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# Well-connected microsphere-nanoparticulate $TiO_2$ composites as high performance photoanode for dye sensitized solar cell

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ABSTRACT

Anatase $TiO_2$ microspheres with smooth and fibrous morphology (SμS and FμS) resembling laddu and dandelion are synthesized by solvothermal and hydrothermal methods, respectively. A detailed analysis of these two microstructures using XRD, UV–vis spectroscopy, electron microscopy and surface area measurement techniques are presented. Photoanodes fabricated using these microspheres and their composites with nanoparticles (Degussa P25) are tested for photovoltaic (PV) performance using a standard Grätzel-type dye-sensitized solar cell (DSSC) configuration. The DSSC made up of SμS and FμS microspheres exhibit an efficiency (η) of 8.4% and 6.4% respectively, in comparison to η≈7.1% for nanoparticulate P25. Further enhancement in η is realized in the composite photoanode films made of porous SμS/FμS microspheres filled with nanoparticulate P25 $TiO_2$. High power conversion efficiency of 8.9% (for cell area of 0.5 $cm^2$ and thickness of ~25 μm) was achieved in composite photoanode film consisting of 80 *wt*% SμS and 20 *wt*% P25. Electrochemical impedance spectroscopy studies reveal a low interfacial resistance in composite photoanodes, which is desired for efficient electron generation and transport. Composite microspheres filled with P25 nanoparticles in their voids show enhanced efficiency than the mesoporous $TiO_2$ microspheres. Thus, SμS-nanoparticle composite $TiO_2$ film possesses essential attributes necessary for an efficient photoanode *viz*. large surface area for dye adsorption, good connectivity between nanocrystallites for the efficient electron transport, and higher scattering properties for better light harvesting efficiency.

## 1. Introduction

Anatase $TiO_2$ is an important material employed in various industrial applications; particularly nanostructured $TiO_2$ is used as a photocatalyst in $H_2$ production [1], as a gas sensing material [2], as photoanodes in solar cell [3], and as anode in Li-ion battery energy storage devices [4]. $TiO_2$ is the most preferred photoanode employed in dye sensitized solar cells (DSSCs) [5]. A significant breakthrough in the development of newer generation solar cells at low cost happened in 1991, when DSSCs with high power conversion efficiency (PCE) of greater than 7% were realized using metal oxide semiconductor (MOS) $TiO_2$ with porous nanostructure [3]. The anode-electrolyte-cathode configuration in DSSC comprise of a monolayer of dye-coated MOS film on a transparent conductive oxide (TCO)-coated glass substrate as anode, an iodide/triiodide ($I^-/I_3^-$) redox couple in an organic solvent as electrolyte, and a platinized TCO-coated glass substrate as cathode [3]. Most importantly this device configuration was also adopted in recently booming perovksite solar cells with a thick layer of perovksite replacing the dye [6]. The heart of a DSSC system is the wide band gap semiconductor film with large surface area for the adsorption of light harvesting molecules, and efficiently extract and transport charge carriers before recombination takes place in the molecules. Over the past two decades, the development in the nanotechnology has created various MOS nanostructures to significantly improve the solar cell device performance on the commercial modules [7]. Several metal oxides such as $TiO_2$, ZnO and $SnO_2$ have been widely studied as photoanodes in DSSCs, due to their matching band structure suitability, excellent physical properties and high electronic mobility [5,8]. Also, these oxides are highly stable, non-toxic and exhibit excellent bulk electron mobility.

Since the morphology of $TiO_2$ is important for uniform dye-adsorption, and efficient charge separation and transport, specific challenge and interest still lies in addressing the improvement of the efficiency by tailoring the morphology. $TiO_2$ nanomaterials with a variety of morphologies have been prepared via different techniques such as wet chemical methods, physical and chemical vapor deposition techniques [9–15]. Notable morphologies of $TiO_2$ that are attractive for various applications are ordered nano-tubes [16], disordered nano-

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tubes [17], nano-porous microstructures [18], microspheres [19], nano-arrays [20], hierarchical nano-tubes (HTNT) [20] and commercially available $TiO_2$ nanoparticles (TNP) synthesized via flame pyrolysis of $TiCl_4$ [21]. Several reports focus on obtaining optimized microstructures of $TiO_2$ photoanode films with important structural attributes. A robust photoanode film should possess three important structural features; high surface area, scattering effect and efficient electron transport. Photoanode films composed of $TiO_2$ nanocrystallites provide large surface area to adsorb sufficient amount of dye molecules. Monolayers of dye molecules on the large surface of nanocrystalline $TiO_2$ photoanode film capture the incident photons and generate electron–hole pairs. However, the nanocrystalline films show high transparency with negligible light scattering, thus exhibiting relatively low optical extinction coefficient, which limit the power conversion efficiency of DSSC [22,23].

In order to enhance the efficiency, large particles are incorporated into the nanocrystalline film which enhances light scattering effects of most intense red light in the solar spectrum thus enhancing the photoresponse. Normally large sized microstructures, with the size comparable to the wavelength of incident light, are preferred as it enhances the light scattering in DSSCs. The mostly used scattering layer nanostructures are hollow microspheres [24], nano-rods [25,26], nano-tubes [27–29], nano-spindles [30], nano-fibers [31], photonic crystals [32], nano-wires [33], nano-sheets [34], nano-dice [35], nano-plates [36], nano-petals [37] and nano-cubes [38]. In recent years, double layer [25,39,40] and composite photoanode film [41] structure consisting of different sized $TiO_2$ particles are explored to exhibit both large specific surface area and light scattering effect to enhance the performance of DSSCs. In the double layer photoanode film, over the bottom layer of 10–15 μm thickness comprising of 10–30 nm sized $TiO_2$ particles, a layer comprising of large particles is formed for scattering of light. This bilayer nanostructure photoanode can offer excellent light harvesting due to longer wavelength absorption and better electron-transport properties [42]. However, this scattering layer cannot enhance the surface area adequately to improve the dye adsorption and also it increases the thickness of photo anode due to which interfacial resistances are increased [41].

Optical path length of incident light in the $TiO_2$ main layer can be increased by fabricating composite photoanode films consisting of large particles. Adding a large fraction of particles will reduce the internal surface area of the $TiO_2$ film and also increase the recombination rate of photo-excited electrons [41]. Therefore the challenge is to obtain highly connected nanoparticular structures in the micron size to provide the better light scattering. A most applicable approach is to produce a new composite structure of small and large particles having both properties of high light scattering and higher surface area. In addition to efficient light absorption, the morphology and stoichiometry of $TiO_2$ nanoparticles is a critical parameter for improving electron mobility and subsequent photovoltaic response [43,44].

In this report we propose a well-connected $TiO_2$ microstructural composite comprising of porous microspheres and nanocrystallites as suitable photoanode for DSSCs. These composites exhibit high light scattering coefficient and efficient electron transport. Porous smooth microsphere and hollow/fibrous microspheres of $TiO_2$ were synthesized by solvothermal hydrothermal method respectively. A systematic investigation revealing the effects of microsphere to nanocrystallite ratio on the performance of DSSCs is carried out in comparison to the commercial P25 $TiO_2$ anodes. Large surface area for dye adsorption, good connectivity between $TiO_2$ particle for the efficient electron transport, and large light scattering for better light harvesting efficiency is demonstrated by $TiO_2$ microstructural-composites. High power conversion efficiency of 8.9% (for cell area of 0.5 $cm^2$ and thickness of ~25 μm) was achieved in composite photo-anode film consisting of 80 *wt.* % SμS and 20 *wt.* % P25.

## 2. Experimental

### 2.1. Materials

Titanium (IV) isopropoxide -Alfa Aesar (97%), glacial acetic acid – Vetec (AR > 99.8%), ethanol (AR-99.9%), poly ethylene glycol 4-*tert*-octyl phenyl ether- Triton X-100 (SRL), Degussa P25 $TiO_2$ nanocrystallites, Ru N719 dye – Solaronix, acetonitrile (HPLC grade-99.8%), Butanol- Emplura (> 99%), Lithium iodide (LiI), Iodine, 4-tertiary butyl pyridine (TBP) - Aldrich (96%), and fluorine doped tin oxide coated transparent (FTO) glass (8 Ω/Sq, 2.2 mm thick) were purchased and used without any purification.

### 2.2. Synthesis of titanium dioxide microsphere

(i) **Smooth surface $TiO_2$ microsphere (SμS) by solvothermal method:** 0.25 mol of titanium (IV) isopropoxide was added into 200 ml of ethanol. The pH of the ethanol was adjusted to 3 using glacial acetic acid before the addition of titanium (IV) isopropoxide. The solution was stirred vigorously to get homogeneous mixture and then transferred to an autoclave. The autoclave was maintained at 200 °C for 2 h. After the solvothermal treatment, the remaining solvent in the reaction mixture was slowly evaporated to get a white powder. This powder was washed with de-ionized water several times to reach pH about 7 and then calcined at 450 °C for 3 h to obtain crystalline anatase $TiO_2$ microspheres.

(ii) **Hollow/fibrous $TiO_2$ microsphere (FμS) by hydrothermal method** [19]**:** 0.1 g of Degussa P25 particle added into 60 ml of 10 M NaOH solution was ultrasonicated and stirred for 5 min each alternatively for 3 times. The solution was transferred to Teflon autoclave and 8 ml of hydrogen peroxide was added. The autoclave was maintained at 160 °C for 2 h. The white powder obtained was filtered and washed several times till the pH reached ~7. The powder was finally calcinated at 450 °C for 3 h to obtain crystalline $TiO_2$ microsphere.

### 2.3. Characterization

The crystallographic phase of the $TiO_2$ microsphere was studied using X-ray diffraction (XRD) patterns recorded on a X'Pert-Pro, Panalytical powder diffractometer (Cu-Kα radiation). Microstructural details were studied using scanning electron microscopy (SEM: FEI Quanta FEG 400) and high-resolution transmission electron microscopy (HRTEM: FEI Tecnai $G^2$ T20). The phase and local structural details of $TiO_2$ were obtained from the Raman spectroscopy with a 632 nm red excitation line of He-Ne laser using Horiba Jobin-Yvon (HR 800 UV) micro-Raman spectrometer. The diffuse reflectance spectra (DRS) of $TiO_2$ photoanode film were studied using integrated sphere configuration in a PVE 300 (Bentham) quantum efficiency measurement system. In DRS the scattered light excluding the specular reflection from the sample is measured with respect to a $BaSO_4$ reference sample. The band gap of microspheres (SμS and FμS) and P25 sample were estimated by converting this diffuse reflectance spectra to absorption coefficient equivalent using Kubelka-Munk (K-M) function, $F(R_\infty)$ as given below

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{\alpha}{S}, \quad (1)$$

where $R_\infty$ is the reflectance of infinitely thick sample; 'α' and 'S' are absorption and scattering coefficients. But in case of a sample having finite thickness, the reflectance is,

$$R_\infty = \frac{R(measured)}{R(standard)} \quad (2)$$

The energy (E) dependence of absorption coefficient (α) for semiconductor with band edge absorption energy ($E_g$) is given