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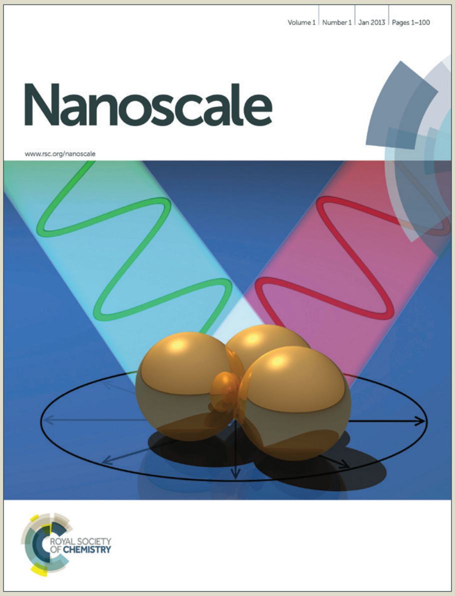

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# Geometrical implication of ion transporters employing ellipsoidal hollow structure in pseudo-solid electrolytes

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We demonstrate facilitated ion transport in oligomer electrolytes by introducing $TiO_2$ hollow particles of ellipsoidal and spherical shapes. It was found that the $TiO_2$ hollow particles of ellipsoidal shape are much more effective to construct ionic diffusion paths for the Grotthuss mechanism, resulting in highly enhanced diffusion coefficients of ions such as $I^-$ and $I_3^-$ in oligomer electrolytes. Compared to the hollow spheres of $TiO_2$ component, the ellipsoidal hollow particles of $TiO_2$ component provide 11% larger ionic diffusion coefficients, because of their geometry with a relatively small diffusion resistance. Since the facilitated ion transport can render fast redox reactions at both photo and counter electrodes, the solid state dye-sensitized solar cells employing oligomer electrolytes based on the $TiO_2$ hollow ellipsoids exhibit highly improved photovoltaic performances including highly improved energy-conversion efficiency without destabilizing the cell.

## Introduction

Since particles of hollow structure have unique properties, for example, low density, large surface area, and large scattering effect of light,[1, 2] they have a variety of potential applications such as catalysts, batteries, capacitors, and solar cells.[3-8] Typically, the hollow structure is constructed by deposition of nanoparticles onto templates and then removing the templates.[9, 10] While hollow particles have been developed mostly based on templates of spherical shape (denoted HSs) to date, spherical shape is not the only form that the hollow particles can have. Recently, the preparation and performance examination of non-spherical hollow particles have been given lots of interest.[11-13] Nevertheless, the fabrication of non-spherical hollow particles still remains highly challenging due to the tendency of disastrous structural collapses during the removal of template components.[14, 15]

Employment of hollow particles of $TiO_2$ with spherical shape, that is $TiO_2$ HSs, has been reported successful as additives for oligomer electrolytes of solid state dye-sensitized solar cells (DSSCs).[16] The hollow particles are capable of inducing the Grotthuss mechanism, which explains ion transport via an ion-exchange reaction between adjacent ions. Since the Grotthuss mechanism is much faster than the conventional ion transport governed by Fick's law in oligomer electrolytes,[17] the overall ionic diffusion could be facilitated by adding hollow particles. However, the HSs may not be optimal additives to construct diffusion paths for the Grotthuss mechanism, since the contact area between spherical particles is relatively small, indicating less efficient networks for ionic diffusion paths. Compared with the HSs, it can be expected that hollow ellipsoids (denoted HEs) would be more effective additives to enhance ion transport due to their shape with a low curvature and a high aspect ratio, causing a much larger contact area between the particles and thus a relatively small diffusion resistance of ions.[18, 19]

In this study, the effect of the geometrical shape of hollow particles on ionic diffusion in electrolytes of solid state DSSCs is investigated. The HEs of uniform size and shape were fabricated and then introduced into oligomer electrolytes as additives, which were utilized for solid state DSSCs. We confirmed that the hollow particles with ellipsoidal shape have a large advantage in increasing ionic diffusion coefficients in oligomer electrolytes, which enables the DSSCs to improve their energy-conversion efficiency.

## Experimental

**Preparation of ellipsoidal hollow particles.** Spherical polystyrene (PS) beads were synthesized by emulsion polymerization.[20] Styrene (20 g) and sodium dodecyl sulfate (0.2 g) were mixed with deionized water (200 ml) via mechanical stirring at 500 rpm. Under a nitrogen atmosphere, the temperature of the solution was maintained at 70 ºC. 0.1 g of ammonium persulfate was added into the solution to initiate polymerization and the reaction was performed for 16 h. After purifying via dialysis, the product was collected by centrifugation. Ellipsoidal PS templates for hollow particles were obtained by uniaxial stretching of the PS beads. The prepared PS beads were mixed with an aqueous solution (10 wt%) of poly(vinyl alcohol) (PVA, $M_w$ = ~50,000 g/mol) and then the PVA films containing the PS beads were prepared via solution casting. The resulting films with a thickness of ~100 μm were cut into a strip of 120 × 35 $mm^2$, which were stretched at 200 ºC to change the shape of the embedded PS beads. The aspect ratio of the elongated particles was controlled by the degree of the elongation of each film. Since the PVA part in the strip can be dissolved in a mixture of deionized water and isopropanol at 60 ºC, the elongated PS particles are obtained by filtration. The $TiO_2$ shell was constructed on the surface of the ellipsoidal PS particles using a hydrolysis reaction of $TiCl_4$ solution (0.2 M) at 50 ºC for 1 h.[6, 16] The $TiO_2$ coated particles were rinsed with deionized water and then collected via centrifugation. The hollow structure for $TiO_2$ ellipsoidal particles was constructed by removing the PS cores with thermal treatment at 500 ℃ for 1 h. For comparison, $TiO_2$ HSs were also prepared by using the spherical PS beads before elongation. All other processes were identical to the fabrication of the HEs.

**Fabrication of DSSCs.** A reference electrolyte consists of 0.8 M 1-butyl-3-methylimidazolium iodide, 0.1 M iodine and 0.1 M N-methylbenzimidazole in poly(ethylene glycol) dimethylether ($M_w$ = 250 g $mol^{-1}$).[21] The composite electrolytes were prepared by adding either 10 wt% of ellipsoidal or spherical $TiO_2$ hollow particles into the reference electrolyte. The fabrication process for photo and counter electrodes of DSSCs has been described in references.[21-23] To construct a photoelectrode, $TiO_2$ paste (Dyesol, 18NR-T) was cast on fluorine-doped tin oxide (FTO) glass (Pilkington, TEC-8, 8 Ω $sq^{-1}$), and then sintered at 500 ℃ for 15 min. The resulting $TiO_2$ electrode with a thickness of 12.0 μm was sensitized with a purified N719 dye solution. The counter electrode was formed on FTO glass by spin-coating of a $H_2PtCl_6$ solution (0.01 M in isopropanol) and annealing at 400 ℃ for 20 min. The photo and counter electrodes were assembled by using a thermal adhesive film (60 μm thick). The space between two electrodes was filled with the prepared electrolytes through the holes at the counter electrode.

**Characterization.** The morphology of the pristine PS beads, elongated PS particles, $TiO_2$-coated PS ellipsoidal particles and $TiO_2$ HEs was observed with scanning electron microscopy (SEM). In particular, the hollow structure of the particles was confirmed by using transmission electron microscopy (TEM). The crystal structure of the $TiO_2$ hollow particles was characterized with X-ray diffraction (XRD). The specific surface area of the hollow particles was quantified by Brunauer–Emmett–Teller (BET) measurements. Through the linear sweep voltammetry method with an ultramicroelectrode,[24, 25] steady-state currents were measured to obtain the diffusion coefficients of $I^-$ and $I_3^-$ in oligomer electrolytes. The incident photon-to-current conversion efficiency (IPCE) of the DSSCs was measured under a monochromatic beam generated from a Xenon lamp of 75 W. The photovoltaic characteristics and long-term stability of the DSSCs were investigated under 1 sun condition (100 mW $cm^{-2}$, AM 1.5) using Keithley 2400 and a Xenon lamp of 1000 W.

## Results and discussion

To investigate how the geometrical shape of hollow particles affects ionic diffusivity in oligomer electrolytes, we tried to prepare hollow particles with different aspect ratios. Such hollow particles can be obtained by deposition of oxide nanoparticles on surface of polymer templates with designed shape and subsequently removing the templates via thermal treatment. Figure 1(a) shows the morphology of the pristine PS beads prepared via emulsion polymerization. They are monodisperse and have a perfectly spherical shape with mean diameter of ~240 nm. When the size of the templates was larger than 500 nm, we observed that the hollow structure of the ellipsoidal particles mostly collapsed due to the asymmetric volume shrinkage during the template removal. Conventionally, the coating layers with increased thickness have been utilized to avoid the collapse.[26] However, the hollow particles with a thick shell will not be highly effective to enhance ionic diffusion coefficients due to their small specific surface area. To address this issue, we selected relatively small templates and coated thin $TiO_2$ layers for the fabrication of ellipsoidal hollow particles. The prepared PS beads were embedded in PVA films and then elongated in a uniaxial direction above the glass transition temperatures of PS and PVA. This process resulted in the shape change of the embedded PS particles from a sphere to an ellipsoid. Moreover, the aspect ratio of the products could be controlled by the degree of the elongation, as shown in Figure 1(b), (c), and (d). The aspect ratio of PS beads to degree of elongation for PVA films containing PS beads is illustrated in Figure S1 in Supplementary Information. The elongated particles were employed as the templates for HEs.

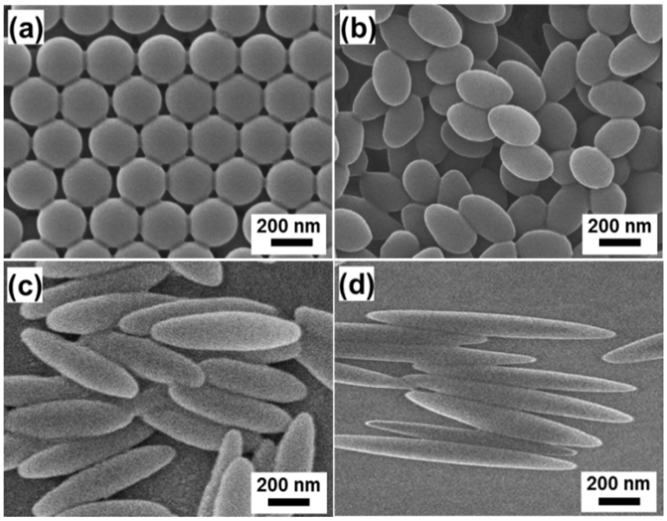

**Fig. 1**. SEM images of (a) spherical PS beads and ellipsoidal PS particles with aspect ratios of (b) 2:1, (c) 4:1, and (d) 8:1, respectively.

$TiO_2$ is one of the well-known materials to adsorb cations due to the negative surface charges.[27] In addition, when using $TiO_2$ particles as additives for oligomer electrolytes, the Coulomb interaction between cations and anions in the electrolytes allows the ion pairs to be arranged around the $TiO_2$ particles, constructing ion diffusion paths.[16, 28] To increase the surface area and thereby to enhance the ion transfer behavior of $TiO_2$ components in oligomer electrolytes, the connected structure of nano-sized $TiO_2$ particles is desirable, and thus, the surfaces of elongated PS particles were coated with $TiO_2$ nanoparticles.

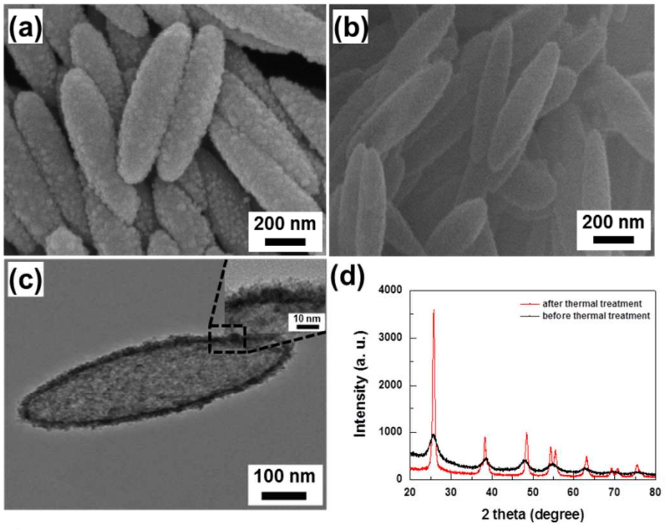

**Fig. 2**. SEM images of (a) ellipsoidal PS/$TiO_2$ core-shell particles and (b) $TiO_2$ HEs. (c) TEM image of $TiO_2$ HEs. (d) XRD spectra of ellipsoidal PS/$TiO_2$ core-shell particles and corresponding $TiO_2$ HEs.

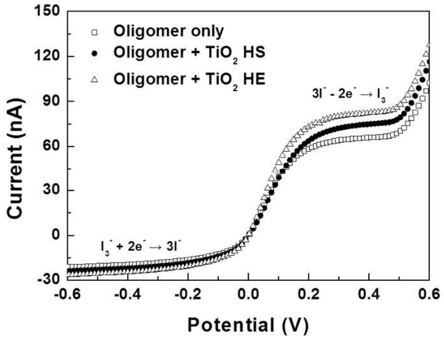

**Fig. 3**. Steady-state voltammograms of oligomer-based electrolytes with/without hollow particles. The curves were measured with a scan rate of 10 mV/s.

In particular, when the PS particles with aspect ratio of 8:1 were used as template, it was very hard to obtain hollow structure of $TiO_2$ components due to the disastrous collapse of $TiO_2$ framework during thermal treatment. In addition, in the case of PS particles with the aspect ratio lower than 4:1, it was hardly to meet monodisperse morphology, which is a critical factor in evaluating the shape factor effect. Since the primary aim in this work is to examine the effect of morphological shape factor of electrolyte additives on the ion transport, i.e. the difference between sphere and ellipsoid, the aspect ratio was fixed at 4:1 in this work, and the fabrications of $TiO_2$-coated PS ellipsoids and hollowed $TiO_2$ ellipsoids were conducted, as shown in Figure 2. Figure 2(b) and (c) show the morphology of the prepared HEs. The length and width of the $TiO_2$ HEs are about 630 and 150 nm, respectively, and the thickness of the walls is around 10 nm, as shown in Figure 2(c). The spherical $TiO_2$ hollow particles were prepared by using same procedure except for a elongation step. The diameter and thickness of the $TiO_2$ HSs are about 250 nm and 20 nm, respectively (Figure S2 in Supplementary Information). The specific surface areas of the $TiO_2$ HEs and HSs are 43 and 37 $m^2g^{-1}$, respectively. As shown in the XRD spectra of Figure 2(d), while the initial nature of the $TiO_2$ shells on PS particles was mostly amorphous, the thermal treatment for removal of the PS core imparted an anatase phase of high crystallinity to the $TiO_2$ components.

Poly(ethylene glycol) dimethyl ether-based oligomer electrolytes were mixed with 10 wt% of the $TiO_2$ hollow particles with different shapes, which are HEs and HSs, respectively. On the basis of the previous research,[16] introducing 10 wt% of $TiO_2$ hollow particles into oligomer electrolyte was thought to be the most effective in enhancing ionic diffusion coefficients. Moreover, the 10 wt% of the $TiO_2$ HEs were nearly the maximum wettable amount by the oligomer electrolyte. The $TiO_2$ HEs seem to be randomly distributed in oligomer electrolytes because they have a large volume per unit mass as shown in Figure S3 in Supplementary Information, indicating a low packing density of the particles.[18, 29] The change in the ionic diffusivity of the oligomer electrolytes was investigated in terms of the shape of the $TiO_2$ particles. The diffusion coefficients of $I^-$ and $I_3^-$ in the electrolytes can be evaluated from the steady-state current ($I_{ss}$) using the following equation.[16, 22, 28]

$$I_{ss} = 4nFDCr,$$

where n is the electron number per molecule, F is the Faraday constant, D is the diffusion coefficient, C is the bulk concentration of the electroactive species and r is the radius of the Pt microelectrode (~ 8 µm). We assumed that the concentration change of the electrolytes due to adding the hollow additives is negligible.

Figure 3 describes the steady-state voltammograms of the oligomer electrolytes with and without $TiO_2$ hollow additives. The composite electrolyte containing 10 wt% of the additives exhibit much higher steady-state currents than the reference electrolyte without any additives. Based on the steady-state current values, the diffusion coefficients of $I^-$ and $I_3^-$ in each electrolyte were calculated, as shown in Table 1. Compared to the reference electrolyte, the composite electrolyte with $TiO_2$ HEs exhibited about 25% larger diffusion coefficients of both $I^-$ and $I_3^-$. The diffusion of these anions in the oligomer electrolytes is conducted by two mechanisms, which are ion transport according to the Fick's law and ion exchange due to the Grotthuss mechanism.[17, 28] The $TiO_2$ hollow additives hardly affect the ion transport by Fick's law because the concentration change of the electrolytes is negligible when introducing the additives,[28, 30] and thus, it can be reasonable to conclude that the increase in the diffusion coefficients of the composite electrolytes is mainly imparted by the enhancement of the ion exchange process.[16]

The Grotthuss-like mechanism in oligomer electrolytes can be described as exchange reactions between $I^-$ and $I_3^-$ anions (Figure 4). Since the imidazolium cations in the electrolytes are adsorbed on the surfaces of the $TiO_2$ particles, $I^-$ an $I_3^-$ in the electrolytes can be arranged around the $TiO_2$ particles by an electrostatic force.[28, 31] Those $I^-$ and $I_3^-$ have high chances to contact with each other, resulting in facilitated ion transport by the ion-exchange reactions. We observed that the anions in the electrolytes with $TiO_2$ HEs can be diffused faster than those in the electrolyte with $TiO_2$ HSs (Table 1), indicating that the $TiO_2$ HEs provide more effective diffusion paths for ions than even the $TiO_2$ HSs. It is because the HEs have a desired geometry with a large contact area between particles, providing a benefit for the ion-exchange process.[18, 19, 32] Furthermore, since the ion exchange occurs along the surfaces of the hollow particles, the long axis of the HEs would be beneficial to transport ions further without hopping between particles.

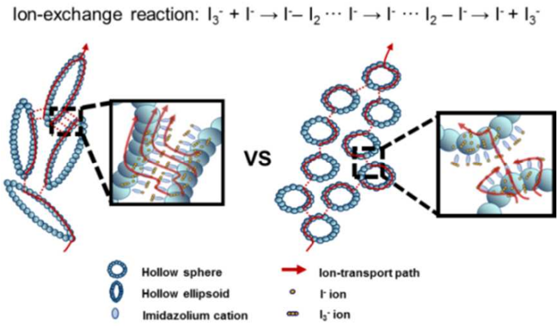

**Fig. 4**. Schematic diagram of proposed ion-transport mechanism in oligomer electrolytes via $TiO_2$ HEs or $TiO_2$ HSs.

**Table 1**. Diffusion coefficients of active species in oligomer-based electrolytes with/without hollow particles and photovoltaic characteristics of DSSCs employing the electrolytes.

| Electrolyte | Diffusion coefficient ($10^{-7}$ cm$^2$ s$^{-1}$) | | Cell performance | | | |
|---|---|---|---|---|---|---|
| | $I^-$ | $I_3^-$ | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | η (%) |
| Oligomer only | 4.44 | 2.66 | 0.66 | 10.32 | 0.60 | 4.06 |
| Oligomer + 10 wt% $TiO_2$ HS | 5.01 | 2.99 | 0.65 | 12.74 | 0.61 | 5.04 |
| Oligomer + 10 wt% $TiO_2$ HE | 5.56 | 3.32 | 0.66 | 14.71 | 0.62 | 6.06 |

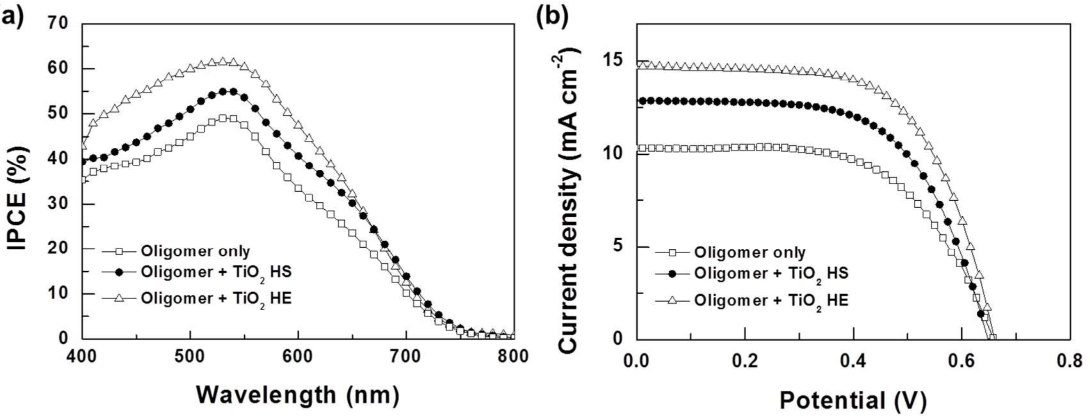

**Fig. 5**. (a) IPCE spectra and (b) J-V curves of DSSCs employing oligomer-based electrolytes with/without hollow particles.

Figure 4 illustrates the proposed ion-transport mechanism in oligomer electrolytes with $TiO_2$ HEs or HSs. Based on these, the HEs can reduce a resistance in the ion-exchange process and thus fast transport of the anions compared to the HSs. Typically, the rate of redox reactions at photo- and counter-electrodes in DSSCs is determined by the diffusion rate of ions in electrolytes. Oligomer electrolytes particularly are suffering from the slow diffusion of $I^-$ and $I_3^-$, resulting in a low energy-conversion efficiency of the DSSCs.[32] The large increase in the diffusion coefficients of $I^-$ and $I_3^-$ in oligomer electrolytes due to adding the HSs can be helpful in improving the performance of the oligomer-based DSSCs.

Figure 5(a) shows the IPCE spectra of the DSSCs employing the oligomer electrolytes with and without $TiO_2$ hollow additives. The additives can increase the IPCE values by two possible reasons. One is the light scattering and the other is the facilitated ion transport. The light scattering is dominant at the relatively long wavelengths (over 600 nm) while the facilitated ion transport is effective in the entire range of wavelengths.[33] Since the increase in the IPCE values of the DSSCs is observed in the entire range of wavelengths, it seems mainly related to the enhancement in the ionic diffusion coefficients by adding the hollow additives.[16] Moreover, as expected from the diffusion coefficients of $I^-$ and $I_3^-$ in the electrolytes, the $TiO_2$ HEs are more efficient to enhance the IPCE values compared to the $TiO_2$ HSs. Regardless of the shape of the hollow particles, the DSSCs with the different additives show comparable IPCE values at the wavelengths of over 650 nm where the light scattering is effective. Accordingly, we believe that the IPCE spectra were also affected by the light scattering and the HSs induced relatively large light-scattering effect compared to the HEs.

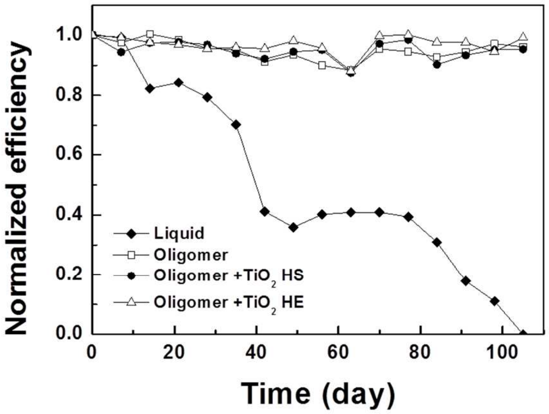

**Fig. 6**. Long-term stability of DSSCs employing various electrolytes.

The improvement of the IPCE values results in the increase in the short-circuit current ($J_{sc}$) of the DSSCs, as shown in Figure 5(b). When utilizing the $TiO_2$ HEs, the DSSCs show 43% increased $J_{sc}$ without deteriorating other characteristics such as the open-circuit voltage and fill factor. The escalated level in the $J_{sc}$ is mainly caused by the facilitated ion transport that brings out fast redox reactions at both photo and counter electrodes. As a consequence, the DSSCs containing the $TiO_2$ HEs exhibit a notable change in the photovoltaic performance; the energy-conversion efficiency improvement was about 20% over the cells with $TiO_2$ HSs, and more than 50% with no additives.In fact, we need a further effort to improve the somewhat low energy-conversion efficiency of the cells employing the $TiO_2$ HEs (6.06%), which might be possibly due to the partial lack of structural perfection in the hollow ellipsoids such as surface roughness or structural defects. Nevertheless, it can be told that the ion transport behavior in oligomer electrolytes is simply facilitated by the adoption of morphology control of $TiO_2$ additives. We believe there is a room for practical improvement, such as further increasing diffusion coefficient of ionic components via the use of better-controlled surface of $TiO_2$ HEs tunable by chemical preparation condition as well as the geometry of assembly.

The long-term stability of the DSSCs employing various electrolytes is also examined. As shown in Figure 6, even after over 100 days, all oligomer-based DSSCs maintained over 95% of their initial efficiency regardless of the hollow additives. On the contrary, the DSSCs with a volatile solvent electrolyte (acetonitrile and 3-methoxypropionitrile) showed gradually deteriorated performance with time and were extinguished at the end. Based on this result, we confirm that the oligomer electrolytes containing the $TiO_2$ hollow additives would be beneficial in energy-conversion efficiency without destabilizing the cell.

## Conclusions

Ellipsoidal $TiO_2$ hollow particles have been introduced to facilitate ion transport in oligomer electrolytes of large diffusion resistance of ions. The hollow ellipsoids of $TiO_2$ increase notably the diffusion coefficients of $I^-$ and $I_3^-$ in oligomer electrolytes due to the enhancement in the ion exchange process by means of the Grotthuss mechanism. Compared with the hollow spheres, the hollow ellipsoids provide more effective diffusion paths for ions, resulting from the desired geometry with a relatively small diffusion resistance. The facilitated ion transport via the $TiO_2$ hollow ellipsoids can lead to the faster redox reactions at the photo and counter electrodes in DSSCs hence improve the photovoltaic performance of the DSSCs. Moreover, the DSSCs employing the oligomer electrolytes with $TiO_2$ hollow ellipsoids showed a highly stable performance for several months. Consequently, we conclude that $TiO_2$ hollow ellipsoids can act as effective additives for oligomer electrolytes of DSSCs.

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## Notes and references

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Electronic Supplementary Information (ESI) available: [Figure S1. Aspect ratio of PS particles to degree of elongation for PVA films containing PS particles. / Figure S2. SEM images of the pristine spherical PS particles and the $TiO_2$ hollow spheres derived from formation of $TiO_2$/PS core-shell hybrid particles and subsequent removal of PS component and TEM image of the $TiO_2$ hollow spheres. / Figure S3. Photographs of 0.9 g of oligomer electrolyte, 0.1 g of $TiO_2$ hollow ellipsoidal particles, and composite electrolyte prepared via pouring the oligomer electrolyte onto the hollow particles and after complete mixing them.]. See DOI: 10.1039/b000000x/

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