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$_2$ photoanodes sintered at 450°C.

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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 $\sim$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 (\(\gamma_{gb}\)) of nanoparticles by 2/3 compared to solid/vapor surface energy (\(\gamma_{sv}\)) 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.
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 SnO2 [18], CdS [19] etc., coupled with wide band gap semiconductors such as TiO2 and ZnO. Several groups have claimed improved IPCE through hetero-junctions such as ZnO/TiO2 [20], poly(phenylenevinylene)/C60 [21] and CdTe/TiO2 [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 TiO2–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 3.2 eV). 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 TiO2 layer to improve the optical performance of TiO2 layer. In another related study [26], the effect of functionalized Ge (QDs) has been studied on the performance of TiO2 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 TiO2. 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 TiO2–Ge nanocomposite with different wt% of Ge using colloidal suspension method has been prepared and applied on 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. TiO2 (supplier by Sigma Aldrich, size range 100–150 nm) and Ge (supplier 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 1 hr and then stirred over night. The two suspensions were mixed together and again sonicated for 1 hr followed by stirring for 12 hr. 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) TiO2–0.5 wt%Ge, (2) TiO2–2 wt%Ge, (3) TiO2–5 wt%Ge and (4) TiO2–10 wt%Ge have been prepared with a control specimen fabricated using pure TiO2 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 °C for 30 min in vacuum glove box. Pure TiO2 photoanode was sintered at 450 °C for comparison. The sintered substrates were immersed in Ru(dcbpy)2(NCS)2 (dcbpy 1/4 2,2-bipyridyl–4,4-dicarboxylato) dye solution (535-bisTBA (N719), Solaronix) with acetonitrile/ethanol mixture and rinsed with ethanol. Counter electrodes were prepared using Pt sputtercoating 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 electron 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 (Voc), short circuit current (Jsc), fill factor (FF) and IPCE at AM1.5 sun (1000 W/m² 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
Table 1

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Specimen ID</th>
<th>Weight of FTO glass (g)</th>
<th>Weight of deposited FTO glass (g)</th>
<th>Weight of deposited layer (g)</th>
<th>Dye loading (x10^-7/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO₂</td>
<td>0.888 ± 0.001</td>
<td>0.977 ± 0.001</td>
<td>0.089 ± 0.001</td>
<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td>TiO₂-0.5%Ge</td>
<td>0.913 ± 0.001</td>
<td>0.995 ± 0.001</td>
<td>0.082 ± 0.001</td>
<td>1.14</td>
</tr>
<tr>
<td>3</td>
<td>TiO₂-2%Ge</td>
<td>0.878 ± 0.001</td>
<td>0.974 ± 0.001</td>
<td>0.094 ± 0.001</td>
<td>1.33</td>
</tr>
<tr>
<td>4</td>
<td>TiO₂-5%Ge</td>
<td>0.821 ± 0.001</td>
<td>0.901 ± 0.001</td>
<td>0.080 ± 0.001</td>
<td>1.74</td>
</tr>
<tr>
<td>5</td>
<td>TiO₂-10%Ge</td>
<td>0.916 ± 0.001</td>
<td>1.002 ± 0.001</td>
<td>0.086 ± 0.001</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Fig. 1. SEM micrographs of un-sintered and sintered raw TiO₂ nanoparticles (a) low magnification image of coating (b) high magnification un-sintered TiO₂ nanoparticles and (c) sintered TiO₂ nanoparticles.

Sintering at 400 °C for TiO₂-Ge nanocomposite photoanodes and 450 °C for reference TiO₂ photoanode. For dye adsorption the weight method is not reliable that is why adsorption-desorption method has been performed in the present study. NaOH-ethanol solution was used to desorb the dye loaded on the photoanodes [27].

With increase in wt% of Ge in TiO₂ matrix, amount of dye adsorption increased which can be due to lower surface energies and oxygen vacancies of sintered nanoparticles. Further increase to 10 wt% cause reduction is dye pick up due to excessive necking and less surface area.

3.1. Morphological study

Fig. 1 is showing SEM images of coated reference TiO₂ nanoparticles before and after sintering at 450 °C. Particle size ranges between 100–150 nm and possess irregular shapes. Low magnification TiO₂ coating can be seen in Fig. 1a. Inter-particle contact have been improved in sintered coating (Fig. 1c) compared to un-sintered coating (Fig. 1b) due to boundary diffusion at high temperatures.

Fig. 2 is showing TiO₂-Ge nanocomposite coating of specimens before and after sintering at 400 °C. Homogenous and agglomeration free mixing of un-sintered nanocomposite photoanodes can be observed in Fig. 1(a,a1-3). Backscattered images of specimens (Fig. 1(c,c1-3)) have also been taken to visualize homogenous mixing. Fig. 1(b,b1-3) is showing sintered TiO₂-Ge nanocomposite coatings at 400 °C. It can be clearly observed that with the introduction of Ge in TiO₂ matrix, the inter–particle contact has been improved (shown using circles) compared to reference TiO₂ photoanode specimens sintered at 450 °C (Fig. 1). Furthermore, an increasing trend in inter-particle contact has been observed (Fig. 2(b1-3)) with increment in the wt% of Ge in TiO₂ matrix.

This increase in inter-particle contact (Fig. 2) can be explained using the process of sintering of two different elements as can be seen in Fig. 3. Fig. 3 is showing development of inter-particle contact between nanoparticles. Fig. 3(a(i)) is illustrating surface contact between TiO₂ nanoparticle and Fig. 3(a(ii)) is showing surface contact between TiO₂ & Ge nanoparticles along with inter-atomic arrangements illustrated in Fig. 3(b(i,ii)). The melting point of TiO₂ and Ge is approximately 1843 °C and 938 °C respectively. As the sintering temperature is assumed to be 0.5–0.9 of the melting temperature, at 400 °C Ge nanoparticles lose more surface/boundary energy (γgb) compared to TiO₂ nanoparticles which facilitates necking between the particles by introducing capillary forces [28,29]. The addition of capillary forces due to low melting point second phase i.e. Ge along with heat energy improved the inter–particle contact which is a decisive parameter to increase the efficiency of DSSC.

X-ray diffraction (XRD) analysis has also been performed (Fig. 4) to observe any effect of capillary forces on the structure of TiO₂. Fig. 4 showed no any observable structural changes in TiO₂ matrix. Anatase phase is a dominant phase which is highly required for DSSC applications due to its superior optoelectronic properties compared to rutile phase. It can also be observed that the oxide layer of GeO2 has been successfully removed using thermal treatment.

The optical characterization of three constituent materials has also been performed (Fig. 1–3s (supplementary material)). The optical absorption edge of TiO₂ lies in UV region while Ge showed optical absorption in near infrared region (the absorption edge starts from 900 nm), N719 dye showed optical absorption in visible region of the spectrum.
3.2. Electron transfer

To study the effect of Ge on the charge transfer capability of TiO₂ matrix, EIS has been performed which is supposed to be a powerful tool to study electron transfer resistance in materials. Fig. 5 is showing impedance spectroscopy of the TiO₂-Ge nanocomposites along with band energy diagram. The charge transfer efficiency has been improved with increment in wt% of Ge nanoparticles. With the addition of 0.5 wt% Ge, the charge transfer resistance reduced, which is further reduced with the addition of 2 wt% Ge nanoparticles. Furthermore, a further decrease in recombination reaction has been measured with the addition of 5 wt% Ge nanoparticles in TiO₂ matrix, further addition of Ge nanoparticles to 10 wt% cause increase in recombination reactions which is attributed to high concentration of impurities and surface defects.

Two operative mechanisms i.e. high inter-particle connection due to capillary forces and thermodynamic suitability of hetero-structure carrier pathway have improved the charge transfer ability of photoanode material. The neck formation reduced the boundary electron transfer resistance due to more or less ordered atomic arrangement. Another reason is suitable electronic path of TiO₂-Ge nanocomposite which is thermodynamically more suitable compared to reference TiO₂ specimen (Fig. 5(b)). Excited electrons from lower unoccupied molecular orbit (LUMO) of N719 dye are injected to the conduction band of Ge nanoparticles before TiO₂ due to the slightly negative conduction band edge of Ge. This hetero-junction arrangement minimizes the recombination reactions and in turn improves the current density of DSSC.
Fig. 3. Sintering mechanism of particles (a(i)) surface diffusion between TiO$_2$ nanoparticle, (a(ii)) surface diffusion between TiO$_2$ & Ge nanoparticles, (b(i)) absence of atomic arrangement at interface and (b(ii)) ordered atomic arrangement in neck area.

Fig. 4. XRD analysis of as received raw materials and sintered TiO$_2$–10wt%Ge nanocomposite.

Fig. 5. Electrochemical impedance analysis of specimens (a) EIS and (b) Energy band diagram.
3.3. I–V curves

Photocurrent verses voltage (I–V) curves have been studied to understand the overall photo conversion properties of DSSCs assemble using TiO$_2$–Ge nanocomposite photoanodes. Fig. 6 is showing I–V curves of specimens under investigation and other parameters i.e. $V_{oc}$, $J_{sc}$, FF and efficiency are listed in Table 2. An increase in overall performance can be observed with increment in Ge nanoparticles. TiO$_2$–0.5 wt%Ge specimen showed 10.3 mA short current density with IPCE of 4.42% which is 9.6% higher than the reference TiO$_2$ photoanode. Specimens containing 2 wt% Ge nanoparticles showed 4.97% IPCE value which is 23.3% higher than the reference specimens. With the addition of 5 wt% Ge nanoparticle, an increase in IPCE of 5.65% has been recorded which is 40% higher than the reference specimens. Further addition of Ge nanoparticles didn’t improve the IPCE rather the efficiency dropped with further addition up to 10 wt% Ge. This is due to high concentration of impurity levels which produces defects and electron trapping sites [30].

High current density in nanocomposite specimens is due to high dye loading and high electrical conduction characteristics of nanocomposite photoanodes. Ge nanoparticles possess more electro-negativity value (1.85) compared to TiO$_2$ (1.45), and the bond energy of Ge with oxygen (O) atoms is approximately 6657.4 KJ/mol which is double the bond energy of Ti and O atoms [31]. This change in bond energy may have disturbed the bonds between Ti and O atoms and produce oxygen vacancy which caused higher dye anchoring in nanocomposite photoanode [32,33]. High incident photo energy absorption of nanocomposite photoanodes facilitates dye molecules to absorb high amount of energy and inject more electrons to conduction band of photoanode. Furthermore, an increase in $V_{oc}$ can be due to upward shift of Fermi level of TiO$_2$ with the addition of Ge nanoparticles [34]. Increased oxygen vacancies, high light absorption and improved electron transfer of TiO$_2$–Ge nanocomposite photoanodes improved the overall IPCE of the DSSC. This investigation revealed that Ge is a promising additive in TiO$_2$ photoanode for various types of nanostructured solar devices and photo-electrochemical systems.

4. Conclusions

In this study, TiO$_2$–Ge nanocomposite photoanode materials have been investigated for their performance in DSSCs. Specimens were prepared using colloidal suspension method with 0.5 wt%Ge, 2 wt%Ge, 5 wt%Ge and 10 wt%Ge in TiO$_2$ matrix. High inter-particle contact at relatively lower temperature has been achieved which improved the commercial viability of DSSC technology. Morphological studies revealed that particles had developed necks on the surfaces due to high surface diffusion. Light absorption and impedance spectra showed high light absorption and electron transfer capability. An increase in overall photo conversion efficiency of 40% compared to reference TiO$_2$ has been measured when doped with 5 wt%Ge. This improvement can be co-related with high light absorption ability, increased electron transfer ability due to neck formation and hetero-junction symmetry and high dye loading capacity. Further addition of Ge nanoparticles up to 10 wt% reduces the IPCE mainly due to high concentration of impurity levels and reduction in dye loading capacity due to excessive necking.
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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jiieo.2017.11.073.

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