## The examination of the most appropriate size of ZnO nanorods in organic-inorganic hybrid solar cells

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## 1. Introduction

The organic-inorganic hybrid solar cells by using ZnO nanorods and P3HT were fabricated. Fabrication of hybrid solar cells was to grow the ZnO nanorods vertically on the ITO substrates and fill with the bulk heterojunction polymers. The interface between organic and inorganic nanostructures influences the performance of organic-inorganic hybrid solar cells. In this paper, the most appropriate size of ZnO nanorods was examined when ZnO nanorods were used in organic-inorganic hybrid solar cells. After the most appropriate size of ZnO nanorods was clarified, organic-inorganic hybrid solar cells were fabricated using P3HT and PCBM blend polymer.

#### 2.Experimental procedure

#### Fabrication of ZnO nanoparticle layer

A 40 ml solution of zinc acetate dehydrate, 2-methoxyethanol and 2-aminoethanol was stirred for 2 h at room temperature. The concentration of zinc acetate dehydrate was 0.5 M. A clean ITO substrate was dip coated by immersion in the solution and subsequently raised at 1 mm/s, which provided a zinc acetate dehydrate template layer. The coated ITO was annealed at 200 °C for 1 h in air, which formed a freestanding ZnO nanoparticle layer on the ITO.

## Fabrication of the ZnO nanorods[1][2]

A 100 ml solution of zinc nitrate hexahydrate, ammonium chloride, urea and ammonia solution was stirred for 1 h at room temperature. The concentration of zinc nitrate hexahydrate was 0.1 M. The ZnO nanoparticle layered ITO substrates were immersed in the solution at 90 °C for 15-210 min, which formed ZnO nanorods on the surface of the ZnO nanoparticle layer. Substrates were removed from solution, rinsed with ultrapure water and then dried under N<sub>2</sub>. ZnO nanorods were characterized by FE-SEM, film thickness measurements.

## Fabrication of the organic-inorganic hybrid solar cells

A 500  $\mu$ l solution of P3HT, monochlorobenzene and chloroform was produced. The concentration of P3HT was 40 mg/ml. The solution(60  $\mu$ l) was deposited on the ZnO nanorods by spin-coating at 800 rpm. Then, the samples were immediately annealed at 50 °C for 10 min in order to form high crystalline of polymer. Finally, silver electrodes

were deposited on the top of the photoactive layer under high vacuum in the evaporation system.

After the most appropriate size of ZnO nanorods was clarified, organic-inorganic hybrid solar cells were fabricated using P3HT and PCBM blend polymer. The concentration of both P3HT and PCBM was 40 mg/ml.

The current density-voltage(J-V) characteristics were measured by using optical modelex under air and simulation light, AM1.5, 100 mW/cm<sup>2</sup>. The active area of the device irradiated by the light was defined as  $0.25 \text{ cm}^2$  by using a photomask.

#### 3. Results and discussion

# Crystalline, orientation, morphology and Growth process of ZnO nanorods[3]

ZnO nanorods were vertical, well-aligned and uniformly distributed on the ITO substrate. Average crystal width of ZnO nanorods increased linearly up to 90 min immersion time and then stopped. Average crystal width eventually became constant at ~500 nm. Moreover, thickness of ZnO nanorods increased linearly up to 90 min immersion time and then stopped. ZnO film thickness eventually became constant at ~5  $\mu$ m.

Characteristics of the organic-inorganic hybrid solar cells

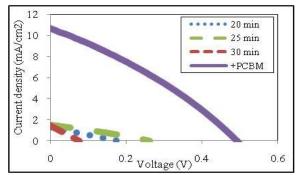


Fig.1 The J-V characteristics of the organic-inorganic hybrid solar cells using ZnO nanorods immersed for 20, 25, 30 min, +PCBM.

Table I The  $J_{SC}$ - $V_{OC}$  characteristics of the organic-inorganic hybrid solar cells using ZnO nanorods immersed for 20, 25, 30 min, +PCBM.

	V <sub>OC</sub>	J <sub>SC</sub>	FF	PCE
	(V)	$(mA/cm^2)$		(%)
20 min	0.180	1.261	0.065	0.057
25 min	0.262	1.514	0.105	0.115
30 min	0.073	1.394	0.028	0.026
+PCBM	0.498	10.663	0.214	1.643

ZnO nanorods immersed for 15-90 min were applied to the organic-inorganic hybrid solar cells. Then, hybrid solar cells using ZnO nanorods immersed for 15, 45, 60, 75, 90 min didn't generate electric power. Meanwhile, hybrid solar cells using ZnO nanorods immersed for 20, 25, 30 min generate electric power.

The  $J_{SC}$ - $V_{OC}$  characteristics of the organic-inorganic hybrid solar cells which generate electric power are shown in Fig.1 and Table.1 for comparison.

The hybrid solar cell performance was best when ZnO nanorods immersed for 25 min was used. In this case, crystal length was 110 nm and thickness was 1.5  $\mu$ m(Fig.2).

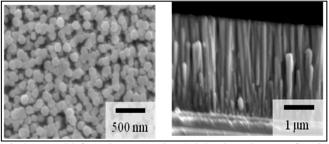


Fig.2 Frontal(left) and cross-sectional(right) SEM images of ZnO nanorods(25 min immersion).

In order to consider the result from the viewpoint of the junction area between ZnO nanorods and P3HT, surface area of one ZnO nanorod was calculated. If one ZnO nanorod is considered to be a regular hexagon column, surface area(S) was the following.

$$S = \sqrt{3a(a+2b)}$$
 (a:crystal length,b:thickness) (1)

The surface area of ZnO nanorod immersed for 15-90 min was calculated by eq. (1), respectively. Fig.3 shows the relationship between conversion efficiency and surface area.

The hybrid solar cells generated electric power only within  $1.0 \sim 10.0 \times 10^5 \text{ (nm)}^2$ . Then, the hybrid solar cell performance was best when surface area was  $5.87 \times 10^5 \text{ (nm)}^2$ (crystal length:110 nm, thickness:1.5 µm).

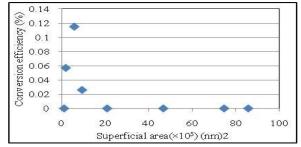


Fig.3 Relationship between conversion efficiency and surface area.

Considered from surface area, the surface area was divided into three situations. The first situation was  $S < 1.0 \times 10^5 \text{ (nm)}^2$ . The second situation was  $1.0 \times 10^5 \text{ (nm)}^2 < S < 10.0 \times 10^5 \text{ (nm)}^2$ . The third situation was  $10.0 \times 10^5 \text{ (nm)}^2 < S$ (Fig.4).

In the first situation, the charge separation didn't occur because junction area was small. Therefore, photocurrent was not produced. In the third situation, we considered that the charge recombination occurred than the charge separation. Therefore, photocurrent was not produced. In the second situation, we considered that the charge separation occurred than the charge recombination. Therefore, photocurrent was produced. If surface area of ZnO nanorods was  $5.87 \times 10^5$  (nm)<sup>2</sup>, we considered that the charge separation occurred most effectively.

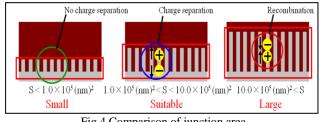


Fig.4 Comparison of junction area

When P3HT and PCBM blend polymer was used under using ZnO nanorods immersed for 25 min, the hybrid solar cell exhibits a  $J_{SC}$  of 10.663 mA/cm<sup>2</sup>, a  $V_{OC}$  of 0.498 V, an FF of 0.214, a PCE of 1.643 %(Fig.1, Table I).

#### 4. Summary and further work

In this paper, the most appropriate size of ZnO nanorods was examined when ZnO nanorods were used in organic-inorganic hybrid solar cells.

The most appropriate size of ZnO nanorods was the following. The crystal length was 110 nm, thickness was 1.5  $\mu$ m, and surface area was  $5.87 \times 10^5$  (nm)<sup>2</sup>. When P3HT and PCBM blend polymer was used under using these ZnO nanorods, conversion efficiency was 1.643 %. The interface between ZnO nanorods and blend polymer will be improved as further work.

#### References

- [1].Xiulan Hu, J. Am. Ceram. Soc.,92[4] 922–926 (2009)[2].Xavier Bulliard, Adv. Funct. Mater.,20,4381-4387(2010)
- [3].T.ichikawa, Inorg. Chem., 50, 999-1004(2011)