results and discussion

Specimens were weighed at each fabrication step i.e. before and after deposition of nanocomposite layer on FTO glass. Table 1 is illustrating the weight of the specimens under investigation (weight of deposited layer has been measured after