Highly dispersed mesoporous TiO₂ spheres via acid treatment and its application for dye-sensitized solar cells

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A R T I C L E   I N F O

Article history:
Received 22 August 2012
Received in revised form 30 January 2013
Accepted 23 February 2013
Available online 4 March 2013

Keywords:
Dye-sensitized solar cell
Scattering layer
Acid treatment
Compression method

A B S T R A C T

Photoelectrodes composed of mesoporous TiO₂ spheres as scattering centers and TiO₂ nanoparticles as the binder were fabricated and tested with the aim of improving the energy conversion efficiency of dye-sensitized solar cells (DSSCs). In order to achieve the dispersion of the TiO₂ spheres in suspension and improve their connectivity in the electrodes, acid treatment and a compression method were applied. These electrodes composed of TiO₂ spheres and nanoparticles enable the fabrication of high performance DSSCs, because of the light scattering of the TiO₂ spheres and the dye-loading capacity of their high surface areas. The energy conversion efficiency of composite-type photoelectrode was found to be 7.66%, which is higher than that of nanocrystal electrode (4.50%). We can thus conclude that high energy conversion efficiency was achieved with a composite-type photoelectrode, without the use of an anti-reflection coating or a back-scattering layer.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have recently been extensively investigated due to their attractive properties: low fabrication cost, less toxic manufacture, relatively high energy conversion efficiency, and substrates that are more flexible than those of silicon-based solar cells [1–11]. Typical DSSCs are comprised of a fluorine-doped SnO₂ substrate, a titanium dioxide film, a sensitizing dye, an electrolyte, and a counter electrode. A simple introduction to the mechanism involved in DSSCs is described as below: The electrons generated from the excited dye molecules upon irradiation with visible light are injected into the conduction band of the TiO₂ electrode. The oxidized dye molecules are regenerated by I⁻ ions in the electrolyte, and the I⁻ ions are oxidized to I³⁻ ions. The I³⁻ ions are reduced to I⁻ ions by accepting electrons at the counter electrode, and the process is repeated [12–14].

A TiO₂ electrode with a high surface area is essential for the loading of large numbers of sensitizing dye molecules that engender photoelectrons upon the absorption of the incident light [15–17]. Typical photoelectrodes are thus composed of porous TiO₂ nanocrystallites (~20 nm), which maximize the uptake of dye molecules. However, small nanocrystallites with large surface areas do not always produce the best performance due to the increased number of grain boundaries and defects on their surfaces, which can delay the electron transport; such TiO₂ nanocrystal electrodes can cause the exhibition of high transparency and insufficient light scattering in the visible light region due to the small particle size, which results in poor light-harvesting efficiency.

Many studies have been carried out in the attempt to enhance the light harvesting efficiency of DSSCs. One approach is to improve light harvesting by adding a scattering layer to the TiO₂ nanocrystal electrode [18]. It has been demonstrated that scattering layers improve light harvesting and thus enhance the light conversion efficiency of solar cells. According to Mie theory, the particles utilized to scatter visible light should be large; and it has been verified that sub-micron-sized particles result in the effective light scattering [19]. When incident light collides with the sub-micron-sized particles, the light will be scattered violently, which increases the light path length in the nanocrystalline TiO₂ films.

However, the small surface-to-volume ratio of sub-micron-sized TiO₂ particles limits the adsorption of dye molecules. The incorporation of a light scattering over-layer results in an increase in film thickness and the loss of photons traveling through the electrolyte-filled TiO₂ electrodes, as well as increases in the recombination rate and the path length of the injected photo-electrons [20,21]. To address these issues, submicron-sized TiO₂ beads that enhance the light-harvesting capability of the TiO₂ electrode, without reducing the area of the surface accessible to dye loading, have been reported recently. Lee et al. [7], Kim et al. [22], and Murayama et al. [23] prepared hollow submicron-sized TiO₂ spheres, consisting of primary nanocrystallites, via a sol-gel reaction with polystyrene beads as the template. They found that a DSSC with the TiO₂ hollow spheres exhibits enhanced light harvesting efficiency. This improvement results from the multiple reflecting and scattering of incident light by the hollow spheres. However, the introduction of hollow spheres as scattering centers reduces the dye-loading capacity of the electrodes due to the large voids in the hollow spheres.

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http://dx.doi.org/10.1016/j.powtec.2013.02.036
Chen et al. designed a working electrode containing spherical TiO₂ beads consisting of TiO₂ nanocrystallites, which was found to be able to enhance the light-harvesting efficiency of the associated DSSC, and therefore improves the energy-conversion efficiency [3]. Shao et al. synthesized porous spherical TiO₂ aggregates via an interfacial confined formation, which were found to enhance electron transfer and light scattering in DSSCs. However, the voids between the aggregated TiO₂ particles in the TiO₂ electrodes are larger than those in the TiO₂ nanocrystallite electrodes. The comparatively large sizes of the voids result in poor connectivity and ineffective charge transfer between the aggregated TiO₂. Such poor connectivity between aggregated TiO₂ often limits the effectiveness of charge transfer, which leads to reduced DSSC performance [24,25].

In this paper, we reported the preparation of mesoporous TiO₂ spheres with various aggregated sizes. These spheres were synthesized by using surfactants with ethylene oxide groups of various lengths. To achieve satisfactory dispersion of the TiO₂ spheres in suspensions, treatment with nitric acid was performed. We fabricated composite-type photoelectrodes consisting of TiO₂ spheres mixed with small TiO₂ particles as the binder. In order to further improve the connectivity between the TiO₂ spheres, we used the hot-pressing compression technique to prepare TiO₂ electrodes on fluorine doped tin oxide (FTO) substrates. This hot-press technique was found to improve the connectivity between the TiO₂ spheres, as well as the mechanical adhesion of the TiO₂ electrode to the FTO substrate. These composite-type electrodes were used as scattering layers and working electrodes in DSCC devices and their effects on the conversion efficiency of the devices were investigated.

2. Experimental section

2.1. Materials

Titanium(IV) isopropoxide (TTIP, Ti(OPr)₄), Pluronic P123 (P123, EO₂₃PO₇₀EO₂₀), Pluronic F127 (F127, EO₁₀₈PO₇₀EO₁₀₈), 2,4-pentanedione (acetylacetone, AcAc), sulfuric acid, nitric acid poly(ethylene glycol) (PEG, average MW = 10,000) and poly(ethylene oxide) (PEO, average MW = 100,000) were all purchased from Sigma-Aldrich and used as received without further purification. cis-Diisothiocyanato-bis(2,2-bipyridyl-4,4-dicarboxylato) ruthenium(II) bis (tetrabutylammonium) (D719), fluorine doped tin oxide (FTO) substrates and Ti-nanoxide T pastes were purchased from Solaronix. The water used in all syntheses was distilled and deionized.

2.2. Preparation of mesoporous TiO₂ spheres

The mesoporous TiO₂ spheres were synthesized with the sol-gel method by using triblock copolymer surfactants (P123 and F127 for sample S1 and S2, respectively) in aqueous solution. The general procedure was carried out as follows. First, 1.0 mmol of each surfactant was dissolved in 100 mL of deionized water, and the mixture was stirred vigorously at 50 °C to give a transparent solution. After the surfactant had dissolved sufficiently, 1.5 g of sulfuric acid was added to the aqueous surfactant solution. TTIP (7.84 g) was mixed with AcAc (2.76 g) in a separate beaker and dropped into the aqueous surfactant solution with vigorous stirring for 30 min at 50 °C. The resulting materials were treated hydrothermally at 90 °C for 10 h.

To achieve dispersion of the TiO₂ spheres (S1 and S2) in suspension, the TiO₂ spheres were hydrothermally treated with nitric acid (HNO₃). The procedure was carried out as follows. 4 mL of HNO₃ was added to 100 mL of the above suspension. This mixture was then vigorously stirred at 50 °C for 2 h. The suspension was transferred into an autoclave, sealed, and then maintained 200 °C. After a reaction time of 24 h the autoclave was cooled to room temperature. The HNO₃ treatment produced a milky suspension.

2.3. Fabrication of TiO₂ nanoparticle/mesoporous sphere composite films

The weight content of the nitric acid treated spheres in the suspension is 40 wt %. The pastes were prepared by admixing the 10 g of suspension with 0.12 g of PEG, and 0.12 g of PEO, and then TiO₂ nanoparticle incorporated mesoporous sphere (S1 and S2) composite pastes were prepared by mixing with 2 g of Ti-nanoxide-T paste, and the resulting pastes were doctor-bladed onto the FTO substrates (N-S1 and N-S2, respectively). In order to further improve connectivity between the TiO₂ spheres, the coated composite TiO₂ films (N-S1 and N-S2) were then pressed (N-S1-P and N-S2-P, respectively). Typical pressures were 12 MPa with plates preheated to 120 °C for 10 min. Teflon plates were inserted between the composite TiO₂ films and the plate to prevent the films sticking to the plate. The films were then calcined at 450 °C for 30 min in air.

2.4. Assembly of the DSCCs

Before adsorbing the dye, the composite TiO₂ electrode was treated with heat for 30 min at 200 °C and dried in a vacuum oven for 2 h at 90 °C in order to remove any excess water and organic residues. The composite TiO₂ electrodes were immersed in an ethanolic solution containing a ruthenium sensitizer dye, 3 × 10⁻⁴ M D719 for 12 h. The platinized counter electrode was placed on top of the dye-coated TiO₂ photo-electrode sealed with a Surlyn film (25 μm thick, DuPont), and the electrolyte, which was composed of 1-butyl-3-methyl-imidazolium iodide (BMI, 0.7 M, Merck), I₂ (0.03 M), guanidinium thiocyanate (GSCN, 0.1 M, Aldrich), and 4-tert-butylpyridine (TBP, 0.5 M, Aldrich) in acetonitrile and valeronitrile (85:15 v/v), was injected through a hole in the counter electrode.

Fig. 1. FE-SEM images of (a) S1 and (b) S2.
2.5. Characterization

The surface features and morphologies of the TiO2 spheres were investigated by using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6330 F) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2000 FX II). The crystallite structures of the TiO2 spheres were investigated by analyzing the wide angle X-ray diffraction (XRD) patterns obtained with a MAC/Sci MXP 18XHF-22SRA diffractometer equipped with Cu Kα irradiation (λ = 0.154 nm) and a fixed power source (40 kV, 200 mA) at a step width of 0.02°. The crystallite sizes were calculated by using the Scherrer equation (Φ = Kλ / βcosθ), where Φ is the crystallite size, λ is 0.154 nm (the wavelength of the X-ray irradiation), K is usually assumed to be 0.89, β is the full width at half-maximum intensity (FWHM), and θ is the diffraction angle of the (101) peak for anatase (2θ = 25.3°). Differential scanning calorimetry (DSC) measurements were performed using a DSC200 F3 Maia system under flowing nitrogen with a heating rate of 5° C min⁻¹. The specific surface areas and pore size distributions of the TiO2 spheres were characterized by analyzing the N2 adsorption and desorption isotherms obtained at 77 K with a Micrometrics ASAP 2000 equipment (Table 1). All the samples were degassed at 200 °C and 10⁻⁶ Torr for 10 h prior to these measurements. The surface areas were calculated with the Brunauer–Emmett–Teller (BET) equation, and pore-size distributions were determined from the adsorption and desorption branches by using the Barrett–Joyner–Halenda (BJH) formula. The average size and size distribution of the TiO2 spheres were measured by dynamic light scattering (DLS), using a Photal DLS-7000 spectrophotometer equipped with a Photal GC-1000 digital autocorrelator (Otsuka Electronics Co., Ltd.). In this procedure, the wavelength (λ) of the argon laser was 488 nm, and the scattering angle was 90° with respect to the incident beam. Intensity-average and number-average particle size distributions were analyzed by the conventional CONTIN algorithm to estimate the diameter of the TiO2 spheres. The zeta potential was measured by a zeta potential analyzer using ELS-8000 spectrophotometer (Otsuka Electronics Co., Ltd.) using Smoluchowski relationship. UV–visible spectroscopy was performed with a Lambda 25 instrument manufactured by Perkin Elmer.

Photovoltaic measurements were conducted by illuminating the DSSCs with light from a 450 W Xe lamp that had been directed through an AM 1.5 solar simulator. The intensity of the simulated light was calibrated by using a Si reference solar cell equipped with a BK7 filter to approximate AM 1.5, 100 mW cm⁻² global radiation. The photovoltaic characteristics of the DSSCs were obtained by applying an external potential bias to the cells and measuring the generated photocurrent with a Keithley 2400 source meter. IPCEs were measured as a function of wavelength from 350 to 800 nm using a specially designed IPCE system for dye-sensitized solar cells (PV Measurements, Inc.). A 75 W xenon lamp was used as the light source for generating a monochromatic beam. Calibration was performed using a NIST-calibrated silicon photodetector.

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![Fig. 2. Representative HR-TEM images of (a) S1 and (b) S2.](image)

![Fig. 3. X-ray diffraction patterns of (a) S1 and (b) S2 before and after calcination.](image)
3. Results and discussion

3.1. Morphology and structure of mesoporous TiO₂ spheres

FE-SEM images of the mesoporous TiO₂ spheres (S1 and S2) after hydrothermal treatment with various surfactants are shown in Fig. 1a and b, respectively. The aggregates of these materials all have spherical morphologies. The spherical TiO₂ structures (S1 and S2) are highly monodispersed with sizes of ≈ 550 nm and ≈ 1000 nm, respectively. Even though a same precursor was used, the surface of TiO₂ spherical particles had a distinct toughness which is predicted to be caused by different surfactants. Both P123 and F127, consisting of a central hydrophilic PPO chain and two hydrophilic PEO tails, have been used as the structure-directing agents for the construction of mesoporous structure for TiO₂. Both P123 and F127 are triblock copolymer and are constituted as EO–PO–EO. The two surfactants have the same length of 70 PO chains but P123's end groups have 20 while F127 have 108 EO chains. Therefore, compared to P123, F127 has a comparably hydrophilic EO chain forming a long micelle. It has been generally accepted that the nucleation takes place at the hydrophilic part of each surfactants, EO chain, when TiO₂ is formed from Ti precursor by sol-gel method. This implies that TiO₂ prepared with P123, the shorter EO-chain holder, has a coarser surface than that with F127, given that the longer EO chain, TiO₂ particles are easier to be agglomerated. For comparison, several preparation processes for TiO₂ with different surfactants have been carried out under the same experimental condition as mentioned (Figs. S1 and S2). As a result, the product particles prepared with F68 (PEO₇₅PPO₃₀PEO₇₅, Mw = 8,400), and F127 are smoother than those made with L121 (PEO₅PPO₇₀PEO₅, Mw = 4,400) and P123 which has a relatively shorter EO than the former ones. Due to this phenomenon, it can be confirmed that the surface of spherical particle in S1 was coarser that in S2 since the hydrophilic part of surfactant was influential for formation of the particle. In accordance with these results, the effect of EO on block copolymer based synthesis of spherical TiO₂ has been predicted. When symmetrical block copolymers are dissolved in water solution, a large number of spherical micelles are formed due to the interaction of the two segment types of the block copolymers. The block copolymer micelle was composed of a core dominated by PO and a corona dominated by EO segments. The core of the micelles was believed to be free of water, while the swollen corona was hydrated. The aggregation behavior of the block copolymer under thermodynamic conditions may affect the TiO₂ particle size and morphology. The TiO₂ spheres were synthesized with the sol-gel method from hydrolysis of a titanium precursor. Hydrolysis and condensation (nucleation and growth) of the titanium precursor lead to the formation of primary particles, which spontaneously aggregated to form the large spherical clusters in the solvent due to the strong surface tension. The driving force for aggregation of the primary particles is a decrease in the high surface energy of the tiny primary particles. It is generally accepted that the functional groups of the surfactant have coordination bonds with the nanoparticles. In this system, surface hydroxyl groups in the surfactant coordinate with primary TiO₂ particles in the water. It is assumed that micelles surround the primary TiO₂ particles, playing an important role in the formation of TiO₂ aggregates. It appears that as the hydrophilic chain of EO becomes longer, the nucleation and growth of TiO₂ become easier and hence increase the size of TiO₂.

Fig. 4. DSC curves for (a) P123, S1 before and after calcination and (b) F127, S2 before and after calcination.
Typical HR-TEM images for the mesoporous TiO2 spheres are shown in Fig. 2 and reveal that the materials have well-defined spherical structures with primary particle sizes of ≈ 10 nm. All of the samples have mesoporous structures, and the wormhole-like mesopores form special closely interconnected nanoparticles. From these results, we conclude that the pore walls consist of aggregated TiO2 nanoparticles. Fig. 3a and b shows the XRD patterns for S1 and S2, respectively, which indicate that all of the particles possess highly crystallized anatase structures (JCPDS card no. 73-1764) without any impurity phases. The average crystallite sizes of S1 and S2, as determined from the (101) peak with an estimation based on the Scherrer formula, are 13 nm and 7 nm, respectively, which implies that the mesoporous spheres are composed of smaller nanocrystals.

Fig. 4(a) and (b) shows the DSC patterns of S1 and S2 before and after calcination at 500 °C, respectively. In all cases, below 200 °C, the weight loss is attributed to the loss of adsorbed water and decomposition of organic residue on the surface of the powder. Due to the high surface area of TiO2 sphere, even after calcination, the adsorption functions of water or residues were optimal. Therefore, the samples that have been calcinated and those that were not, showed a similar endothermic peak with regards to the loss of adsorbed water and decomposition of organic residues. For S1 (see Fig. 4(a)), no characteristic exothermic peak was observed, which is attributed to the presence of TiO2 anatase crystallites, since all the TiO2 nanoparticles in the spheres crystallized during the hydrothermal treatment. In contrast, as shown in Fig. 4(b), for S2, there is an exothermic crystallization peak at approximately 300 °C. It is known that the transformation from amorphous to anatase crystallites depends on intimate contact with OH−. S2 contains large spheres, so there is less chance for the particles to come into contact with OH− during hydrothermal treatment, which results in a lesser degree of crystallization, as confirmed by the XRD result. It is known that the transformation from amorphous to nanocrystalline anatase is governed by interface nucleation and surface nucleation. Accordingly, the intensity of the exothermic crystallization peak of packed TiO2 is lower than that of loose TiO2. According to DSC analysis, the crystallization of amorphous TiO2 to anatase crystallite usually occurs at approximately 440 °C, whereas crystallization in S2 occurs at approximately 300 °C through the self-assembling aggregation of spheres. The exothermic changes disappear from the S2 pattern after calcination.

The specific surface areas of S1 and S2 characterized by using nitrogen gas adsorption–desorption and are shown in Fig. 5(a) and (b), respectively. The physical characteristics are summarized in Table 1. The specific surface area of the NC is only 51.84 m² g⁻¹ (see Fig. S3) and there are no obvious porous characteristic, which indicates that they are amorphous hybrid beads with a dense structure. All the isotherms of the S1 and S2 are of classical type IV with H2 hysteresis between the adsorption and desorption curves, which indicates the presence of an ink-bottle pore structure with a large cavity. The surface areas of S1 and S2 calcined at 500 °C were determined with the BET method and found to be similar, 223.76 and 192.06 m² g⁻¹, respectively. The surface areas of S1 and S2 are 4.3 and 3.7 times respectively that of the TiO2 nanoparticle, which clearly indicates that these spherical structures have high internal surface areas. The pore-size distributions of S1 and S2 estimated by employing the Barrett–Joyner–Halenda (BJH) method, as shown in Fig. 6(a) and (b), respectively. As shown in Fig. 6(a), the average pore size of S1 was 12.51 nm, a seemingly reasonable result considering the particle size. It was reported that the area occupied by the dye molecule on the TiO2 surface was calculated to be 1.6 nm²/molecule [26]. This result suggests that the surfaces inside the TiO2 spheres can be readily accessed by the dye molecules. Conspicuously, two kinds of pores were observed in S1. The 12.51 nm sized pores are regarded as the internal pores, which were originated from the surfactant, of the mesoporous TiO2 spheres, whereas the 126.2 nm pores originated from the interstitial voids formed by packed spheres. Conversely, for S2 (Fig. 6(b)), 16.06 nm and 111.8 nm sized pores were generated from S2.

Fig. 7 shows the average aggregate diameters of the mesoporous TiO2 spheres in aqueous solution, as determined with DLS. DLS measures the Brownian motion of the particles and relates it to their size. The correlation functions were analyzed by means of the constrained regulation (CONTIN algorithm) method to determine the distribution decay rates. The average aggregate sizes of S1 and S2 are 2549.4 (average % error: 0.8) and 2149.0 nm (average % error: 2.2%), respectively. Although the FE-SEM images of these TiO2 spheres show that they have submicrometer sizes, these spheres aggregated in aqueous solutions. Considerable aggregation was observed for both types of TiO2 spheres, resulting in the formation of flocs. The aggregate sizes of these spheres are on the micrometer scale, presumably due to the hydrophobic nature of the TiO2 spheres’ surfaces and the electrostatic attraction of the spheres. Therefore, these TiO2 spheres aggregate in solvents to sizes that reach even the micrometer scale. To improve TiO2 sphere dispersion, acid treatment was tested. Acid treatment is an effective tool for dispersing TiO2 spheres in aqueous solution without damaging their spherical structure. The aggregate sizes of S1 and S2 were reduced by treatment with HNO3 to 545.8 (average % error: 0.5) and 1139.0 (average % error: 0.4) nm, respectively, which is in good agreement with the FE-SEM results. Thus the spheres are well-dispersed in the suspension. The spheres maintained their morphologies after dispersion of TiO2 in

Table 1
Specific surface area and average pore size of S1 and S2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific surface area (m²/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>223.76</td>
<td>12.51</td>
</tr>
<tr>
<td>S2</td>
<td>192.06</td>
<td>16.06</td>
</tr>
</tbody>
</table>

![Fig. 5. N₂ adsorption–desorption isotherms for (a) S1 and (b) S2.](image-url)
the solvent, because no physical pressure was applied during the HNO₃ treatment. So any destruction of morphology was minimized.

Fig. 8 shows the zeta-potential values of S1 with and without acid treatment. The zeta-potential (ζ) of a suspension is a function of surface charge. In a dispersion where ζ is close to zero (the isoelectric point), particles in the suspensions tend to agglomerate. At highly positive or negative ζ (|ζ| > 30 mV), particles in suspensions tend to repel each other and therefore do not agglomerate. After treating with HNO₃, when looking at the zeta potential value of TiO₂ sphere, it can be found that the HNO₃ treated TiO₂ spheres had a high zeta-potential value in the pH domain, which indicates that the HNO₃ treatment within the solvent of TiO₂ sphere prevents aggregation between spheres. Particularly, when the pH level is not adjusted, the TiO₂ sphere that has not been treated with HNO₃, resulted in a pH value of 4 in the water. The zeta-potential of the TiO₂ spheres before acid treatment is approximately −5 mV at pH 4, which is in the range of strong agglomeration (|ζ| < 5 mV). However, after being treated with HNO₃, the pH value of TiO₂ in water was 3, while the zeta-potential value was approximately −15 mV, which means that the acid treatment increases the steric repulsion between the TiO₂ spheres, showing that TiO₂ spheres treated with HNO₃ become moderately dispersed in water. Through this, dispersed TiO₂ spheres could be made into TiO₂ paste.

3.2. Morphology and optical properties of mesoporous TiO₂ sphere/nanocrystalline TiO₂ composite film

Fig. 9(a), (b), and (c) shows FE-SEM images of film surfaces composed of S1, and of TiO₂ spheres/nanoparticles before and after compression, respectively. Voids, larger than 1 μm, can be found in the film composed of TiO₂ spheres, whereas the voids in the film composed of TiO₂ spheres/nanoparticles are much smaller. The presence of these large voids between the TiO₂ spheres limits their connectivity and prevents effective charge transfer. Such a poor connectivity is likely to result in an increased electron diffusion distance and reduced energy conversion efficiency. FE-SEM cross-sectional images of TiO₂ films fabricated on FTO substrates are shown in Fig. 9(d) and (e). The thicknesses of the mesoporous TiO₂ sphere film without hot-press treatment and of TiO₂ composite films with press treatment are as follows:
were approximately 20 μm and 10 μm, respectively. The magnitude of the reduction in film thickness as a result of the compression process is approximately 50%.

The films consisting of TiO2 nanoparticles appear semi-transparent, which indicates the partial transmittance of incident visible radiation. An increase in the light scattering ability of the film is important for enhancing the light-harvesting efficiency and thus the photon to current conversion efficiency of the associated DSSC. As shown in the transmittance spectra of nanocrystalline TiO2 (P25, labeled NC) and the as-prepared TiO2 spheres (S1 and S2) (Fig. 10), NC is more transparent with respect to visible light than the films with TiO2 spheres, which indicates that the TiO2 spheres trap more light. This property means that the films composed of TiO2 spheres can prevent visible light from escaping the devices. As discussed above, the scattering of light by the TiO2 spheres enhances light trapping and hence light utilization in the film.

3.3. Photovoltaic performance of mesoporous TiO2 sphere/nanocrystalline TiO2 composite film

Fig. 11 shows that the performances of J–V curves of DSSCs based on photoelectrodes made of TiO2 spheres (S1 and S2), TiO2 spheres/TiO2 nanoparticle composite (N-S1 and N-S2), TiO2 spheres/TiO2 nanoparticle composite with compression (N-S1-P and N-S2-P) and nanocrystalline TiO2 (NC): D719 were used as a sensitizer without any chemical modification or anti-reflection coating. The open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF), and energy conversion efficiency ($\eta$) of the DSSCs are also summarized in Table 2. The DSSC with the photoelectrode consisting of TiO2 spheres (S1 and S2) reached an energy conversion efficiency of 5.83% and 5.47%, respectively, whereas that of NC

![Fig. 9. Surface FE-SEM images for films prepared from (a) S1, (b) N-S1, (c) N-S1-P and cross-section FE-SEM images of films prepared (d) N-S1 and (e) N-S1-P.](image)

![Fig. 10. UV-visible transmittance spectra of films prepared S1, S2, and NC.](image)
achieved an energy conversion efficiency of 4.50%. The admixing of TiO\textsubscript{2} spheres into TiO\textsubscript{2} nanoparticles results in an enhancement in DSSC performance. As shown in Table 2, all the values of the samples except \( J_{sc} \) are similar. Therefore, on the basis of the TiO\textsubscript{2} electrode characteristics, we suggest that the increase in energy conversion efficiency is ascribed to the improvement of \( J_{sc} \).

The improvement in the efficiency of the DSSCs with a photoelectrode consisting of TiO\textsubscript{2} spheres/nanoparticles can be explained as follows. Submicron sized TiO\textsubscript{2} spheres improve the light scattering efficiency and thus increase the probability of photon capture from the incident light [27], the cause of \( J_{sc} \) improvement could be due to the scattering effect of TiO\textsubscript{2} sphere, as well as the mesoporous structure of TiO\textsubscript{2} sphere. The amounts of adsorbed dye were determined by measuring the dye concentration eluted from the mesoporous TiO\textsubscript{2} spheres with UV-vis absorption spectroscopy. The result of dye adsorption experiment shown in Table 3, depicts that dye adsorption of S1 and S2 compared to that of NC, was by approximately 1.89 and 1.72 folds higher, respectively, which is in good agreement with the BET/BJH results. It is inferred that the improved DSSCs fabricated from TiO\textsubscript{2} spheres are closely related to larger amounts of anchored dye sensitizers.

In order to compare the photovoltaic performance of S1, S2 and NC, incident photon to current conversion efficiency (IPCE) spectra of the TiO\textsubscript{2} electrodes were recorded. Fig. 12 displays the IPCE spectra of the DSSCs fabricated with electrodes consisting of S1, S2 and NC. The dye-loading capacity of each photoelectrode is reflected on the corresponding IPCE in the shorter wavelength region (400–600 nm), while the light scattering efficiency can be explained by the IPCE value in the longer wavelength region (above 600 nm). As shown in Fig. 12, the TiO\textsubscript{2} films prepared from S1 and S2 possessed higher IPCE values over a wide range than films of NC of similar thickness. Compared to the NC electrodes, the increase in IPCE values for S1 and S2 at short wavelength region could be mainly attributed to their higher dye loading capacities [27]. In the long wavelength region, the higher IPCE values of S1 and S2 could be ascribed to the enhanced light scattering capacities, which promotes the light harvesting of the D719 dye in the region [18,19,28]. Therefore, the higher IPCE value above 600 nm can be attributed to the light scattering abilities of the photoelectrodes, which leads to increase the probability of interaction between the photons and the dye molecules that adsorb on the TiO\textsubscript{2} surface. In the case of N-S1 and N-S2, the dye-loading is slightly increased because the TiO\textsubscript{2} nanoparticles fill the voids between the TiO\textsubscript{2} spheres. However, no significant difference was found between the dye adsorption of the electrodes with TiO\textsubscript{2} spheres (S1 and S2) and of the composite-type electrodes (N-S1 and N-S2). It is deduced that the dye-loading capacity of the TiO\textsubscript{2} spheres is superior to that of the TiO\textsubscript{2} nanoparticle used as binder. The performance of the cells produced by the compression technique was evaluated in terms of their \( J–V \) characteristics under white light illumination: Table 2 summarizes the results. The maximum energy conversion efficiency of the pressed electrodes (N-S1-P) was measured to be 7.66% with \( J_{sc} = 14.53 \) mA cm\(^{-2}\), \( V_{oc} = 0.79 \) V, and FF = 0.66.

After compression, \( V_{oc} \) of N-S1 and N-S2 (0.69 V and 0.96 V, respectively) improved compared to N-S1-P and N-S2-P (0.79 V and 0.72 V, respectively). It is known that \( V_{oc} \) depends on the back-reaction of the injected photo-electrons [29]. The improvement of \( V_{oc} \) may be explained due to the improved connectivity between spheres and the increased number of electron pathways and therefore less resistance to electron transfer to the sphere interface. The increased light scattering, dye-loading capacity of the electrode with TiO\textsubscript{2} spheres answers for the improved performance of DSSC. And the compression process improves the connectivity between TiO\textsubscript{2} spheres, which can decrease the serious resistance and enhance the \( V_{oc} \).

### 4. Conclusions

In summary, highly dispersed TiO\textsubscript{2} spheres with tunable cluster sizes (approximately 500 nm and 1000 nm) in suspension have been prepared through treatment with nitric acid. We fabricated TiO\textsubscript{2} electrodes based on mesoporous TiO\textsubscript{2} spheres, which have 2–3 times higher dye-loading capacity than nanocrystal electrode. The effects of filling the voids between the TiO\textsubscript{2} spheres with TiO\textsubscript{2} nanoparticles as the binder

<table>
<thead>
<tr>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>FF</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 0.70 ± 0.2</td>
<td>12.93 ± 0.1</td>
<td>0.64 ± 0.3</td>
<td>5.83 ± 0.06</td>
</tr>
<tr>
<td>N-S1 0.69 ± 0.0</td>
<td>14.13 ± 0.2</td>
<td>0.62 ± 0.1</td>
<td>6.17 ± 0.07</td>
</tr>
<tr>
<td>N-S1-P 0.79 ± 0.1</td>
<td>14.53 ± 0.1</td>
<td>0.66 ± 0.3</td>
<td>7.66 ± 0.04</td>
</tr>
<tr>
<td>S2 0.72 ± 0.2</td>
<td>11.75 ± 0.1</td>
<td>0.64 ± 0.2</td>
<td>5.47 ± 0.07</td>
</tr>
<tr>
<td>N-S2 0.69 ± 0.1</td>
<td>13.67 ± 0.3</td>
<td>0.60 ± 0.3</td>
<td>5.72 ± 0.04</td>
</tr>
<tr>
<td>N-S2-P 0.72 ± 0.0</td>
<td>14.03 ± 0.1</td>
<td>0.63 ± 0.2</td>
<td>6.19 ± 0.06</td>
</tr>
<tr>
<td>NC 0.70 ± 0.1</td>
<td>10.05 ± 0.0</td>
<td>0.64 ± 0.2</td>
<td>4.50 ± 0.05</td>
</tr>
</tbody>
</table>

#### Table 3

Dye-loading capacity of the various photoelectrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Amount of adsorbed dye per unit area (μmol/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>209.96</td>
</tr>
<tr>
<td>N-S1</td>
<td>255.34</td>
</tr>
<tr>
<td>N-S1-P</td>
<td>253.50</td>
</tr>
<tr>
<td>S2</td>
<td>191.48</td>
</tr>
<tr>
<td>N-S2</td>
<td>224.03</td>
</tr>
<tr>
<td>N-S2-P</td>
<td>218.91</td>
</tr>
<tr>
<td>NC</td>
<td>110.97</td>
</tr>
</tbody>
</table>

![Fig. 12. IPCE spectra of the DSSCs prepared from S1, S2 and NC.](Image)
were investigated. The mesoporous TiO2 spheres act as scattering centers that improved light scattering without damaging the dye-loading capacity of the internal surface area, and the TiO2 nanoparticles successfully filled the large voids between the TiO2 spheres and improved the connectivity for charge transport. The TiO2 electrodes were compressed to improve the connectivity between the large TiO2 spheres and the adhesion of the film with the FTO substrate. This compression was found to result in higher energy conversion efficiency than the one obtained with TiO2 nanoparticles alone. The improved dye-loading capacity and light scattering efficiency, and better electrical connectivity of the film are important characteristics of the electrodes produced by these methods. An overall energy conversion efficiency of 7.66% has been achieved by using these TiO2 sphere/nanoparticle composite electrodes in DSSCs, which is significantly higher than that one arose from TiO2 nanoparticle electrodes of similar thickness (4.50%).

Acknowledgment

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (R11-2005-065).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.powtec.2013.02.036.

References