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ZnO hierarchical structures for efficient quasi-solid dye-sensitized solar cells†

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We report a direct precipitation method for mass production of ZnO microflowers (MFs) containing hierarchical structures. The ZnO MFs are constructed by interlaced single crystalline and porous nanosheets which are ideal photoanode material for dye-sensitized solar cells (DSCs) because the MFs can largely improve the energy harvesting performance and the efficiency of DSCs. Compared with other forms of nano-sized structures, the novel hierarchical structures show obvious advantages in DSC application because of their large surface area for dye-loading, good light scattering efficiency and excellent electrical transport property. The quasi-solid state DSCs fabricated with the MF hierarchical structures exhibited an efficiency of 4.12%, much higher than that of ZnO nanoparticle-based DSCs, indicating a great potential for the development of highly-efficient quasi-solid DSCs.

Dye-sensitized solar cells (DSCs) have been considered as a promising alternative to conventional silicon-based solar cells owing to their low cost and relatively high efficiency. In DSCs, mesoporous TiO$_2$ is usually employed as the photoanode material. In recent years, ZnO nanostructures have been extensively investigated as a promising photoanode material for dye-sensitized solar cells because they possess a similar band-gap structure, excellent electrical properties and flexibly controlled morphologies. However, the photoanodes simply made from ZnO nanoparticles (NPs) usually suffer from deficient light-scattering efficiency and even with adequate dye-loading being offered.

ZnO hierarchically structured photoanodes have been known to be more efficient for DSCs since dye-loading and light-scattering can be optimized simultaneously. However, most of the ZnO hierarchical structures so far reported were constructed by simply packing the primary nano-sized particles together. In this case, the photogenerated electrons still need to hop across massive boundaries before being collected, leading to a serious charge recombination and a low electron collection efficiency. In addition, for traditional DSCs, the utilization of a liquid electrolyte brings practical problems for their long-term stability (e.g., volatilization and leakage). So far, ZnO hierarchical structures with improved electron transport properties for DSCs have been merely reported.

Herein, we present a facile direct precipitation process for synthesizing ZnO microflowers (MFs) that are uniquely constructed by interlaced single crystalline nanosheets. We further demonstrate excellent performance of these hierarchically structured ZnO MFs in quasi-solid DSCs. The photoanodes made from the MFs exhibit sufficient dye-loading, excellent light scattering and significantly improved electron transport property by optimizing the electron transport pathway with minimized hopping interfaces, in which the electron diffusion coefficient is nearly one order of that in the photoanodes made from pure ZnO NPs. Furthermore, the ZnO MF photoanodes possessing abundant micro-channels favor the penetration of gel electrolyte in the photoanodes of quasi-solid DSCs. The highest energy conversion efficiency up to 4.12% has been achieved in quasi-solid DSCs without further optimization.

Different from conventional fabrication methods for ZnO nanostructures such as hydrothermal reaction, chemical bath deposition and thermal pyrolysis, our ZnO MFs were synthesized by the direct precipitation of zinc salt in an alkaline environment at room temperature. Typically, a 0.5 L zinc nitrate hexahydrate aqueous solution (0.2 M) was slowly added to a 0.5 L sodium hydroxide aqueous solution (1 M) with stirring for 0.5 h. Then, the resulting white precipitate was filtered and washed with deionized water. Scanning electron microscopy (SEM) and TEM images clearly revealed the hierarchical morphologies of the as-synthesized ZnO MFs. The MFs have a very uniform spherical morphology with diameters ranging from 1 to 3 μm (Fig. 1a) and each MF is constructed by a high density of nanosheets that are interlaced with each other to form a special flower-like morphology (Fig. 1b). These nanosheets are micro and sub-micrometre in width and about 20 nm in thickness. It is noted that the surfaces of these nanosheets are quite rough with a high density of pits (less than 10 nm in size). The pits are shown by the bright thickness contrast as revealed in Fig. 1c and d. The high-resolution TEM (HRTEM) image in Fig. 1d identifies that the nanosheet is a single crystalline Wurtzite...
structure with dominated planes \{\{1\bar{1}00\}\}. The clear two-dimensional (2D) crystal lattice image in Fig. 1d indicates good crystallinity of the nanosheet. Although flower-like ZnO structures have been synthesized and studied previously,\textsuperscript{14,21–23} to the best of our knowledge, these hierarchical structures constructed uniquely by interlaced monocrystalline ZnO nanosheets which contain a high density of nano-pits have not been reported.

In order to enhance the electrical connection between the MFs and the FTO glass electrode, a small amount (5.0 wt\%) of ZnO NPs (20 nm in diameter) were mixed with ZnO MFs. The photoanode films formed by this method were stable and compact (see Fig. S1, ESI). For comparison, the photoanode samples consisting of pure ZnO NPs (20 nm in diameter) were also prepared and tested under the same experimental conditions. Fig. 2a and b illustrate SEM cross-sectional images of the NP- and MF-based photoanodes, from which the thicknesses of these two films are determined to be \(\sim 10\ \mu m\) and \(20\ \mu m\), respectively. In the MF-based photoanode, there are less than ten layers of ZnO MFs stacking from bottom to top while in the NP-based film about 500 layers of 20 nm-sized particles have to be packed as schematically illustrated in Fig. 2c.

Fig. 2d demonstrates the \(J-V\) characteristics of the DSCs made from ZnO NPs and MFs. \(J\) is the current density of the DSC. Some of the experimental results are summarized in Table 1. We determined that the MF-based DSC has a conversion efficiency of 4.12\% at 100 mW cm\(^{-2}\) light illumination, much higher than the efficiency of the NP-based DSCs (normally about 1.26\%). Apparently, the excellent performance of ZnO MF DSCs is partially due to the improvement of the short-circuit current density \(J_{SC} = 11.31\ \text{mA cm}^{-2}\), indicating a significant improvement for the collection efficiency of photo-generated electrons in the MF-based photoanodes. Up to now, this efficiency is the highest record reported for the quasi-solid DSCs that were fabricated with polymer gel electrolyte and ZnO photoanodes.

We believe that the novel hierarchical structures of the ZnO MFs make the MF photoanode possess advantages in the following aspects, which largely benefit the performance of the MF-based DSCs. Firstly, the massive thin nanosheets in ZnO MFs contain a high density of pits. This results in rough surfaces and can offer a large surface area for dye-loading. The measured surface area of MFs is 21.48 m\(^2\) g\(^{-1}\), comparable to that of NPs (38.47 m\(^2\) g\(^{-1}\)). To evaluate the exact amount of N719 dye anchored on the photoanodes, the two saturated dyed films (MFs and NPs) were immersed into the NaOH solution for dye-desorption according to a previous report.\textsuperscript{24} We obtained that the dye-loading of the MF-based photoanode is \(0.95 \times 10^{-7}\ \text{mol cm}^{-2}\), about half of that of the NP-based one \(1.86 \times 10^{-7}\ \text{mol cm}^{-2}\) in the same film thickness, indicating that the hierarchical MF structure can

<table>
<thead>
<tr>
<th>Sample (DSC)</th>
<th>Dye-loading ((10^{-7}\ \text{mol cm}^{-2}))</th>
<th>(J_{SC}/\text{mA cm}^{-2})</th>
<th>(V_{OC}/\text{V})</th>
<th>FF (%)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>0.93</td>
<td>2.67</td>
<td>0.63</td>
<td>74.3</td>
<td>1.26</td>
</tr>
<tr>
<td>MF</td>
<td>1.01</td>
<td>11.31</td>
<td>0.68</td>
<td>53.2</td>
<td>4.12</td>
</tr>
</tbody>
</table>

Table 1 Performance and some characteristics of the DSCs based on NPs and MFs

![Fig. 1](image1.png) (a) The SEM image of as-fabricated ZnO MFs; (b) a magnified SEM image of an individual MF; (c) TEM image of a single crystalline ZnO nanosheet; (d) HRTEM image of the nanosheet shown in (c).

![Fig. 2](image2.png) (a) and (b) Cross-sectional SEM images of the NP-based and MF-based photoanodes respectively; (c) schematic diagrams of the NP-based and MF-based photoanode structures; (d) \(J-V\) curves of the quasi-solid DSCs fabricated using NP- and MF-based photoanodes.

![Fig. 3](image3.png) (a) Properties of the NP and MF-based photoanodes: (a) optical absorbance of solutions containing dyes desorbed from these two photoanodes; (b) pore distributions; (c) diffuse transmission spectra; (d) electron diffusion coefficients as a function of light intensity.
ensure to adsorb a comparable amount of dye molecules (Fig. 3a). The dye-loading results are consistent with their surface area data. Secondly, the micro-channels among MFs and the pores formed by the intersection of the nanosheets in MFs favor the penetration of the viscous PEO gel electrolyte. In Fig. 3b, it is clearly seen that the MF-based photoanode has not only a macroporous structure around 600 nm that can be denoted as packing pores by adjacent MFs, but also a continuous pore structure with sizes ranging from 50 nm to 400 nm that might stem from abundant channels constructed by these interlaced nanosheets. For the highly viscous quasi-solid electrolytes, the macroporous structure is favorable for their penetration into the matrix of the photoanode, thus facilitating the interfacial contact and the charge exchange between redox couples ($\Gamma^-/I_3^-$) and dye molecules. Thirdly, the micrometre-sized MFs (1–3 $\mu$m) containing a variety of different forms of nanosheets enable the MFs as efficient light-scattering centers. Fig. 3c shows the diffuse transmission spectra of the MF and NP-based photoanodes before dye sensitization. Obviously, the MF-based photoanode has a largely improved light scattering effect compared with the NP-based one. This distinguished enhancement of light scattering is attributed to the unique hierarchical structure of the MFs. The randomly oriented and intersected nanosheets with different widths from 300 nm to 1.5 $\mu$m (comparable to the wavelengths of the solar light) can increase the optical path length within the photoanode due to multiple scattering. Furthermore, these hierarchical spherical aggregates may also lead to a photon localization effect that comes from the confined light scattering in closed loops. Therefore, the opportunities for incident photons to be captured by the dye molecules should be increased in MF-based photoanodes. Finally, but most importantly, the MF-based photoanodes provide an optimized pathway for electron transport. Although some flower-like spheres have been reported by several groups, there is no report on the improvement of the electron transport property with these flower-like ZnO structures. In our MF particles, the hierarchical structure is made of many interlaced thin monocrystalline nanosheets. These plates are not simply assembled together layer by layer but grow directly from the core of the MFs. Therefore, the photogenerated electrons can transport easily in each MF. Furthermore, since the path for the photogenerated electrons to reach the FTO substrate is short (less than ten ZnO MFs to pass through as shown in Fig. 2c), the photogenerated electrons are much easier to be collected by the FTO substrate after hopping across limited interfaces.

To verify our analysis of the structural advantages of the ZnO MFs, we have investigated the electron transport in the MFs using the intensity-modulated photocurrent spectroscopy (IMPS). Fig. 3d plots the diffusion coefficient $D_n$ of the photo-generated electrons as a function of illumination intensity. We observed that $D_n$ of the MF-based photoanode was nearly one order of magnitude higher than that of the NP-based photoanode. Obviously, the special hierarchical structures in ZnO MFs not only generate a large surface area for dye-loading, but also behave as good light scattering centers and enhance the electrical transport property. In recent years, various ZnO nanostructures, such as nanowire arrays, submicron-sized aggregation of NPs and nanosheets have been extensively investigated with an aim to improve the performance of DSCs by increasing surface area, providing rapid pathways for electron transport and enhancing light scattering. However, there was no significant improvement in the DSC performance because it is a difficult task to improve all these three factors mentioned above for a material at one time. Here, the ZnO MFs with hierarchical structures have been proved to perform well in all these three factors. Through further optimization of its structure and morphology, this material should be an ideal candidate for high performance DSCs.

Conclusions

In summary, a simple and effective direct precipitation method has been developed for the fabrication of ZnO MFs containing novel hierarchical structures in large scale. The hierarchical ZnO MFs are constructed by interlaced single crystal nanosheets which can largely improve the energy harvesting performance and the efficiency of quasi-solid DSCs. The nano-micro-porous structures not only generate a large surface area for dye-loading, but also behave as good light scattering centers and enhance the electrical transport property. Quasi-solid DSCs fabricated using these novel hierarchical structures and PEO gel electrolyte exhibit a conversion efficiency of 4.12%.

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References