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Photovoltaic Performance of Vertically Grown ZnO nanorods in Dye-sensitized Solar Cells

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For an application to the photoelectrode in dye-sensitized solar cells (DSSCs), we fabricated ZnO nanorod arrays on fluorine-doped tin oxide (FTO) coated glass substrate by chemical bath deposition, and modified its surface through sodium silicate coating. Effects of the surface modification on the morphology of ZnO nanorod arrays, as well as the photoelectric conversion properties in DSSCs were investigated. From the field-emission scanning electron microscopy (FE-SEM) images, ZnO nanorods are observed to be vertically grown on FTO substrate. The surface treatment via dip coating within sodium silicate solution gives rise to increase the photocurrent, resulting in the increase of solar-to-electrical power conversion efficiency. This may be originated from that the surface-treated ZnO photoelectrode has higher conduction edge to introduce an energy barrier for increasing charge separation and suppressing recombination rate at the photoelectrode-electrolyte interface.

Keywords Dye-sensitized solar cells; photovoltaic performance; surface modification; ZnO nanorod array

1. Introduction

Nanostructured metal oxide materials, such as TiO_2, ZnO, SnO_2 and Nb_2O_5, are an interesting research area with many potential applications [1]. Among them, ZnO was investigated and applied as a promising key material for UV light emitters, field emissions, bio-sensors, field effect transistors, and solar cells, due to their intrinsic properties of non-toxicity, good electrical and optical behaviors [2,3].

On the other hand, dye-sensitized solar cells (DSSCs) has become the most important alternative to conventional silicon based solar cells because of low cost, ease of handling, relatively high photon-to-current conversion efficiency for low energy consumption, and simple fabrication process [4]. The DSSC is composed of dye molecule attached

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nanocrystalline TiO_2 electrode, and electrolytes containing a redox couple, and Pt as a counter electrode. The photon-to-current conversion mechanism of DSSC is based on the injection of electrons from the excited dyes into the conduction band of nano-crystalline TiO_2. The oxidized photosensitizers are reduced by electron injection from the electrolyte.

The nanostructured ZnO is a wide band gap II-VI semiconductor oxide (3.37 eV) possessing a similar energy band gap structure with TiO_2 with higher electronic mobility that would be favorable for electron transport in dye-sensitized solar cells (DSSCs) with reduced recombination loss. However, the photovoltaic performance of DSSC composed of ZnO semiconductor as a photoanode was much lower than that of TiO_2 electrode mainly due to the lower light harvesting and charge collection efficiency, which resulted in the lower IPCE in the DSSC [5]. In spite of the low photon-to-current efficiency in DSSC [6], the improvement of their photovoltaic performance has continued to be an important research area, due to the ease crystallization and anisotropic growth of ZnO electrode that makes it possible to prepare variety of nanostructures in large quantities with wide area by the low temperature process and low cost technique [6–9].

In this paper, we prepared the vertically aligned ZnO nanorod on the FTO with the chemical bath deposition (CBD) method in various temperatures to use it as a photoelectrode in DSSCs. The ZnO photoelectrode was treated with metal oxide to modify their surface that could enhance the short-curcult current (J_{sc}), significantly [10]. The photovoltaic properties of the DSSC composed of ZnO photoelectrode were measured and evaluated with I-V curves, incident photon-to-current (IPCE) efficiencies, and impedance analysis.

2. Experimentals

2.1 Synthesis of Vertically Aligned ZnO Nanorods

The ZnO nanorod arrays were fabricated via two steps. Firstly, ZnO seed layer was prepared on the fluorine doped tin oxide (FTO, sheet resistance: $\sim$10 Ω/cm^2). The substrate is coated with a droplet of 10 mM or 20 mM of zinc acetate dihydrate (99.99%, Sigma-Aldrich) in ethanol. And then, the substrate, the fluorine doped tin oxide with droplet of ZnO seed solution was spin coated with 500 rpm for 1 minute. After spin coating, it dried several hours at room temperature. The coated substrate was heated over 150°C to evacuate some organic substances for 4 hours to prepare the seed layer. The deposited ZnO seed substrate was immersed into an aqueous solution of 0.1 mM of zinc nitrate hexahydrate (99%, Sigma-Aldrich) and 0.1 mM of hexamethylene tetramine at 95°C for 9 hours, respectively. In addition, the growth of ZnO nanorod was carried out in a sealed bath. The solution was refreshed every 3 hours in order to retain a constant growth rate since the reagent concentration decreases as growth proceeded.

2.2 Surface Treatment with Sodium Metal-Silicate

The ZnO nanorods electrodes were treated with sodium metal-silicate solution prepared from sodium metal-silicate (Na_2SiO_3, 0.1 mmol) and deionized water (100 mL) by the simple dip-coating technique. When soaking the Glass/FTO/ZnO nanorods, as an active layer in electrode, it was dipped for 5 minutes. After resulting electrodes were rinsed with deionized water and ethanol, the electrode dried in dry oven for 10 minutes at 60$\sim$70°C.

2.3 Fabrication of DSSC and Measurements

The FTO glasses (FTO, sheet resistance: $\sim$10 Ω/cm^2) were washed in acetone for 20 min. by sonication and were again washed in methanol and deionized water with several times.

The active ZnO nanorods layer was sintered at 500°C for 30 minutes. For dye adsorption, the annealed ZnO electrodes was immersed into a 0.3 mM of N3 dye solution (solaronix) at room temperature for 30 minutes. For the counter electrode, a Pt layer was formed on pre-cleaned FTO glass substrate by using doctor-blade with Pt paste (Dyesol) and then it was sintered at 500°C for 30 minutes. The dye-adsorbed ZnO nanorods electrode and Pt counter electrode were assembled with the 60 μm-thicks Surlyn (Dupont1702) as a bonding agent. The electrolyte (Dyesol, AN-50) was introduced into the cells.

The FE-SEM images are measured by S-4100 (HITACHI, LTD). The I-V curves were determined using a potentiostat/galvanostat (263A, EG&G Princeton Applied Research, USA) under an illumination of 10-100 mW cm^{-2} by a 50-500 W Xe lamp (Thermo Oriel Instruments, USA). The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system.

3. Results and Discussion

3.1 Growth of ZnO Nanorods

We prepared the vertically grown ZnO nanorods on the FTO substrate by using the CBD method to prepare the ZnO-DSSC, since the CBD technique allow us to make it with inexpensive and convenient for large area of DSSCs. The CBD process is based on two steps as nucleation and particle growth. [6] We used of the solution of zinc acetate dehydrate in ethanol as a seed solutions (10 mM and 20 mM) for the nucleation process. The ZnO nanorod arrays were grown in aqueous solution of 0.1 mM of zinc nitrate hexahydrate at 95°C for 9 hours respectively, and their ZnO surface morphologies and the cross-section image were shown in Fig. 1. The SEM image prepared from the 25 mM of zinc acetate seed solution showed well vertically aligned ZnO nanorods on FTO substrate with the enhanced surface area to compare with that of 290 mM solution. We also changed temperatures of the crystal growth process of ZnO nanorod arrays, and their comparison between ZnO morphologies in different crystal growth temperatures were shown in Fig. 2. The photovoltaic performance of vertically grown ZnO electrode on FTO in different crystal growth temperatures was evaluated with the current-voltage characteristics and impedance analysis.

3.2 Photovoltaic Performance of ZnO Nanorod in DSSC

The ZnO nanorods prepared in different synthetic temperatures, 90, 95, and 99°C on FTO were immersed into a dye solution (N3 and N719) to prepare the DSSC, respectively. The DSSC was assembled with the dye adsorbed ZnO electrode, Pt counter electrode, and electrolyte containing a redox couple. Fig. 3 shows the current-voltage characteristics of ZnO-DSSC, and the results are summarized in Table 1. The ZnO-DSSC sensitized with N719 shows the lower photovoltaic performance to compare with that of N3 sensitized one, due to mainly the smaller amount of dye loaded in ZnO surfaces. Short-circuit current values sensitized Ru-complex dyes in ZnO-DSSC show significantly low to compare with that of the TiO_2-DSSC as shown in Table 1. It had been reported that the chemical stability of ZnO semiconductors are quite low, specially, in their acid solution. The proton in carboxylic acid in dye structure could affect the surface of ZnO electrode and dissociate the Zn ion from their surface. [11] Thus, during the dye adsorption process, the Zn^{2+}/dye aggregates could be formed on the ZnO electrode surface, which might reduce the electron injection efficiency and photovoltaic performance during the irradiation in DSSCs, because

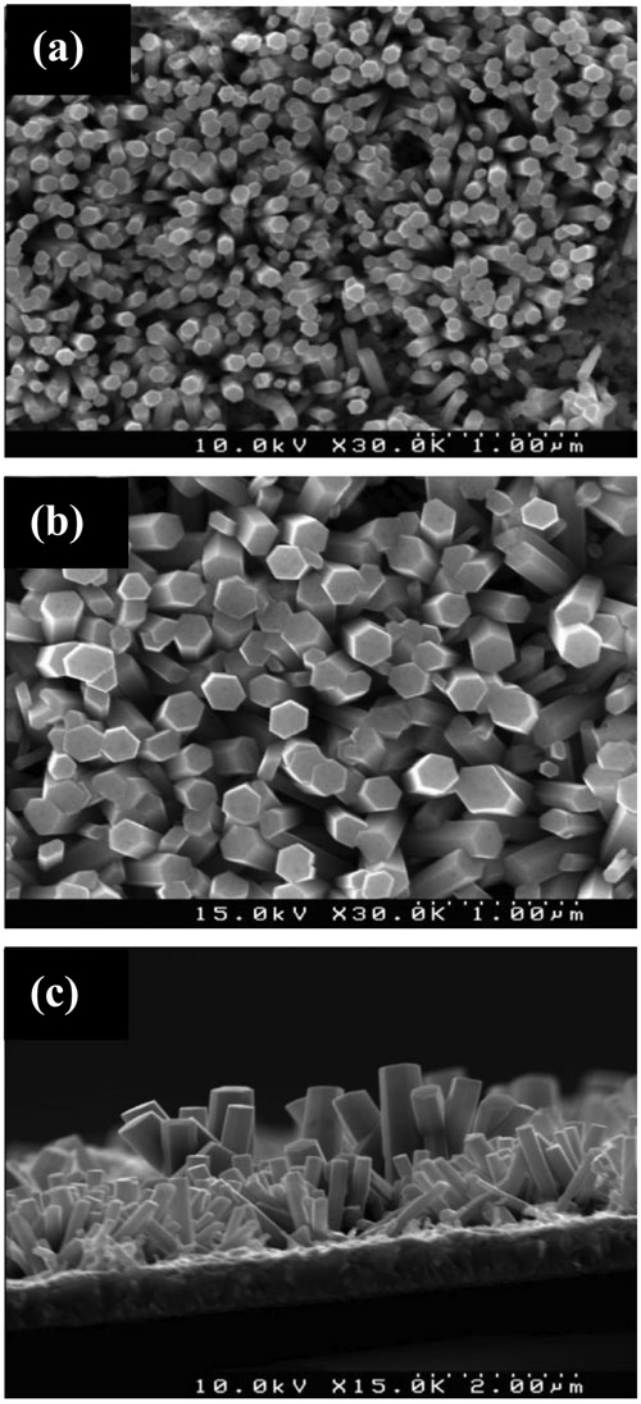

Figure 1. Field-emission scanning electron microscopy (FE-SEM) images of ZnO nanorod arrays grown in different concentration of zinc acetate seed solutions; (a) 20 mM, (b) 25 mM, (c) the cross sectional image of ZnO electode grown in the solution of 20 mM concentration. All ZnO nanorods were synthesized for 9 hours at 90°C.

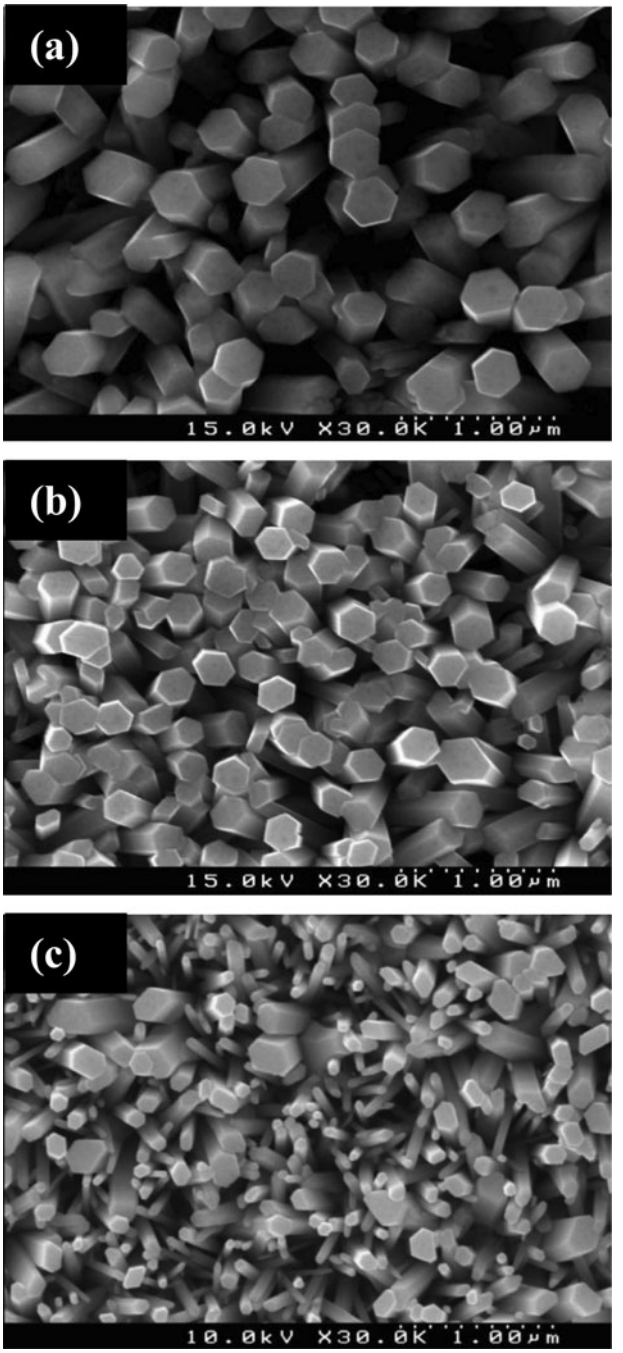

Figure 2. FE-SEM images of ZnO nanorod arrays grown at different temperatures; (a) 80°C, (b) 90°C, (c) 95°C, (d) the cross sectional image of ZnO electrode. All ZnO nanorods synthesized for 9 hours. *(Continued)*

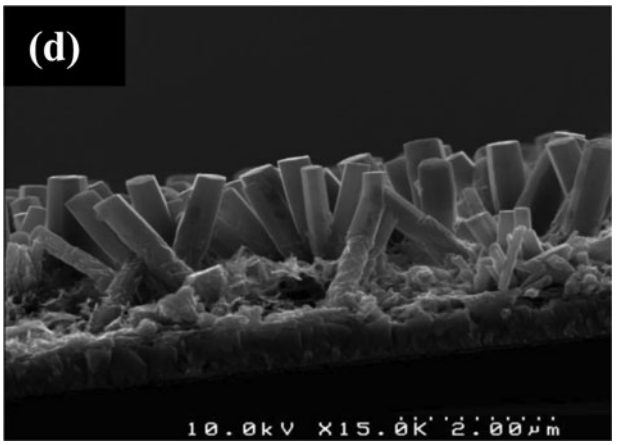

Figure 2. (Continued)

the intrinsic photon-to-current efficiency (IPCE) of a solar cell is the product of the light harvesting efficiency for photons of wavelength λ (LHE(λ)), electron injection efficiency from the excited sensitizer to the conduction band of semiconductor oxide (η_{inj}), and electron collection efficiency (η_{cc}) as shown in Equation (1) [11,12].

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \cdot \eta_{inj} \cdot \eta_{cc} \tag{1}$$

Since the bad characteristics in the short circuit current value in ZnO-DSSC were derived from the surface properties in ZnO electrode, we also observed the change in ZnO

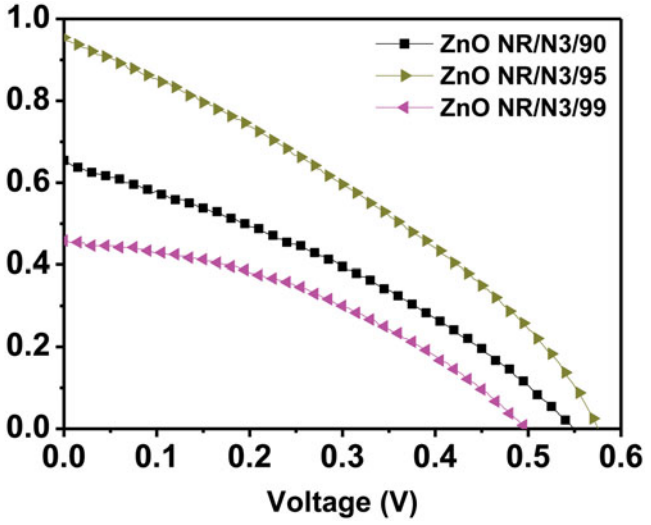

Figure 3. *I-V* characteristics of DSSC fabricated with ZnO nanorods prepared in different synthetic process temperature, 90, 95, and 99°C.

Table 1. Comparison of the photovoltaic performances of DSSC fabricated by ZnO nanorods (sensitized with N3) in different synthesis temperature, 90∼99°C. The I-V character of TiO_2-DSSC prepared in same condition also included for the comparison purpose

Photoelectrode	J_{sc} [mA/cm^2]	V_{oc} [V]	FF [%]	η [%]
ZnO/N3[a]/90[b]	0.64	0.55	33.9	0.12
ZnO/N3[a]/95[b]	0.94	0.59	33.4	0.20
ZnO/N3[a]/99[b]	0.46	0.50	34.0	0.09
ZnO/N719[a]/90[b]	0.67	0.58	40.4	0.16
TiO_2/N3[a]	8.28	0.77	67.6	4.05
S.T[c] ZnO/N3[a]	1.15	0.65	32.7	0.24
S.T[c] ZnO/N719[a]	1.78	0.61	36.5	0.40

[a]Photosensitizing dye
[b]The crystal growth temperature
[c]After the surface treatment

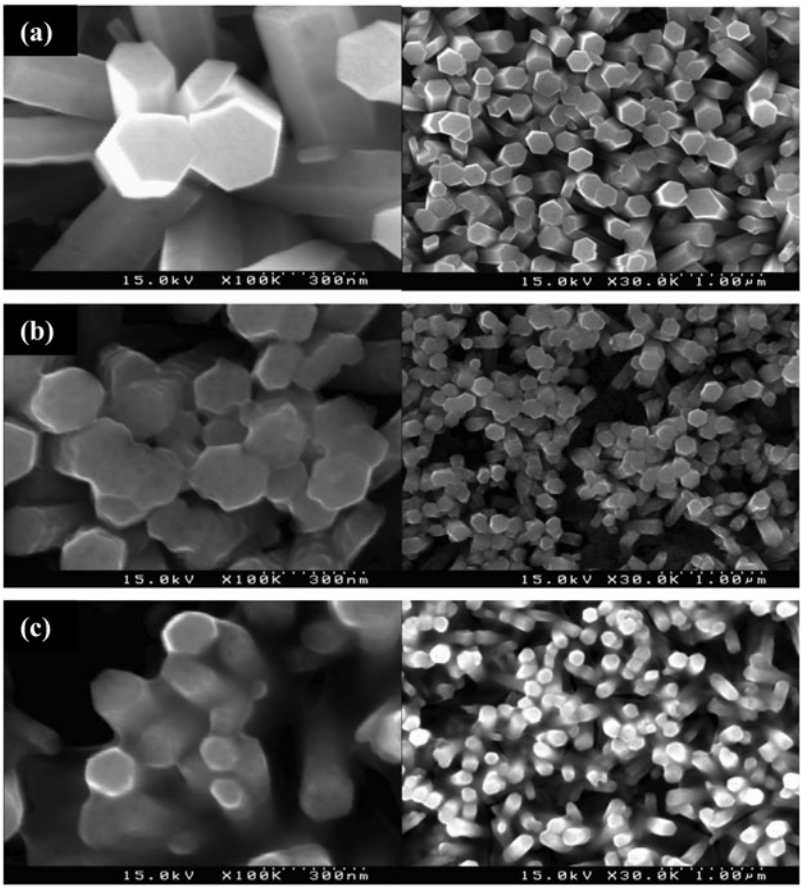

Figure 4. Comparison of FE-SEM images of ZnO nanorod arrays between before (a) and after the dyeing process with N3 for (b) 30 minutes and (c) 2 hours of dyeing process at room temperature.

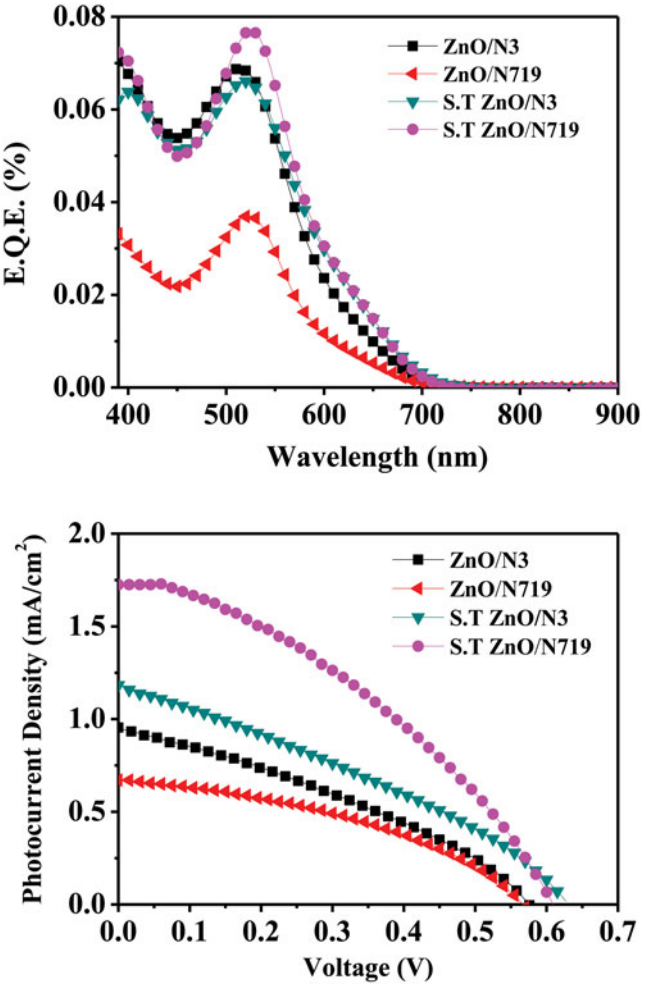

Figure 5. The *I-V* characteristics of ZnO- DSSC sensitized with N3 and N719 dyes, after and before surface treatment (S.T) with 0.1 mM sodium silicate aqueous solution for 5 minutes.

surface morphology during the dyeing process at room temperature, and were shown in Fig. 4. The fine structure of ZnO electrode surface was decreased significantly after 30 min., and then, the surface of ZnO rod dissolved to make aggregates with dyes as shown in Fig. 4(c).

Table 2. Comparison of the electrochemical impedance data between before and after the surface treatment

The Photo-electrode	Rs [ohm]	R1 [ohm]	R2 [ohm]
ZnO NR/N3	20.32	24.45	681.9
ZnO NR/N719	14.98	17.155	877.02
S.T ZnO NR/N3	27.12	3.186	414.9
S.T ZnO NR/N719	22.69	1.399	482.2

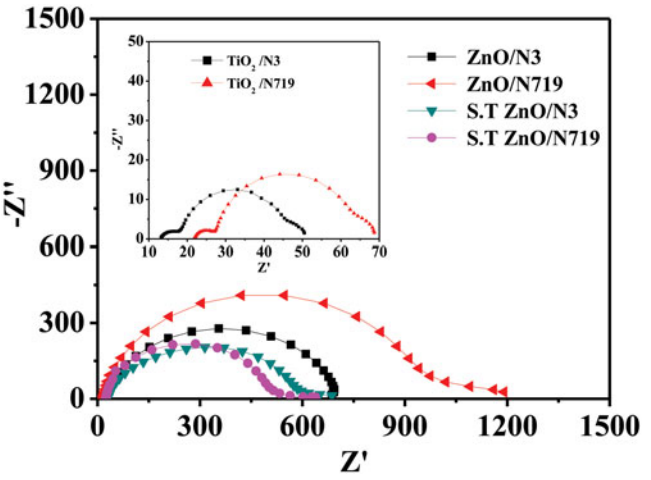

Figure 6. The Niquist diagram of ZnO nanorods DSSCs before and after surface treatment (S.T).

3.3 Surface Treatments of ZnO Nanorod

To improve the short-curcult current (Jsc) in ZnO-DSSC, we treated the ZnO electrode with aqueous solution of sodium silicate by the simple dip-coating technique that could avoid the formation of [Zn^{2+}/Dye] aggregates in their surface. The results are shown in Fig. 5 and compared with the pristine DSSC result prepared in same condition in Table 1. The result reveals that the J_{sc} value in ZnO-DSSCs treated with sodium silicate aqueous solution increased from 0.64 mA/cm^2 to 1.15 mA/cm^2 for N3 sensitized DSSC, and from 0.67 mA/cm^2 to 1.78 mA/cm^2 for N719, respectively.

Electrochemical impedance spectroscopy (EIS) analysis (Fig. 6) was performed to study the interfacial transfer process in ZnO-DSSCs after surface treatment, and the results were shown in Table 2. After the surface treatment with sodium silicate solution, the resistance at the ZnO nanorod/dye/electrolyte interface increases. The increase in the resistance indicates that surface coating with sodium silicate suppressed electron transfer from the ZnO nanorod photoelectrodes to the electrolyte, owing to the shift of ZnO conduction band edge due to sodium silicate coating.

4. Conclusions

We fabricated ZnO nanorod arrays on fluorine-doped tin oxide (FTO) coated glass substrate by chemical bath deposition, and investigated their properties and the application to the photoelectrode in DSSCs. In addition, effects of the surface modification via sodium silicate coating on the morphology of ZnO nanorod arrays were investigated. ZnO nanorods are observed to be vertically grown on FTO substrate from the FE-SEM images. The surface treatment by dip coating within sodium silicate solution gives rise to increase the photocurrent, resulting in the increase of solar-to-electrical power conversion efficiency. Although, photovoltaic performance of the DSSCs with ZnO nanorods grown by CBD method is low, CBD method has particular interest in large-area fabrication and low temperature process, which are compatible with plastic substrates for flexible DSSCs. Hence, it is in progress to improve photovoltaic performance of ZnO nanorod in DSSC and to attempt the application to flexible DSSC.

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