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The improvement on the performance of quantum dot-sensitized solar cells with functionalized Si

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ABSTRACT

Quantum dots (QDs) have been attractive recently with their multiple exciton generation characteristics. QD solar cells can more effectively use the incident energy because one or more electrons are generated with the photon of high energy. They have less heat loss and higher theoretical efficiency (44%) than single exciton generation solar cells (33%). This work focused on Si as alternative to conventional QD materials. Si has QD's unique characteristics such as the quantum size effect and quantum confinement with non-toxicity and abundance. Si QDs were fabricated by the multi-hollow discharge plasma chemical vapor deposition and applied to QD-sensitized solar cells (QDSCs). Contrary to the good characteristics of Si QDs, Si QDSCs had poor performance as compared with conventional QDSCs because of the weak combination between Si QDs and TiO_2. Small amounts of adsorbed Si QD on TiO_2 made low photocurrent and TiO_2 surface widely exposed to redox electrolyte caused charge recombination, the decrease of open-circuit voltage, and low fill factor. For improving their combination, Si QDs were functionalized. The electron transfer from Si to TiO_2 and the bonding with TiO_2 were improved and more Si QDs were adsorbed by the functionalization. In the functionalization process, the linking source is one of the key parameters. Therefore, 4-vinylbenzoic acid was controlled and its effect was analyzed. The change in the photovoltaic parameters according to the concentration of 4-vinylbenzoic acid and the performance dependence were investigated. In order to verify their characteristics, the effects in terms of the photovoltaic performance, electrochemical impedance, and optical properties were examined.

1. Introduction

Quantum dot-sensitized solar cells (QDSCs) have recently attracted considerable attention in the research field of photochemical solar cells. They have been expected to realize high efficiency with QD's unique characteristics such as hot carrier [1,2], intermediate band [3,4], and multiple exciton generation (MEG) [5–8]. Especially, MEG characteristics generated multiple excitons by single photon absorption and enhanced the theoretical efficiency of QDSC over 44% [9] from 33% of Shockley and Queisser limit [10]. There are many kinds of QDs such as CdSe, CdS, PbSe, PbS, Ag_2S and so on developed so far [11–21]. QDSCs based on Cd or Pb compounds have high conversion efficiency currently and most of QDSC researches are concentrating on them. However, these QD materials have some disadvantages such as toxicity and scarcity. On the other hand, Si QD investigated in this work is one of the good QD materials as a dominant material in the photovoltaics. Its abundance and absence of toxicity are advantageous for photovoltaics. In addition, Si QD has high stability against light soaking as compared with a-Si:H films and a high optical absorption coefficient due to its quantum size effect as compared with μc-Si films. Quantum characteristics of Si QD were already proved in previous researches [7,22] and some papers were published about the characteristics of Si QD. However, there are no published reports about Si QDSC. Difficult collection of Si particles is one of the main reasons. In related researches, Si QD fabrication is mostly based on Si substrate because Si QDs were made by etching or growing from Si substrate [23–25]. In other words, these Si QDs were not particles actually because they were sticked to Si films. Therefore, these methods could not collect Si particles. This work solved it using multi-hollow discharge plasma chemical vapor deposition (CVD). Proposed method was possible to fabricate and collect Si particles. This method did not need Si substrate because Si QDs were directly generated from gas containing Si source. In this process, the crystallinity, particle size and optical properties of Si were controllable and these characteristics were the evidence of QD. Accordingly, Si QDs with different particle size and optical property were applicable to Si QDSC.

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Another reason of rare Si QDSC research is the weak adhesion of Si QDs on TiO_2. Only a few Si QDs were adsorbed on TiO_2 surface by conventional soaking method and it caused too low photocurrent and photovoltage of Si QDSC. In this work, the functionalization was introduced to Si QDs for improving the bonding between Si and TiO_2. More Si QDs were adsorbed by the functionalization and they make larger photocurrent and reduce the charge recombination. In this work, Si QDSCs were fabricated on the basis of these techniques. Consequently, Si QDs with visible light absorption were fabricated and functionalized Si QDs led to improve the overall performance. In order to verify their characteristics, the photovoltaic performance, internal electrochemical impedance, and the optical properties were examined.

2. Experimental details

2.1. Synthesis of Si QDs

Si QDs were synthesized by multi-hollow discharge plasma CVD [26,27]. Its dominant reaction is as follows. Silane (SiH_4) and hydrogen (H_2) were injected from the bottom of the reactor. It flowed through hollows of electrodes and pumped out from the top of the reactor. SiH_4 was converted to high-ordered silane with SiH_2 and ionized. Then, crystalline Si particles were nucleated and grown in the discharge plasma region. Eq. (1) simplified this process [28]. AC 200 W power with 60 MHz was applied to the electrode for the discharge with the temperature of 250 °C. Generated Si QDs were transported to the downstream region with gas flow and captured by stainless meshes. Si QDs were obtained by sonicating these meshes. Their crystallinity and size were changed according to the gas ratio of SiH_4 and H_2, and working pressure, respectively. Si QDs were structurally characterized by a transmission electron microscopy (TEM, JEM-2010, JEOL) with operating voltage of 2 kV.

$$\begin{aligned} &SiH_4 + e^- \rightarrow SiH_2 + H_2 + e^- \\ &SiH_4 + SiH_2 \rightarrow Si_2H_6 \\ &Si_2H_6 + SiH_2 \rightarrow Si_3H_8 \\ &Si_3H_8 + SiH_2 \rightarrow Si_4H_{10} \\ &Si_4H_{10} + e^- \rightarrow Si_4H_{10}{}^- (\text{grow}) \end{aligned} \quad (1)$$

2.2. Fabrication of Si QDSCs

Si QDSCs were fabricated as follows. FTO (F-doped tin oxide) substrates (30 Ω per sq., Asahi Glass Co.) were used as the transparent conductive oxide (TCO) to make the photo and counter electrodes. The substrates were sequentially cleaned by sonicating in acetone, ethyl alcohol, and distilled water, and dried using a stream of nitrogen. A uniform TiO_2 with a thickness of about 50 μm was pasted on the cleaned FTO substrate by the doctor blade method. After sintering at 450 °C for 30 min, the thickness of the prepared film was reduced to about 7 μm and its structure became nano-porous. FTO/TiO_2 electrodes were soaked in Si QD solution for 24 h. For the functionalization, Si QDs were immersed in ethanol with 4-vinylbenzoic acid as the linking source and chloroplatinic acid as the catalyst. The reaction was completed after mixed solution was sonicated for 4 h. The transmittance and reflectance of FTO/TiO_2/Si QD electrodes were measured in the region from 300 to 800 nm by UV/VIS spectrophotometer (V-570, Jasco). Au counter electrode with a thickness of about 100 nm was deposited by DC sputter (JEC-550, JEOL) at a power of 1.5 kVA and a working pressure of 2 Pa. Polysulfide electrolyte is suitable as the redox couple in case of QDSC because QDs are degraded by I^-/I_3^- electrolyte [14]. Then, polysulfide electrolyte allows strong interactions between Pt and S^{2-}. S^{2-} ions adsorb onto the surface of Pt counter electrode and suppress the conductivity and catalytic activity unlike Au counter electrode [29]. After that, the photo and counter electrodes were sealed using a thermoplastic sealant (Meltonix 1170–25, Solaronix) with a thickness of 25 μm. The sealed Si QDSCs were completed by injecting a redox electrolyte through a pre-drilled hole into the counter electrode. The redox electrolyte consisted of 1 M Na_2S, 2 M S and 0.4 M KCl in water and methanol mixed solution at a volume ratio of 3:7.

2.3. Characterization

Before their characterization, the completed cells were stored in the dark under open-circuit conditions for 24 h to allow the electrolyte to penetrate into the pores. The photovoltaic performance was measured under 1 sun (air mass 1.5, 100 mW/cm^2) by a source meter (Model 2400, Keithley Instrument, Inc.). During their irradiance and characterization, the cells were covered with a black mask fitting the active area. The irradiated cell area was 0.20 cm^2. I–V characteristic curve and Eq. (2) were used to calculate the short-circuit current (I_{SC}) and density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and the overall efficiency (η). The electrochemical analysis instrument (SP-150, Biologic SAS) was used to analyze the electrochemical impedance spectroscopy (EIS). EIS spectra were measured in the frequency range from 10 MHz to 1 MHz at room temperature. The applied bias voltage and AC amplitude were set at V_{OC} of QDSC and 10 mV, respectively. The electrical impedances were characterized using the Nyquist diagram.

$$\eta = \frac{P_{max}}{P_{in}} \times 100 = \frac{FF \cdot V_{oc} \cdot Jsc}{P_{in}} \times 100(\%) \quad (2)$$

3. Results and discussion

The controllable crystallinity and particle size were verified in our previous research [27]. Si was turned from amorphous to crystalline with the increase H_2 gas rate. Crystalline Si particles were obtained below 0.5% of SiH_4. Therefore, SiH_4 and H_2 gas streams of 2 and 448 cm^3/min were used at the subsequent experiments. The particle size of crystalline Si was larger with the increase of pressure. Fig. 1 shows TEM images of Si according to working pressure. Under high pressure, more particles were injected to the reactor and mean free path was shortened. Then, Si particles stayed in the discharge region for a longer time. That is, it was enough to react like Eq. (1) and generate more high-ordered silane as the seed of Si nano-particles. Accordingly, large Si particles were fabricated under high working pressure. Si particle size was changed from 5 nm to 17 nm under the working pressure from 266.6 to 799.9 Pa. In this work, Si QDs with a diameter of 9 nm were used under working pressure of 666.6 Pa.

The characteristics of Si QDs were verified by absorbed photon to current conversion efficiency (APCE). Fig. 2 shows APCE of Si QDSC [30]. For the penetration of short wavelength, Al sputtered quartz substituted for FTO substrate. APCE was increased from 400 nm and rapidly climbed at 2, e.g (band-gap energy) point (280 nm). Although the measurement in the range of below 250 nm was impossible by the limitation of equipment, the rapid increase from 2 e.g point confirmed MEG effect.

Generated Si QDs were applied to Si QDSC. Before Si adsorption on TiO_2, the cell was extremely poor with V_{OC} of 0.07 V and J_{SC} of 0.11 mA/cm^2. After Si QDs were adsorbed on TiO_2, the overall photovoltaic parameters were increased as V_{OC} of 0.21 V, J_{SC} of 0.14 mA/cm^2, FF of 0.40 and efficiency of 0.012%. But the enhancement of performance was not much because of the weak adhesion of Si QD on TiO_2. Adsorbed Si QDs were easily removed due to bad bonding. Weak adhesion made less Si QDs adsorbed and wide TiO_2 surface exposed to redox electrolyte. Then, photo voltage and current were decreased and many electrons were recombined with redox electrolyte through exposed TiO_2 surface. For the improvement of this adhesion, the functionalization was introduced to Si QDs. Functionalization made a kind of linker on Si particles and this linker was solidly connected with TiO_2. With strengthened adhesion, more Si QDs were adsorbed and photo-generated electrons were