Morphology-controllable 1D-3D nanostructured TiO2 bilayer photoanodes for dye-sensitized solar cells

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Abstract
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Keywords
1d, 3d, nanostructured, tio2, bilayer, photoanodes, dye, sensitized, solar, cells, morphology, controllable

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Morphology-controlled bilayer TiO₂ nanostructures consisting of one-dimensional (1D) nanowire bottom arrays and three-dimensional (3D) dendritic microsphere top layer were synthesized via one-step hydrothermal method. These novel 1D/3D bilayer photoanodes demonstrated the highest energy conversion efficiency of 7.2% for rutile TiO₂ dye-sensitized solar cells to date, with TiCl₄ post-treatment.

Innovations in materials technology in the fields of photovoltaic cells and photocatalysis are playing a key role in the paradigm shift from fossil fuels to renewable sources. Economically viable and stable energy conversion devices with efficiencies surpassing those presently available are fundamental to such a transition, requiring a new generation of materials that offer broad-spectrum light harvesting and superior charge transport properties. Dye-sensitized solar cells (DSCs) have been recognized as one of the most promising devices for low-cost solar-to-electricity energy conversion. The improvement in DSC performance, however, has been impeded by the disordered structure of the mesoporous TiO₂ films in current DSCs, which induce a short electron diffusion length (10-35 µm) by interfacial dissipating, trapping and detrapping. Usually, two ways to increase solar energy harvesting/conversion efficiency are employed by enhancing electron diffusion length and light harvesting in DSCs. The one is the application of vertically aligned one-dimensional (1D) nanostructures, which has been identified as a promising way to enhance the electron diffusion length (up to ~100 µm). One key challenge in using vertically aligned 1D nanostructures in DSCs is that they have a low internal surface area, resulting in insufficient dye adsorption, and therefore, low light-harvesting efficiency. The other way is adopting large nanostructures in sizes of ~400-800 nm to enhance the light scattering. Unfortunately, the large particle size of the nanoparticles significantly lowers the surface area and the amount of dye uptake. In general, high specific surface area, long electron diffusion length, and a pronounced light-scattering effect are indispensable to a high-performance photoanode, but these factors are often incompatible with one another.

To accommodate all of these favourable characteristics, we propose an innovative one-step approach to synthesize double-layered structures with controlled morphology to act as DSC photoanode. In our design of the bilayer TiO₂ nanostructures, the bottom layer is vertically aligned 1D TiO₂ nanowires, which feature high photoinjected electron collection efficiency, fast...
TTIP$_{aq}$:EG = 1:1 were examined by SEM and TEM, as shown in Figure 1. Fig. 1(a) shows a cross-sectional SEM image of the synthesized bilayer structure. It reveals that a continuous 3D TiO$_2$ dendritic nanostructures has formed as the top layer with a thickness of ~40 µm, and the particle size of the TiO$_2$ microspheres is in the range of 2-3 µm (Fig. 1(b)). It is very interesting that the TiO$_2$ microspheres are not dense solid balls, but 3D dendritic nanostructures made up of nanowires approximately 10 nm in diameter as nano-units (inset in Fig. 1(b)). This 3D dendritic TiO$_2$ nanostructure has been proved to possess high specific surface area and superior electrochemical properties compared to nanoparticles with smooth surfaces. The bottom nanowire arrays had a similar shape and dimensions to those of the constituent units of the 3D dendrites. The thickness of the TiO$_2$ nanowire arrays was around 1.5 µm (Fig. 1(c-d)). As shown in Fig. 1(c), a strong mechanical connection between the microspheres or between the microspheres and the nanowire arrays was observed on a fractured surface. The growth directions and microstructures of the constituent nanowires of the 1D nanostructure arrays and the 3D dendrites were examined by HRTEM (Fig. 1(e-f)). The nanowires are well-crystallized in rutile TiO$_2$ single-crystals, where the growth direction is along the [001] orientation and the side surfaces are {110} facets. The single-crystal characteristics of the nanowires are very crucial in DSC application, as they will provide fast electronic transport through the wires, and most importantly, avoid the surface defect trapping derived by poor crystallization. The XRD patterns show that the obtained TiO$_2$ nanostructures were well-crystallized as rutile phase (Fig. S1).

By adjusting the TTIP$_{aq}$/EG volume ratio, the 1D/3D bilayer nanostructures with different constituent nanowire diameters were synthesized. The diameter of the nanowires synthesized from the mixed solution with a volume ratio of TTIP$_{aq}$:EG = 1:1 was around 10 nm, as can be seen in Fig. 1 (denoted as NW-C), then changed to ~6 nm when TTIP$_{aq}$:EG = 1:4, and to ~4 nm with TTIP$_{aq}$:EG = 1:6 (denoted as NW-F, Fig. 2). Due to the dilution of Ti-containing precursor by EG in the reaction solutions, both the thicknesses of the nanowire arrays and the overall size of 3D dendrites were decreased as the increasing of EG contents. By repeating the deposition 2-5 times, the thickness of the dendritic microsphere scattering layer can be increased to 40 µm. This repeated treatment, however, has no effect on increasing the thickness of the bottom nanowire array. Owing to the thinness of the bilayer nanostructures synthesized from the solutions with TTIP$_{aq}$:EG = 1:6, we picked the bilayer thin films obtained from the solutions of TTIP$_{aq}$:EG = 1:1 (NW-C) and TTIP$_{aq}$:EG = 1:4 (NW-F) for further photochemical characterizations.

In the UV-Vis spectra (Fig. S2), the cut-off edge of the nanowire single-layer thin film spectrum is around 390 nm, corresponding to a band-gap of 3.2 eV, which is much wider than the band-gap of bulk rutile TiO$_2$ (3.0 eV), attributing to the quantum size effect of the small nanowires. However, two conspicuous peaks were detected in the absorbance spectrum of the 1D/3D bilayer structure. The first peak located at 350 nm...
should be assigned to the absorption of the constituent nanowires. The second absorption at ~400 nm (3.1 eV) was contributed by the large-size cores of the 3D dendritic microspheres. The most interesting phenomenon in the UV-Vis absorption spectra is that there is a strong scattering effect from the bilayer thin films in visible light regime, which is helpful for confining and harvesting the incident light within the electrode.

Fig. 3 shows typical photocurrent density - photovoltage (J-V) curves (Fig. 3(a)) and the external quantum efficiencies in the 400-800 nm wavelength range (Fig. 3(b)) of the solar cells made from photoanodes with the following configurations: single-layer 1D TiO$_2$ nanowire arrays (NW-C arrays, ~1 µm in thickness), single-layer commercial P25 nanoparticles (~10 µm in thickness), and bifunctional TiO$_2$ nanostructures (NW-C bilayers and NW-F bilayers, ~1.0 µm 1D TiO$_2$ nanowire array underlayer plus ~19 µm 3D TiO$_2$ microsphere top layer). The measured results on these solar cells are summarized in Table 1.

The solar cells with NW-C array photoanode showed the lowest energy conversion efficiency, where the $V_{oc}$ was 0.61 V, $J_{sc}$ was 4.86 mA·cm$^{-2}$, $FF$ was 0.58, and $\eta$ was 1.7%. For the NW-C bilayer photoanodes, the energy conversion was significantly enhanced to 4.3%, corresponding to an enhancement of 150% over the NW-C single-layer photoanode. In the IPCE action spectrum of the NW-C bilayers, there is obvious visible light energy conversion in the wavelength range from 600-750 nm. The solar cell efficiency was further improved by employing NW-F bilayer photoanodes, which exhibited a $V_{oc}$ of 0.68 V, $J_{sc}$ of 14.70 mA·cm$^{-2}$, $FF$ of 0.56, and $\eta$ of 5.6%, better than the commercial P25 TiO$_2$ nanoparticle photoanode.

Even though improvements in $V_{oc}$ and $J_{sc}$ were observed in the 1D/3D bilayer photoanode, the $FF$ showed a decrease from 0.69 for P25 photoanodes to 0.44 for the ones with NW-C bilayer photoanodes and 0.56 for the ones with NW-F bilayer photoanodes. This kind of $FF$ decrease for the bilayer photoanodes is likely to be the high internal resistance in the 3D dendritic TiO$_2$ microsphere scattering layer. TiCl$_4$ soaking was used to overcome this disadvantage, as it can increase the contact among the 3D dendritic microspheres and thus decrease the internal resistance of the TiO$_2$ bilayer photoanodes (Fig. S3). On comparing the solar cell performance of the NW-F bilayer photoanodes before and after TiCl$_4$ treatment, the $FF$ improved significantly from 0.56 to 0.68, and contributed to a cell efficiency enhancement from 5.6% to 7.2%. The TiCl$_4$ post-treatments exhibited a significant enhancement on the DSC efficiency, due to the improved connection among the 1D and 3D nanostructures. The high efficiency of DSCs achieved by the bifunctional photoanodes demonstrates the success of our strategy of designing novel 1D/3D bilayer nanostructures that simultaneously combines previously incompatible factors for superior DSCs, such as high specific surface area, long electron diffusion length, and a pronounced light-scattering effect.

## Conclusions

Novel morphology-controlled 1D/3D bilayer TiO$_2$ nanostructures were synthesized via a simple one-step hydrothermal method. These bilayer nanostructures simultaneously possess the incompatible features of high specific surface area, fast electron transport, and a pronounced light-scattering effect, and provide DSCs an energy conversion efficiency of 7.2% after TiCl$_4$ treatment, compared to 4.7% for the commercial P25 TiO$_2$ nanoparticle photoanode. The successful synthesis of these novel photoanodes opens up a new way to improve the performance of DSCs.

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## Notes and references

1. This journal is © The Royal Society of Chemistry [year]
2. [vol], 00–00 | 3
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### Table 1. Photovoltaic performance of the solar cells with different photoanodes.

<table>
<thead>
<tr>
<th>Photoanodes</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW-C array</td>
<td>0.61</td>
<td>4.86</td>
<td>0.58</td>
<td>1.7</td>
</tr>
<tr>
<td>P25 particle</td>
<td>0.66</td>
<td>10.32</td>
<td>0.69</td>
<td>4.7</td>
</tr>
<tr>
<td>NW-C bilayer</td>
<td>0.74</td>
<td>12.95</td>
<td>0.44</td>
<td>4.3</td>
</tr>
<tr>
<td>NW-F bilayer</td>
<td>0.68</td>
<td>14.70</td>
<td>0.56</td>
<td>5.6</td>
</tr>
<tr>
<td>NW-F bilayer with TiCl$_4$</td>
<td>0.72</td>
<td>14.51</td>
<td>0.68</td>
<td>7.2</td>
</tr>
</tbody>
</table>