

ZnO Nanorod Arrays Fabricated by Hydrothermal Method Using Different Thicknesses of Seed Layers for Applications in Hybrid Photovoltaic Cells

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ZnO nanorod arrays have been synthesized on seed-coated indium tin oxide (ITO) substrates by a hydrothermal method from different thicknesses of seed layers. The ZnO nanorods obtained were investigated by scanning electron microscopy (SEM) to study the influence of different seed layer thicknesses on the orientation of the nanorods. The diameter of ZnO nanorods increased with increasing seed layer thickness. An X-ray diffractometer was used to verify the formation of ZnO nanorods on ITO. Well-aligned ZnO nanorods from various seed layer thicknesses were used as electron transporting layers in hybrid photovoltaic cells. Photovoltaic properties and power conversion efficiency (PCE) of devices made of ZnO nanorod arrays were investigated. PCE of up to 1.02% can be achieved from a cell made of ZnO nanorods grown on two suitable seed layers.

1. Introduction

Currently, researchers in solar energy have given much attention to solving increasing demands for energy. The conversion of solar energy into electricity is clean, and the sun is renewable resource. Silicon solar cells dominate the photovoltaic market and have been reported to have power conversion efficiencies (PCEs) of up to 25%. Although the efficiency of silicon-based solar cells is high, manufacturing is still expensive. The development of solar cells with reduced production costs has led to solar cells made of organic materials. Organic photovoltaic cells

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are of great interest owing to the ability to process them in solution, low manufacturing costs, and light weight.^(1,2) In the organic system, an electron donor has the role of absorbing photons and generating excitons. When excitons diffuse to the interface between two components and dissociate, the electron acceptor receives electrons and transfers them to an electrode, while the electron donor carries holes to another electrode. The absorber layer in devices is composed of a conjugated polymer and a soluble fullerene. Many reports of organic photovoltaic cells are focused on poly(3-hexylthiophene) (P3HT) as a donor and 6,6-phenyl-C₆₁-butyric acid methylester (PCBM) as an acceptor. However, the PCEs of organic photovoltaic cells are still very low, because of low stability and low mobility associated with transferring excited electrons or holes. Therefore, hybrid photovoltaic cells, which combine organic and inorganic materials, have been studied to solve the problem of low charge mobility and to improve efficiency by using inorganic nanostructures as electron collecting layers.^(3,4)

Among several kinds of inorganic semiconductors, metal oxides have been extensively used in hybrid photovoltaic cells because they have high conductivities and can be prepared as different nanostructures such as nanorods, nanotubes, and nanoparticles. Zinc oxide (ZnO) is an attractive metal oxide that can be used in photovoltaic devices because of its wide band gap (3.37 eV), high electron transport characteristics, and excellent chemical and thermal stability. It can be easily formed as nanorods, which have a direct pathway to transport charges.^(4,5) ZnO nanorod arrays have been fabricated by various preparation methods such as vapor–liquid–solid techniques,⁽⁶⁾ chemical vapor deposition,⁽⁷⁾ electrochemical deposition,⁽⁸⁾ and hydrothermal methods.^(5,9,10) A hydrothermal method is a simple and cheap technique when compared with the others because it requires no vacuum, no expensive equipment, and no special substrates.⁽¹¹⁾

There are many studies about controlling the parameters such as reaction time,⁽¹²⁾ temperature,⁽¹³⁾ concentration of precursor,⁽¹⁴⁾ and seed layer thicknesses,^(15,16) which affect the growth of ZnO nanorod arrays by hydrothermal methods. However, there are no reports of hybrid photovoltaic cells made of ZnO nanorods fabricated from seed layers with different thicknesses.

In this work, ZnO nanorod arrays were synthesized under different conditions of seed layer thickness. The morphology of the grown ZnO nanorod arrays was investigated, and the applications of ZnO nanorod arrays to hybrid photovoltaic cells were studied.

2. Materials and Methods

2.1 Preparation of ZnO nanorod arrays

ZnO nanorod arrays were prepared on indium tin oxide (ITO) substrates, which were cleaned ultrasonically in deionized water, ethanol, and acetone. Zinc acetate in ethanol (0.01 M) was spin-coated on the cleaned ITO substrate. The seed-coated substrate was annealed at 260 °C for 5 h in the air to form crystal seeds on the substrate. ZnO nanorods were grown perpendicularly on the seed layer by immersing ZnO-coated glass substrates into 0.04 M of zinc nitrate and 0.8 M of sodium hydroxide at 110 °C for 20 min. After immersion, the ITO substrates with aligned ZnO nanorod arrays were washed with deionized water to remove the residual material and dried in the air.

2.2 Fabrication of hybrid photovoltaic cell

A mixture of P3HT and PCBM (1:0.8 w/w) in dichlorobenzene (500 μl) was coated on the ZnO nanorod arrays. Subsequently, the sample was thermally annealed at 165 $^{\circ}\text{C}$ for 20 min in a dry environment. After the heat treatment, tungsten trioxide (WO_3) was coated on the blended polymers using a solution process. Finally, a Ag layer, which served as an anode, was deposited on the fabricated structure by thermal evaporation.

2.3 Characterization

The morphology and structure of the nanorod arrays were characterized by scanning electron microscopy (SEM, JEOL JSM-6610LV) with an accelerating voltage of 20 kV. The crystalline structure was characterized by X-ray diffraction (XRD, Bruker D8 Advance). Photocurrent density–voltage (J – V) curves were measured under simulated solar light (AM 1.5, 100 mW/cm^2).

3. Results and Discussion

ZnO nanorod arrays were grown by the hydrothermal method at a temperature of 110 $^{\circ}\text{C}$ for 20 min. The morphology of ZnO nanorod arrays deposited on ITO substrates that were coated with seed layers of different thicknesses was investigated by SEM. Figure 1(a) shows ZnO nanorod arrays grown on one layer of seed thickness; ZnO nanorods have high density and small diameter (~ 350 nm). The growth of ZnO nanorod arrays on two seed layers is shown in Fig. 1(b); the ZnO nanorods have the Wurtzite hexagonal structure and the rod diameter increased (~ 600 nm). As can be seen in Fig. 1(c), the diameter of ZnO nanorod arrays grown on three seed layers was the largest (~ 1 μm) and the density of the rods was low.

It was found that a thinner seed layer resulted in a higher density of ZnO nanorod arrays. This results from the nucleation sites on the surface of the seed layer decreasing when the thickness of the seed layers increases. Moreover, the diameter of nanorods depends on the particle size in the seed layer, because an increase in seed layer thickness affects the increase of the particle size in the seed layer. Therefore, the thickness of the seed layer plays a role in determining the diameter of ZnO nanorod arrays.⁽¹⁶⁾

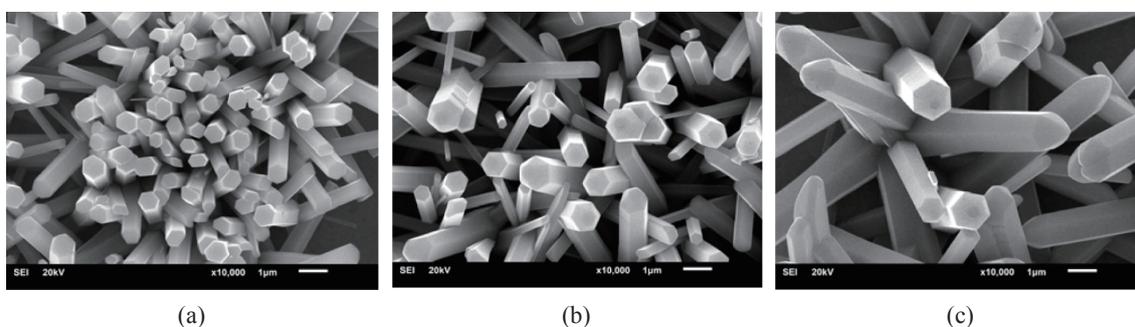


Fig. 1. SEM images of ZnO nanorod arrays grown on seed layers of varying thickness: (a) one, (b) two, and (c) three seed layer(s).

The XRD pattern of a cleaned ITO substrate is shown in Fig. 2(a). Figure 2(b) shows the XRD result of the thickness of two seed layers on an ITO substrate after annealing. The XRD pattern of ZnO nanorod arrays grown on coated ITO with two seed layers is shown in Fig. 2(c). Many peaks in the pattern of ZnO nanorods on ITO are totally different from those seen as pristine ITO, which are the characteristic peaks of ZnO.

The ZnO nanorod arrays with various seed layer thicknesses were applied as electron transporting layers on hybrid photovoltaic cells. The structure of a cell is ITO/ZnO nanorods/PCBM/P3HT/WO₃/Ag, as shown in Fig. 3. Figure 4 shows J - V curves of hybrid photovoltaic cells made of ZnO nanorods grown on ZnO seeds for different seed thicknesses. Table 1 shows characteristic photovoltaic properties, i.e. short-circuit photocurrent density (J_{sc}), open-circuit

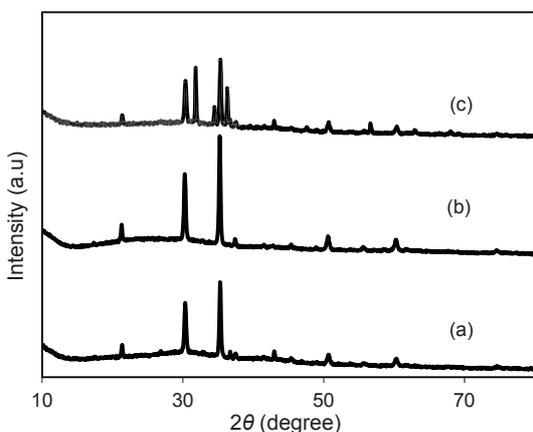


Fig. 2. XRD pattern of (a) ITO substrate, (b) ZnO seeded ITO substrate, and (c) ZnO nanorod arrays on ITO substrate.

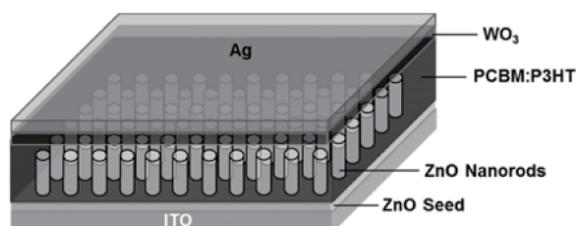


Fig. 3. Cell structure of hybrid photovoltaic cells made of ZnO nanorods.

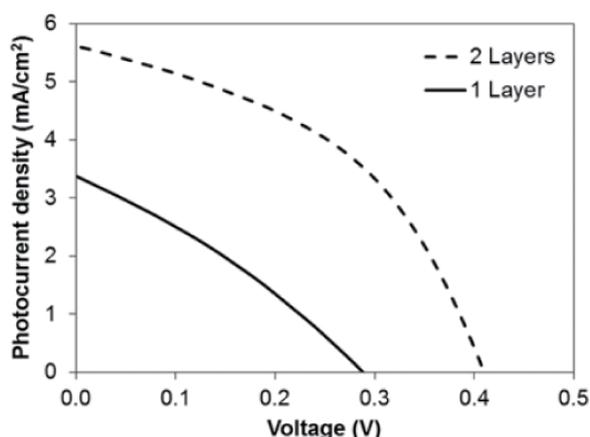


Fig. 4. J - V curves of hybrid photovoltaic cells made of ZnO nanorods grown on ZnO seeds for different seed thicknesses.

Table 1
Photovoltaic characteristic properties of cells made of ZnO nanorods arrays grown on ZnO seeds with number of different seed layers.

Seed	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
1 layer	3.38	0.29	0.32	0.29
2 layers	5.62	0.41	0.44	1.02
3 layers	n/a	n/a	n/a	n/a

voltage (V_{oc}), fill factor (FF), and PCE (PCE), of the cells investigated. It was observed that ZnO nanorods grown on ZnO seeds with one seed layer showed low PCE. Even if the diameter of cell was small, the density of nanorods was high, so the active PCBM:P3HT could not easily penetrate to the nanorod later. The PCE of the cells increased when the number of seed layers was increased to two. Even if the diameter of rods was larger, which reduced the surface area, the density of rods was suitable for the penetration of the active layer. Lastly, with three layers of seed, the cell short circuited, because the diameter of nanorods standing over the active layer was too large and contacted the Ag electrode. From this observation, we concluded that the suitable number of seed layers for ZnO seeding was two.

4. Conclusions

ZnO nanorod arrays have been synthesized on seed-coated ITO substrates using a hydrothermal method from different thicknesses of seed layers. The seed layer thicknesses influences the diameter and density of nanorods. The ZnO nanorods had low density and increased in diameter as seed layer thickness was increased. Well-aligned ZnO nanorods from the suitable seed layer thickness were used as an electron transporting layer in hybrid photovoltaic cells. A PCE of 1.02% can be achieved to from a cell made of ZnO nanorods grown on two seed layers.

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