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Anatase TiO_2 Hollow Microspheres Fabricated by Continuous Spray Pyrolysis as a Scattering Layer in Dye-Sensitised Solar Cells

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Abstract

TiO_2 hollow spheres, synthesised using Continuous Spray Pyrolysis (CoSP) reactor, were utilised as a scattering layer in dye-sensitised solar cells (DSSC) and the device performance was investigated. The size of the TiO_2 hollow spheres was about 170-300 nm and the thickness of the shell was about 55-60 nm. DSSC fabrication involved screen printing the TiO_2 hollow spheres (HSs) as a scattering layer on top of TiO_2 transparent layer (10 µm thick; 20 nm particle size) making a total thickness of 15 µm. The results suggested that the DSSC containing TiO_2 HSs layer showed power conversion efficiency of 7.46% which is better than that containing single layer TiO_2 transparent film (7.1%). This might be attributed to TiO_2 HSs layer acting as light scattering layer. Hence the cell exhibits an enhanced light-harvesting performance, therefore leading to an increment of photovoltaic performance compared to that for pure TiO_2 transparent film.

Keywords: TiO_2; scattering layer; DSSC; spray

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1. Introduction

Apart from the design and synthesis of more efficient and low-cost dyes in dye-sensitised solar cells (DSSCs), various TiO_2 structures such as nanoparticles, nanorods and nanotubes have been applied to enhance the performance of TiO_2 photoanodes [1-4]. The molar extinction coefficient in the red region for most of the dyes are low and hence thicker nanocrystalline (~20 nm particle size) layers of mesoporous titanium oxide are needed to efficiently absorb the photons with longer wavelengths. However, thicker transparent layers (> 10 µm) result in the loss of photogenerated carriers from the far end of current collector (fluorine doped tin oxide, for instance) due to the limitation of electron diffusion length in TiO_2. In addition, due to high surface area, thicker photoanodes can lead to a significant loss of open-circuit potential of the device [5]. In order to overcome the aforementioned issues, bilayer configuration has been proposed to introduce an additional scattering layer on the nanocrystalline transparent film to efficiently confine the photons within the photoanode film. Addition of the scattering layers with the large particles (~200-400 nm) ensures adequate light trapping in the device [6], due to the increase of absorption path length of photons and optical confinement. To this extent, hollow microspheres of TiO_2 have now been used as scattering material because of multiple-reflection effect occurring inside the interior cavities which could trap the incident light in the photoanode for longer duration.

In this work, DSSCs with TiO_2 hollow microspheres as scattering layer were fabricated from organic precursor via continuous spray Pyrolysis (CoSP) reactor to improve the light harvest efficiency of the dye-adsorbed TiO_2 electrode by light scattering. The as-synthesised microspheres which had an average size of ~ 300 nm and shell thickness ~ 55 nm were used as a scattering layer in DSSC. The technique in itself is "one-step" and also less time consuming as compared to other template based and hydrothermal approaches. TiO_2 electrode of the DSSC device was composed of TiO_2 particles of 20 nm as the average diameter. It was found that the power conversion efficiency under 1 sun intensity increased from ~7.1 to 7.5% due to mainly increase of the short-circuit current from 13.3 to 14.3 mA/cm^2 with scattering layer. Since the CoSP technique is capable of fabricating the microspheres in large quantity, the scattering layers can be easily incorporated for improved large area DSSC performance.

2. Experimental details

Well-defined anatase TiO_2 hollow microspheres were prepared via one step technique (Continuous Spray Pyrolysis Reactor (CoSP)) using titanium isopropoxide (TTIP) as organic precursor and ethanol as solvent [7]. A milky white titanium precursor, obtained after 1 hr of constant stirring, was sprayed through a three zone reactor with all the three zones maintained at different temperatures with N_2 as the carrier gas. TiO_2 powder was collected from the outlet connected to the third zone of the furnace. This powder was then utilised to make TiO_2 paste in a mortar pestle using ethanol as solvent following the steps mentioned by S. Ito *et al.* [8]. Nanocrystalline TiO_2 paste (20 nm) forming the transparent layer was from Dyesol. X-ray diffraction (XRD) studies were done using X-ray diffractometer (Phillips X'PERT PRO), having CuKα incident beam (λ = 1.54Å). Surface morphology was done using a ZEISS EVO-50 model scanning electron microscope (SEM).

To prepare the DSC working electrodes, the FTO (fluorine doped tin oxide) glass used as current collector (TEC 7, Solaronix, Switzerland) was first cleaned in a detergent solution using an ultrasonic bath for 30 min, and then rinsed with water and ethanol which is followed by a thermal treatment at 500 °C for 20 min. The FTO is passivated by an underlayer using $TiCl_4$ treatment (40 mM solution in water, 75 °C, 30 min). Nanocrystalline TiO_2 paste (20 nm particle size, 67% porosity) was screen printed on the FTO glass to make a thickness of 10 µm on top of which the hollow microspheres paste was screen printed again, resulting in a light scattering TiO_2 film of 4-5 µm, and total thickness of 15 µm. The printed films are sintered following different temperature profiles upto 500 °C as described by S. Ito *et al.* [8]. The mesoporous sintered films are treated using $TiCl_4$ similar to the underlayer passivation to enhance the necking of mesoporous nanocrystalline particles. The photoanodes are heated again to 500 °C for 30 min before dipping them in a Ru(II) bipyridyl sensitiser solution coded C106 [9]. The films are sensitised for 14 hours in dark and washed in acetonitrile for 30 min to remove any loosely bound dye molecules. The Pt-coated counter electrode is made by drop casting the H_2PtCl_6 solution on a pre-cleaned FTO glass followed by a heat treatment at 400 °C for 15 min.

The photoanode and the counter electrode are then sealed using a 25 Surlyn film. The electrolyte composed of 1 M DMII (Imidazolium Iodide Salt), 0.03 M I_2, 0.1 M guanidinium thiocyanate and 0.5 M 4-tert-butylpyridine and 0.05 M LiI in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15) is injected in the cell by vacuum backfilling through a hole created in the counter electrode. The devices are then sealed using a thin glass and contacts are made using an ultrasonic solder. The J-V characteristics under dark and illumination (AM 1.5 Global, 100 mW/cm^2) of the DSSCs are measured using a home-made mac-interfaced Keithley setup fitted with an Oriel 450 W Xenon lamp as solar illumination source. The distance between the sample and the lamp was about 7cm. The active area is defined by a black mask and the illuminated area was equal to 0.159 cm^2.

Incident photon-to-current conversion efficiency measurements were determined using a 300 W xenon light source (ILC Technology, USA). A Gemini-180 double monochromator Jobin Yvon Ltd. (UK) was used to select and increment the wavelength. The monochromatic incident light was passed through a chopper running at 2 Hz frequency and the on / off ratio was measured by a lockin amplifier. The monochromatic light was superimposed on a white light bias corresponding to 5 mW/cm^2 intensity.

3. Results and discussion

The hollow microspheres (HSs) are characterised using X-ray diffraction and SEM (scanning electron microscopy) to verify crystallinity and microstructure, respectively. Figure 1 (a) shows the micrograph of the hollow spheres and it can be noted that they are hollow and possess spheres of uniform size.

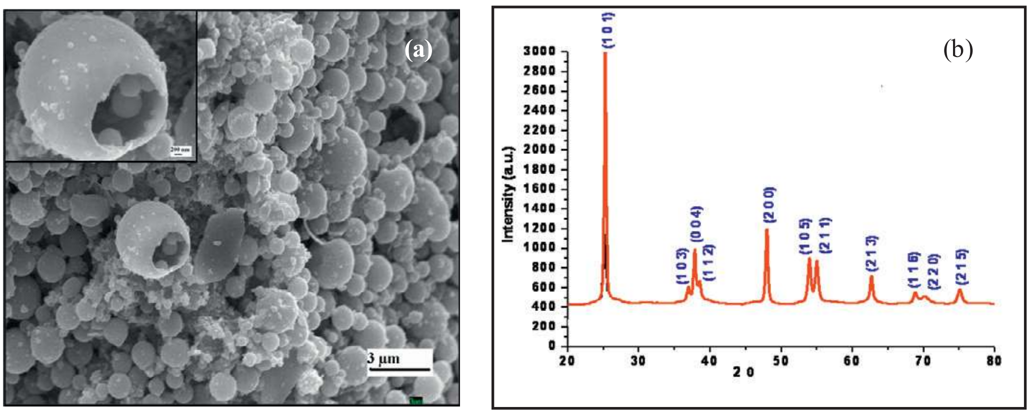

Fig. 1. (a) SEM image of hollow microspheres; inset depicts the magnified image (b) X-ray diffractogram of TiO_2 HSs and the numbers indicated in the brackets are the (*hkl*) planes of the corresponding peaks.

The diffraction pattern of the corresponding film is shown in Fig. 1(b). Several peaks related to a crystalline phase are observed and the Bragg reflections can be attributed to the TiO_2 crystallised in the anatase structure (JCPDS 71-1169) exhibiting a space group symmetry of $I\,4_1/amd$.

Figure 2 (a) shows typical photocurrent density-photovoltage curves for the resulting DSSCs, and the related photovoltaic parameters of two kinds of DSSCs are summarised in Table.1. After TiO_2 HSs were introduced as scattering overlayer, the short-circuit current density (J_{sc}) was increased from 13.3mA/cm^2 to 14.3 mA/cm^2, while open-circuit voltage remains almost same. As a result, the cell showed a higher cell performance than that of cell having only transparent layer, and the efficiency of DSSCs was improved from 7.1% to 7.5%, which should be attributed to the enhanced light harvesting efficiency of TiO_2 hollow spheres, and is in accordance with the previous discussion. The increase in the J_{SC} is verified using IPCE (Incident Photon to Charge Carrier Efficiency) measurements and Fig. 2(b) shows the plot of IPCE as the function of wavelength. One can observe that the IPCE of the reference transparent device is lower compared to the device with scattering layer over all the wavelength range. The integrated current under the IPCE spectra roughly equals the observed J_{SC} in the photovoltaic J-V measurement and the trend is consistent.

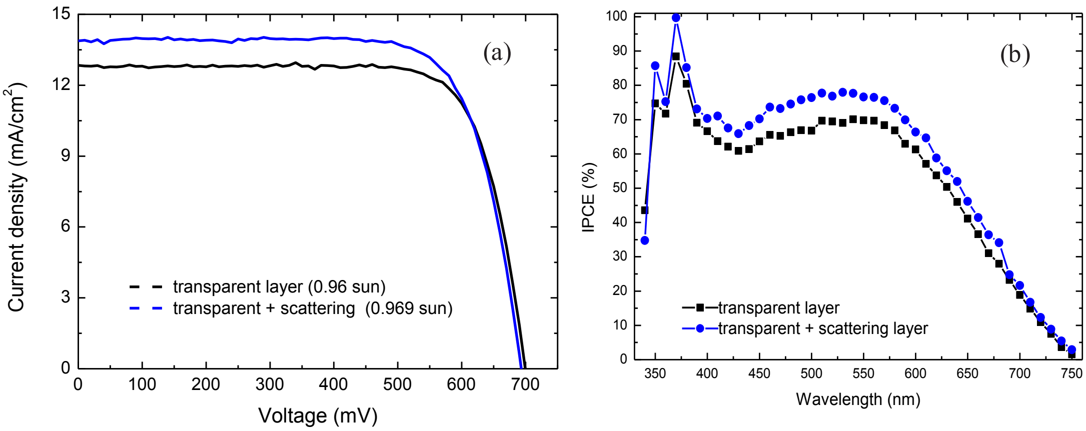

Fig. 2. (a) J-V characteristics of TiO_2 DSSC with and without scattering layer. The numbers indicated in the parenthesis in the legend correspond to the illumination intensity during measurement; (b) IPCE plot of the DSSC with and without HSs scattering layer.

Table 1. Photovoltaic parameters of TiO_2 DSSC showing the effect of TiO_2 HSs as scattering layer.

Name	V_{oc} (mV)	J_{sc} (mA/cm^2)[a]	Fill Factor	η (%)
Only transparent layer (10 μm)	699.2	13.3	0.763	7.1
Transparent +scattering layer (10+5 μm)	692.2	14.32	0.752	7.46

[a]current density normalised to 1 sun

4. Conclusion

In summary, TiO_2 HSs were synthesised successfully by continuous spray pyrolysis reactor and their role as scattering layer to improve the photovoltaic performance in DSSC was investigated. The double-layered structured DSSC employing the hollow spheres as scattering layer demonstrated a high conversion efficiency of 7.5%, in contrast to 7.1% for the cell using single layer nanoparticles film. The enhancement in efficiency was mainly attributed to the high light-scattering performance of TiO_2 HSs. The size effect of TiO_2 HSs is under investigation to further enhance the diffuse scattering in the red regime of the visible light.

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