Facile hydrothermal preparation of hierarchically assembled, porous single-crystalline ZnO nanoplates and their application in dye-sensitized solar cells†

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Bottom-up engineering of semiconductor nanostructures holds high potential for designing the next generation of solar cells. A superstructure of meso/micro-porous single-crystalline ZnO nanoplates is created by controlled thermal decomposition of a nanoplate precursor prepared from a hydrothermal process. This unique porous nanoplate structure has proved to be an excellent candidate for constructing photoanodes of low-cost and high-performance dye-sensitized solar cells (DSSC).

I. Introduction

The noncentrosymmetric wurtzite ZnO semiconductor has attracted much attention in the bottom-up engineering of nanostructures because of its versatility as an excellent nano-structure-former and its unique electronic properties with a wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV. A number of synthetic strategies have been reported for the preparation of one-dimensional (1D) ZnO nanostructures by the vapor–liquid–solid (VLS) and vapor–solid (VS) methods. In particular, the 1D ZnO nanostructures with monocrystallinity have received a great deal of research efforts due to their excellent device performance in optoelectronics, gas sensors, field emission, as well as UV lasers, light-emitting diodes (LED), and photo-anodes for photovoltaic and dye-sensitized solar cell (DSSC) applications. Although single-crystalline ZnO nanorods, nanowires, nanotubes and nanobelts have been amply synthesized and employed for building advanced devices, there has been paucity of investigations on 2D nanostructures of single crystalline ZnO. This is partly due to the fact that the synthesis of 2D nanostructures of single crystalline ZnO entails a different strategy from those for their 1D counterpart, especially when they need to be porous and thus possess a high specific surface area.

As a promising candidate for the photoanode of DSSCs, nanostructured ZnO with different morphologies have been extensively studied in recent years due to the similarity of the band-gap and the electron-injection process of ZnO to that of TiO₂. An electrode made of polydisperse aggregates of ZnO nanocrystallites was reported to yield a DSSC with an overall power conversion efficiency of 5.4%, which is much higher than those of DSSCs based on the ordinary ZnO nanocrystals due to an enhanced light-scattering effect and thus improved light-harvesting efficiency. By using upright standing ZnO nanosheets based electrodes, researchers have produced a DSSC (η = 3.9%) with a higher fill factor due to fast transport of the redox couple (I²/I₃⁻) between the electrodes through the vertical channels and therefore the decrease in the resistance of the cell and the recombination of the injected electrons. In this work, we demonstrate the synthesis and assembly of porous single-crystalline ZnO nanoplates by a simple hydrothermal method. The key is the formation and decomposition of a nanoscale plate-like precursor [hydrozincite Zn₅(CO₃)₂(OH)₆]; the former appears to proceed by oriented conglomeration of hydrozincite building blocks, while the latter creates the ZnO nanoplates with numerous pores. In addition, we have for the first time used the porous nanoplates to prepare photoanodes for DSSCs and, by tuning the pore size and investigating the charge transport characteristics, obtained a high energy conversion efficiency of up to 5.05% from our preliminary experiments. The efficiency we achieved is higher than those of most ZnO based DSSCs with increased dye loading, enhanced light scattering and increased electron lifetime, making the porous single crystalline ZnO nanoplates a viable candidate for the development of novel DSSCs.

II. Experimental

Preparation of porous ZnO nanoplates

For the precursor preparation, zinc acetate dihydrate (1 mmol) and urea (2 mmol) were dissolved in 30 mL of distilled water, and into the aqueous solution was CTAB (10 mM) added with vigorous stirring for 1 h. The mixture was sealed in a Teflon-lined stainless-steel autoclave of 50 mL capacity, kept at 130 °C for 10 h, and then allowed to cool down to room temperature naturally. A white precipitate was collected and rinsed with distilled water and absolute ethanol several times. Finally, the precursor product was filtered and dried at 70 °C for 24 h. Finally, for obtaining the porous single crystalline ZnO nanoplates, the precursor product was heated to 400 °C and kept for 1 h in oxygen atmosphere.

Fabrication of porous ZnO photoanode films

The as-prepared precursor powder was ground in an agate mortar to homogenize the sample, and then was dispersed in water and poly(ethylene glycol) by stirring overnight, resulting in
a viscous precursor paste. To make films, the paste was applied onto the conducting substrate (FTO-coated glass, 14 Ω/square, Nippon Sheet Glass, Japan) by doctor blading using adhesive tape (Scotch brand) as a frame and spacer. The films were then allowed to dry at 70 °C for 10 h, and finally subjected to heat treatment at 400 °C in different heating rates.

Characterization

The as-prepared products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) measurements. The morphologies were directly examined by SEM using a JEOL 6700F at an accelerating voltage of 5 kV. For TEM observations, the porous ZnO nanoplates were ultrasonically dispersed in ethanol and then dropped onto carbon-coated copper grids. TEM observations were carried out on JEOL 2100F and JEOL 2010 microscopes both operating at 200 kV. An energy-dispersive X-ray spectrometer (EDX) was attached to the JEOL 2100F. The XRD analyses were performed on a Philips PW-1830 X-ray diffractometer with Cu Ka radiation (λ = 1.5406 Å) at a scanning speed of 0.025° s⁻¹ over the 2θ range of 10–80°. A conductive glass slide sputter-coated with 100 nm of Pt was used as the counter-electrode. The electrodes were separated by a 40 μm thick Surlyn hot-melt gasket. The dye was desorbed from the film by immersing in a 1 mM NaOH water–ethanol (1 : 1, v/v) solution. The J–V characteristic curves were recorded using a computerized Keithley 236 source measure unit or a CHI 600A electrochemical analyzer. The light source (Oriel solar simulator, 450 W, AM 1.5 global filter) was calibrated to be 1 sun (100 mW cm⁻²) using a power meter. The active electrode area was typically 0.16 cm².

III. Results and discussion

The as-prepared precursor after hydrothermal treatment of zinc acetate and urea in the presence of CTAB was examined by powder XRD and SEM techniques. As the low magnification SEM image in Fig. 1a shows, the product has a spherical or nearly spherical morphology with an open internal structure and a size of a few microns, and appears to be hierarchically assembled from numerous nanoplates. The thickness of the nanoplates is estimated to be ~17 nm from the high magnification SEM image in the inset of Fig. 1a. The surfaces of the precursor nanoplates are found to be rough from the transmission electron microscopy (TEM) image in Fig. 2a. High-resolution TEM (HRTEM) images and selected-area electron diffraction (SAED) patterns reveal that the nanoplates are polycrystalline (Fig. 2b–c). Energy-dispersive X-ray spectroscopy (EDX) analysis confirmed that the body of the nanoplates is exclusively composed of Zn, C and O except for the Cu peak arising from the copper grid of the TEM sample holder (see Fig. 2d). The PXRD peaks of the precursor in Fig. 1b can be indexed to [hydrozincite...
\( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) (JCPDS card no.19-1458). This assignment is also supported by the FTIR spectrum of the precursor (Fig. S1, in the ESI†). The broad band centered at 3364 cm\(^{-1}\) is ascribed to O–H stretching vibrations of the OH\(^{-}\) group and water molecules. The intense sharp peaks at 1547–1502 and 1397 cm\(^{-1}\) are assigned to the \( \nu_2 \) mode of the CO\(_3^{2-}\) group, and the peaks at the 831 and 707 cm\(^{-1}\) are associated with the \( \nu_2 \) and \( \nu_4 \) modes of the CO\(_3^{2-}\) group, respectively.\(^{10}\) The minor peaks at 2924 and 2856 cm\(^{-1}\) are ascribed to C–H stretching vibrations of CTAB surfactants attached onto the precursor surfaces.\(^{11}\)

Thermogravimetric (TG) analysis was employed to follow the heat treatment process of the precursor under compressed air (Fig. S2, in the ESI†). The first weight loss of 3.82% from 50 to 210 °C can be attributed to the loss of water molecules, while a second sharp weight loss of 22.68% in the temperature range of 210–280 °C is assigned to the release of CO\(_2\) and H\(_2\)O due to the thermal decomposition of the precursor. The final weight loss of 2.98% from 280 to 385 °C is ascribed to the combustion of CTAB. After the heat treatment of \( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) at 400 °C for 1 h accompanied by the release of CO\(_2\) and H\(_2\)O, the nanoplate morphology has been retained, but numerous through pores are now distributed throughout the nanoplates as can be seen from the SEM images in Fig. 1c. The composition of the transformed porous nanoplates is determined to be hexagonal ZnO (JCPDS card no. 36-1451) on the basis of the PXRD pattern in Fig. 1d. The sharp and strong XRD peaks also confirm the good crystallinity and high purity of the product.

The porous ZnO nanoplates were subjected to further investigations by TEM, HTREM and SAED. Shown in Fig. 3a is a representative TEM image of the porous ZnO nanoplates, which reveals pores with various shapes and sizes of 2–50 nm. The corresponding SAED pattern in the inset of Fig. 3a displays well-defined spots, which are readily indexed to wurtzite ZnO in agreement with the XRD analysis. The HRTEM image of a single ZnO nanoplate exhibits clear and coherent lattice fringes running through the whole nanoplate (Fig. 3b). The lattice spacing of 2.6 Å is recognized and can be ascribed to the (002) planes of the hexagonal phase of ZnO. Therefore both the SAED pattern and the HRTEM image show that these nanoplates are actually high quality single crystals. This important result sets our single crystalline porous ZnO nanoplates apart from the polycrystalline porous ZnO nanoplates reported by Jing and Zhan,\(^{12}\) which resulted from the decomposition of different precursors under very different experimental conditions.

During the process of precursor formation, decomposition of urea is believed to play an important role in the homogeneous hydrolysis of the Zn\(^{2+}\) salt. More specifically, OH\(^{-}\) and CO\(_3^{2-}\) ions can be generated by the decomposition of urea at a given temperature, which precipitates the zinc ions, thus leading to the nucleation and growth of \( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) nanoplates. The growth of \( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) nuclei can be controlled by the release rate of NH\(_3\) and CO\(_2\) from urea.\(^{13}\) It is likely that small nanoparticles of \( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) are initially nucleated and their growth is accompanied by the capping with the CTAB surfactant. Because at low reagent concentrations, the incipient \( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) prefers to form a layered structure with the positively charged CTAB preferentially interacting with the negatively charged layers of OH\(^{-}\) and CO\(_3^{2-}\) ions. Indeed, as shown in the SEM images of the precursor (see the ESI, Fig. S3†), the nanoplates appear to be aggregates of \( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) nanoparticles. This is further revealed by the HRTEM image and SAED pattern, the corresponding fast Fourier transform (FFT) pattern (see Fig. 2) and the strong (200) XRD peak of the precursor. According to the present results (see the ESI, Fig. S3†) and those reported previously,\(^{14}\) a plausible mechanism for the assembly of the nanoparticles into microflower morphology can be proposed as illustrated in Fig. S4†. It begins with the formation of nanoparticles capped by CTAB. The nanoparticles, owing to their layered structure, then undergo oriented attachment sideways, leading to the formation of nanoplates with the surface capping of CTAB. The nanoplates, due to their lateral interactions, are further assembled at a higher level to form a flower-like sphere or pseudosphere with an open microporous/mesoporous framework.

The monoclinic hydrozincite \( \text{Zn}_2(\text{CO}_3)_{2}(\text{OH})_6 \) structure (space group \( \text{C}_2/m \)) with lattice constants of \( a = 13.58 \) Å, \( b = 6.28 \) Å and \( c = 5.41 \) Å, \( \beta = 95.6^\circ \), where each layer in the [001] direction is constructed by the assembly of zinc octahedrons and tetrahexedrons (see the ESI, Fig. S5†). The hexagonal wurtzite ZnO structure (space group \( \text{P} \text{6}_3 \text{mc} \)) with lattice constants of \( a = 3.253 \) Å and \( c = 5.213 \) Å, is constructed from alternately interconnection of zinc tetrahexedrons, the separation between two neighboring zinc or oxygen atoms is \( 3.2 \) Å (see the ESI, Fig. S6†). As mentioned above, the porous single-crystalline ZnO nanoplates are considered to form through the thermal decomposition of the precursor, during which the zinc octahehedrons collapse and reorganize to form tetrahexedrons upon the release of CO\(_2\) and H\(_2\)O. The high temperature in the heat treatment step has the effect of consolidating the oriented attached nanoparticles and thus makes the final ZnO phase much better crystallized.

In a preliminary attempt, porous ZnO nanoplate photoanodes for dye sensitized solar cell (DSSC) tests were fabricated by depositing a \( \sim 15 \) µm thick precursor film on fluorine-doped tin oxide (FTO) glass, followed by heating from room temperature to 400 °C in oxygen atmosphere at heating rates of 15 °C min\(^{-1}\) (nanoplate-1) and 30 °C min\(^{-1}\) (nanoplate-2), respectively. After annealing, the porous ZnO nanoplate films prepared in this way are uniform (see the film morphology in the ESI, Fig. S7†) with a thickness of approximately 12 µm. For comparison, commercial ZnO particles \( \sim 20 \) nm in diameter were also used to prepare

**Fig. 3** Typical TEM image (a) and HRTEM image (b) of the porous ZnO nanoplates. Inset of (a): the corresponding SAED pattern.
Table 1  Structural and performance characteristics of DSSCs based on photoanodes of DSC-1, DSC-2, and DSC-3

<table>
<thead>
<tr>
<th>Samples</th>
<th>$V_{oc}$/mV</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
<th>BET surface area/m$^2$ g$^{-1}$</th>
<th>Adsorbed dye/mol cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC-1</td>
<td>628</td>
<td>14.4</td>
<td>55.8</td>
<td>5.05</td>
<td>46.9</td>
<td>1.15 x 10$^{-7}$</td>
</tr>
<tr>
<td>DSC-2</td>
<td>626</td>
<td>13.1</td>
<td>51.8</td>
<td>4.25</td>
<td>44.3</td>
<td>1.05 x 10$^{-7}$</td>
</tr>
<tr>
<td>DSC-3</td>
<td>620</td>
<td>8.9</td>
<td>53.5</td>
<td>2.95</td>
<td>35.7</td>
<td>9.25 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

A ZnO film (ZnO NP) with the same thickness (see the film morphology in the ESI, Fig. S8†). As shown in Table 1, the Brunauer–Emmett–Teller (BET) surface areas of these films are 46.9, 44.3, and 35.7 m$^2$ g$^{-1}$, respectively. The increased surface areas of nanoplate-1 and nanoplate-2 by a factor of 1.31 and 1.25, respectively, compared to that of the ZnO nanoparticle film (ZnO NP), clearly benefit from the highly porous structure of our ZnO nanoplates. Fig. 4 compares the pore-size-distributions of the three films determined from their N$_2$ absorption/desorption isotherms. The film of ZnO NP displays only a single type of pores in the size range from 10 to 25 nm due to the close-packing of irregularly shaped and sized ZnO nanoparticles, whereas two kinds of pores are observed for the porous nanoplate films, which measure 15 nm and 25–50 nm for nanoplate-1 and 13 nm and 22–80 nm for nanoplate-2. Clearly, the smaller-sized pores are intrinsic within the ZnO nanoplates (through pores), whereas the larger-sized pores are mainly due to interstices between the nanoplates. The variation of the pore sizes was achieved by annealing at different heating rates. As expected, the size and distribution of the pores within the ZnO nanoplates are not appreciably different for the two nanoplate films, but the interstitial pore sizes become much more broadly distributed when the heating rate is higher.

The nanoplate-1 (DSC-1), nanoplate-2 (DSC-2) and ZnO NP (DSC-3) photoanodes were comparatively investigated. Fig. 5 presents the characteristic current ($J$)–voltage ($V$) curves of these DSSCs, and the resulting photovoltaic parameters are summarized in Table 1. DSC-2 achieved an overall solar to electric energy conversion efficiency ($\eta$) of 4.25% with a current density ($J_{sc}$) of 13.1 mA cm$^{-2}$, open-circuit voltage ($V_{oc}$) of 626 mV, and fill factor (FF) of 51.8%, much higher than the performance of DSC-3 derived from ZnO nanoparticles ($\eta = 2.95\%$). Interestingly, DSC-1 demonstrated a higher $J_{sc}$ (14.4 mA cm$^{-2}$) and FF (55.8%) and slightly higher $V_{oc}$ (628 mV) than those of DSC-2, thus with the corresponding $\eta$ climbing to 5.05%. As will be discussed below, the enhanced $J_{sc}$ for DSC-1 is most likely a result of enhanced light harvesting due to increased dye loading and enhanced light reflection and scattering of the photoanode, as well as improved charge collection due to increased electron lifetime.

The adsorbed amounts of N719 dye on these porous ZnO films listed in Table 1 were determined by thorough desorption in a 1 mM NaOH solution. The dye-loadings of DSC-1 and DSC-2 are, respectively, 1.24 and 1.14 times that of DSC-3, in concurrence with the corresponding BET surface area measurements. Therefore, the increased surface area of our porous superstructure primarily accounts for the increment in dye adsorption, thus partially explaining the increased light harvesting of the porous ZnO nanoplates.

Light scattering of a photoanode film has been shown to significantly improve light-harvesting efficiency, and this has whipped up much recent interest for developing mesoporous hierarchical spherical structures to boost photon to current conversion efficiency of DSSCs. By the same token, our porous ZnO nanoplate films also make good in having excellent light scattering characteristics. It is believed that the porous nanoplates could not only provide good light reflection, but also scatter the incident light of different wavelengths in the visible range. By glancing over the diffuse reflectance spectra of the nanoplate-1, nanoplate-2 and ZnO NP films in Fig. 6, one is immediately struck by the significantly heightened diffuse reflection of the porous nanoplate films in the wavelength range of visible light compared to that of the ZnO NP film.

Fig. 7a presents incident photon-to-current efficiency (IPCE) spectra for the three representative DSSCs. The maximum quantum efficiencies for all the three DSSCs with the N719 dye are approximately located at ~530 nm. For DSC-2, the peak
quantum efficiency is ~65%, which is higher than that of the DSSC derived from ZnO NP. The quantum efficiency of DSC-1 is increased relative to that of the ZnO NP film to a much larger extent over the whole spectral range with a maximum of ~71.5%. As a result, the highest solar to electric energy conversion efficiency ($\eta$) of 5.05% is achieved for DSC-1.

To gain further insight into charge collection, electron transit times $\tau_D$ and lifetimes $\tau_n$ of photogenerated electrons in the ZnO layers of the photoanodes were determined by the intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS), respectively.\textsuperscript{16} While $\tau_D$ is allied to the relative electron diffusion given the lack of an electric field, $\tau_n$ is related to back reaction with oxidized species in the electrolyte.\textsuperscript{16} Experimentally, $\tau_n$ and $\tau_D$ were, respectively, estimated from the IMVS response by $\tau_n = 1/\omega_{min} = 1/2\pi f_{min}$ and from the IMPS response by $\tau_D = 1/\omega_{min} = 1/2\pi f_{min}$. Fig. 7b plots electron lifetimes and electron transit times at different light intensities for the three DSCs. Several features merit attention. First, DSC-1 and DSC-2, particularly DSC-1, show longer lifetimes than DSC-3, suggesting the presence of fewer surface trap sites on the porous nanoplates than on the nanoparticles for mediating recombination with $I_3^-$ in the electrolyte. This can be explained by the good single crystallinity of the porous ZnO nanoplates with well-defined surfaces, which are to be compared with the more variable ZnO nanoparticle surfaces. Second, electron transit times for DSC-1 and DSC-2 are longer than that of DSC-3. This at first appears to be unexpected, but one can imagine that the porous nanoplates, although good for the internal electron transport, have difficulty to communicate electrons with each other due to packing constrained disjoints for the nanoplate morphology. This could be remedied by post treatment in the future. Nevertheless, from the IMPS and IMVS results, the charge collection efficiency of DSC-1 is still comparable to that of DSC-3 and higher than that of DSC-2. The IPCE can be partitioned according to the relation $\text{IPCE}(\lambda) = \text{LHE}(\lambda) \phi_{\text{inj}} \eta_c$, where $\phi_{\text{inj}}$ is the quantum yield of charge injection from the excited dye to the conduction band of ZnO, and $\eta_c$ is charge collection efficiency. It thus appears that the relatively higher IPCE for our porous ZnO nanoplate photoanodes is mainly caused by the enhanced light harvesting efficiency LHE($\lambda$), more specifically, the enhanced light reflection, scattering, and absorption.

IV. Conclusions

In conclusion, we have synthesized a superstructure of porous single-crystalline ZnO nanoplates by the thermal transformation of a morphologically analogous precursor. The precursor was obtained by hydrothermal treatment of a zinc salt and urea. The synthetic method for the porous structure is simple, scalable and very reproducible, and the pore size is tunable. The hierarchical, porous and single crystalline structure of ZnO is inimitable and would be difficult to obtain by other means. This novel nanostructure bodes well for photoanodes of DSSCs owing to the possibility to finely demarcate and separate bicontinuous transport pathways of electrons and holes and to enhance light reflection and scattering. Indeed, our initial survey has already evinced a decent energy conversion efficiency of 5.05% with the new type of photoanode. We expect that the porous single-crystalline ZnO nanoplate based photoanodes can be further optimized by improving film fabrication, dye loading, electrolyte composition, etc. This work will not only inspire rational preparation and hierarchical assembly of other novel porous single crystalline nanostructures but also open up new opportunities for the development of photoanodes for DSSCs, among others.

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References


