Yolk@shell anatase TiO₂ hierarchical microspheres with exposed {001} facets for high-performance dye sensitized solar cells

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We report a facile, template-free and nontoxic one-pot solvothermal route of synthesizing submicrometer-sized yolk@shell hierarchical spheres, which possess a permeable shell self-assembled by ultrathin anatase TiO₂ Nanosheets (NSs) with nearly 90% of exposed {001} facets and mesoporous inner sphere with a high specific surface area. Compared to the {001} faceted TiO₂ NSs and standard Degussa P25, the anatase TiO₂ yolk@shell hierarchical spheres (TiO₂ YSHSs) were obtained with surface area up to 245.1 m²·g⁻¹ and their submicrometer scale simultaneously promoted light scattering in visible region. A light to electricity conversion efficiency (η) of 6.01% was achieved for the DSSCs with TiO₂ YSHSs as its photoanode, under 100 mW cm⁻² illumination, indicating 49.9% and 34.8% increases compared to the DSSCs with TiO₂ NSs (4.01%) and the standard Degussa P25 (4.46%) as photoanodes, respectively. The enhancement can be mainly attributed to the higher dye loading on TiO₂ YSHSs (4.35×10⁻⁵ mol·cm⁻²) than that of TiO₂ NSs (3.14×10⁻⁵ mol·cm⁻²) and P25 (3.32×10⁻⁵ mol·cm⁻²); longer lifetime of the injected electrons in TiO₂ YSHSs film (65.79 ms) than that of in TiO₂ NSs film (57.90 ms); and the good capability of light scattering of TiO₂ YSHSs in visible light region, which are confirmed by UV-vis spectrophotometer and electrochemical impedance spectroscopy (EIS). The growth mechanism of the TiO₂ YSHSs has also been investigated in detail.

1. Introduction

Since the report of dye sensitized solar cells (DSSCs) by O'Regan and Grätzel in 1991, DSSCs have captured extensive research interest for their ease of fabrication, theoretical high efficiency and low manufacturing cost compared with silicon-based photovoltaic devices.1–5 So far, the power conversion efficiency of DSSC has broken through 12% under 1 sun of illumination reported by Yella et al. with a specially designed redox mediator containing cobalt (Co) complexes and zinc porphyrin dye as sensitizer.6 Besides the presentation of new sensitizing dyes and redox couples for DSSCs, considerable efforts have been devoted to the development of more efficient photoanode materials including a wide range of TiO₂ nanoparticles with desirable shape, structure and crystallinity.5–12

Typically, the most available anatase TiO₂ nanoparticles used in photoanodes are dominated by the thermodynamically stable {101} facets (more than 94%, according to the Wulff construction).13–15 In 2008, on the basis of theoretical predictions, Yang et al. firstly synthesized micrometer-sized anatase single crystals with 47% of the highly reactive {001} facets by using hydrofluoric acid (HF) as a capping agent under hydrothermal conditions.15 Following this breakthrough, extensive efforts have been made in synthesis, characterization, and application of these anatase TiO₂ with {001} facets.16–18 According to the theoretical structures, all of the Ti atoms on ideal {001} facets are five-fold-coordinated (5c) and only half of the Ti atoms on {101} facets are not fully coordinated. The comparatively more dye molecules adsorption is thus expected to occur on {001} facets, which is also supported by theoretical and experimental results.19–21 Moreover, the band edges of anatase TiO₂ {001} facets are more negative than {101} facets.22 However, to the best of our knowledge, most of these anatase TiO₂ exposed by {001} facets used in DSSCs are 2D sheetlike nanocrystals or microspheres closely packed by micro/submicro-sized anatase TiO₂ nanosheets (TiO₂ NSs).20, 23–26 Due to the layer-by-layer stacking of anatase TiO₂ NSs and the large size of the packed TiO₂ NSs, the specific surface areas of photoanode films composed of these anatase...
TiO₂ are comparatively lower than those TiO₂ nanoparticles (TiO₂ NPs), which may to some extent inhibit the performance of DSSCs.\textsuperscript{19, 27} It is now well accepted that a high-efficiency photoanode for DSSCs requires not only a high surface area for dye molecules loading but also a good capability of light scattering for enhancing the light-harvesting. Among various morphologies for TiO₂ nanostructures such as nanowires, nanotube and nanosheets,\textsuperscript{5, 8, 25} hollow structures and mesoporous beads have a low density, high surface area and efficient light scattering and may applied as multifunctional photovoltaic materials in DSSCs.\textsuperscript{9, 11} Recently, “yolk@shell” nanostructures or so-called “rattle-type” nanomaterials are emerging as an interesting new member of the family of hollow nanoarchitectures.\textsuperscript{28, 29} The unique physical properties of yolk@shell nanostructures enable them as attractive materials in applications of optical, electronic, magnetic, catalytic, and sensing devices.\textsuperscript{30, 31} More importantly, the void space as well as shells and inner yolks in the yolk@shell nanostructure could be easily altered alongside numerous synthetic methods including the bottom-up, soft templating or selective etching approaches, etc.\textsuperscript{28, 32} However, the application of this kind of hierarchical architectures in DSSCs is up to date extremely sparse.\textsuperscript{34} For this reason, it is of a great opportunity to design and synthesize a multifunctional photoanode material on the base of yolk@shell nanostructures.

Herein, we report a facile, template-free and nontoxic one-pot solvothermal route of synthesizing submicrometer-sized yolk@shell hierarchical spheres, which possess a permeable shell self-assembled by ultrathin anatase TiO₂ NSs with nearly 90% of exposed {001} facets and mesoporous inner sphere with a high specific surface area. Compared to the {001} faceted TiO₂ NSs and standard Degussa P25, the anatase TiO₂ yolk@shell hierarchical spheres (TiO₂ YSHSs) were obtained with surface area up to 245.1 m² g⁻¹ and their submicrometer scale simultaneously promoted light scattering in visible region. As a result, overall light conversion efficiency (η) of 6.01% has been achieved, indicating 49.9% and 34.8% increases compared to the TiO₂ NSs (4.01%) and the standard Degussa P25 (4.46%) photoanodes, respectively.

2. Experimental

2.1 Materials Synthesis

a. The anatase TiO₂ YSHSs were synthesized with a modification to the previous report.\textsuperscript{35} In a typical synthesis, 0.03-0.05 mL of diethylentetriamine (DETA; 99%, Sigma-Aldrich) was added to 40 mL of isopropyl alcohol (IPA; 99.5%, Sinopharm) in a Teflon-lined autoclave (90 mL in volume) and the resulting mixture was stirred constantly for 5 min. Then, 1.5 mL of titanium (IV) isopropoxide (TIP; 97%, Sigma-Aldrich) was added to the above mixture under vigorous stirring for another 10 min. After the reaction at 200 °C for 24 h in an electric oven, light yellow precipitate was harvested via centrifugation, washed with ethanol three times, and dried at 60 °C overnight. Finally, the TiO₂ YSHSs was calcined at 400 °C for 2 h with a heating rate of 2 °C min⁻¹ in air atmosphere to obtain a highly crystalline anatase phase.

b. Anatase TiO₂ NSs were prepared by a hydrothermal method as reported previously.\textsuperscript{42} Briefly, 5 mL of TIP and 0.6 mL of HF (48 wt%, Sigma-Aldrich) were mixed in a Teflon-lined 50 mL autoclave at room temperature, and then kept at 180 °C for 24 h. After hydrothermal reaction, white precipitates were collected and washed with 0.1 M NaOH aqueous solution, deionized water and ethanol for several times to cleaning the adsorbed fluorine ions, and finally dried in an oven at 60 °C overnight.

2.2 Fabrication of DSSCs

For preparation of the TiO₂ photoanodes with TiO₂ YSHSs, TiO₂ NSs and P25, the viscous pastes were prepared by the following procedure. 0.5 g of the above samples were first dispersed into a mixture of 15 mL ethanol, 2.03 mL terpinol (mixture of isomer, Sigma-Aldrich) and 0.26 g ethyl cellulose (#46070, Sigma-Aldrich) and ultrasonicated for 30 min. The solvent was then evaporated at 45 °C to obtain the viscous paste. The prepared TiO₂ pastes were spread uniformly on the surface of the FTO glasses using the screen-printing technique and gradually heated in air at 325 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. After cooling to 80 °C, the TiO₂ photoanodes were soaked into 0.5 mM N719 dye solution in a mixture of acetonitrile (99.8%, Sigma-Aldrich) and tert-butyl alcohol (99.8%, Alfa Aesar) (volume ratio, 1:1) for 24 h at room temperature and then washed with ethanol and dried in air. The average thickness of the obtained TiO₂ nanoporous films was about 10 µm. Subsequently, the dye-covered TiO₂ photoanode and a thermal decomposition Pt counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 µm thickness made of the ionomer Surlyn 1702 (DuPont). The size of the TiO₂ film used was 0.25 cm² (5 mm × 5 mm). A drop of the redox electrolyte (0.6 M 1-Butyl-3-methylimidazolium iodide (BMI), 0.03 M I₂, 0.10 M guanidinium thiocyanate and 0.5 M 4-tet-butylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15) was introduced via vacuum back-filling.

2.3 Characterizations

The crystal structure was determined using X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer with Cu Kα radiation). Scanning electron microscopy (FESEM, HITACHI S4800) and transmission electron microscopy (TEM, J EM 2100F) were used to examine the structure of the samples. Brunauer-Emmett-Teller (BET) surface areas were determined by an ASAP 2010 nitrogen sorption isotherms apparatus. The amount of adsorbed dye was measured by desorbing the dye into 0.1 mM NaOH solution and by absorption measurement of the solution using the adsorption peak intensity of N719 at 530 nm by using a Cary 500 spectrophotometer. Photovoltaic properties of DSSCs were performed under one sun condition using a solar light simulator (Oriel, 91160, AM 1.5 globe). The power of the simulated light was calibrated to 100 mW cm⁻² using a Newport Oriel PV reference cell system (model 91150 V). I-V curve were measured and recorded by a Keithley model 2400 digital source meter by applying an external bias to the cells. The incident photon to current conversion efficiency (IPCE) test system was consisted of a model SR830 DSP Lock-In Amplifier and model SR540 Optical Chopper (Stanford Research Corporation, U.S.A.), a 7IL/PX 150 xenon lamp and power supply, and a 7ISW301 spectrometer. The EIS measurements were carried out
with an impedance analyzer (Parstat 2273, Princeton) in darkness at a bias potential of -0.65 V and 10 mV of amplitude over the frequency range of 0.1 Hz ~ 100 kHz. The diffuse-reflectance spectra were measured by using a Cary 500 spectrophotometer.

3. Results and discussion

Fig. 1 indicates the unique yolk@shell hierarchical structures of the calcined TiO$_2$ YSHSs (see the Experimental Section). As can be seen from the FESEM images in Fig. 1a, a number of perfect TiO$_2$ YSHSs with the size ranging from 1-1.5 µm are evenly distributed. As shown in the high magnification micrographs (Fig. 1b), the closely packed nanosheets (NSs) are clearly visible and randomly assemble on the surfaces of microspheres. From the cross-section of the cracked microspheres (Fig. 1c), the hierarchically structured outer spherical shell with a thickness of approximately 200 nm can be visualized to consist of constituent ultrathin NSs. Compared to the shell, the inner sphere with a diameter of about 650 nm has a much more smooth surface due to the closely accumulation of tiny TiO$_2$ nanocrystals. As mentioned above, the two kinds of hierarchical structures of shell and yolk may enormously enlarge the surface area of TiO$_2$ film and thereby enhance dye absorption and injection efficiency of photoexcited electrons into semiconductors. In addition, it is expected that the multilayered hollow-sphere structure should produce a multireflection of incident light in-between the hierarchical hollow spheres, so as to improve the efficiency of light harvesting. As shown in Fig. 1d, the crystallographic structures of the TiO$_2$ YSHSs have been confirmed by powder XRD to be the tetragonal anatase phase (JCPDS card no. 21/1272; space group $I4_1/amd$; $a_0 = 3.7852$ Å, $c_0 = 9.5139$ Å).

![Fig. 1 FESEM images (a-c) and XRD pattern (d) of the calcined anatase TiO$_2$ YSHSs.](image)

The detailed microstructures of the TiO$_2$ YSHSs were further investigated by TEM and HRTEM (Fig. 2). The gradual contrast of the TEM image (Fig. 2a) from the edge to the center of the sphere indicates that the entire sphere is indeed composed of a yolk-shell structure. As shown in Fig. 2b, it is reconfirmed that the self-organized NSs formed the shell of the sphere in a random orientations. Compare to the rectangular TiO$_2$ NSs obtained by HF-mediated condition (Fig. S1), the NSs on shell show a larger average size of about 100-200 nm and a thinner thickness ranging from 4 nm to 7 nm (Fig. 2c). The High-resolution TEM (HRTEM) image of a single NS on shell (Fig. 2d, inset) demonstrates a typical top-viewed indicative of {001} facets on anatase TiO$_2$. It can be observed that sets of the lattices oriented perpendicular to each other with an equal fringe spacing of 0.19 nm are in well agreement with the (200) and (020) planes of anatase TiO$_2$. The visible lattice fringes on other area of the NS also reveal with a distance of 0.19 nm (Fig. 2d). Therefore, it can be concluded that the NSs on shell are all single crystals and are bounded by {001} facets on both the top and bottom. On the basis of the above TEM and HRTEM results, we can roughly calculate the percentage of exposed {001} facets on the NSs and typical TiO$_2$ NSs obtained by using HF capping agent. The percentage of exposed {001} facets on shell NSs is about 87% which is a little bit higher than that of TiO$_2$ NSs synthesized in HF solution (75%). The crystal structures of the inner spheres were also investigated from a crashed TiO$_2$ YSHSs (Fig. 2 e-f). Lattice images are clearly observed, indicating the inner sphere composed of tiny TiO$_2$ beads with diameters of about 10 nm have high crystallinity despite the closely random aggregation. The HRTEM image shown in Figure 2f, allows the lattice fringes of the crystals to be correlated with the (101) plane of the anatase TiO$_2$. These suggested that the shells and inner spheres of the TiO$_2$ YSHSs are mainly exposed by different kinds of crystalline facets. The formation of this structure may result from a Ostwald ripening effect and the selective adsorption of diethylenetriamine (DETA) molecules on the specific crystalline surface of TiO$_2$, which have influence on the structures and exposed facets of the hierarchical structures.

![Fig. 2 TEM and HRTEM images of the annealed TiO$_2$ YSHSs (a-d) and crashed hemispherical TiO$_2$ YSHSs (e-f) prepared at 200 °C for 24 h.](image)

To clarify the growth mechanism of the as-prepared products, time-dependant experiments were carried out to reveal the formation process of TiO$_2$ YSHSs in more details (Fig. 3). In the
initial reaction stage, solid spheres have formed due to the alcoholysis of Ti(O-i-C\(_3\)H\(_7\))\(_4\) shown in Fig. 3a. The diethylenetriamine (DETA) plays an important role in the alcoholysis of Ti(O-i-C\(_3\)H\(_7\))\(_4\), since no solid products can be collected even after solvothermal treatment of Ti(O-i-C\(_3\)H\(_7\))\(_4\) with isopropl alcohol (IPA) alone for 2 h. The presence of IPA may control alcoholysis and polycondensation reaction and lead to an even distribution of the solid spheres (Fig. 3a, S2a). The initial solid spheres show a poor crystalline quality (Fig. S3). It is generally thought that the initial solid spheres have higher surface energies and are more easily redissolved. So as solvothermal reaction proceeds to 12 h, the solid spheres shrink over time and newly alcoholysed spike-like nanoparticle occur and then assemble around the solid spheres (Fig. 3b, S2c-d) due to the Ostwald ripening process.\(^{34}\) The shell nanoparticles are not stable and will transfer from spike shape to sheet like structure with a prolonged ageing time (24 h). The tridentate DETA in the solvothermal system is hypothesized to play a key role in effectively stabilizing the emerging high-energy {001} facets and prohibiting the growth along [001] direction during ripening.\(^{35}\) The hydrogen bonds through the unreacted amino-groups on DETA which interconnect the alcoholysis products may be the another reason for the formation of a 2 D sheet-like nanostructure.\(^{36}\) The shell of the yolk@shell nanoparticles finally peels off from the surface of the yolk after 72 h of reaction (Fig. S2e-f).

To obtain an insight into the hierarchical structure of the shells and the porous structure of the inner spheres, we determined the pore-size distribution and BET surface area of the TiO\(_2\) YSHSs using nitrogen adsorption and desorption isotherms (Fig. 4). The TiO\(_2\) NSs sample was also tested here as a benchmark. It was found that the BET surface area of the TiO\(_2\) YSHSs presents quite a high value, 245.1 m\(^2\)/g, nearly two times than that of TiO\(_2\) NSs (88.9 m\(^2\)/g). The isotherms corresponding to the TiO\(_2\) YSHSs display the typical type IV curve according to the IUPAC classification, indicating a hysteresis loop at high relatively pressures associated with capillary condensation of gases within mesopores. The hysteresis loop is of type H2, which is consistent with pores with necks and wider bodies. The pore size distribution (Fig. 4b) calculated from the desorption branch of the nitrogen isotherm by the BJH method shows a wide range from 2 to 80 and distributions centred at with two salient peaks of 4 nm and 8 nm, respectively, which might be attributed to the different porous structures of yolk and shell.\(^{25, 26, 35}\) However, for the sample of TiO\(_2\) NSs, the shapes of the hysteresis loops change from type H2 to H3, demonstrating the presence of slit-like pores.

The high absorption at high relative pressure (P/P\(_0\)) in isotherms also indicates the formation of large mesopores and macropores. As reported earlier, the existing nanopores are from the aggregation of TiO\(_2\) NSs.\(^{26}\) The large BET surface area and mesopores structures of TiO\(_2\) YSHSs are thus believed to promote better transport of electrolyte and more adsorption of the dye molecules than TiO\(_2\) NSs.

In order to investigate the performance of TiO\(_2\) YSHSs as photoanodes for DSSCs, the TiO\(_2\) YSHSs photoanodes were tested under an illumination of one sun condition (AM 1.5 globe, 100 mW·cm\(^{-2}\)) and compared to these photoanodes made of TiO\(_2\) NSs and commercial TiO\(_2\) (P25). The DSSC is a very complicated system that requires electrodes to be similar in order to achieve a meaningful comparison. Thus, all electrodes for DSSCs tests were prepared by screen printing a thin TiO\(_2\) film on fluorine-doped tin oxide (FTO) glass and sintered at the same batch. The thickness of electrodes was controlled by the screen printing times, showing a similar value of about 10 µm. The characteristic current (I) vs voltage (V) curves and IPCE spectra of these DSSCs are given in Fig. 5, and their detail photovoltaic parameters derived from the I-V curves are summarized in Table 1. It can be seen that both the open-circuit photovoltage of the TiO\(_2\) NSs (V\(_{oc}\) = 790 mV) and TiO\(_2\) YSHSs (V\(_{oc}\) = 760 mV) are comparatively higher than that obtained from the commercial P25 DSSCs (V\(_{oc}\) = 733 mV). This is expectable because the flatband potential of the {001} facets was reported about 60 mV more negative than that of {101} facets and this leads to the increase of
open-circuit photovoltage of TiO$_2$ NSs and TiO$_2$ YSHSs photoanodes. Such alterations in open circuit and shifts in the flat band potential along crystallographic orientation have also been observed before in some SnO$_2$ based DSSCs. However, the slightly lower $V_{oc}$ value for TiO$_2$ YSHSs than that for the TiO$_2$ NSs sample implies that only the shells of TiO$_2$ YSHSs are dominated by {001} facets, and the inner spheres are composed of anatase TiO$_2$ nanocrystals with lower exposure of {001} facets.

However, due to the layer by layer stacking and oriental attachment of the TiO$_2$ NSs, the adsorption capacity of N719 on TiO$_2$ NSs is smaller than that on TiO$_2$ P25, which leads to the lower $J_{sc}$ value of TiO$_2$ NSs than that of TiO$_2$ P25. The overall photoconversion efficiency ($\eta$) of the TiO$_2$ YSHSs DSSC is about 6.01%, remarkably higher than those of TiO$_2$ P25 (4.46%) and TiO$_2$ NSs (4.01%) measured in our parallel experiments. It is deduced that the enhanced $\eta$ of the TiO$_2$ YSHSs DSSC is closely related with its larger amounts of anchored dye molecules. Fig. 5 displays the incident photo to current efficiency (IPCE) spectra for the several DSSCs. The IPCE is in good agreement with the $\eta$ of the solar cells. The IPCE is determined by the light absorption efficiency of the dye, the quantum yield of electron injection, and the efficiency of collecting the injected electrons at the conducting glass substrate, which is strongly affected by the photoanode properties of the DSSCs. Compared with the TiO$_2$ P25 and TiO$_2$ NSs films, the film of TiO$_2$ YSHSs had a higher IPCE over the whole range from 400 nm to 800nm. At the maximum value of the IPCE spectra at 530 nm, the IPCE of the film of the TiO$_2$ YSHSs was approximately 60.4 %, obviously higher than that of the TiO$_2$ P25 (44.6 %) and TiO$_2$ NSs (24.4 %) films.

The distinct photovoltaic performance of the TiO$_2$ YSHSs is largely due to its higher short-circuit current ($J_{sc}$ =13.1 mA cm$^{-2}$) compared with TiO$_2$ NSs ($J_{sc}$ =7.5 mA cm$^{-2}$) and TiO$_2$ P25 ($J_{sc}$ =10.2 mA cm$^{-2}$). Moreover, as is given in Table 1, the sequences of $J_{sc}$ values of these DSSCs are constant to that of the eluted dye concentration from these TiO$_2$ films. Therefore, this enhanced photocurrent could be attributed to better dye adsorption and light-harvesting efficiency, due to its extraordinarily high surface area and the special yolk@shell hollow spherical structure.

![Diagram](image)

**Fig. 5** I-V characteristics (a) and IPCE spectra (b) of DSSCs with photoelectrode films composed of TiO$_2$ P25, TiO$_2$ NSs and TiO$_2$ YSHSs, respectively.

<table>
<thead>
<tr>
<th>DSSCs</th>
<th>Adsorbed dye [$\times 10^3$ mol·cm$^{-2}$]</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$V_{oc}$ [mV]</th>
<th>FF</th>
<th>$\eta$ [%]</th>
</tr>
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<tbody>
<tr>
<td>P25</td>
<td>3.32</td>
<td>10.2</td>
<td>733</td>
<td>0.60</td>
<td>4.46</td>
</tr>
<tr>
<td>NSs</td>
<td>3.14</td>
<td>7.5</td>
<td>790</td>
<td>0.68</td>
<td>4.01</td>
</tr>
<tr>
<td>YSHSs</td>
<td>4.35</td>
<td>13.1</td>
<td>760</td>
<td>0.60</td>
<td>6.01</td>
</tr>
</tbody>
</table>

**Table 1** Comparison of short-circuit photocurrent density ($J_{sc}$), open-circuit photovoltage ($V_{oc}$), fill factor (FF), overall photo-conversion efficiency ($\eta$) along with the amount of adsorbed dye N719 for the films composed of TiO$_2$ P25, TiO$_2$ NSs and TiO$_2$ YSHSs, respectively.

![Diagram](image)

**Fig. 6** (a) Schematic illustration of the multiple reflecting and scattering of light in the TiO$_2$ YSHSs. (b) Diffuse-reflectance spectra of the films of TiO$_2$ YSHSs, TiO$_2$ NSs and TiO$_2$ P25 with the similar thickness of about 10 µm.

Fig. 6a illustrates the possible reflecting and scattering of light...
in film of TiO$_2$ YSHSs and inside of the single TiO$_2$ YSHS. It is believed that the out shell assembled by the random oriented NSs in a micro-sized TiO$_2$ YSHS can not only multireflect, but also scatter the incident light of different wavelengths in the whole range of visible light.\textsuperscript{38} UV-vis diffuse reflectance spectra of the three TiO$_2$ films were thus investigated here (Fig. 6b) to explore their different light scattering and transmittance capabilities. Comparatively, the TiO$_2$ NSs and TiO$_2$ P25 films present little diffuse reflectance in the visible region and a rapid decrease in diffuse reflection capacities were observed for both films as the wavelength increased from 400 to 800 nm due to their small particle size. This would cause the unabsorbed light to penetrate through the films without being back scattered to enhance light absorption. In contrast, the TiO$_2$ YSHS film exhibit high diffuse reflectance in the visible range of 400-700 nm and only a slight decline could be noticed beginning at 700 nm. Overall, the reflectance of the film of TiO$_2$ YSHS is much higher than that of TiO$_2$ NSs and TiO$_2$ P25 in the whole wavelength range from 400 to 800 nm, pointing at the key role of the yolk@shell hierarchical microspheres in the film in dominating the light scattering behavior. Therefore, the TiO$_2$ YSHS as bi-functional photoanode materials can not only drastically increase the dye loading rate but also maximize the absorption of light in the range of 400 to 800 nm, and thus enhance the light harvesting efficiency.

Electrical impedance spectroscopy (EIS) can provide additional information and deeper understanding on the dynamics of electron transport and recombination in electrodes, electron transfer between the counter electrode and electrolyte, and I$_3^-$ diffusion in the electrolyte.\textsuperscript{38-41} To reveal the difference in the interfacial characteristics of the TiO$_2$ YSHSs and TiO$_2$ NSs photoanodes, EIS spectra of the DSSCs were tested in dark at a bias DC voltage of 0.65 V and 10 mV of amplitude over the frequency range of 0.1 Hz-100 kHz. Fig. 7a shows the Nyquist plots under the open-circuit condition for the DSSCs using TiO$_2$ YSHSs and TiO$_2$ NSs as photoanodes, respectively. An equivalent circuit model (see the inset in Fig. 7a) was given to recognize the total series resistance (R$_s$), charge-transfer resistance (R) and the corresponding constant phase angle element (CPE) in DSSCs. In general, the first semicircle in the high frequency region ($10^2$-10$^3$ Hz) represents the impedance corresponding to the reoxidation of $\Gamma$/$I_3^-$ at the Pt/electrolyte interface (R$_s$), while the semicircles in intermediate frequencies ($10^1$-10 Hz) and low frequency region (10-0.1 Hz) give information on the impedance at oxide/dye/electrolyte interface (R$_2$) related to the charge transport/recombination and finite diffusion of the electrolyte (R$_1$), respectively.\textsuperscript{39-41} The fitted data are all listed in Table 2 indicating several features of the two TiO$_2$ photoanodes. Firstly, the R$_2$ and R$_1$ values for both the DSSCs are similar, simply because both the TiO$_2$ electrodes and counter electrodes used in DSSCs assembly were printed and heated under the same conditions. Secondly, the R$_2$ value of TiO$_2$ YSHSs is slightly higher than that of the TiO$_2$ NSs electrodes. Here, R$_3$ is usually considered to be mainly determined by the charge recombination resistance, with partial contribution from transport resistance, suggesting that the TiO$_2$ YSHSs film contributed to an increase in the charge transfer resistance. This result can be explained by the fact that the specific surface area of the TiO$_2$ YSHSs photoanode is larger than that of the TiO$_2$ NSs electrode and leads to much more grain boundaries in the TiO$_2$ interface, thereby increasing the recombination rate in the film. Finally, from the values of R$_3$, The TiO$_2$ YSHSs photoanode is expected to have a better penetration of the redox $\Gamma$/$I_3^-$ for its comparatively lower R$_3$ value.

![Fig. 7 Electrical impedance spectroscopy (EIS) measurements; (a) Nyquist plots of the TiO$_2$ YSHSs and TiO$_2$ NSs films in the dark; and (b) the corresponding Bode plots. The inset in (a) displays the equivalent circuit model.](image)

Table 2 EIS parameters of the DSSCs determined by fitting the experimental data to the equivalent circuit model (see Fig. 7)

<table>
<thead>
<tr>
<th>DSSCs</th>
<th>R$_s$ (Ω)</th>
<th>R$_2$ (Ω)</th>
<th>R$_1$ (Ω)</th>
<th>$\omega_{max}$ (Hz)</th>
<th>$\tau_r$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSs</td>
<td>16.50</td>
<td>5.63</td>
<td>12.36</td>
<td>7.99</td>
<td>17.27</td>
</tr>
<tr>
<td>YSHSs</td>
<td>14.58</td>
<td>5.67</td>
<td>15.53</td>
<td>6.01</td>
<td>15.2</td>
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</table>

Bode phase plots (Fig. 7b) can be drawn from the Nyquist plots in Fig. 7a Two main frequency peaks and a slight frequency peak are observed. These peaks correspond to the charge transfer process at different interfaces within the DSSCs. It is found that the maximum frequency peak in the intermediate frequency regime, which is related to electron transfer in the TiO$_2$ YSHSs film, is lower than that of the TiO$_2$ film. According to the EIS model, the lifetime of injected electrons in the oxide film ($\tau_r$) can be estimated from the maximum angular frequency ($\omega_{max}$) of the impedance semicircle at middle frequencies in the Bode spectrum, according to the following relationship, $\tau_r = 1/\omega_{max} = 1/2\pi f_{max}$ where $f_{max}$ is the maximum frequency of the mid-frequency peak.\textsuperscript{38,41} From Table 2, it can be found that the $\tau_r$ for DSSCs with TiO$_2$ YSHSs and TiO$_2$ NSs photoanodes were
65.79 and 57.90 ms, respectively. These data suggest that the electron lifetime in the TiO$_2$ YSHSs photoanode is longer than that of the TiO$_2$ NSs photoanode. The measurement was taken at the open circuit condition and no current could pass through the external circuit. So the injected electrons must recombine with I$_3^-$ ions at the TiO$_2$ YSHSs film/dye/electrode interface. Therefore, the increase in the electron lifetime means that the produced electrons can diffuse further without interruption, such as recombination and trap within the film. The enhanced electron lifetime can be explained by the higher electron mobility through the single crystalline anatase TiO$_2$ YSHSs film. These factors are directly related to the improved efficiency of the DSSC using TiO$_2$ YSHSs as photoanode.

4. Conclusions

In summary, it is found that the photoanode of anatase TiO$_2$ YSHSs with an outer shell assembled by the NSs exposed by nearly 90% of [001] facets and a mesoporous inner microsphere exhibited a high photoconversion efficiency of 6.01%, indicating 44.9% and 34.8% improvement compared to the TiO$_2$ NSs and TiO$_2$ P25. The performance improvement is attributed to the high surface area and light scattering effect, as well as the high electron mobility of the TiO$_2$ YSHSs. The unique structure of TiO$_2$ YSHSs successfully takes advantage of the more negative band edge of [001] facets to increase the value of $V_{oc}$ and electron mobility without sacrificing the internal surface area needed for effective dye-uptake. In addition, the technique for synthesis TiO$_2$ YSHSs may be adopted to fabricate other multilayered hollow spheres with a hierarchical porous structure for clean energy applications.

Acknowledgements

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Notes and references

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Submicrometer-sized anatase TiO$_2$ yolk@shell possesses a permeable shell self assembled by ultrathin anatase TiO$_2$ nanosheets with nearly 90% of exposed {001} facets and a mesoporous inner sphere with a high specific surface area. As a result, overall light conversion efficiency ($\eta$) of 6.01% has been achieved.
Supporting Information

Yolk@shell anatase TiO₂ hierarchical microspheres with exposed \{001\} facets for high-performance dye-sensitized solar cells

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Fig. S1 SEM (a) and TEM (b-d) images of TiO₂ NSs synthesized through hydrothermal reaction of 5 mL of Ti(C₂H₅O)₄ and 0.6 mL of HF (48%) at 180 °C for 24 h.
Fig. S2 SEM images of the samples obtained after different reaction durations (a, b) 2 h, (c, d) 12 h, (d, f) 72 h.
Fig. S3 XRD patterns of the samples obtained after different reaction durations.
Dear Editors,

I am pleased to submit the manuscript titled “Yolk@shell anatase TiO$_2$ hierarchical microspheres with exposed {00} facets for high-performance dye-sensitized solar cells” for your kind consideration as full papers to *Journal of Materials Chemistry*. I certify that this is an original manuscript that has not been submitted elsewhere for publication. The following is a short description of the work and why we think it merits publication in *Journal of Materials Chemistry*.

Typically, the most available anatase TiO$_2$ nanoparticles used in photoanodes of dye sensitized solar cells are dominated by the thermodynamically stable {101} facets (more than 94%, according to the Wulff construction). In 2008, on the basis of theoretical predictions, we firstly synthesized micrometer-sized anatase single crystals with 47% of the highly reactive {001} facets by using hydrofluoric acid (HF) as a capping agent under hydrothermal conditions (Yang et al, *Nature*, 453, 2008, 638). Following this breakthrough, extensive efforts have been made in synthesis, characterization, and application of these anatase TiO$_2$ with {001} facets. According to the theoretical structures, all of the Ti atoms on ideal {001} facets are five-fold-coordinated (5c) and only half of the Ti atoms on {101} facets are not fully coordinated. The comparatively more dye molecules adsorption is thus expected to occur on {001} facets, which is also supported by theoretical and experimental results. Moreover, the band edges of anatase TiO$_2$ {001} facets are more negative than {101} facets. However, to the best of our knowledge, most of these anatase TiO$_2$ exposed by {001} facets used in DSSCs are 2D sheetlike nanocrystals or microspheres closely packed by micro/submicro-sized anatase TiO$_2$ nanosheets (TiO$_2$ NSs). Due to the layer-by-layer stacking of anatase TiO$_2$ NSs and the large size of the packed TiO$_2$ NSs, the specific surface areas of photoanode films composed of these anatase TiO$_2$ are comparatively lower than those TiO$_2$ nanoparticles (TiO$_2$ NP), which may to some extent inhibit the performance of DSSCs. Additionally, it is now well-accepted that a high-efficiency photoanode for DSSCs requires not only a high surface area for dye molecules loading but also a good capability of light scattering for enhancing the light-harvesting. Recently, “yolk@shell” nanostructures or so-called “rattle-type” nanomaterials are emerging as an interesting new member of the family of hollow nanoarchitectures. The unique physical properties of yolk@shell nanostructures...
enable them as attractive materials in applications of optical, electronic, magnetic, catalytic, and sensing devices. More importantly, the void space as well as shells and inner yolks in the yolk@shell nanostructure could be easily altered alongside numerous synthetic methods including the bottom-up, soft templating or selective etching approaches, etc. However, the application of this kind of hierarchical architectures in DSSCs is up to date extremely sparse. For this reason, it is of a great opportunity to design and synthesize a multifunctional photoanode material on the base of yolk@shell nanostructures.

Herein, we report a facile, template-free and nontoxic one-pot solvothermal route of synthesizing submicrometer-sized yolk@shell hierarchical spheres, which possess a permeable shell self-assembled by ultrathin anatase TiO$_2$ NSs with nearly 90% of exposed {001} facets and mesoporous inner sphere with a high specific surface area. Compared to the {001} faceted TiO$_2$ NSs and standard Degussa P25, the anatase TiO$_2$ yolk@shell hierarchical spheres (TiO$_2$ YSHSs) were obtained with surface area up to 245.1 m$^2$·g$^{-1}$ and their submicrometer scale simultaneously promoted light scattering in visible region. As a result, overall light conversion efficiency (η) of 6.01% has been achieved, indicating 49.9% and 34.8% increases compared to the TiO$_2$ NSs (4.01%) and the standard Degussa P25 (4.46%) photoanodes, respectively.

We are looking forward to hearing from you soon

Best Regards

Huagui Yang (Prof. Dr.)