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Enhancing interparticle connectivity in TiO_2 film in preparation of photoanode for dye sensitized solar cell

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Abstract:
In dye sensitized solar cells the electron transport through the particulate network in the TiO_2 film depends upon the interparticle connectivity and is of prime importance for the cell performance. Thus, to enhance particle connectivity we have explored a hybrid technique using in-situ combustion by incorporation of relevant additive in the TiO_2 film in dye sensitized solar cells. In situ solution combustion synthesis in the TiO_2 film itself has been used to prepare nanosized TiO_2 by using titanyl nitrate[$TiO(NO_3)_2$] and glycine (H_2N-CH_2-COOH). This in situ combustion synthesis is aimed to introduce small sized TiO_2 nanoparticle among larger TiO_2 nanoaggregate facilitating to enhance interparticle connectivity. Moreover, the combustion synthesis being an exothermic process; the localized heat generated during synthesis varies from 1000 to 1800 K. This heat produced during synthesis in the TiO_2 film could achieve neck formation among TiO_2 nanoparticles. The current increment observed was from 4.57 mA cm^{-2} to 6.77 mA cm^{-2} while the efficiency enhanced from 2.53% to 3.44% with the increment of titanyl nitrate from 0 to 30 wt%.

Keywords: Dye sensitized solar cells, combustion synthesis, and interparticle connectivity

Introduction

To-date, the choice of the semiconductor for Dye sensitized solar cells(DSSCs) is the n-type TiO_2 with band gap of 3.2 eV and appropriate electronic band structure along with remarkable chemical stability[1,2,3]. Undoubtedly, highly efficient titania based photoanode for DSSCs requires not only a high surface area for a large amount of dye loading, but also an optimum interconnected construction of the material for light harvesting and fast electron transport[2,3,4]. In this regard tremendous efforts have been made on the design of the chemical composition, structure and morphology of the semiconductor materials such as zero dimensional (0D) nanoparticle, quasi-one dimensional (quasi-1D)/one dimensional(1D) nanostructures and hierarchical nanoarchitectures[5]. The titania electrodes are usually prepared by coating a titania paste containing organic binders on the TCO glass substrate with subsequent sintering process, usually around 500^{o}C to achieve mechanically stable TiO_2 film and electrical contact between TiO_2 particles. However, coating of viscous TiO_2 paste on a TCO glass substrate with subsequent calcination to remove organic additives results in porous TiO_2 films in which the particles are separated by the removal of organic additives, resulting in a loose particle packing network thereby hindering electron transport[6]. It has been observed that the cell efficiency increases with increasing annealing temperature from 300^{o}C to 500^{o}C and further increase in temperature (600^{o}C) decreases the cell efficiency. The decrease in cell efficiency beyond 500^{o}C annealing temperature is correlated with the coarsening of TiO_2 nanoparticles leading to decrease in surface area and hence decrease in dye loading[7,8,9]. Thus, though the interparticle connectivity in TiO_2

film could be achieved by increasing annealing temperature to enhance electron transport is of no use due to decrease in dye loading and hence lower cell efficiency[7,8,9]. Post treatment of porous TiO_2 electrode with $TiCl_4$ is successful strategy to enhance the interparticle connectivity and thus electron transport[10,11].

Combustion synthesis has been known for long as an important technique for the synthesis and processing of oxide and non-oxide ceramics [12]. The important features of combustion synthesis are localized high temperatures, fast heating rates and short reaction times, thus making it an attractive option for the material synthesis. Since the combustion synthesis is based on exothermic reaction, the localised heat generated during synthesis varies from 1000 to 1800K. Other advantages of combustion synthesis are that it requires simple equipment; product formed is of high purity product.

In the present study we are reporting the use of in-situ combustion synthesis to enhance interparticle connectivity and specific surface area in titania films for photoanode. The purpose of this in situ combustion synthesis is to introduce small sized TiO_2 nanoparticle among larger TiO_2 nanoaggregate serving to imporve interparticle connectivity as well achieving neck formation through localised heating.

Experimental and Characterization:

Synthesis of titanyl nitrate as oxidizer

Synthesis of $TiO(NO_3)_2$ has been carried out as per the literature[12]. First a 20ml of isopropyl alcohol was taken in a three neck flask followed by maintaining an inert atmosphere of nitrogen. Then 10ml of TTIP was added under inert conditions. To this 1.8ml of deionised water was added drop wise under vigorous stirring for 1h at 273K. At this stage we got a white precipitate. Subsequently the precipitate was dissolved with excess 37% nitric acid (1:1 ratio). Here the excess nitric acid taken was 20ml. After dissolving, yellow colour transparent liquid was obtained, which after evaporation resulted in slightly yellowish-white colour titanyl nitrate powder.

A water based titania particulate slurry was made so as to incorporate the $TiO(NO_3)_2$ as an oxidiser and glycine as fuel in slurry keeping the nature of slurry relatively unchanged. Water based slurry was made as follows: 2.5 gm of P25(TiO_2) was ground in mortar pestle with 200 ul of acetyl acetone and 1 ml DW. To it 1 gm PEG 20K was added (such that vol % of TiO_2 is 40 % in the film) and DW was added slowly such that it always remains as a thick paste. Eventually rest 19 ml DW was added and mixed properly. To this 200 ul Triton X100 and 20 gm zirconia beads were added in a dropping bottle and left on roller mill for 4hrs.For in situ combustion synthesis 10, 20 and 30wt % of $TiO(NO_3)_2$ with respect to TiO_2 was added in a slurry with glycine as 1:1 ratio with $TiO(NO_3)_2$. Here the content of P25 (TiO_2) is same in each slurry. Using these slurries the films were coated on cleaned FTO glass with the adhesive tape to control the thickness and area (1cm×1cm) of the film. After drying, the film was fired at 450ºC for one hr. After cooling to 100ºC the film was sensitised in a 0.3mM solution of N3 dye for 24 hr. The dyed film was then sandwiched together with platinised FTO counter electrode and the electrolyte was then injected into the cell from the edges by capillarity. The content of the

electrolyte is 0.1M LiI, 0.05 M I_2, 0.5M 4-tert-butylpyridine (TBP) and 0.6M 1-propyl-3-methylimidazolium iodide (PMII) in acetonitrile.

The surface morphology of the Titanyl powder and TiO_2 photoanode was analyzed using field emission scanning electron microscope (FEG-SEM; JEOL JSM 7600 F). Photocurrent-voltage (J-V) characteristics were obtained using a Keithley model 2420 source meter and a solar simulator with a 150W Xenon arc-lamp (Newport) under 1 sun illumination (AM 1.5, 100 mW cm^{-2}). Dye loading was determined by desorption of the adsorbed dye with 1 N NaOH solution and comparing with a calibrated curve in UV-Visible spectrometer (Jasco V650).

Results and discussion:

Figure 1 shows the SEM images of Titanyl powder. Image shows that the titanyl nitrate is highly aggregated. The aggregate size varies from 100-500nm. Also, it seems that the primary particle is very fine which may act as binder or nanoglue when mixed with P25 (TiO_2) powder.

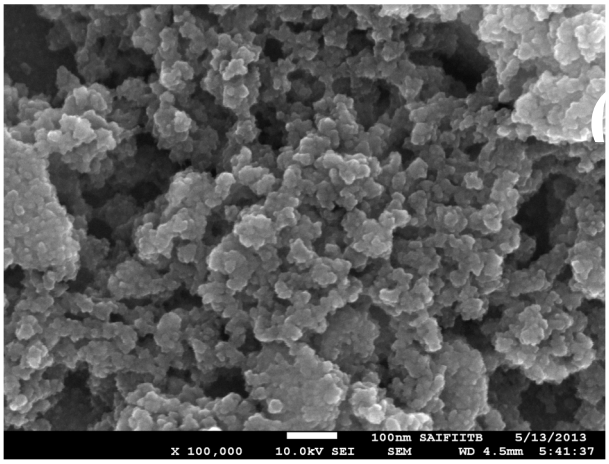

Fig. 1 FEG-SEM image of Titanyl Powder

The morphological properties of films containing 0, 10, 20 and 30 wt% of $TiO(NO_3)_2$ dispersed in a TiO_2 photoanode respectively were characterized by scanning electron microscopy (SEM). Clearly in figure 2b, c and d the randomly distributed big clusters are seen and are nothing but the aggregates of TiO_2 resulting from the in situ combustion of titanyl nitrate. Moreover, it appears that the in situ combustion in photoanode has resulted in more compact and dense film structure compared to that of without in situ combustion in TiO_2 photoanode (figure 2a)

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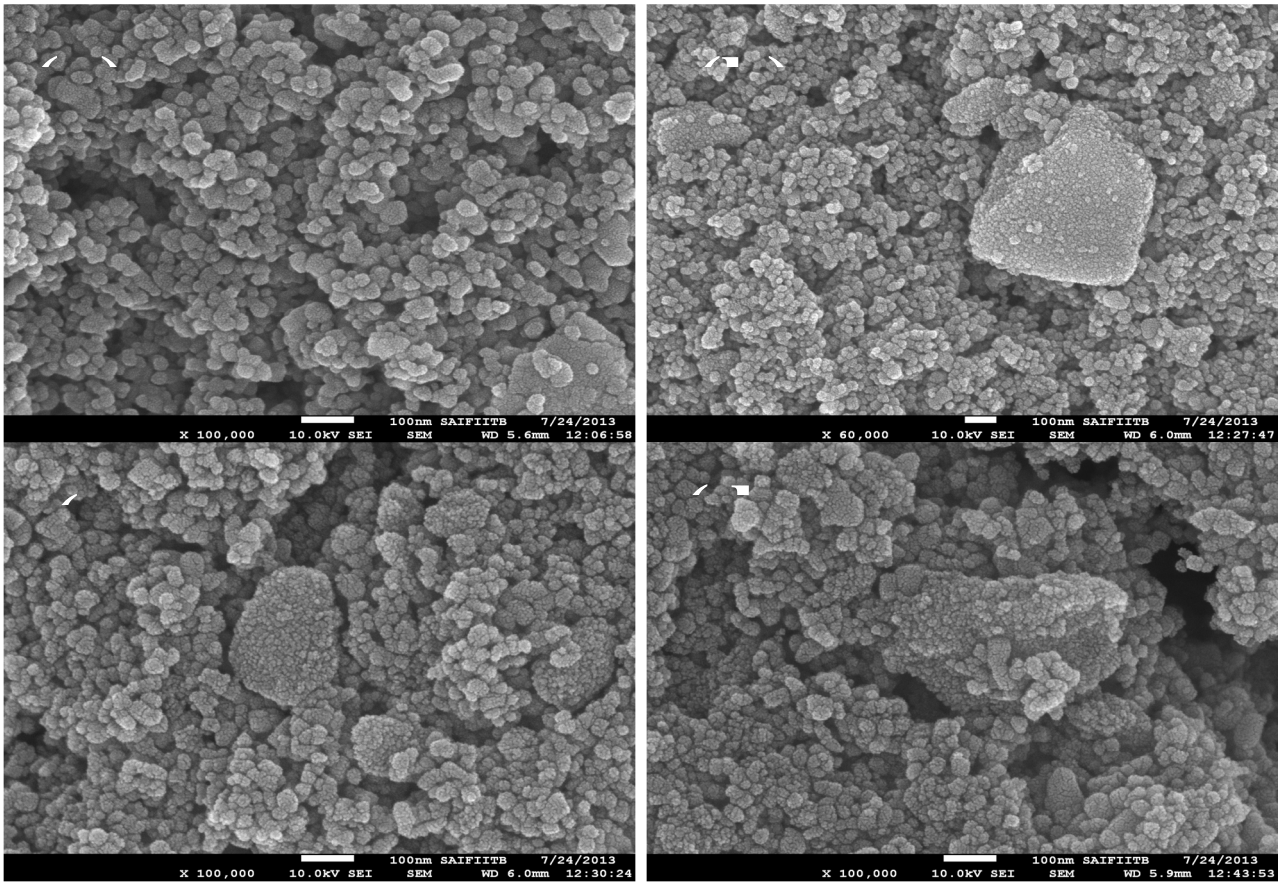

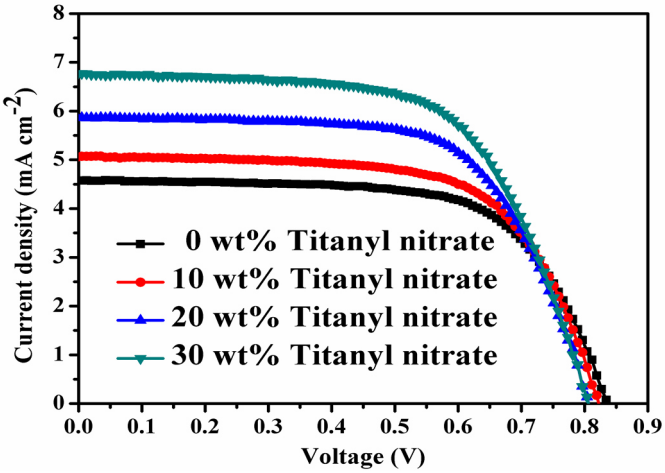

The performance of the DSSCs without and with in situ combustion (containing different wt % of titanyl nitrate) in the TiO_2 photoanode was evaluated by their current density (J)-voltage (V) characteristic under AM 1.5 solar illumination at 100 mW cm^{-2} and the results are shown in figure 3. In addition the corresponding photovoltaic parameters such as short circuit current (J_{sc}), open circuit voltage (V), fill factor (FF), adsorbed dye and power conversion efficiency are summarised in table 1. Thus, from figure 3 and table 1, it is clear that with the increase in the content of titanyl nitrate in the film, current density is enhanced from 4.57 $mAcm^{-2}$ for 0 wt% of titanyl nitrate to 6.77 mA cm^{-2} for 30 wt% of titanyl nitrate, whereas open circuit voltage and fill

factor are relatively unchanged. Thus, due to the increase in current density the overall power conversion efficiency was found to increase from 2.53 % for 0 wt % of titanyl nitrate to 3.44 % for 30 wt % titanyl nitrate. From table 1, it was found that there is an increase in the amount of dye adsorbed with the increase in the content of titanyl nitrate for in-situ combustion and is attributed to the TiO_2 nanoparticle aggregates in the photoanode resulting from in situ combustion in the photoanode, thus explaining the increase in current density.

Titanyl nitrate (wt%)	J_{sc} ($mAcm^{-2}$)	V_{oc}(mV)	FF	η%	Dye loading ($\times 10^{-8}$ mol cm^{-2}))
0	4.57	834	0.66	2.53	2.70
10	5.07	819	0.65	2.72	2.75
20	5.86	804	0.66	3.10	3.03
30	6.77	804	0.63	3.44	3.81

Table 1 Photovoltaic performance of DSSCs without and with different wt% of titanyl nitrate in Photoanode at AM 1.5 and irradiance of 100 mW cm^{-2}

Fig. 3 *J-V* characteristic of DSSCs without and with different wt% of titanyl nitrate in Photoanode

However, from SEM images shown in figure 2 b, c and d, TiO_2 nanoparticles in the photoanode film resulting from in situ combustion are aggregated and not uniformly distributed throughout the film. This is due to the aggregated nature of titanyl nitrate as shown in figure 1. To achieve uniform distribution of small TiO_2 nanoparticle, better interparticle connectivity and neck formation among TiO_2 nanoparticles through localized heating resulting from in situ combustion in the TiO_2 photoanode, slight changes were made in the recipe of the slurry. As mentioned in the experimental section, glycine as a fuel was directly added to the sol of titanyl nitrate and the resulting precursor for in situ combustion was then added in the water based TiO_2 slurry. However, this approach was not successful due to the changes in the properties of slurry causing difficulty in the doctor blade coating along with fluffy nature of the film after sintering. Thus, it leaves further opportunities to develop the strategy for efficient in situ combustion in TiO_2 photoanode to get benefit of interparticle connectivity through small sized nanoparticles, localized heating for neck formation, morphology, compactness, pore size and and thus eventually the performance of DSSCs.

Conclusion:

Here in this work, in situ combustion synthesis of TiO_2 nanoparticles by incorporation of relevant additive in the TiO_2 photoanode film was carried out. The resulted TiO_2 photoanode in DSSCs showed enhanced photocurrent density, thereby enhanced power conversion efficiency with the increase in the Titanyl nitrate content in the TiO_2 Photoanode film as compated to pristine TiO_2 film. The improved photovoltaic performance for modified TiO_2 photoanode by in situ combustion synthesis is attributed to enhanced dye loading in TiO_2 photoanode film.

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