Nanosheet-assembling Hierarchical Zinc Stannate Microspheres for Enhanced Efficiency of Dye-Sensitized Solar Cells

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Abstract
Nanosheet-assembling hierarchical Zn2SnO4 microspheres (NHMSs) are synthesized via one-pot solvothermal route and used as photoanodes for dye-sensitized solar cells (DSSCs). An overall photoconversion efficiency of 3.43% has been achieved with this ternary metal oxide and structure, significantly higher than that derived from dispersed nanosheets (DNSs) electrode (2.06%). The hierarchical Zn2SnO4 microsphere structure is proven to be favorable for enhancement of overall dye-sensitized solar cells photoconversion efficiency via (1) the hierarchical Zn2SnO4 microspheres can function as efficient light scatterers to enhance the light-harvesting efficiency; (2) intersectional contact with one another of the nanosheets of densely packed neighboring microspheres offers the transport channel for fast electron transport, avoiding the high resistance existing in the nanoparticle-based microspheres due to the relatively small interface resistance; (3) these spherical assemblies form large external pores for dye loading, at the same time, provide a "main trunk" for the quick electrolyte diffusion throughout the Zn2SnO4 layer in the film.

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1. Introduction

Over the past decades, dye-sensitized solar cells (DSSCs) have attracted extensive attention due to their facile fabrication process, low fabrication cost and relatively high efficiency [1–4]. Previous studies have described the application of simple binary oxides, TiO2, ZnO, SnO2, Nb2O5 and In2O3, as photoanodes in DSSCs [5–9]. In comparison with simple binary oxides, ternary metal oxides such as Zn2SnO4, Zn2TiO4, SrTiO3, etc. have several advantages in certain respects [10–12]. First, ternary metal oxides have more freedom to tune the materials' chemical and physical properties by altering the compositions [13]. To DSSCs, this ability to adjust these properties is crucial for better control of carrier transport and collection [14]. Second, ternary metal oxides exhibit better corrosion resistance than many binary oxides, which could improve the long-term chemical stability of the DSSCs under the real world conditions [10]. In addition, ternary metal oxides would broaden material spectrum for DSSCs applications. Among ternary metal oxides, the higher electron mobility (10–15 cm² V⁻¹s⁻¹) of Zn2SnO4 than TiO2 (0.1–1.0 cm² V⁻¹s⁻¹) enables photoinduced electrons in Zn2SnO4 for a faster diffusion transport [15]. The larger band gap (3.6 eV) of Zn2SnO4 than anatase TiO2 (3.2 eV) also allows for fewer oxidative holes in the valence band, benefiting the long-term stability of DSSCs [15]. Moreover, as the DSSCs electrode material, Zn2SnO4 overcomes the stability problem associated with ZnO in the presence of acidic dyes [10,16]. Meanwhile, it is also an earth-abundant material, which ensures that it is suitable for the fabrication of low-cost DSSCs [13]. So, low-dimensional Zn2SnO4 nanostructures have been utilized as photoanodes in DSSCs, such as zero-dimensional (0D) nanoparticles [10,17,18], one-dimensional (1D) nanorods [19] and nanowires [20].

It is widely accepted that a high-efficiency photoelectrode for DSSCs generally simultaneously possesses a high surface area for light harvesting and a densely packed structure for fast electron transport [1]. To meet these harsh requirements, considerable effort has recently made for exploration of three-dimensional (3D) hierarchical microstructures consisting of low-dimensional nano-sized building blocks [21–23]. On the one hand, the primary building blocks, such as nanowires, nanotubes or nanosheets, can provide the high surface area for dye loading to enhance the current density (Isc) and photoconversion efficiency (η) of DSSCs. At the same time, those 1D or 2D nanostructures furnish direct
electrical pathways for photogenerated electrons, which greatly enhance electron transport rates [24–26]. On the other hand, hierarchical microspheres with subunit size comparable to the wavelength of visible light enable enhancement of the light-harvesting efficiency via the scattering effect through increase of the light transport length within the photoanode film [23]. Simultaneously, the densely packed neighboring microspheres offer the transport channel for fast electron transport [27]. As examples, nanosheet-based TiO$_2$ hierarchical spheres [21], and our previous work of hierarchically assembled microspheres consisting of ZnO nanosheets [28] and nanowire-covering Zn-doped SnO$_2$ microspheres [29] have been proved to be efficient structure to improve photoconversion efficiency as photoanodes for DSSCs. However, to the best of our knowledge, the 3D hierarchical

![Fig. 1. SEM images of the NHMSs (a-d) and DNSs (e-h) at different magnification.](image-url)
Zn$_2$SnO$_4$ nanostructures as photoanode for DSSCs have rarely been reported.

In this paper, we investigate the synthesis of nanosheet-assembling hierarchical Zn$_2$SnO$_4$ microspheres (NHMSs) and apply them as a photoanode for DSSCs. An overall photoconversion efficiency of 3.43% has been achieved, significantly higher than that derived from dispersed nanosheets (DNs) electrode (2.06%). The hierarchical microsphere structure is proven to be favorable for enhancement of overall DSSCs photoconversion efficiency via (1) the hierarchical Zn$_2$SnO$_4$ microspheres can function as efficient light scatters to enhance the light-harvesting efficiency; (2) intersectional contact with one another of the nanosheets of densely packed neighboring microspheres offers the transport channel for fast electron transport, avoiding the high resistance existing in the nanoparticle-based microspheres due to too many contact interfaces among the nanoparticles; (3) these spherical assemblies form large external pores for dye loading, at the same time, provide a "main trunk" for the quick electrolyte diffusion throughout the Zn$_2$SnO$_4$ layer in the film.

2. Experimental

2.1. Synthesis of NHMSs

2 mmol of Zn(CH$_3$COO)$_2$·2H$_2$O and 0.6 mmol of SnCl$_4$·4H$_2$O were dissolved in a solvent containing 10 mL of 1–3 propanedi-amine and 20 mL of H$_2$O. After 10 min of stirring, 7 mmol of NaOH was added to the stirred solution. The obtained compound was transferred to a 50 mL stainless Teflon-lined autoclave and treated at 200 °C for 24 h in an electric oven. The resulting gray precipitate was filtered, washed with distilled water and dried in air. Finally, the powder was calcined at 500 °C for 0.5 h in air with a heating rate of 5 °C/min. For comparison, the individual Zn$_2$SnO$_4$ nanosheet was obtained with a mixed solvent of 1 mL of 1–3 propanedi-amine and 29 mL of H$_2$O while keeping all other conditions unaltered.

2.2. Preparation of the electrode

The working electrodes were constituted according to our previous paper [30]. The photoanodes were soaked in N719 ethanol solution for 6 hrs. The FTO substrate, dye-impregnated film, and Pt counter electrode fabricated a sandwich-like cell. A drop of the electrolyte was introduced into the cell, filling the space of the FTO substrate, a Pt counter electrode, and an I$_2$-LiI solution. The FTO substrate, dye-impregnated film, and Pt counter electrode fabricated a sandwich-like cell. The electrolyte was added to the stirred solution. The obtained compound was transferred to a 50 mL stainless Teflon-lined autoclave and treated at 200 °C for 24 h in an electric oven. The resulting gray precipitate was filtered, washed with distilled water and dried in air. Finally, the powder was calcined at 500 °C for 0.5 h in air with a heating rate of 5 °C/min. For comparison, the individual Zn$_2$SnO$_4$ nanosheet was obtained with a mixed solvent of 1 mL of 1–3 propanedi-amine and 29 mL of H$_2$O while keeping all other conditions unaltered.

2.3. Characterization

The morphology and crystallinity of the samples were characterized by the scanning electron microscopy (SEM, FEI NOVA NanoSEM230, USA) and transmission electron microscopy (TEM, JEOL 3010, Japan). The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALab MKII X-ray photoelectron spectrometer. The X-ray diffraction (XRD) data were obtained using X-ray diffractometer with Cu-Kα radiation at 200 mA and 40 kV. The Brunauer-Emmett-Teller (BET) surface area was measured on Tristar micromeritics surface area. The diffuse reflectance and optical absorption spectrum of powder were recorded with a UV–vis spectrophotometer (UV-2550, Shimadzu). To quantify the amount of desorbed N719, the dye-impregnated film was immerged into a 0.1 M NaOH aqueous solution, whose optical absorption spectra was recorded. The incident-photon-to-current conversion efficiency (IPCE) spectra were collected by PEC-S20 (Peccell Technology Co. Ltd.). The photocurrent–voltage characteristics (I–V) were performed using a sunlight simulator (Oriel 92251A-1000, AM 1.5 globe, 100 mW·cm$^{-2}$) with an active area of 0.132 cm$^2$. Electrochemical impedance spectroscopy (EIS) curves were observed with PAR2273 workstation (Princeton Applied Research, USA).

3. Results and discussion

3.1. Characteristics and structural properties of NHMSs

The SEM images show that the synthesized NHMSs are regular and uniform with an average diameter of about 1.2 μm (Fig. 1a and b). High-resolution SEM image shows that the Zn$_2$SnO$_4$ nanosheet building block in the hierarchical structures is ~80 nm in thickness (Fig. 1c) and closely interconnected to form the microsphere (Fig. 1d). The TEM image further reveals that the Zn$_2$SnO$_4$ nanosheet in the hierarchical microsphere was hexagonal with ~300 nm length (Fig. 2a). The high-resolution TEM (HRTEM) image shows the resolved lattice fringes separated by 0.49 nm, corresponding to the (111) plane of the cubic Zn$_2$SnO$_4$ phase (Fig. 2b).

All the XRD peaks for the Zn$_2$SnO$_4$ can be assigned to the cubic phase (a = b = c = 0.865 nm, α = 8β = γ = 90°). The X-ray diffraction patterns (XRD) with 2θ ranging from 5 degrees to 80 degrees and the corresponding diffraction peaks are indexed to the cubic phase with (100), (002), (101), (102), (110), (112), (200), (201), (210), and (211) planes of Zn$_2$SnO$_4$. The relative intensities of the XRD peaks are in good agreement with the JCPDS Card No. 74–2184(Fig. 3). The XPS spectra also demonstrate the presence of Zn, Sn, and O elements (Supplementary Fig. S1a). Supplementary Fig. S1b presents the binding energies of Sn 3 d$_{5/2}$ and Sn 3 d$_{3/2}$ corresponding to 485.7 and 494.5 eV, respectively.

Fig. 2. (a) TEM and (b) HRTEM image of the Zn$_2$SnO$_4$ nanosheet in the NHMSs.
Zn2SnO4/dye/electrolyte system as the two photoanodes are reasonable to assume the same injection efficiency. With 19.1 μm thickness and in close proximity to those of Zn2SnO4 nanoparticles (3.8%), the distinct photovoltaic behavior of the NHMS is its large diffusion recombination in photoanodes, originating from the disparate structure morphology of the Zn2SnO4. It is generally known that the existence of light scattering significantly extend the traveling distance of the light within the photoelectrode film and thus intensively increase the probability of the incident photons interacting with the dye molecules. This finally resulted in an enhancement in the light harvesting efficiency of the photoelectrode as well as an improvement in the solar cell’s performance.

The amount of diffusely scattered light as a result of a beam of irradiation on the film can be quantified by diffuse reflectance spectroscopy [33]. Fig. 5 and Supplementary Fig. S2 present the UV–vis diffuse reflectance spectra of the two films before and after the dye adsorption, respectively. Relative to the DNS film, the NHMS film possesses higher diffuse reflection in the wavelength range between 400 and 800 nm both before and after the dye adsorption, indicating that the NHMS film has a higher light-scattering ability than the DNS film. As shown in Supplementary Fig. S2, the reflectance of the two dye-adsorbed films decreases drastically due to light absorption by the N-719 molecules. Similar diffuse reflectance spectra of hierarchical microspheres with and without dye were also previously reported to explain the improved light-harvesting capability for the samples and different charge transport and recombination in photoanodes, originating from the disparate structure morphology of the Zn2SnO4. It is generally known that the existence of light scattering significantly extend the traveling distance of the light within the photoelectrode film and thus intensively increase the probability of the incident photons interacting with the dye molecules. This finally resulted in an enhancement in the light harvesting efficiency of the photoelectrode as well as an improvement in the solar cell’s performance.

The performance of the DNS-based DSSCs with various film thicknesses follows the same trend as that of the NHMS-based DSSCs. The highest η achieved from the NHMS cell is 3.43% with a 19.1 μm film thickness, whereas the 19.6 μm thick DNS electrode showed the η of 2.06%, a 67% improvement in the η compared to the DNS electrode. The η of 3.43% of the NHMS is higher than those of previous nanocrystalline Zn2SnO4 (3.08%) [18], Zn2SnO4 fibers (2.8%) [20], Zn2SnO4 micro-octahedron (3.1%)–based DSSCs [30], and in close proximity to those of Zn2SnO4 nanoparticles (3.8%) [10], and amorphous Zn2SnO4 nanofibers (3.7%)–based DSSCs [31].

Table 1: Photovoltaic properties of the DSSCs assembled by using electrodes made from NHMSs and DNSs of different thickness.

<table>
<thead>
<tr>
<th>Films</th>
<th>NHMS</th>
<th>DNS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (μm)</td>
<td>8.90</td>
<td>13.9</td>
</tr>
<tr>
<td>V oc (V)</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>I sc (mA/cm²)</td>
<td>4.32</td>
<td>5.82</td>
</tr>
<tr>
<td>FF (%)</td>
<td>72.9</td>
<td>72.5</td>
</tr>
<tr>
<td>η (%)</td>
<td>1.87</td>
<td>2.52</td>
</tr>
</tbody>
</table>

3.2. Photovoltaic performance of NHMSs

The nanosheet-assembling hierarchical Zn2SnO4 microspheres were utilized as a photoanode for DSSCs. For comparison, the dispersed Zn2SnO4 nanosheets were also fabricated through a similar solvothermal reaction (Fig. 1e-h and Fig. 3). The open-circuit voltages (Voc), fill factors (FF), I sc and η for NHMS and DNS electrodes with different thicknesses are given in Table 1. To NHMS-based DSSCs, the I sc and η increase initially from the cell film with a thickness of 8.90 μm to 19.1 μm, and finally drop down to 23.6 μm. The performance of the DNS-based DSSCs with various film thicknesses follows the same trend as that of the NHMS-based DSSCs. The highest η achieved from the NHMS cell is 3.43% with a 19.1 μm film thickness, whereas the 19.6 μm thick DNS electrode showed the η of 2.06%, a 67% improvement in the η compared to the DNS electrode. The η of 3.43% of the NHMS is higher than those of previous nanocrystalline Zn2SnO4 (3.08%) [18], Zn2SnO4 wires (2.8%) [20], Zn2SnO4 micro-octahedron (3.1%)–based DSSCs [30], and in close proximity to those of Zn2SnO4 nanoparticles (3.8%) [10], and amorphous Zn2SnO4 nanofibers (3.7%)–based DSSCs [31].

Fig. 4 compares the solar cell I–V based on the NHMS electrode with 19.1 μm thickness and DNS electrode with 19.6 μm thickness. While the NHMS and DNS-based DSSCs change little on V oc and FF, the distinct photovoltaic behavior of the NHMS is its large I sc (7.62 mA/cm²), which is much higher than DNS (5.48 mA/cm²). As well known, the I sc in the DSSCs is determined by the light harvesting efficiency (ηlh), the electron injection efficiency (ηinj) and the efficiency of collecting the injected charge at the back contact (ηoc), which can be calculated by the following expression [32]:

\[
I_{sc} = qF_{inj}η_{lh}η_{oc}I_0
\]

where q is the elementary charge, and I0 is the light flux. It is reasonable to assume the same injection efficiency for the given Zn2SnO4/dye/electrolyte system as the two photoanodes are composed of similar Zn2SnO4 materials. Obviously, both the ηlh and ηoc can influence the I sc. Then, the ηlh is determined by the dye loading and the light scattering ability. However, the amount of dye adsorption on the NHMS with the surface areas of 5.79 m² g⁻¹ (5.05 × 10⁻⁷ mol/cm² mμm) is smaller than that of DNS with the surface areas of 7.92 m² g⁻¹ (6.23 × 10⁻⁷ mol/cm² mμm). Therefore, the different values of I sc can be ascribed to the light-harvesting capability for the samples and different charge transport and recombination in photoanodes, originating from the disparate structure morphology of the Zn2SnO4. It is generally known that the existence of light scattering significantly extend the traveling distance of the light within the photoelectrode film and thus intensively increase the probability of the incident photons interacting with the dye molecules. This finally resulted in an enhancement in the light harvesting efficiency of the photoelectrode as well as an improvement in the solar cell’s performance. The amount of diffusely scattered light as a result of a beam of irradiation on the film can be quantified by diffuse reflectance spectroscopy [33]. Fig. 5 and Supplementary Fig. S2 present the UV–vis diffuse reflectance spectra of the two films before and after the dye adsorption, respectively. Relative to the DNS film, the NHMS film possesses higher diffuse reflection in the wavelength range between 400 and 800 nm both before and after the dye adsorption, indicating that the NHMS film has a higher light-scattering ability than the DNS film. As shown in Supplementary Fig. S2, the reflectance of the two dye-adsorbed films decreases drastically due to light absorption by the N-719 molecules. Similar diffuse reflectance spectra of hierarchical microspheres with and without dye were also previously reported to explain the improved light-harvesting capability for the samples and different charge transport and recombination in photoanodes, originating from the disparate structure morphology of the Zn2SnO4. It is generally known that the existence of light scattering significantly extend the traveling distance of the light within the photoelectrode film and thus intensively increase the probability of the incident photons interacting with the dye molecules. This finally resulted in an enhancement in the light harvesting efficiency of the photoelectrode as well as an improvement in the solar cell’s performance.

The amount of diffusely scattered light as a result of a beam of irradiation on the film can be quantified by diffuse reflectance spectroscopy [33]. Fig. 5 and Supplementary Fig. S2 present the UV–vis diffuse reflectance spectra of the two films before and after the dye adsorption, respectively. Relative to the DNS film, the NHMS film possesses higher diffuse reflection in the wavelength range between 400 and 800 nm both before and after the dye adsorption, indicating that the NHMS film has a higher light-scattering ability than the DNS film. As shown in Supplementary Fig. S2, the reflectance of the two dye-adsorbed films decreases drastically due to light absorption by the N-719 molecules. Similar diffuse reflectance spectra of hierarchical microspheres with and without dye were also previously reported to explain the improved scattering effect [34,35]. The IPCE spectra of the devices are further characterized (Fig. 6). Compared with DNS, NHMS exhibits similar IPCE in the short wavelength region (400–560 nm), which may be attributed to similar dye loading amount. However, NHMS possesses a higher IPCE value than DNS over the wavelengths range from 570–800, which is probably the consequence of better light-scattering efficiency [36]. The similar observations have also been demonstrated [33–35,37]. These can reasonably explain the above I–V results: although the dye amounts on the NHMS is lower,
microspheres, which favors the electron transport through a longer connectivity caused by the tightly packed nanosheets in the low transfer resistance could be due to better inter-sheets face ($R_{ct}$), which is the most important and decisive factor in DSSCs electron transfer resistance at the Zn$_2$SnO$_4$/dye/electrolyte inter-
and the larger one at the lower frequency region re process occurring at the counter electrode/electrolyte interface, is attributed to the impedance related to the charge transfer semicircles, the smaller semicircle occurring at higher frequencies (51.9 Hz) is much smaller than that of DNS (30.1 Hz). The electron lifetime ($\tau_e$) for recombination is estimated to be 12.45 ms and 5.29 ms, respectively. A significant increase in the $\tau_e$ value reveals the effective retardation of the charge recombination reaction between photo-injected electrons with I$_3^-$ during the electron transport through the film of NHMS, as compared to DNS-based film. Undoubtedly, the enhanced electron lifetime enable NHMS film to achieve higher overall photoconversion efficiency. Meanwhile, the characteristic frequency in the Bode phase plot of the NHMS device shifted to a lower frequency relative to those of the DNS device (Fig. 7b), further indicating that the charge-recombination rate is reduced in the microspheres systems and leads to the capture of more electrons and the enhancement of the cell efficiency [27].

4. Conclusions

A facile method has been developed for the synthesis of nanosheet-assembling hierarchical Zn$_2$SnO$_4$ microspheres. The unique hierarchical bifunctional structure provides a direct transfer pathway for the rapid collection of photogenerated electrons and an apparent microstructure can function as efficient light scatterers to enhance the light-harvesting efficiency, increase the photoconversion efficiency. With the hierarchical Zn$_2$SnO$_4$ microspheres as anode material, the DSSCs with an overall 3.43% photoconversion efficiency was obtained, which was a 67% improvement over the DSSCs that uses dispersed Zn$_2$SnO$_4$ nanosheets as anode. It is expected that the conversion efficiency of the present Zn$_2$SnO$_4$ can be further improved through coupling with other semiconductor such as SnO$_2$ to more efficiently separate photogenerated charges.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.electacta.2014.11.106.

References


