

Flexible Solar-Cell from Zinc Oxide Nanocrystalline Sheets Self-Assembled by an *In-Situ* Electrodeposition Process

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Zinc oxide nanocrystalline sheets were self-assembled on a flexible polymer substrate to act as the electrode of dye-sensitized solar cells by an *in situ*-construction electrodeposition process. It was discovered that the nanosheet-based solar cell exhibited better performance than a nanoparticle-based solar cell or a well-oriented nanowire-based solar cell. The nanosheet microstructure has advantages which include the depression of loss during photoelectron transport, the increase of dye compound adsorption, and the enhance of incident light capture. As a result, the performance of dye-sensitized solar cells can be obviously improved. This success provides a feasible bottom-up approach for integrating a solar cell together with nanodevices and microcircuits on a flexible substrate which can work with self-supplied solar energy.

Keywords: Zinc Oxide, Nanosheet, Self-Assembly, *In Situ*-Construction Electrodeposition, Flexible Solar Cell.

1. INTRODUCTION

Current trends in miniaturization of electronic and optical systems have stimulated the development of nanodevices.^{1,2} The devices, especially those integrated on flexible substrates, are expected to be applied in many fields, such as very large scale integration (VLSI) and integrated optical systems, since they can offer many advantages, including suitability for any complex shape, minimal size, low power consumption, and high performance. In recent years, many investigations have been carried out to integrate nanodevices and microcircuits on flexible substrates.^{3,4} In our previous studies, we have demonstrated that it is feasible to integrate nanodevices and microcircuits on flexible polymer substrate by a self-assembly process.^{5,6} Furthermore, it is presumed that solar cells can be integrated together with nanodevices and microcircuits on the same substrate to form independent nanosystems, which can be expected to work with self-sufficient energy supply. Figure 1 shows the scheme of a nanosystem where a solar cell and microcircuits are integrated on the two faces of one substrate.

To obtain these nanosystems, the integration of solar cells on the flexible polymer substrate is a big challenge.

There are some reports on the fabrication of porous nanocrystalline semiconductor films for dye-sensitized solar cells (DSSCs) on polymer substrate by methods such as microwave irradiation, hydrothermal process, chemical vapor deposition (CVD), and others.⁷⁻⁹ However, these methods are too expensive or too complex, and the performance of solar cells obtained by these methods are not satisfactory. A feasible method for improving the conversion efficiency of dye-sensitized solar cells is optimizing the microstructure of the semiconductor film.

Recently, there have been some reports of well-oriented nanostructures for developing nanodevices. Cembrero et al. obtained nanocolumnar ZnO films for photovoltaic applications,¹⁰ and Groenen et al. fabricated surface-textured ZnO films for thin film solar cells.¹¹ As for dye sensitized solar cells, Baxter and Aydil have developed ZnO nanowire-based solar cells by metallorganic chemical vapor deposition, with a conversion efficiency of 0.5%.¹²

To further improve the performance of solar cells, here we show a novel *in situ*-construction electrodeposition process for synthesizing zinc oxide films having a nanosheet microstructure. This remarkable microstructure is not oriented very well but appeared as a matrix of randomly aggregated nanosheets. This structure lends itself to the combining of the film with the flexible substrate

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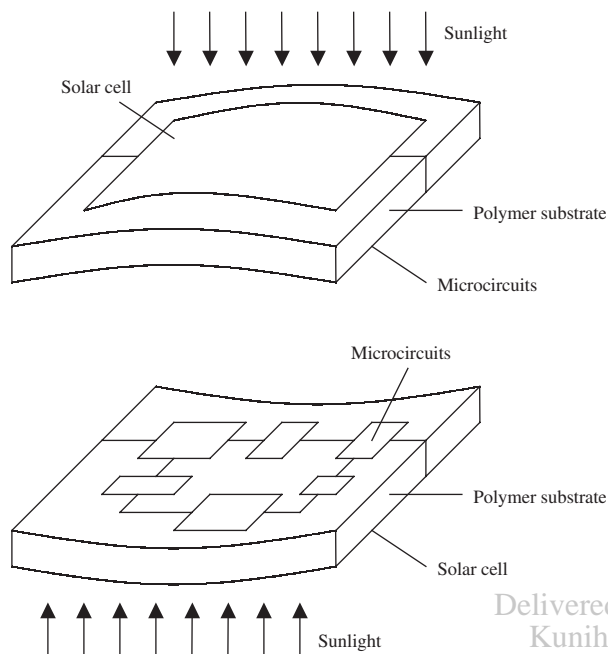


Fig. 1. Scheme of integrated solar cell and microcircuits.

more stably than a well-oriented one would, and handles deformation well. Besides, the not-well-oriented structure is helpful to increase photon capture by inducing a multiple scattering effect.^{13, 14} Therefore, it can be expected that the performance of the solar cell is a great improvement over previous methods.

2. EXPERIMENTAL DETAILS

2.1. *In Situ*-Construction Electrodeposition of Zinc Oxide Film

Flexible poly(ethylene terephthalate) (PET), coated with In_2O_3 -doped SnO_2 (ITO) transparent conductive oxide film, was selected as polymer substrate. The substrate was rinsed in an ultrasonic bath with distilled water, ethanol, and acetone, sequentially, for 5 min, and dried in air. A Pt electrode was etched in 0.1-M HCl and rinsed with distilled water. An aqueous solution of zinc nitrate (0.1 M) was maintained at 50 °C in a water bath. The pH value was adjusted to remain in the range of 2.0 to 6.0. Electrodeposition was performed in the solution at 2.0 V for 1 h. A small amount of ammonium chloride was added to the solution to control the microstructure of an electrodeposited film.

2.2. Fabrication of Dye-Sensitized Solar Cell

The obtained zinc oxide film was dried in air at 130 °C, and immersed in an ethanol solution of ruthenium(II) *cis*-(dithiocyano)-*bis*-(2,2'-bipyridil-4,4'-dicarboxylic acid) for 12 h at room temperature, to be fully adsorbed with the dye compound. Then it acted as a working electrode.

A counter electrode was prepared by sputtering platinum onto another substrate. Home-made electrolyte was sandwiched between the working and counter electrode to fabricate a dye-sensitized solar cell.

2.3. Characterization

The microstructure of zinc oxide film was observed by scanning electron microscope (SEM) (S-3000N, Hitachi Ltd.). The amount of the dye adsorbed on zinc oxide film was evaluated by colorimetry (UV-1600PC, Shimadzu Co. Ltd., Japan). The *I*-*V* properties were measured under the quasi-sunlight of AM-1.5 at 100 mW cm⁻² irradiated directly on the cell.

3. RESULTS AND DISCUSSION

ZnO has nearly the same bandgap and electron affinity as TiO_2 , and ZnO DSSCs built using ZnO nanoparticles have shown the second highest efficiencies (5%), after TiO_2 .¹⁵ ZnO films can be obtained under a mild reaction condition by electrodeposition process.¹⁶⁻¹⁸ From an SEM image (Fig. 2(a)), it can be seen that the microstructure of a zinc oxide film obtained by the electrodeposition process appears to consist of aggregated particles, and the diameters of the particles range from about 200 nm to 500 nm. The thickness of the film is about 5 μm. This microstructure is similar to that of the films commonly reported in the literature.¹⁹⁻²²

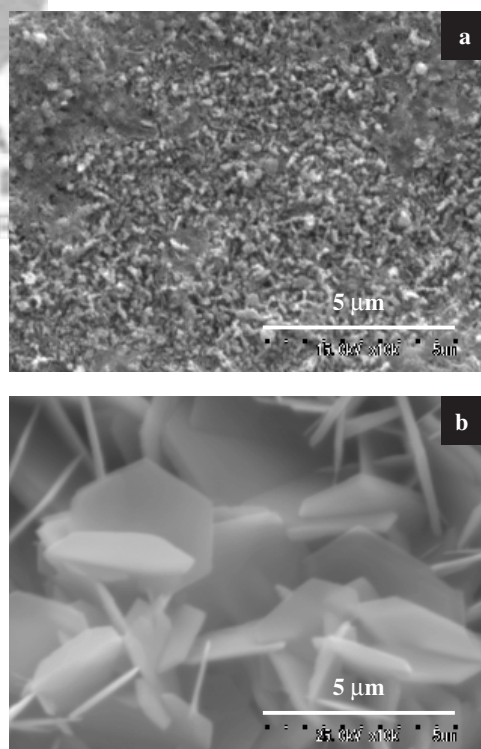
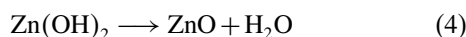
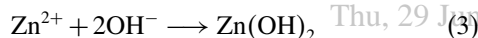
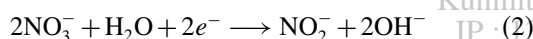
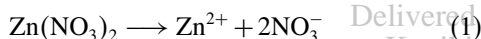


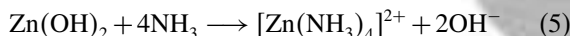
Fig. 2. SEM image of ZnO film synthesized by electrodeposition; (a) without NH_4Cl employed and (b) with NH_4Cl employed.

In order to further increase the specific surface area of zinc oxide films, we brought forward an *in situ*-construction method. Ammonium chloride was added to the solution to control the microstructure of the zinc oxide film during electrodeposition. Figure 2(b) shows the SEM image of zinc oxide film synthesized by the *in situ*-construction electrodeposition. The film appears to be composed of agglomerated thin sheets. The thickness of each sheet is $\sim 30\text{--}50$ nm, and the diameter is $\sim 2\text{--}3$ μm . All the nanosheets are crosslinked randomly, constructing a loose matrix. The thickness of the film is about 5 μm . This film adsorbs dye compound much more than a nanoparticle-based film would do. According to the colorimetry method, the amount of dye adsorption of the nanosheet-based film was 9.25×10^{-5} mol L^{-1} , and that of the nanoparticle-based film was 3.51×10^{-5} mol L^{-1} .

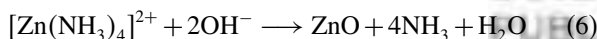
The mechanism of electrodeposition of zinc oxide film was suggested by Gal-Or and Switzer as follows:¹⁸



In this reaction system, zinc oxide is nucleated and tends to generate spherical particles (Fig. 2(a)). If ammonium chloride is added to the solution, the reaction becomes different. It is common sense that zinc hydroxide can form complex ions with ammonium ions:

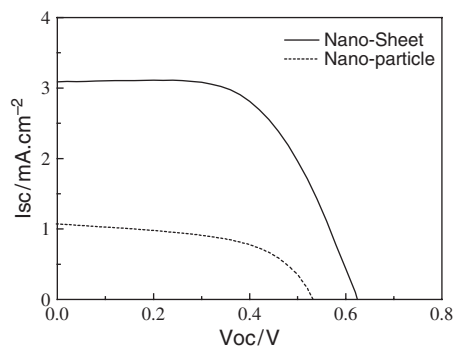


The complex ions are not stable and can easily react with hydroxyl ions, resulting in the formation of zinc oxide again:

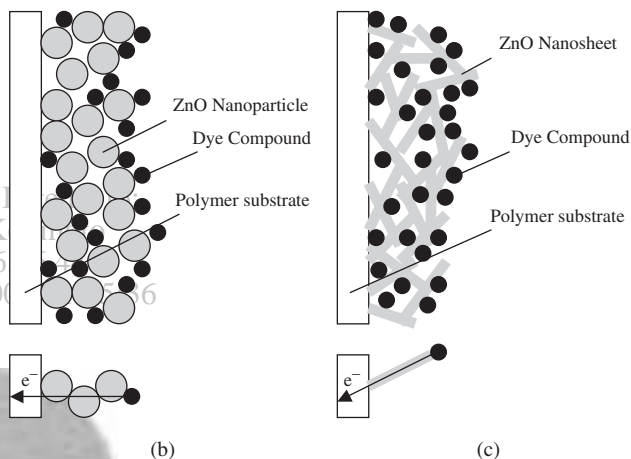


Therefore, the surface atoms of zinc oxide particles would tend to combine with ammonium ions and dissolve into the solution during the course of electrodeposition. We suggest that the cooperation of the reactions (1)–(6) result in an asymmetric (or oriented) growth of zinc oxide. So, the obtained zinc oxide appeared as nanosheets (Fig. 2(b)) instead of as particles. All of the nanosheets are crosslinked randomly. Thus, the matrix of nanosheets was *in situ*-constructed. The amount of ammonium chloride added to the electrolyte solution is the key step in obtaining such a structure. More details arose out of further investigation.

Dye-sensitized solar cells were fabricated with zinc oxide films, which consisted of either particles or nanosheets; their *I*–*V* curves are compared in Figure 3(a). Table I shows their *I*–*V* properties. It is to be noted that the performance of cells was obviously varied with the different microstructure of ZnO films. For the present sample



(a)



(b)

(c)

Fig. 3. (a) *I*–*V* property of ZnO film solar cell, (b) scheme of photoelectron transfer in the film consisting of particles, and (c) scheme of photoelectron transport in the film consisting of nanosheets.

with nanosheet microstructure, the open circuit voltage and fill factor were about the same as when the film consisted of particles, but the short circuit current of the former was more than three times higher than that of the latter. As a result, a conversion efficiency for the former of 1.13% was attained, which is much higher than that of the latter, 0.31%.

The difference in *I*–*V* properties is mainly due to the dissimilarity in the microstructure of zinc oxide films. Film consisting of particles has an inter-connected porous structure. Figure 3(b) shows a scheme of photoelectron transport in particle-based film. During the solar cell operation,

Table I. Comparison of different solar cells.^a

	Nanosheet-based	Nanoparticle-based	Nanowire-based ¹²
Microstructure	Nanosheet	Nanoparticle	Nanowire
Substrate	Flexible Polymer	Flexible Polymer	Glass
Isc [mA cm ⁻²]	3.09	1.07	1.62
Voc [V ⁻¹]	0.62	0.53	0.74
ff	0.59	0.55	0.38
Eff [%]	1.13	0.31	0.50

^aWherein Isc is short circuit current, Voc is open circuit voltage, ff is fill factor, and Eff is conversion efficiency.

photoelectrons should be transported from one particle to another until they arrive at the outer circuit. They would be scattered by particle surfaces and grain boundaries, with their transport frequently being interrupted. On the other hand, the film consisting of nanosheets had an *in situ*-constructed inter-connected structure. Figure 3(c) shows a scheme of photoelectron transport in the nanosheet-based film. In this film, photoelectrons could be transported along the direction parallel to the nanosheet surface. The microstructure within each one of the nanosheets is more condensed than that in a particle-based film. As a result, the chances of encountering surface defects and particle boundaries are largely reduced. As a result, the loss of photoelectrons was depressed, and the short circuit current was increased.

From Table I, it can be seen that the performance of the nanosheet-based solar cell is better than that of the nanowire-based solar cell, and that the conversion efficiency of the nanosheet-based one is more than two times than that of the nanowire-based one, which is mainly due to the large short circuit current of the nanosheet-based solar cell. We suggest that the difference in short circuit current between these two samples is derived from the microstructure.

In the nanosheet-based solar cell, the nanosheets aggregated randomly to form a loose matrix, which is beneficial to reflection and refraction of incident light within the film, and would lead to a multiple scattering effect.^{13, 14} As a result, the incident light capture was largely improved and the amount of photoelectrons was increased. On the other hand, for the nanowire-based solar cell, all of the nanowires are well-oriented. The incident light cannot be reflected and refracted sufficiently. So the incident light capture of the nanowire-based solar cell is not as effective as that of the nanosheet-based one. According to this model, the short circuit current of the nanosheet-based solar cell (3.09 mA cm⁻²) can be much larger than that of the nanowire-based one (1.62 mA cm⁻²), and the conversion efficiency (1.13%) is about two times higher than that of the nanowire-based one (0.50%).

In the present study, the performance of present nanosheet-based solar cells, such as the short circuit current and conversion efficiency, are not as high as those reported previously.^{15, 23} This is mainly due to the fact that the substrate of the present cell is a flexible polymer substrate, not glass substrate as that of those reported in the previous studies.^{15, 23} It is commonly recognized that the polymer substrate can not be as transparent as a glass substrate—but its flexibility is the particular advantage for the solar cell. Further effort to improve the performance of the present polymer-based solar cell is on-going.

4. CONCLUSIONS

In summary, dye-sensitized solar cells made up of nanosheet-based zinc oxide films have been successfully fabricated on a flexible polymer substrate. The nanosheet

microstructure was obtained by an *in situ*-construction electrodeposition process under mild reaction conditions. The conversion efficiency of the nanosheet-based solar cells was more than three times larger than that of nanoparticle-based one, and about two times higher than a well-oriented nanowire-based one. The improvement was mainly due to the depression of loss during photoelectron transport, the adsorption of a larger amount of dye compounds, and the enhanced incident light capture by the multiple scattering effect of the nanosheet structure. This success, as well as previously reported barrier-effect self-assembly process,⁶ permits a feasible bottom-up approach for the integration of solar cells together with nanodevices and microcircuits on flexible substrates to obtain independent nanosystems, which can operate with a self-sufficient energy supply. This approach is expected to play an important role in the fabrication of microelectronic and/or optoelectronic devices on flexible polymer substrates.

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