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Anatase TiO_2 microspheres with exposed mirror-like plane {001} facets for high performance dye-sensitized solar cells (DSSCs)†

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Anatase TiO_2 microspheres with exposed mirror-like plane {001} facets were successfully synthesized *via* a facile hydrothermal process. The photoanode composed of TiO_2 microsphere top layer shows an improved DSSCs efficiency owing to the superior light scattering effect of microspheres and excellent light reflecting ability of the mirror-like plane {001} facets.

Since O'Regan and Grätzel's pioneering work in 1991, a two-decade research effort has made dye-sensitized solar cells (DSSCs) becoming a real alternative to silicon-based solar energy conversion technologies.[1–3] A recently reported solar light-to-electricity conversion efficiency of over 11% marks a new milestone of DSSCs technology.[2] Nanoparticle TiO_2 has been widely used for DSSCs. Photoanodes fabricated using such nanoparticle forms of TiO_2 are transparent to visible light but weak in visible light scattering due to the small particle size.[2,4,5] As a result, a significant portion of input light directly transmits through the nanoparticle TiO_2 layer without being harvested and utilized.[2,4–6] There has been a general consensus that the performance of DSSCs can be further improved by maximizing light harvesting efficiency.[2,5–7] To this end, much effort has been dedicated to explore new means to improve light harvesting efficiency.[5–8] A number of recent studies has demonstrated that incorporating scatterers into photoanode films can enhance light harvesting efficiency, consequently improve the DSSCs performance.[5–7] An earlier strategy of admixing larger sizes of TiO_2 particles into nano-sizes TiO_2 particle films as the scattering centres was used by various research groups.[9–11] Over 10% increase in the light-to-electricity conversion efficiency was achieved when $\sim$100 nm sized TiO_2 particles were employed as the scattering centres.[9] Recently, sub-micrometre-sized mesoporous TiO_2 beads with high surface area were used as scatterers for DSSCs.[5,12] The overall light conversion efficiency was markedly improved using the mesoporous TiO_2 beads photoanode in comparsion to the standard Degussa P25 photoanode.[5,12] Similar approach has also been used for ZnO photoanode based DSSCs.[13,14] The reported photoanodes using sub-micrometre polydisperse ZnO aggregates as scatterers can achieve an overall efficiency of 5.4%, which is significantly higher than that of photoanodes fabricated with ZnO nanocrystalline and ZnO nanowire films.[13,15,16] Although the use of large size scatterers enhances light harvesting efficiency, the increase in particle sizes usually results in decrease in surface area and hence the dye loading.[7] To overcome the issue, Cheng's group newly reported a dual-function scattering layer approach.[6] This approach allows the incorporation of sufficient scatterers while maintains the high level of dye loading capacity.[6] The DSSCs assembled using these photoanodes possess an overall light conversion efficiency of 8.84%.[6]

It has been reported that the anatase TiO_2 crystals with exposed {001} facets possess higher photocatalytic activities compared to the anatase TiO_2 with other crystal facets.[17–19] This type of TiO_2 could be advantageous for fabrication of photoanodes for DSSC applications. Incorporation of large size anatase TiO_2 crystals with exposed {001} facets could, on one hand, serves as effective light scattering centres, and on the other hand, improves the reactivity, both are important attributes for achieving high light harvesting efficiency.

Herein, we report, for the first time, the synthesis of micro-sized anatase TiO_2 spheres with exposed mirror-like plane {001} facets and the application of such microspheres for photoanode fabrication for DSSCs. The synthesis was carried out *via* a facile low-temperature hydrothermal method using metal titanium foil as Ti source in 0.5% (v/v) HF solution (initial pH = 1.3) at 180 °C for 3 h (experimental details in ESI†). Novel hierarchically structured photoanodes were fabricated using the calcined TiO_2 microspheres with exposed mirror-like plane {001} facets as the light scattering top layer and Degussa P25 film as the bottom layer (denoted as TiO_2 microsphere photoanode, ESI†). DSSCs assembled using TiO_2 microsphere photoanodes possess an overall efficiency (η) of 7.91%, which is 17.5% higher when compared with the standard Degussa P25 photoanodes of similar thickness.

Fig. 1a shows typical X-ray diffraction (XRD) pattern of as-synthesized product. It confirms that the obtained product is tetragonal structured anatase TiO_2. Typical scanning electron microscopy (SEM) image of the as-synthesized product given in Fig. 1b revealed a spherical-shaped structure with diameters ranged from 1.5 to 2.1 μm. Interestingly, the surface of these microspheres is covered by square-shaped crystalline facets, as shown in Fig. 1c. A detailed investigation was therefore carried out to characterize the square-shaped crystalline facets. Fig. 1d shows TEM image of an individual microsphere. The corresponding electron diffraction (SAED) patterns (top inset in Fig. 1d) confirm that the square-shaped crystalline is a single crystal, the zone axis is [001], and in turn the squared

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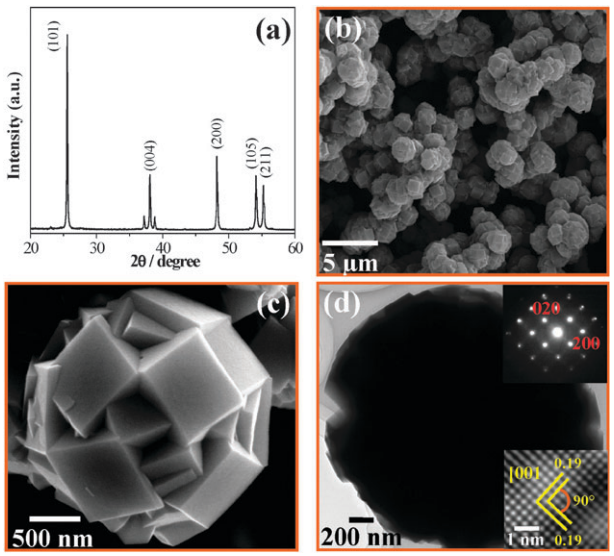

Fig. 1 (a) XRD pattern of the as-synthesized TiO_2 product; (b) and (c) low and high magnification SEM images of the as-synthesized TiO_2 sample, respectively; (d) TEM image of the as-synthesized TiO_2 microsphere with corresponding SAED pattern (top inset) and HRTEM image (bottom inset).

faceted surface is the (001) surface.[18–21] The corresponding high-resolution TEM (HRTEM) image (bottom inset in Fig. 1d) shows the perpendicular lattice spacing of 0.19 nm representing the (200) and (020) atomic planes of the anatase TiO_2.[18–21] It should be noted that the above data were obtained from the ultrasonic treated sample.[22] It is expected that for DSSC applications, when a back-illumination approach is employed, such TiO_2 microspheres with exposed mirror-like plane {001} facets could act alike mirrors reflecting/scattering light, leading to high light harvesting efficiency, as schematically illustrated in Fig. S1 (ESI†).

For TiO_2 microsphere photoanode fabrication, the as-synthesized TiO_2 microspheres were first annealed at 600 °C for 1.5 h to obtain fluorine-free anatase TiO_2 microspheres without change in morphology and crystal phase (Fig. S2 in ESI†).[19,23] The DSSC performance of TiO_2 microsphere photoanode was examined against the photoanode fabricated with Degussa P25 (denoted as P25 photoanode). For TiO_2 microsphere photoanode, a 9.5 μm Degussa P25 layer was first screen-printed onto the FTO substrate and followed by screen-printing a 7.0 μm TiO_2 microsphere layer (Fig. S3a in ESI†). For P25 photoanode, a 16.2 μm Degussa P25 layer was directly screen-printed onto the FTO substrate (Fig. S3b in ESI†). These photoanodes were then calcined at 450 °C for 1 h. The current–voltage characteristics of DSSCs were first investigated, as shown in Fig. 2. The DSSCs assembled with the TiO_2 microsphere photoanodes (16.5 μm) exhibit a short-circuit current density (J_{sc}) of 15.46 mA cm^{-2}, an open circuit voltage (V_{oc}) of ~729 mV, a fill factor (FF) of 70.2% and an overall conversion efficiency (η) of 7.91%, whereas DSSCs assembled with P25 photoanodes possess a J_{sc} of 13.61 mA cm^{-2}, an V_{oc} of ~715 mV, a FF of 69.2% and an overall conversion efficiency of 6.73%. Comparison with P25 photoanodes, a 17.5% improvement in the overall conversion efficiency was achieved by using TiO_2 microsphere photoanodes of similar

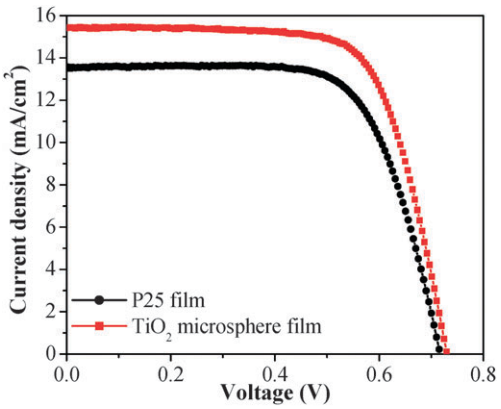

Fig. 2 Photocurrents as a function of photovoltage for DSSCs assembled with TiO_2 microsphere and P25 photoanodes.

thickness. Such a significant increase in overall conversion efficiency could be due to a number of attributes, deserving a further investigation.

It is well known that the performance of DSSCs can be strongly affected by the amount of dye loading to photoanodes.[5,7] The saturation adsorption capacity of N719 dye was therefore measured. The experimental results show that the amounts of dye loading for TiO_2 microsphere and P25 photoanodes are 1.12×10^{-7} mol cm^{-2} and 1.21×10^{-7} mol cm^{-2}, respectively. This decrease in the dye loading capacity of TiO_2 microsphere film can be attributed to low surface area of TiO_2 microspheres (15.6 m^2 g^{-1}), implying that the significant performance improvement of the DSSC assembled using TiO_2 microsphere photoanodes is due to the factors other than the influence of the dye loading capacity.

The light scattering properties have been generally accepted as one of the important attributes in determining the light harvesting efficiency.[5–7] Fig. 3 shows the diffuse reflection spectra of the TiO_2 microsphere and P25 photoanodes. The P25 photoanode shows slightly higher reflectance in the wavelength range between 400 and 450 nm but rapidly decreases as the wavelength increases from 450 to 800 nm due to the small particle size.[5] For the TiO_2 microsphere photoanode, the measured reflectance was found to be markedly higher than that of P25 photoanode over the entire visible and near-infrared regions (from 450 to 800 nm), indicating the

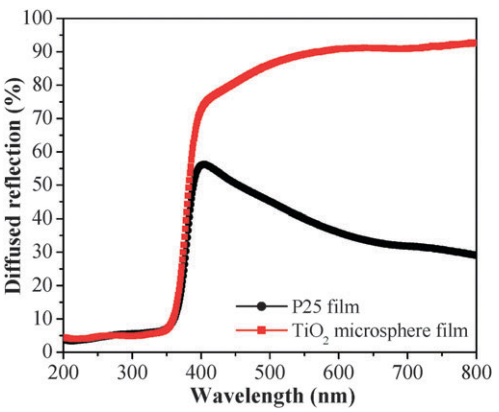

Fig. 3 Diffuse reflectance spectra of the TiO_2 microsphere and P25 films with similar thickness.

superior light scattering effect of the microsphere photoanode. These could mean that the significantly improved performance of DSSCs assembled using microsphere photoanode can be attributed to the dramatically improved light scattering effect introduced by the microsphere layer. The incident-photon-to-current conversion efficiency (IPCE) spectra were then obtained to further confirm the scattering effect of the microsphere layer (Fig. S4 in ESI†). The IPCE values obtained from the TiO_2 microsphere photoanode were approximately 1.2 times of that P25 photoanode at the maximum value of the IPCE spectra at 525 nm. Considering similar thickness were used for both photoanodes, and the lower dye loading capacity of the microsphere photoanode, such a dramatically improved IPCE performance of the TiO_2 microsphere photoanode over the wavelength range of 400–750 nm should be mainly due to the increased light scattering effect of the microsphere layer.

The efficacy of the hierarchically structured microsphere scattering layer is considerably higher when compared to the light scattering effect of previously reported scatterers.[5–7] This superior light scattering effect could be due to the direct light reflection ability of the unique mirror-like plane {001} facets that should be investigated. It is well known that the light scattering effect can be improved by employing large-sized scatterers, however, for a given scatterer size, the effect of introducing mirror-like plane surface on the light scattering efficiency has not been reported. To confirm this, similar size anatase TiO_2 microspheres without mirror-like plane {001} facets were synthesised *via* a hydrothermal process (ESI†). Fig. S5 (see ESI†) shows SEM and TEM images of the resultant microspheres. For DSSCs measurements, the photoanode was screen-printed with a *ca.* 8.0 μm light scattering microsphere layer and a *ca.* 9.3 μm P25 bottom layer (overall thickness of 17.3 μm). The DSSC performance evaluation revealed a J_{sc} of 14.66 mA cm^{-2}, an V_{oc} of $\sim$742 mV, a fill factor (FF) of 69.3% and an overall conversion efficiency of 7.54%. The overall light conversion efficiency of the TiO_2 microsphere photoanode without exposed mirror-like plane {001} facets is obviously higher than that of the P25 photoanode but lower than that of the TiO_2 microsphere photoanode with exposed mirror-like plane {001} facets. Considering the dye loading amount (1.18×10^{-7} mol cm^{-2} for the TiO_2 microsphere film without exposed mirror-like plane {001} facets) and the same layered structural configuration of the photoanodes made of similar size microspheres with or without the mirror-like plane {001} facets, the above results confirm an enhanced light scattering effect by the microspheres with unique mirror-like plane {001} facets. This may be attributed to the mirror-like plane {001} facets with added ability to directly reflect the input light back to the bulk TiO_2 film, the effectiveness of the 400–600 nm square-shaped surface crystals for visible light scattering, and the enhanced effect by the layered configuration, as schematically depicted in Fig. S1 (ESI†). This was further confirmed by diffuse reflectance spectra (Fig. S6 in ESI†.), where the reflectance of the microspheres without exposed mirror-like plane {001} facets over entire visible range was found to be higher than that of P25 photoanode but lower than that of the microsphere photoanode with exposed mirror-like plane {001} facets.

In summary, anatase TiO_2 microspheres with exposed mirror-like plane {001} crystalline facets were successfully fabricated *via* a facile low-temperature hydrothermal method. The DSSC assembled using the microsphere photoanode demonstrated an overall light conversion efficiency of 7.91% which is 1.2 times of the overall efficiency (6.73%) obtained from the P25 photoanode. The performance improvement is due to the improved light harvesting efficiency, attributing to the superior light scattering effect of the TiO_2 microsphere layer. The microsphere scatterers with exposed mirror-like plane {001} facets further benefit the light utilisation efficiency because of their excellent ability to directly reflect the input light back to the bulk film.

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