文章编号:1001-9014(2010)01-0001-05

PREPARATION OF MESOPOROUS ZnO MICROSPHERES AND THEIR APPLICATION IN DYE-SENSITIZED SOLAR CELLS

TAO Jun-Chao, SUN Yan, GE Mei-Ying, CHEN Xin, DAI Ning
(National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China)

Abstract: A novel ZnO photoanode with high specific surface area and good light scattering ability was fabricated for dye-sensitized solar cells (DSSCs). The photoanode comprised of mesoporous ZnO microspheres which were prepared by a solvothermal process. The structures and morphologies of ZnO microspheres were measured and confirmed by means of x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrum (EDS), and multi-point Brunauer-Emmett-Teller (BET) analysis. ZnO microspheres are in sub-micrometer scale and have BET specific surface area of ~ 50$m^2 \cdot g^{-1}$. Furthermore, a ~ 3μm thick photoanode made from ZnO microspheres resultes in a preliminary short-circuit current density (J_{sc}) of ~ 4.5mA · cm^{-2} with an open-circuit voltage (V_{oc}) of ~ 602mV and a conversion efficiency of 1.28% in DSSCs. All these suggest that mesoporous ZnO microspheres can be an alternative and feasible photoanode material for DSSCs.

Key words: ZnO; mesoporous microsphere; dye-sensitized solar cells (DSSCs)
CLC number: TM914.4 **Document**: A

介孔 ZnO 微球的制备及其在染料敏化太阳能电池中的应用

陶俊超, 孙 艳, 葛美英, 陈 鑫, 戴 宁
(中国科学院上海技术物理研究所 红外物理国家重点实验室, 上海 200083)

摘要: 制备了一种新型的染料敏化太阳电池的光阳极, 该电极由溶剂合成的具有高比表面积和良好光散射特性的ZnO介孔微球组成。采用X射线衍射、扫描电子显微镜、能谱仪及N_2吸附脱附等手段, 分析了介孔ZnO微球的结构和形貌。所得介孔微球尺寸在亚微米范围, 比表面积约为50$m^2 \cdot g^{-1}$。将ZnO介孔微球成功应用到染料敏化太阳电池中, 当光阳极为3μm时, 组成的原型器件的短路电流密度约为4.5mA · cm^{-2}, 开路电压约为602mV, 转换效率可达1.28%。研究结果表明, ZnO介孔微球是一种优异的染料敏化太阳电池的光阳极材料。

关 键 词: ZnO; 介孔微球; 染料敏化太阳电池

Introduction

DSSCs have been one of the most promising candidates for solar cells because of low cost and environmental compatibility[1~4]. To improve light conversion efficiency of DSSCs at a desirable cost is a challenge that needs to be met for practical applications. One of critical requirements of photoanode preparations should therefore be an improvement of light harvesting for increasing the conversion efficiency of DSSCs[5,6]. It is known that the light harvesting of DSSCs strongly depends on the photon absorption in the photoanodes. Thus, many efforts have been paid on increasing the surface area[7,8] and the optical enhancement effect[9]

Received date: 2009-06-10, **revised date**: 2009-10-16 **收稿日期**: 2009-06-10, **修回日期**: 2009-10-16
Foudantion item: Suppated by the National Natural Science Fundation of China (20704042, 60225004), the Shanghai City Committee of Science and Technology (06XD14020, 07JC14058, 0752nm016), Shanghai Pujiang Talent Plan (07PJ14095), the Knowledge Innovation Program of the Chinese Academy of Sciences (KSCX2-YW-G-042) and National Basic Research Program of China (2010CB933700).
Biography: Tao Junchao (1982-), male, Shanghai, China, PhD. candidate. Research fields focus on novel materials for DSSCs.

for improving the light harvesting capability of the photoanodes. For instance, mesoporous materials (e. g. mesostructure TiO_2) have been feasible and competent building blocks of photoanodes for increasing the monolayer absorption of dyes, and thus improving the light harvesting depending on the large specitic surface area. On the other hand, the sub-micrometer particles have attracted considerable attention because of the strong light scattering effects that can enhance photon absorption for increasing the short-circuit current density and promoting light conversion efficiency[10,11].

As mentioned above, both microspheres and mesoporous materials can be used in the photoanodes for increasing the light harvesting. However, little attention has been paid to mesostructure ZnO-based microspheres severed as building blocks for photoanodes in DSSCs. In this paper, we presented an alternative ZnO-based photoanode comprised of mesoporous ZnO microspheres. As-prepared ZnO microspheres possess BET specific surface area of ~ 50$m^2 \cdot g^{-1}$. Then, mesoporous ZnO microspheres were successfully applied to prepare the photoanode of ZnO-based DSSCs. The preliminary ZnO-based DSSCs were obtained with a short-circuit current density (J_{sc}) of ~ 4. 5mA · cm^{-2}, an open-circuit voltage (V_{oc}) of ~602 mV and an conversion efficiency of ~1.28 % when the photoanode thickness was ~3 μm.

2 Experimental section

2.1 Preparation of mesoporous ZnO microspheres

Triblock copolymer poly (ethylene glycol)-b-poly (propylene glycol)-b-poly (ethylene glycol) (PEO-PPO-PEO, abbreviated as P123) was purchased from Sigma-Aldrich, and zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was provided by Acros. All chemicals were analytical grade and used as received. In a typical synthesis, 2. 1 g P123 was dissolved in 25 ml ethanol. Then, 0. 3 g $Zn(CH_3COO)_2 \cdot 2H_2O$ and 0. 5 ml diethanol amine were added to the P123 solution in ethanol. The mixed solution was aged for 3 h under vigorous stirring. Finally, 20 ml of the resulting solution was placed in 50 ml Teflon-lined autoclave and heated at 200℃ for 24 h in an oven, and then cooled to room temperature. The white products obtained were centrifugated and washed with ethanol, and subsequently dried at 100℃ for 6h.

2.2 Characterization of mesoporous ZnO microspheres

XRD patterns were performed on Rigaku D/max 2550 diffractometer using a high power Cu Kα source operating at 40 kV and 150 mA. SEM images were obtained on FEI Sirion 200 SEM with an accelerating voltage of 15 kV. Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP 2400 nitrogen adsorption apparatus.

2.3 Fabrication and characterization of DSSCs

The mesoporous ZnO microspheres were re-dispersed in ethanol by using an ultrasonication process, and the weight ratio of ZnO and ethanol was about 5%. ZnO films were obtained on fluorine-tin-oxide (FTO) coated glass substrates by repeating a spin-coating and rapid thermal process. The films were annealed at 450℃ for 2 h and then cooled to ~70℃. Subsequently, they were immersed into a 5×10^{-4} M solution of N719 dye in ethanol for 12 h, and then rinsed with ethanol to remove excess dye on the surface and air-dried at room temperature. The sandwich-like DSSCs were fabricated by using Pt as counterelectrode and iodide-based solution as the liquid electrolyte. The absorption spectra of the photoanode were obtained on Perkin-Elemer Lambda 2S spectrophotometer with scanning rate of 240 nm/s. Mesoporous ZnO microspheres were used as the photoanode in the sandwich-like ZnO-based DSSCs. The ZnO electrode absorbing dye and a counterelectrode with Pt films of ~100 nm thick were assembled and sealed with Dupont Surlyn 1702 (25 μm). The electrolyte employed a solution of 0. 6 M BMII (1-butyl-3-methylimidazolium iodide), 0. 1 M I_2, 0. 1 M LiI and 0. 5 M 4-tertbutylpyridine in acetonitrile. The photocurrent-voltage (I-V) measurements were done using an AM1. 5 solar simulator (16S-002, Solar Light Co. Ltd., USA) as the irradiation source. The incident light intensity was 100 mW/cm^2 calibrated with a standard Si solar cell. The current-voltage curves were obtained by the linear sweep voltammetry (LSV) method using an electrochemical workstation (LK9805, Tianjing Lanlike Co., China).

The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by a Hypermonolight (SM-25, Jasco Co. Ltd., Japan).

3 Results and discussion

Figure 1 shows the small-angle and wide-angle XRD patterns and EDS of ZnO microspheres. The diffraction peaks in wide-angle XRD pattern indicate that ZnO is well crystalline and a hexagonal wurtzite structure, matching with the standard data according to JCPDS card (No. 36-1451). According to Scherrer equation ($D = 0.89\lambda/\beta\cos\theta$, $\lambda = 1.54056$ nm), the average crystallite size is ~12 nm when the (101) diffraction peak (Figure 1(a)) is used for the evaluation. Furthermore, the EDS spectrum demonstrates the formation of crystalline ZnO again that was only comprised of Zn and O elements. A sharp diffraction peak in $2\theta \approx 0.6$ degree in the small-angle XRD pattern represents the mesoporous structure in the ZnO materials. To further confirm the microstructure of ZnO products, BET method was used to study the specific surface area and Barrett-Joyner-Halenda (BJH) method for the average pore diameters. Figure 2 shows the plots of BJH pore-size distribution and nitrogen adsorption/desorption isotherms. The representative type-IV isotherm and the hysteresis (Figure 2) indicate the presence of inkbottle-shaped and cage-type pores in the given materials. The BET specific surface area is ~ $50 m^2 \cdot g^{-1}$, and the BJH analysis shows that the average pore size is about 5 nm. The mesoporous structure is helpful for improving light-harvesting in DSSCs and then light conversion efficiencies.

Figure 3 shows the typical SEM images of mesoporous ZnO microspheres. The overview in Figure 3 (a) indicates that ZnO microspheres are from ~200 nm to ~500 nm in size, and can be controlled as mentioned in our previous work [12]. According to Mie theory, light scattering upon spherical particles may occur when the particle size is comparable to the wavelength of incident light. Thus, ZnO microspheres can be used to increase light scattering and harvesting in DSSCs. The zoom images (Figure 3(b) and 3(c)) indicate that the surfaces of the microspheres are covered by nanoparticles. These nanoparticles accumulate

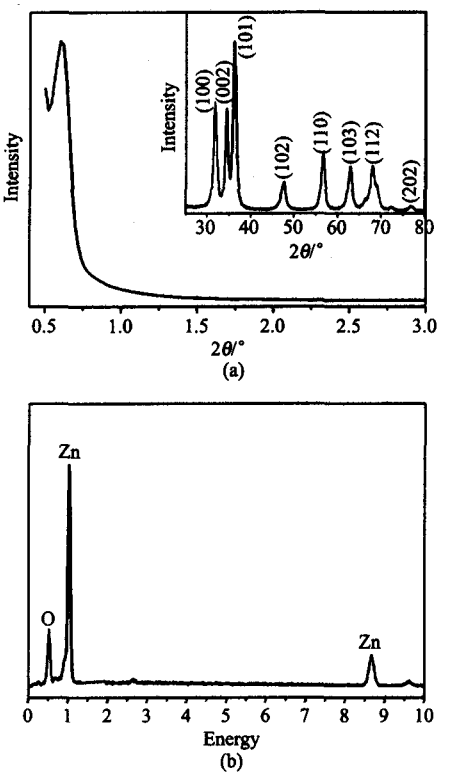

Fig. 1 Small-angle XRD pattern, wide-angle XRD pattern (a) and EDS spectrum (b) of the mesoporous ZnO microspheres
图 1 ZnO 介孔微球的小角 XRD 和广角 XRD(a) EDS 能谱图(b)

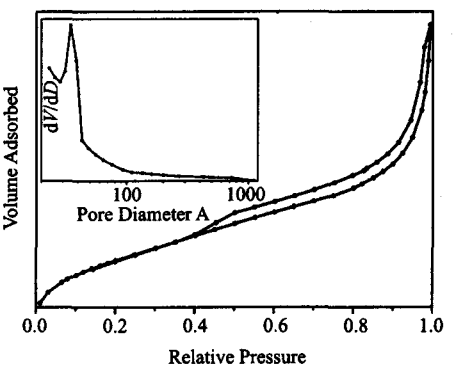

Fig. 2 Plots for N_2 adsorption/desorption isotherms and BJH pore size distribution (the inset) of mesoporous ZnO microspheres.
图 2 ZnO 介孔微球的 N_2 吸附脱附曲线和孔径分布图(插图)

and form mesopores among these nanoparticles. Different from the mesoporous SiO_2 with amorphous phase, the mesopores insides the ZnO microspheres are constituted of ZnO nanocrystallites, i. e. the pore walls are crystalline. As implied in XRD patterns in Figure 1 (a), the average size of the ZnO nanocrystallites is ~

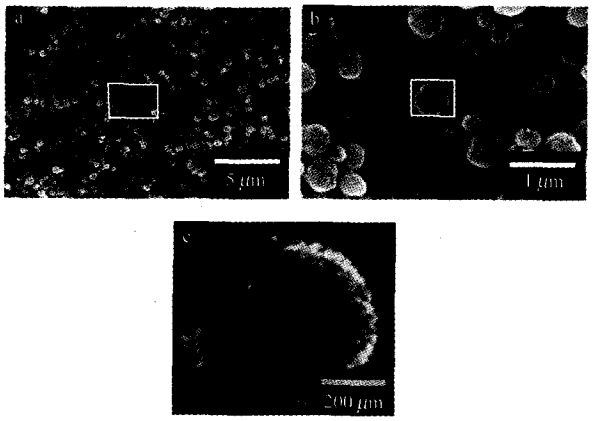

Fig. 3 SEM images of the mesoporous ZnO microspheres (a) overview (b) zoom image of (a) in the red-line area (c) zoom image of (b) in the red - line area.
图3 ZnO介孔微球的SEM图 (a)为总体形貌 (b)为a图里红色区域高放大倍数图 (c)为b图里红色区域高放大倍数图

11 ~ 13 nm and that of the mesopores is several nanometers.

ZnO have been used as an alternative photoanode material in DSSCs due to its large bandgap at ~3.2 eV (similar to that of TiO_2) and the high electron mobility. Mesoporous ZnO microspheres can be used to prepare the feasible photoanodes in DSSCs because they have relative surface area and can also act as light scatterers. Figure 4 shows absorption spectra of the mesoporous ZnO microspheres films (seen from curve a) and the films sensitized with N719 (seen from curve b). The wide absorption scale from 400 to 750 nm was due to the absorption of N719 dye which absorbed on

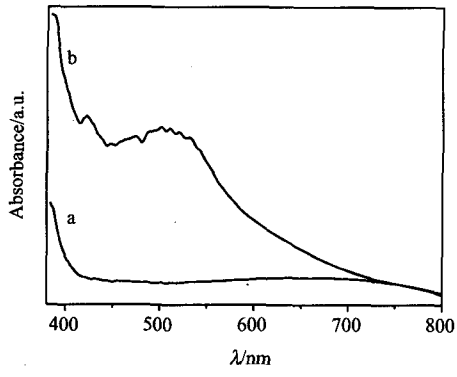

Fig. 4 Absorption spectra of mesoporous ZnO microspheres films (curve a) and mesoporous ZnO microspheres films sensitized with N719 (curve b)
图4 a为ZnO介孔微球膜的吸收光谱,b为染料N719敏化后的ZnO介孔微球膜的吸收光谱

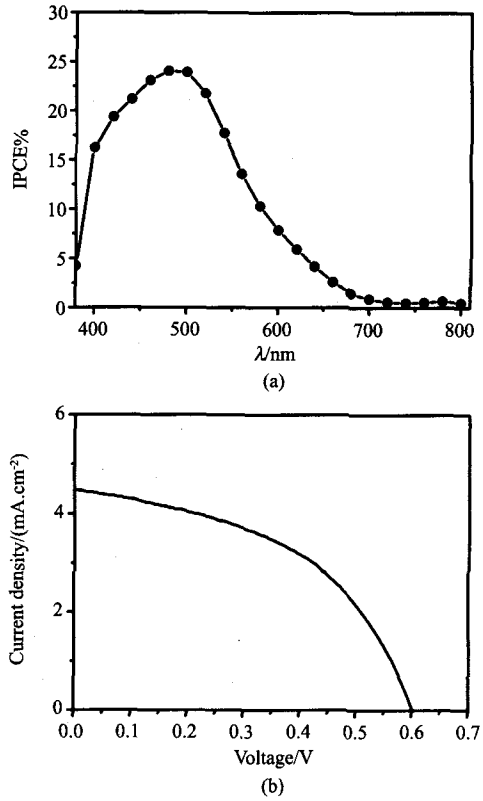

Fig. 5 (a) Photocurrent action spectrum of meseoporous ZnO based DSSCs (b) *I-V* characteristics of the mesoporous ZnO based solar cells under AM 1.5 irradiation
图5 (a)ZnO介孔微球基染料敏化太阳电池在AM1.5下的光电流作用谱,(b)ZnO介孔微球基染料敏化太阳电池在AM1.5下的IV特性曲线

the surface of mesoporous ZnO photoanode.

Figure 5 (a) shows photocurrent action spectrum of meseoporous ZnO based DSSCs. The ZnO electrode with 3 μm in thickness and the active areas of solar cells were about 0.159 cm^{-2}. IPCE was defined as the following, IPCE (%) = $(1240 \times I_{sc})/(\lambda \times P_{in}) \times 100\%$, I_{sc}, λ and P_{in} are short-circuit current density ($\mu A \cdot cm^{-2}$), wavelength of the incident monochromatic light (nm) and light energy ($\mu W \cdot cm^{-2}$), respectively. The photocurrent action spectrum almost covered the whole visible light scale, which is consistent with the absorption spectrum of mesoporous ZnO films sensitized with N719 dye. Figure 5 (b) represents *I-V* characteristics of the mesoporous ZnO based DSSCs under AM1.5 irradiation. The preliminary devices shows desirable photo-electric conversion properties, with a short-circuit current density (J_{sc}) of ~4.5 $mA \cdot cm^{-2}$, an open-circuit voltage (V_{oc}) of ~602

mV. The power conversion efficiency was calculated about 1.28 % from the relationship, $\eta = I_m V_m / P \times 100\%$, where $I_m V_m$ is the maximum multiplied value in the *I-V* curve, and *P* is the illumination power input of ~100 mW/cm^2. All these demonstrate that the mesoporous ZnO microspheres can be used as efficient photoanode materials in DSSCs. We expect that the mesoporous structures with large surface areas are helpful for absorbing more dyes, and increasing light harvesting, electron transfer and electrolyte diffusion. At the same time, the ZnO microsphere structure may help to enhance light scattering and thus increase photon absorption of DSSCs. All those may improve the light-harvesting and light conversion efficiencies. V_{oc}, J_{sc} and fill factor (FF) would be further improved by optimizing ZnO photoanode and device structures.

4 Conclusion

We demonstrated mesoporous ZnO microspheres, an alternative and facile photoanode material prepared by solvothermal processes. The mesopores with a BET specific surface area of 50 m^2 g^{-1} formed by packing ZnO nanocrystallites. The ZnO-based DSSCs were successfully fabricated using mesoporous ZnO microspheres as photoanode, and resulting in short-circuit current density (J_{sc}) of ~4.5 mA · cm^{-2}, open-circuit voltage (V_{oc}) of ~602 mV and conversion efficiency of ~1.28 % with about 3 μm photoanode when N719 dye was used. Ongoing investigations will focus on optimizing the structures and the processes of based on mesoporous ZnO microspheres.

REFERENCES

[1] Grätzel M. Photoelectrochemical cells[J]. *Nature* 2001, **414**:338—344.

[2] Grätzel M. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells[J]. *Inorg. Chem.*, 2005, **44**:6841—6851.

[3] Thomas W H, Rebecca A J, Alex B F M, *et al.* Advancing beyond current generation dye-sensitized solar cells[J]. *Energy Environ. Sci.*, 2008, **1**:66—78.

[4] Ito S, Murakami T N, Comte P, *et al.* Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%[J]. *Thin Solid Films*, 2008, **516**:4613—4619.

[5] Wang P, Wang L, Ma B, *et al.* TiO_2 Surface modification and characterization with nanosized PbS in dye-sensitized solar cells[J]. *J Phys. Chem. B*, 2006, **110**: 14406—14409.

[6] Law M, Greene L E, Johnson J C, *et al.* Nanowire dye-sensitized solar cells[J]. *Nat. Mater.*, 2005, **4**:455—459.

[7] Zukalova M, Zukal A, Kavan L, *et al.* Organized mesoporous TiO_2 films exhibiting greatly enhanced performance in dye-sensitized solar cells[J]. *Nano Lett.*, 2005, **5**: 1789—1792.

[8] Hamann T W, Martinson A F, Elam J W, *et al.* Aerogel templated ZnO dye-sensitized solar cells[J]. *Adv. Mater.*, 2008, **20**:1560—1564.

[9] Chou T P, Zhang Q, Fryxell G E, *et al.* Hierarchically structured ZnO film for dye-sensitized solar cells with enhanced energy conversion efficiency[J]. *Adv. Mater.*, 2007, **19**:2588—2592.

[10] Zhang Q, Chou T P, Russo B, *et al.* Aggregation of ZnO nanocrystallites for high conversion efficiency in dye-sensitized solar cells[J]. *Angew. Chem. Int. Ed.*, 2008, **47**: 2402—2406.

[11] Nishimura S, Abrams N, Lewis B A, *et al.* Standing wave enhancement of red absorbance and photocurrent in dye-sensitized titanium dioxide photoelectrodes coupled to photonic crystals[J]. *J Am. Chem. Soc.*, 2003, **125**:6306—6310.

[12] Tao J, Chen X, Sun Y, *et al.* Controllable preparation of ZnO hollow microspheres by self-assembled block copolymer[J]. *Colloid Surf. A*, 2008, **330**:67—71.