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Preparation of Si Nanoparticles by Laser Ablation in Liquid and Their Application as Photovoltaic Material in Quantum Dot Sensitized Solar Cell

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Abstract. Quantum dot sensitized solar cell was fabricated using silicon nanoparticles prepared by laser ablation in liquid. The obtained particles are spherical and have an average size of 6 nm. These particles were utilized as photosensitizing material in solar cell with polysulfide as an electrolyte. The conversion efficiency of solar cell with silicon nanoparticles was 5.3 times higher than the one with only TiO_2 particles. Electrical impedance spectroscopy also revealed the decrease in resistance in the former case led to higher current density than the latter one.

1. Introduction

Solar cell has attracted much attention from researchers for decades and several models had been proposed. For conventional solar cell, single material was used to convert the entire range of solar spectrum. As a result, there exists Shockley-Queisser limit, which was calculated based on the assumption that each photon resulted in only one electron-hole pair. Based on this assumption, the maximum conversion efficiency for silicon solar cell is limited to only 30% [1]. To overcome this limitation, different concepts have been proposed including intermediate band solar cell, dye-sensitized solar cell (DSSC), multi-junction solar cell, and hot carriers solar cell [2-8].

After the discovery of multiple exciton generation process (MEG) in PbSe quantum dot, the concept of quantum dot sensitized solar cell (QDSSC) has become another possible prospect for improving conversion efficiency [9-10]. This process starts with the absorption of photon with energy at least twice of the energy gap, generating an exciton. Then the excess energy, normally lost into heat, will be utilized to produce other excitons. Thus, one-photon absorption results in two or more electron-hole pairs. If these additional charge carriers are harvested before they recombine, it is possible to enhance the efficiency of photovoltaic device [11]. Later, MEG was proved to occur in several kinds of material including silicon [12-13].

Silicon nanoparticles can be synthesized by diverse techniques such as microemulsion route, chemical vapour deposition, and aerosol synthesis. Unfortunately, these fabrication processes are

complicated and sometimes it is difficult to control the purity of the product [14-16]. Recently, laser ablation in liquid technique was proposed. This process is very simple and the purity of the obtained product is outstanding [17-19]. It also reported that with this technique, silicon nanoparticles could be prepared without oxidation [20].

In this study, silicon nanoparticles were prepared by laser ablation in liquid. After that, these particles are utilized further to fabricate QDSSC. The device characteristics were analyzed and studied.

2. Experiment

2.1. Silicon nanoparticles preparation

P-type <100> silicon wafer (t = 600 μm) was used as a target material immersed in 40 mL of ethanol. This experiment was conducted in the closed system to prevent the evaporation of solvent. Magnetic stirrer was also used. Nd:YAG laser at second harmonic generation (λ = 532 nm) with pulse duration of 13 ns and repetition rate of 10 Hz was employed, and silicon target was irradiated for 30 minutes. After irradiation, the colloidal solution was dropped onto carbon-coated copper grid and dried. Finally, the size and morphology of prepared silicon nanoparticles were observed by Transmission Electron Microscope (H-8100 TEM) with acceleration voltage of 200 kV.

2.2. Fabrication of quantum dot solar cell

Ethanol in the colloidal solution was evaporated in order to obtain silicon nanoparticles powder. FTO glasses were used as photo and counter electrodes. For photo electrode, FTO glass was coated with TiO_2 paste and sintered at 450 ℃ for 30 minutes. This TiO_2-coated electrode was again coated with a mixture of silicon nanoparticles and TiO_2 paste, and sintered for another 30 minutes. For counter electrode, FTO glass was sputtered with gold. Finally, both photo and counter electrodes were assembled together and the gap between two electrodes was filled with polysulfide electrolyte. Another device without silicon nanoparticles was also fabricated as a reference. Their properties were analyzed by solar simulator and electrochemical impedance spectroscopy (EIS).

3. Results and Discussion

3.1. Size and morphology of silicon nanoparticles

Both size and morphology of silicon nanoparticles were observed by TEM. Fig. 1 shows that silicon nanoparticles prepared by laser ablation in ethanol possess spherical shape. Although some agglomeration was observed, most particles well dispersed. From TEM images, the histogram of nanoparticles size was constructed by measuring the diameter of 100 nanoparticles. The result was shown in Fig. 2. The average size obtained was around 6 nm with standard deviation of 2.68 nm. This obtained particle size was smaller than Bohr diameter of silicon (8 nm) [21-23]. Therefore, quantum confinement effect and also MEG can occur.

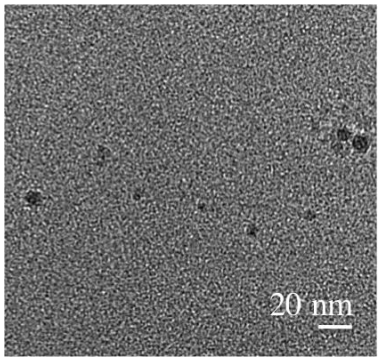

Figure 1. TEM of Si nanoparticles

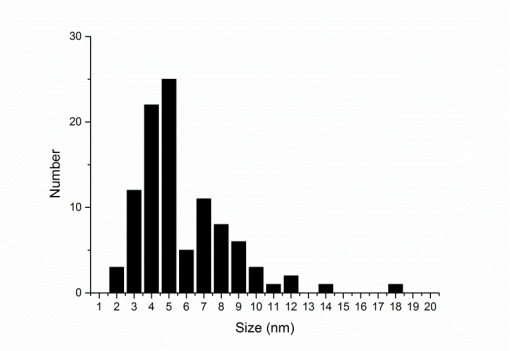

Figure 2. Size distribution obtained from TEM image

3.2. Photovoltaic properties

Fig. 3 shows J-V characteristic of quantum dot sensitized solar cell with silicon nanoparticles along with the one without them. The conversion efficiency of solar cell with silicon nanoparticles was improved up to 0.016% compared to that of the cell with only TiO_2 particles (0.003%). The current density and open circuit voltage of the cell with silicon nanoparticles were also found to be two times higher than that of the device without them. From these results, an improvement of the device performance by the addition of silicon nanoparticles was confirmed. Other electrical parameters are demonstrated in Table 1.

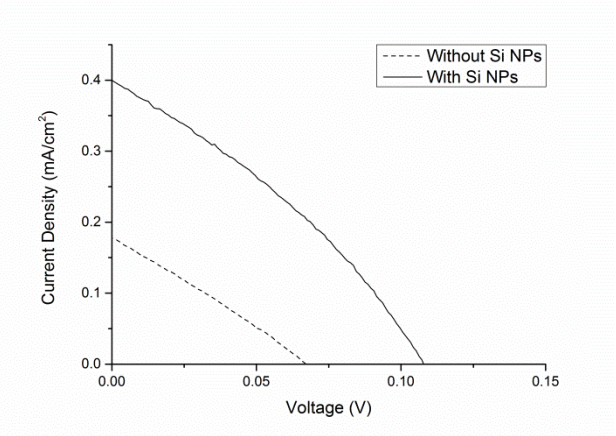

Figure 3. J-V characteristic of solar cell with (solid line) and without silicon nanoparticles (dashed line)

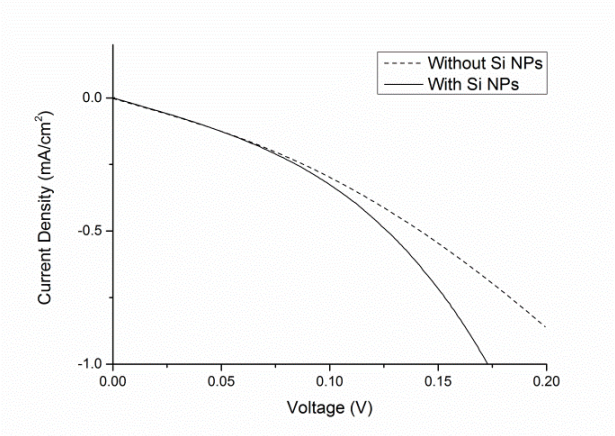

Figure 4. J-V characteristic of dark current with (solid line) and without silicon nanoparticles (dashed line)

Table 1. Electrical parameters of fabricated solar cell.

Sample	V_{oc} (V)	I_{sc} (mA)	J_{sc} (mA/cm^2)	P_{max}	FF	Eff. (%)
Without Si NPs	0.067	0.044	0.178	0.001	0.274	0.003
With Si NPs	0.114	0.104	0.418	0.004	0.330	0.016

Dark current is another important parameter for solar cell. It represents the electron recombination, which in turn, affects the device performance. Ideally, this dark current should be as small as possible for the device to achieve the highest current density. As shown in Fig. 4, the onset of dark current shifted to lower bias for the cell with silicon nanoparticles. This implies an increase in dark current density [24]. Although this unwanted current was enhanced in this case, the total current density were still higher than that of the other one. Since the total current density composed of photo-generated current and dark current, the increase of dark current density might be so small that the total current was dominated by the photo-generated term. As a consequence, the addition of silicon nanoparticles can still increase the total current density of this device.

Electrical impedance spectroscopy (EIS) was used to further study on the device performance. The result is shown in Fig. 5. The intercept at high frequency region corresponds to series resistance including that of electrolyte and conducting electrode. The semi-circle at high frequency range represents charge transfer resistance at counter electrode/electrolyte interface, while the one at low frequency range corresponds to charge transfer resistance by ions in electrolyte [24-27]. Since the electrolyte and counter electrode are the same, the values of series resistance (R_s) in both devices were almost unchanged [24, 27]. However, the resistances at low and middle frequency were decreased in the cell with silicon nanoparticles. This reduction led to higher current density in this device. EIS parameters are listed in Table 2 as additional information.

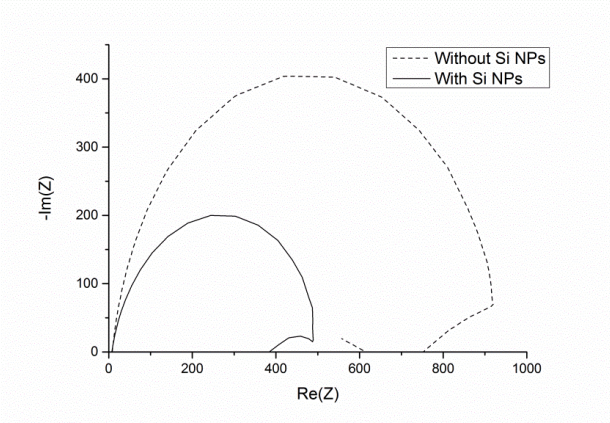

Figure 5. Impedance of solar cell with (solid line) and without silicon nanoparticles (dashed line)

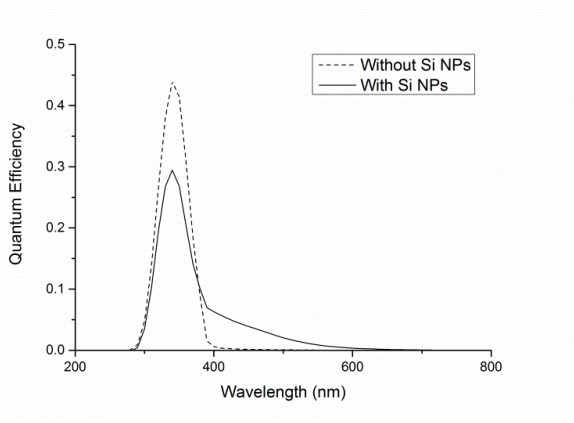

Figure 6. IPCE of solar cell with (solid line) and without silicon nanoparticles (dashed line)

Table 2. EIS parameters of fabricated solar cell.

Sample	R_s (Ω)	Z_1 (Ω)	Z_2 (Ω)
Without Si NPs	8.224	1113	927.8
With Si NPs	7.240	382	487.2

Incident photon-to-current efficiency (IPCE) indicates the ratio of the number of photons incident on photovoltaic device to the number of generated charge carriers. From Fig. 6, IPCE of solar cell with silicon nanoparticles increases in the range of 400-600 nm compared with that of the device without these particles. It seems that the addition of silicon nanoparticles contributes to light absorption at this region. However, no significant change was observed above 600 nm. This result emphasizes that the current density of solar cell with silicon nanoparticles was enhanced leading to an improvement of the device efficiency.

4. Conclusions

Silicon nanoparticles are one of the promising materials in the photovoltaic application. Although several techniques can be employed to prepared silicon nanoparticles, laser ablation in liquid was preferred in this work due to its simplicity and purity of product. The average size of prepared silicon nanoparticles was small enough so that MEG can be expected to occur. The conversion efficiency of QDSSC fabricated by these nanoparticles was shown to be five-fold higher than that of the device without them. This result can be explained by the reduction in electrical impedance and the increase in photon-to-current conversion efficiency from 400 to 600 nm.

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