Synthesis of ZnO Nanocrystals and Application in Inverted Polymer Solar Cells

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Abstract

Controllable synthesis of various ZnO nanocrystals was achieved via a simple and cost-effective hydrothermal process. The morphology evolution of the ZnO nanostructures was well monitored by tuning hydrothermal growth parameters, such as solution concentration, reaction temperature, and surfactant. As-obtained ZnO nanocrystals with different morphologies, e.g., ZnO nanorods, nanotetrapods, nanoflowers, and nanocubes, were further introduced into the organic bulk heterojunction solar cells as the electron transport channel. It was found that the device performance was closely related to the morphology of the ZnO nanocrystals.

Keywords: Zinc oxide, Nanocrystals, Hydrothermal, Solar cells

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Background

Organic bulk heterojunction solar cells using n-type inorganic metal oxide nanostructures as the electron transport channel have attracted considerable attentions because of its improved ambient device stability, low-cost manufacturing, and compatibility to solution fabrication process [1–4]. ZnO nanocrystals, which have high electron mobility, excellent stability, good transparency in the whole visible range, simple preparation process, and easier tailoring of the nanostructures, are promising candidates as the electron transport channel in organic bulk heterojunction solar cells. Recently, various ZnO nanostructures, e.g., nanorods, nanowalls, and nanotetrapods, have been introduced to the organic bulk heterojunction solar cells [5–7]. And it is reported that the device performance is improved by providing a short and continuous pathway for electron transport, enhancing the exciton dissociation ratio, or increasing the ZnO/active layer interface area. However, the relationship between the morphology of the ZnO nanocrystals and the device performance is still controversial.

In this paper, we prepared ZnO nanocrystals with different morphologies via a simple and cost-effective hydrothermal process. The morphology of the ZnO nanostructures was tuned effectively by varying hydrothermal growth parameters, such as the solution concentration, reaction temperature, and surfactant. As-obtained ZnO nanocrystals with different morphologies, e.g., ZnO nanorods, nanotetrapods, nanoflowers, and nanocubes, were further introduced into the organic light absorber as the electron transport channel. The current density-voltage ($J-V$) result reveals that the device performance is closely related to the morphology of the ZnO nanocrystals. To improve the device performance, large surface area and proper space between adjacent ZnO nanocrystals for the infiltration of the organic light absorber, as well as a short and continuous pathway for electron transport, are essential.

Methods

Deposition of ZnO Seed Layer

To grow ZnO nanocrystals on mismatched substrates, the ZnO seed layer is essential. In this paper, the ZnO seed layer is prepared by the dip-coating method, which has been described in our previous paper [8].

Hydrothermal Growth of ZnO Nanocrystals

To grow various ZnO nanostructures, the indium-tin-oxide (ITO) substrate coated with the ZnO seed layer was fixed upside down in the reaction vessel filled with 40 ml aqueous solution of zinc nitrate hexahydrate ($\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$) and hexamethylenetetramine (HMTA) with the identical concentration. Then, a certain amount

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of surfactant, such as polyethylenimine (PEI) or sodium
citrate, was added in the aqueous solution [8]. Next, the
reaction vessel was sealed and kept at a constant
temperature for a certain time. Finally, as-grown ZnO
nanocrystal was taken out, rinsed in deionized water, and
dried in air for use.

Fabrication of the Solar Cells [9]
Firstly, a thin PCBM layer was spin-coated onto the ZnO
nanocrystal from a dichloromethane solution with the con-
centration of 20 mg/ml, at 1000 rpm for 30 s. It was re-
ported that the [6]-phenyl-C 61-butyric acid methyl ester
(PCBM) layer between the ZnO nanocrystal and organic
active layer could improve the infiltration of the active poly-
mer layer into the gaps of ZnO nanocrystals [10]. Then, the
active layer comprising of poly(3-hexylthiophene) (P3HT,
10 mg/ml) and PCBM (16 mg/ml) blending in chloroben-
zene was spin-coated on the top of the PCBM layer at
1000 rpm for 30 s. After that, the samples were baked at
225 °C for 1 min to remove the residual solvent and assist
the polymer infiltrate into the gaps of ZnO nanocrystals.
Next, poly(3,4-ethylene dioxythiophene):poly(styrene sul-
fonate) (PEDOT:PSS) hole transport layer was spin-coated
at 4000 rpm for 40 s, and then thermally annealed at
130 °C for 15 min in air, resulting in a ~35-nm thick
PEDOT:PSS layer. Finally, 100 nm Al was deposited by
thermal evaporation as a cathode to create a device.
Finally, the devices were thermally annealed at 130 °C for
20 min on the hotplate under nitrogen ambient. The final
device structure is shown in Fig. 1.

Characterization
Surface morphologies of the ZnO nanocrystals were
characterized by field emission scanning electron
microscopy (SEM; FE-4800, Hitachi, Tokyo, Japan). The J-V characteristics of solar cells were taken using a
Keithley 2400 source measure unit under 100 mW/cm²
illumination (AM 1.5G).

Results and Discussion
By tuning hydrothermal growth parameters, such as the
solution concentration, reaction temperature, and sur-
factant, ZnO nanocrystals with different morphologies,
e.g., ZnO nanorods, nanotetrapods, nanoflowers, and
nanocubes, were obtained. Among them, patterned and
aligned ZnO nanorod array was synthesized via a hydro-
thermal route by using the TiO 2 ring template deriving
from the polystyrene microsphere self-assembled mono-
layer (inverted self-assembled monolayer template),
which has been demonstrated in our previous work [11].
Figure 2a, b presents the top and 45° tilt view of the as-
grown ZnO nanorod array, grown in the aqueous solu-
tion containing 0.05 M Zn(NO₃)₂·6H₂O and HMTA at
80 °C for 3 h. It can be seen that the ZnO nanorod array
reserves the long-range hexagonal periodicity of the
TiO₂ ring template very well. All of the ZnO nanorods
are perfectly aligned normal to the substrate with the
uniform diameter of 380 nm, which can provide a short
and continuous pathway for electron transport, and only
one ZnO nanorod is grown at each growth site. From
the top view of the as-grown ZnO nanorod array in
Fig. 2a, we can see that the space between adjacent ZnO
nanorods is about 200 nm wide, which is important for
the following infiltration of the organic light absorber. Be-
sides, both the diameter and length of the ZnO nanorods
can be varied easily by varying the solution concentration
and reaction temperature during hydrothermal growth, as
reported in our previous work [11]. The ZnO nanotetra-
pod array, as shown in Fig. 2c, d, was grown at 0.025 M,
50 °C for 6 h by the inverted self-assembled monolayer
template similar with the ZnO nanorod array. The differ-
ence from the ZnO nanorod array is that a certain amount
of PEI (0.1 ml PEI per 40 ml reaction solution) has been
used during the hydrothermal growth, which is reported
to promote the growth in the axial direction, but suppress
the growth in the radial direction [12]. From the top view
(Fig. 2c) and 45° tilt view (Fig. 2d) of the ZnO nanotetra-
pod array, we can see that the nanotetrapod array also re-
serves the long-range hexagonal periodicity of the TiO₂
ring template very well, and each nanotetrapod is com-
posed of three to seven nanorods grown at each growth
site, so the surface area of the ZnO nanotetrapod array is
much larger than the ZnO nanorod array.

Figure 3a, b shows the SEM images of ZnO nano-
flowers and nanocubes, respectively, which are prepared
by a two-step method, as follows. Firstly, ZnO nanorods
were grown via the hydrothermal process in the aqueous
solution containing 0.025 M Zn(NO₃)₂·6H₂O and
HMTA at 85 °C for 3 h. Then, as-grown ZnO nanorods were immersed into different solutions for secondary growth. ZnO nanoflowers were obtained in the solution of 0.0075 M Zn(NO$_3$)$_2$·6H$_2$O and 0.0075 M sodium citrate at 95 °C for 12 h, while ZnO nanocubes were obtained in the solution of 0.0075 M Zn(NO$_3$)$_2$·6H$_2$O and 0.015 M sodium citrate at 95 °C for 6 h. Finally, as-grown ZnO nanoflowers and nanocubes were thoroughly rinsed with deionized water and dried in air to remove residual polymer. From the top view of the ZnO nanoflowers in Fig. 3a, we can see that the ZnO nanoflowers are unordered and crowded, and each nanoflower is composed of many “petals”, so the surface area is increased greatly. However, the space between adjacent “petals” of the ZnO nanoflowers is so small (~30 nm wide), as shown in the zoom-in view of Fig. 3a, that the following infiltration of the organic light absorber become very difficult. Figure 3b presents the top view of the ZnO nanocubes. Obviously, the ZnO nanocubes are uniform in size and the length of the side is about 150 nm. Besides, each ZnO nanocube is separated off from one another, which will influence the electron transport in solar cells, as described later in this article.

Next, the four types of ZnO nanocrystals are introduced into the organic bulk heterojunction solar cells, as shown in Fig. 1. During the fabrication process, four
solar cells were fabricated in each ITO substrate. Among which, if the maximum photon conversion efficiency (PCE) deviation is less than 3% in at least three solar cells with higher PCE values, then their performance parameters will be recorded. The highest PCE values in the records were adopted here for comparison. There, five samples were made for each example, among which, the PCE and other key parameters deviation for each example is less than 3%, thus the results are believable. The $J-V$ characteristics of the solar cell devices with different ZnO nanocrystals under simulated sunlight were shown in Fig. 4, and the corresponding device performance is summarized in Table 1.

It can be seen that the ZnO nanotetrapod device shows a highest PCE of 3.96, followed by the ZnO nanorod and nanoflower device (3.71 and 3.69, respectively), and the ZnO nanocube device showed a lowest PCE of 3.25. The improvement in PCE arises from the higher short-circuit current density ($J_{SC}$), while the open circuit voltage ($V_{OC}$) of the four devices remains almost unchanged. The best performance of ZnO nanotetrapod device can be ascribed to the large surface area and proper space (~300 nm) between adjacent ZnO nanocrystals for the infiltration of the organic light absorber. The ZnO nanorod device suffers from relatively lower surface area, leading to lower dye loading and light harvesting, which will affect the charge extraction, and thus shows a lower $J_{SC}$ compared with the ZnO nanotetrapod device [13]. The ZnO nanoflowers, as shown in Fig. 2c, d, has the largest surface area, but the corresponding device presents lower PCE compared with the ZnO nanotetrapod. Because the space (less than 50 nm) between adjacent “petals” of the ZnO nanoflowers is so close that the infiltration and the combination of the organic light absorber and the ZnO electron transport channel become very poor. As known, to achieve a higher ability of carrier transmission and exciton dissociation, better infiltration and more effective contact are essential. Hence, the ZnO nanoflower device suffers lower $J_{SC}$, compared with the ZnO nanotetrapod. Besides the large surface area and proper space between adjacent ZnO nanocrystals for the infiltration of the organic light absorber, a short and continuous pathway for electron transport is also very important. For the ZnO nanocube device, as each ZnO nanocube is separated off from one another, the pathway for electron transport, which is interrupted by the grain boundary between adjacent nanocubes, is not continuous. As a result, the ZnO nanocube device presents the lowest $J_{SC}$.

**Conclusions**

In conclusion, we have synthesized various ZnO nanocrystals via a simple and cost-effective hydrothermal process. By tuning hydrothermal growth parameters, such as solution concentration, reaction temperature, and surfactant, ZnO nanorods, nanotetrapods, nanoflowers, and nanocubes have been obtained. These ZnO nanocrystals with different morphologies were further introduced into the active layer of organic bulk heterojunction solar cell as the electron transport channel. It was found that the device performance was closely related to the morphology of the ZnO nanocrystals. To improve the device performance, large surface area, proper space between adjacent ZnO nanocrystals, and a short and continuous pathway for electron transport, are essential.

| ZnO nanostructure | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF(%) | PCE(%) | $R_{series}$ (Ω/cm$^2$) |
|-------------------|----------------------|-------------|--------|--------|----------------------|
| Nanorods          | 9.67                 | 0.66        | 58     | 3.71   | 73.7                 |
| Nanotetrapods     | 11.24                | 0.65        | 55     | 3.96   | 71.4                 |
| Nanoflowers       | 10.2                 | 0.66        | 55     | 3.69   | 93.8                 |
| Nanocubes         | 9.01                 | 0.66        | 56     | 3.25   | 109.9                |
Abbreviations
HMTA: Hexamethylenetetramine; ITO: Indium-tin-oxide; \(J_{SC}\): Short-circuit current density; \(J-V\): Current density-voltage; P3HT: Poly(3-hexylthiophene); PCBM: \[6\]-Phenyl-C61-butyric acid methyl ester; PCE: Photon conversion efficiency; PEDOT: PSS: Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate); PEI: Polyethylenimine; SEM: Field emission scanning electron microscopy; \(V_{OC}\): Open circuit voltage

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Authors’ Contributions
JJD designed the experiment, carried out part of the experiment, analyzed the results, and participated in the draft of the manuscript; JW carried out part of the experiment and characterization; HYH supervised the research and revised the manuscript; JX, HL, and HG offered the technique supports. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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References
1. Huynh WU, Dittmer JJ, Alivisatos AP (2002) Hybrid nanorod-polymer solar cells. Science 295:2425–2427
2. Dayal S, Kopidakis N, Olson DC, Ginley DS, Rumbles G (2010) Photovoltaic devices with a low band gap polymer and CdSe nanostructures exceeding 3% efficiency. Nano Lett 10:239–242
3. Ren SQ, Chang LY, Lim SK, Zhao J, Smith M, Zhao N, Bulovic V, Bawendi M, Gradenek 5 (2011) Inorganic-organic hybrid solar cell: bridging quantum dots to conjugated polymer Nanowires. Nano Lett 11:3998–4002
4. Chang JA, Rhee JH, Im SH, Lee YH, Kim HJ, Seok S, Nazaruddin MK, Gratzel M (2010) High-performance Nanostructured inorganic-organic heterojunction solar cells. Nano Lett 10:2609–2612
5. Reek W, Wemk M, Janssen R (2004) Efficient hybrid solar cells from zinc oxide nanoparticles and a conjugated polymer. Adv Mater 16:1009–1013
6. Reek W, Wemk M, Janssen R (2006) Hybrid solar cells from regioregular polythiophene and ZnO nanoparticles. Adv Funct Mater 16:1112–1116
7. Galoppini E, Rochford J, Chen HH, Saraf G, Lu YC, Hagfeldt A, Bosshoo G (2006) Fast electron transport in metal organic vapor deposition grown dye-sensitized ZnO nanorod solar cells. J Phys Chem B 110:16152–16161
8. Dong JJ, Zhen CY, Hao HY, Xing J, Zhang ZL, Zheng ZY, Zhang XW (2013) Controllable synthesis of ZnO nanostructures on the Si substrate by a hydrothermal route. Nanoscale Res Lett 8:378–384
9. Liang ZQ, Gao R, Lan J, Wranachoblayan O, Zhang QF, Li CD, Cao GZ (2013) Growth of vertically aligned ZnO nanowalls for inverted polymer solar cells. Sol Energy Mater Sol Cells 117:34–40
10. Huyn HJ, Chou CY, Lin CF (2010) Enhancing performance of organic-inorganic hybrid solar cells using a fullerene interlayer from a liquid solution processing. Sol Energy Mater Sol Cells 94:182–186
11. Dong JJ, Zhang XW, Yin ZG, Zhang SG, Wang JX, Tan HR, Gao Y, Si FT, Gao HJ (2011) Controllable growth of highly ordered ZnO nanorod arrays via self-assembled monolayer template. ACS Appl Mater Interfaces 3:4388–4395
12. Greene LE, Yuhas BD, Law M, Zitoun D, Yang PD (2006) Solution-grown zinc oxide nanowires. Inorg Chem 45:7535–7543
13. Jiang CY, Sun XW, Lo GQ, Kwong DL (2007) Improved dye-sensitized solar cells with a ZnO-nanoflower photoanode. Appl Phys Lett 90:263501–263503