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Development of porous TiO_2 nanofibers by solvosonication process for high performance quantum dot sensitized solar cell

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ABSTRACT

In the present study, we synthesized TiO_2 nanofibers (NFs) by electrospinning technique and they were subject to solvosonication process using glycerol as a pore forming agent to produce porous TiO_2 NFs. The prepared porous TiO_2 NFs are seen to improve the light harvesting capability as a result of enhanced light scattering inside the TiO_2 NFs and offer a high surface area for maximum adsorption of pre-synthesized CdSe (~4 nm) QDs. The FE-SEM and BET analysis were performed to confirm the surface texture and surface area of porous TiO_2 NFs, respectively. Finally, QDSSCs were fabricated using these porous TiO_2 NFs sensitized with CdSe QDs as the photoanode, Cu_2S nanoparticles as the counter electrode and polysulfide redox couple (S^{2-}/S_x^{2-}) as the electrolyte. The porous TiO_2 NFs obtained by solvosonication at the time duration of 90 min has enhanced photocurrent density (J_{sc}) of 9.21 mA/cm^2 with high power conversion efficiency (η) of 2.15% than the conventional TiO_2 NFs ($\eta \approx 1.50\%$).

1. Introduction

Quantum dots sensitized solar cell (QDSSC) has been identified as a promising area of research for the past one decade due to its tremendous future potential in commercialization after dye sensitized solar cell(DSSC) [1]. Quantum dots such as CdSe [2], CdS [3], PbS [4], $CuInSe_2$ [5] etc, have been used as sensitizers in QDSSCs due to their meritorious properties which includes tunable bandgap, multi-exciton generations, high extinction coefficient (10^5 cm^{-1}), large dipole moments in addition to their intrinsic photostability and low cost of preparation process involved in synthesis of quantum dots etc [6,7]. Among various inorganic semiconductor sensitizers, CdSe QDs do satisfy the criteria of being used as effective sensitizer as it is seen to possess wide absorbance range in the visible region like organic dyes with high stability along with inherent conduction band position of ~ -3.6 eV which is responsible for higher charge separation kinetics of electrons that helps to deliver maximum photocurrent density inside the cell [8,9]. Although, the QDSSC gradually has arrived at the verge of attaining high efficiency still there are few shortcomings that impede them to produce expected power conversion efficiency (PCE). Here, selection of photoanode material holds the major concern of the researcher as it is responsible for the electron transport to the external circuit and provides anchored sites for the QDs. Therefore, to improve the photocurrent density of the cell many studies have been directed towards the development of photoanode material that would comprise of one dimensionality and high specific surface area.

1D- photoanodes are found to be effective in producing high efficiency as electrons are seen to move faster along the length of these structures to the external circuit, which reduces back electron recombinations, while 0D photoanodes are disordered arrangement of nano particles that give enough time for these photoelectrons to back electron recombinations with the electrolyte and thereby producing low photocurrent efficiency in QDSSCs [10]. In this context, 1D-morphologies such as nanorods [11] and nanowires [12] developed by hydrothermal method, where the scope of high surface area found less in compare to 1D-nanofibers produced by electrospinning technique. The one dimensional electrospun TiO_2 NFs has been proved to be an efficient photoanode due to its extraordinary properties such as high internal light scattering [13,14], higher trapping of photons, low transmittance, more adsorption sites for QDs and easy diffusion of electrolyte, higher reproducibility of 1D-structured nanofibers with diameters < 100 nm [15,16]. However, the efficiency of the electrospun TiO_2 NFs based QDSSC was not upto the mark due to the lack of sufficient surface area of the photoanode material essential to adsorb maximum quantity of QDs. Thus, S.Chattopadhyay.et al. [17] group have employed organic polymers/co-block polymers such as PVP and P-127 into the titania precursor solution to introduce pores with high surface area in the TiO_2 NFs. Another method was attempted by

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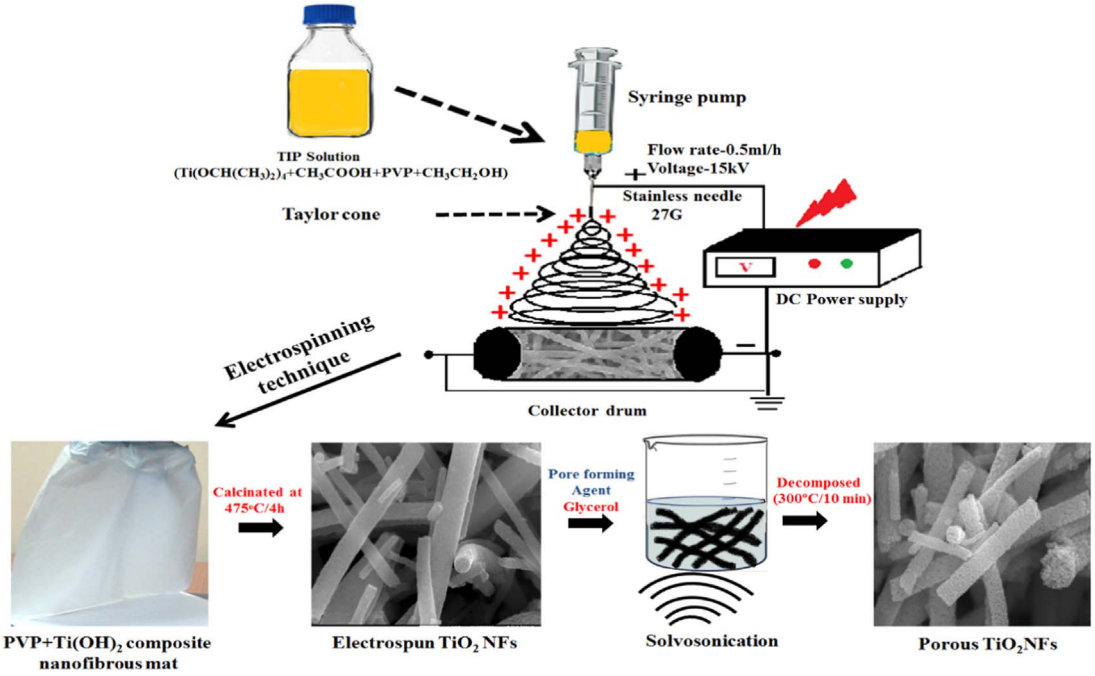

Fig. 1. Schematic procedure for the preparation of porous TiO_2 NFs.

H.Y.Chen et al. [18] to increase the surface area of TiO_2 NFs by adding paraffin oil as pore forming agent into the precursor solution to use as porous photoanode material for DSSC. These methodologies are quite complicated as more parameters are required to control such as viscosity, calcination temperature etc., which may effect the formation of TiO_2 NFs.

Therefore, in the present investigation, we tried to adopt a unique solvosonication method for the preparation of porous and high surface area TiO_2 NFs rather than going for complicated solution process. In this context, we have conducted a solvosonication process which seems a unique combination of electrospinning and influence of ultrasonication using glycerol as pore forming agent to obtain porous electrospun TiO_2 NFs. The effect of solvosonication time duration on the formation of porosity, specific surface area and photovoltaic performances were also investigated in detail.

2. Experimental

2.1. Materials

Titanium(IV) isopropoxide (TiP, 99%), polyvinyl pyrrolidone (PVP, M_w = 1300,000), cadmium chloride ($CdCl_2$, 99.9%), selenium powder (99.9%), oleylamine (technical grade, 70%), 1-Dodecanethiol (> 98%) were procured from the Sigma-Aldrich. Methanol (> 99.5%), ethanol (> 99%), hexane (> 95%), acetic acid glacial (99–100%) and glycerol (GR 87%) were purchased from the Merck India Ltd. without further purification.

2.2. Synthesis of CdSe Quantum dots

CdSe quantum dots were prepared by one pot synthesis method as previously reported [8,9]. However, in the present study, we have synthesized the same with the help of phosphine-free solvent and capping agent having long chain alkylamine (oleylamine) and dodecanethiol to obtain the narrow size of quantum dots. The synthesis was done in two steps. First, selenium precursor solution was prepared where 2 mM of Se powder in 10 mL of oleylamine were taken in a two neck round bottom flask and then refluxed at 150 °C for 1 h to form Se-OAm complex. Second, 0.4 mM of cadmium precursor, 5 mL of OAm (solvent) and 1 mL of 1DDT (capping agent) were taken in a 50 mL round-bottom flask and heated initially upto 150 °C under N_2 gas atmosphere. In this, the pre-prepared Se-OAm complex solution was quickly injected into the flask under continuous stirring that helps in starting the process of nucleation and growth which led to the formation of quantum dots that was evident by the change in color from white to red. Later, the temperature was gradually raised to 210 °C and the reaction was stopped and then the solution was left for cooling followed by precipitation by a 10 mL of cold methanol. The pure QDs were obtained after washing 3 times using ethanol, methanol and they were dispersed in a non-polar solvent (hexane) for further studies.

2.3. Preparation of electrospun porous TiO_2 NFs

The TiO_2 NFs were prepared by electrospinning technique using the procedure in our previous report [19]. A precursor solution containing 0.01 M titanium (IV) isopropoxide (TiP, Aldrich) and 0.04 M acetic acid, 5 wt% polyvinylpyrrolidone (PVP: MW ¼ 1300,000, Sigma Aldrich) in ethanol were taken and stirred for 6 h. The resultant solution was loaded into a syringe equipped with a 27 G stainless steel needle. The spinning rate (0.5 mL min^{-1}) was controlled by using a syringe pump. The electric field of 15 kV was applied between a metal orifice and an electrically grounded stainless steel drum collector. The collector was placed at 12 cm below the tip of the needle. The humidity level inside the electrospinning chamber was maintained below 35% at 25 °C to get electrospun PVP-Ti $(OH)_4$ fibrous mat. These fibrous mats was removed from the collector and calcinated in a muffle furnace (Technico, India) at 475 °C for 5 h at the heating rate of 5 °C min^{-1} in air atmosphere to get pure TiO_2 NFs.

This conventional TiO_2 NFs were solvosonicated using glycerol as the pore forming medium for different time durations (30, 60, 90 and 120 min) in an ultrasonicator (Leela Sonic, 50 W, and 30 kHz) to create pores in TiO_2 NFs. The treated TiO_2 NFs were removed from the glycerol medium and then calcinated at 300 °C for 10 min in a muffle furnace (Technico, India) to eliminate the residual glycerol to get porous TiO_2 NFs.(Fig. 1)