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Effect of Germanium on the TiO_2 Photoanode for Dye Sensitized Solar Cell Applications. A Potential Sintering Aid

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Abstract: Anatase titanium-germanium (TiO_2-Ge) nanocomposite has been prepared by using colloidal suspension process and investigated for photoanode to be used in dye sensitized solar cell. Ge possesses lower band gap energy compared to TiO_2 and has the capability to absorb infrared region of solar spectrum. Its remarkable absorption and good electron transfer ability due to lower band gap energy makes it a potential candidate material in the field of DSSCs to counter important disadvantages such as high probability of electron recombination reactions and absorption of small region (UV region) of solar spectrum. Another advantage is its low sintering temperature which proved to be an added advantage to increase inter-particle contact which in turn leads to improved electron transfer. Scanning electron microscopy (SEM), uv-vis spectroscopy and electron impedance spectroscopy (EIS) have been employed to evaluate the effect of Ge on TiO_2photoanode.

1. Introduction:

Today, the increasing energy demand leads to more CO_2 emission and other pollutants in our environment which is the basic problem in sustainable development[1]. To cope with the energy demand and to save the environment, a concept of renewable or green energy is getting pace and the major challenge for scientists working in the field of technology is to develop an efficient and cost effective renewable technology to harvest energy from natural and renewable resources[2]. Photovoltaic cells in this regard are the strong candidates to effectively harvest solar energy directly into electricity. Silicon based solar cells achieve 25% efficiency [3]and 41% efficiency [2]has been claimed with three junction photovoltaic cells. Still this efficiency is well below their theoretical limits and these technologies require expensive processes and fabrication equipments. In this regards Dye sensitized solar cells (DSSCs) are cost effective and easy to fabricate with moderate efficiency.

DSSCs work on the principle of photosynthesis [4]. In brief, there are three main components of DSSC (1) photoanode (TiO_2 nanostructure), (2) dye sensitizer (ruthenium based dye to absorb sun light) and (3) electrolyte (Iodide/tri-iodide redox couple). Photons are absorbed by the dye sensitizer and an electron has been ejected from dye to conduction band of photoanode material. This electron travels from photoanode towards external circuit. Meanwhile, the positively charged dye pick electron from electrolyte and become stable. The charged electrolyte pick electron from the outer circuit and hence the process continues [5]. Various approaches have been trialed to improve the incident photon conversion efficiency (IPCE) of DSSCs such as size quantization, development of different nano-architectures, surface Plasmon effect and doping with different cations & anions [5-6]. With improvement in light absorption capacity, recombination reactions and dye loading characteristics, the maximum claimed IPEC reached to 12-14% [7-8].

Noval titania/germanium (TiO_2-Ge)nanocomposites and sandwich structures have beendeveloped recently for the removal of environmental pollutants [9]and for high performance thin film photovoltaic devices[10-12].Bulk Ge has direct band gap of 0.8eV(band gap of TiO_2 is 3.2ev). And an indirect band gap of 0.66eVat room temperature[10]. These characteristics make it a potential candidate in the field of DSSCs.In this study, we report for the first time the effect of Ge on TiO_2photoanode and support our conclusion in the light of results obtained through SEM, uv-vis spectroscopy and EIS techniques.

2. Experimental:

TiO_2(sigma Aldrich 100 to 200 nm, irregular shape) and Ge (sigma Aldrich 100 to 200nm size range, irregular shape) nanoparticles were weighed and stirred using in acetone separately for two hrs with subsequent sonication (model XA2600) for 1hr and then stirred over nigh. The two suspensions were mixed together and again sonicated for 1hr followed by stirring for 12hrs. The mixture was then filtered using filter paper and dried at 80^{o}C for 4hrs. Three specimens i.e. (1) TiO_2 nanoparticles, (2) Ge nanoparticles and (3) TiO_2-2wt%Ge nanocomposite have been investigated. SEM was performed to examine and investigate the surface morphology of particles. Field emission scanning electron microscope (FE–SEM) (QUANTA FEG 450) was used in secondary electron imaging (SEI) mode and back scattered electron mode with an accelerating voltage of 1-10kV. Uv-vis spectroscopy (model: uv 2600 spectrometer) and EIS studies have been conducted to evaluate Ge nanoparticles as potential nanomaterial to improve the performance of DSSCs.

3. Results and discussion:

3.1. Surface morphology: scanning electron micrographs (Figure 1) were taken to examine the surface morphology, shape and size of as received nanoparticles. Figure 1(a&b) is showing irregular shaped TiO_2 nanoparticles, the size of these particles ranges between 90 to 150nm. Some TiO_2 nanoparticles larger than 150nm can also be seen in the SEM micrographs. Figure 1(c&d), is showing as received Ge nanoparticles. The shape of Ge particles was observed to be irregular. Ge particles range between 100 to 200 nm.

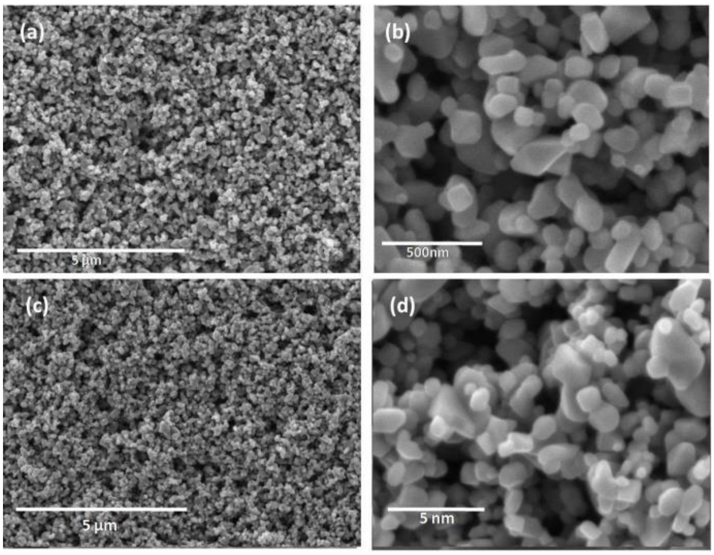

Figure 1. SEM micrographs of raw powders (a,b) TiO_2 nanoparticles and (c,d) Ge submicron particles.

Figure 2 is showing SEM micrographs of un-annealed and annealed (annealed at 450^{o}C to 30 min at the rate of 5^{o}C/min) nanocomposite specimen. Homogeneous and agglomeration free mixing of individual particles can be seen in these micrographs. Excellent mixing has been achieved by employing vigorous stirring and ultrasonication for extended period of time. Figure 2(a,a1) is illustrating un-annealed specimen i.e. pure TiO_2 and TiO_2-2wt%Ge nanocomposite, it can be observed that there is no surface diffusion among nanoaprticles which is the major reason of increase in charge recombination among the semiconductor, dye and electrolyte interface. Semiconductor nanoparticles due to lack of good contact cannot efficiently transfer electrons from sensitizer to the transparent conducting electrode. To facilitate efficient charge transfer from the semiconductor, the contact between the surfaces of semiconductor nanoparticles is improved with the aid of thermal energy which reduces the surface tension of the particles and facilitates surface diffusion. Heating to the temperature range 450-500^{o}C is expected to give optimum results [12]. Annealed composite specimen can be seen in Figure 2(b,b1). Round red circles are indicating surface diffusion of nanoparticles. At this stage complete sintering is not favorable as complete sintering will render a highly compact surface layer with less surface area. High surface area porous layers are highly desirable for photoanode to improve pickup of dye sensitizer molecules along with sufficient inter-particle contact.

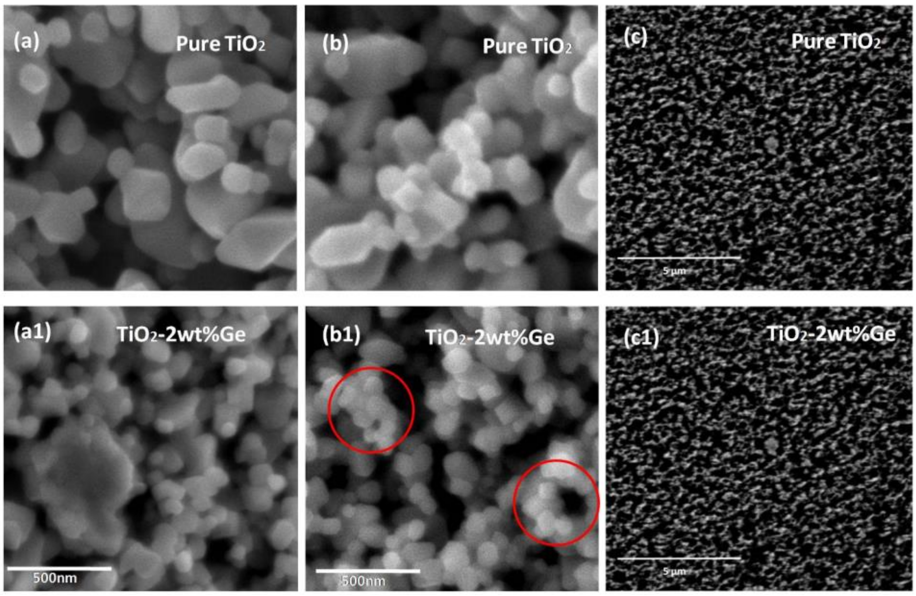

Figure 2 SEM micrographs of annealed and un-annealed composite specimen (a,a1) un-annealed TiO_2&TiO_2-2wt%Ge nanocomposite (b,b1) annealed TiO_2 & TiO_2-2wt%Ge nanocomposite and (c) backscattered SEM images of TiO_2 & TiO_2-2wt%Ge nanocomposite.

It has been observed that with the incorporation of Ge particles, the surface tendency of nanoparticles to diffusion increased. Higher surface diffusion has been observed in TiO_2-2wt%Ge nanocomposite specimen. This effect can be co-related with the specific heat and melting temperature of Ge (938^{o}C) and TiO_2(1843^{o}C). Ge require less energy to activate surface diffusion compared to that of TiO_2 that is why with the addition of Ge, nanocomposite underwent higher degree of surface diffusion which is required to improve the contact between nanoparticles to pave the way for uninterrupted transport of electrons from dye sensitizer to the external circuit and to reduce recombination reactions at the capacitive interface.

3.2. Light absorption

Solar spectrum mainly consists of ultraviolet (Uv), visible (vis) and infrared light (IR). For efficient working of photoanode it is necessary to absorb as much incident spectrum as possible to facilitate the dye sensitizer to eject electron from its valance band. TiO_2 can only absorb Uv spectrum. As Ge has the ability to absorb near infrared region of solar spectrum, combining these two semiconductor elements (i.e. TiO_2 and Ge) will absorb more incident energy and in-turn increase the ability of photoanode to harvest more energy. Figure 3 is showing the optical characteristics of TiO_2 and Ge under different regions of solar spectrum. It is evident from the graph that TiO_2 can only absorb UV region of solar spectrum while Ge is showing absorption in near infrared region. Iso-propyle alcohol

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has been used to prepare specimens for Uv-vis spectroscopy. Nanocomposite prepared by using these two elements will be able to absorb light from UV and near-infrared region of solar spectrum and in-turn improve the light absorption characteristics of photoanode to facilitate dye sensitizer. This improved light absorption capability improves the incident photo conversion efficiency of solar device.

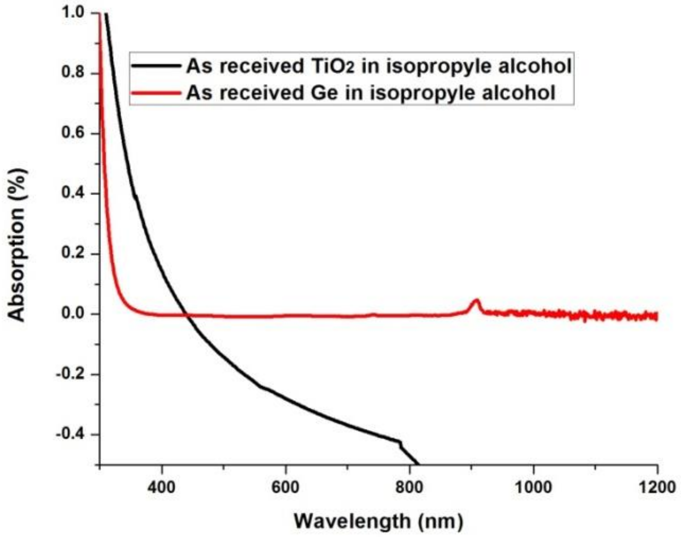

Figure 3. Uv-vis spectra of Ge and TiO_2

3.3. EIS response

The EIS study has been conducted (frequency range was 0.01Hz to 1MHz and ac voltage of 10mV have been chosen for experiments) to examine the capacitance i.e charge transfer ability of Ge and its nanocomposite with TiO_2. It is a powerful tool to study the kinetic behavior of electron transfer from photoanode. The charge transfer properties of TiO_2 and TiO_2 – 2wt% Ge nanocomposite is shown in Figure 4.

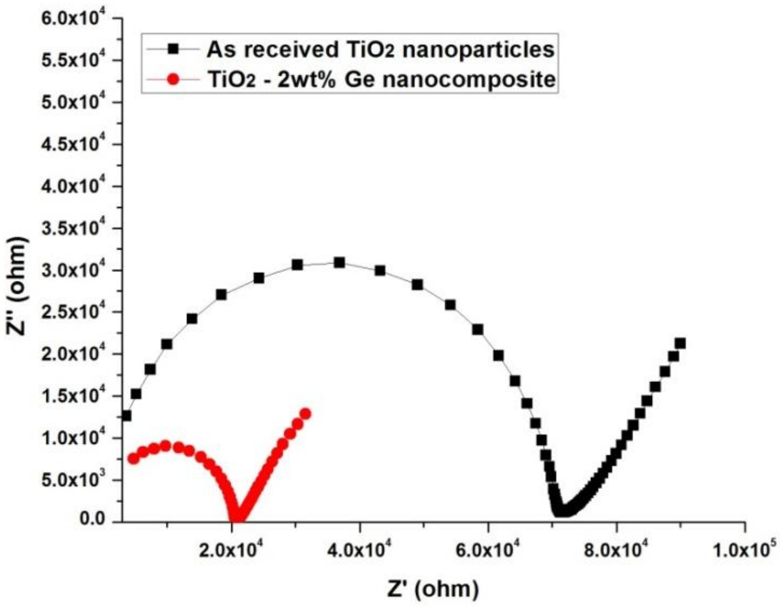

Figure 4. Nyquest plot of TiO_2 and Ge measured through EIS

The TiO_2 - 2wt% Ge nanoparticles show good electron transfer ability compared to TiO_2 nanoparticles. It is evident from the nyquest plot that with the addition of Ge in TiO_2 matrix, the charge transfer ability of photoanode has been increased and electron will have the opportunity to be first picked up by the Ge nanoparticles from the dye efficiently and then transfer to TiO_2 semiconductor matrix. This hetro-junction so called step approach effectively controls the recombination reactions and will improve the photo conversion efficiency of the device.

4. Conclusion:

The effect of Ge on the TiO_2 nanoparticle photoanode has been investigated as potential candidate material to improve the efficiency of dye sensitized solar device. Morphological observations conducted through SEM suggested improved surface diffusion between nanoparticles. Uv-vis analysis has been performed to study the light absorption capability of Ge and TiO_2 individually and EIS study has been conducted to understand the electronic charge transfer capability of TiO_2 with the addition of Ge nanoparticles. Results clearly showed that with the addition of Ge the surface diffusion and light harvesting capability have been improved. Also with the incorporation of Ge, the electron transfer capability has been increased. From the above results and discussion it can be concluded that Ge has the potential to improve the performance of DSSCs and should be further explored for optimization.

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