Research Article

Sb₂S₃ Quantum-Dot Sensitized Solar Cells with Silicon Nanowire Photoelectrode

You-Da Hsieh,¹ Ming-Way Lee,² and Gou-Jen Wang¹,³

¹Department of Mechanical Engineering, National Chung-Hsing University, Taichung 40227, Taiwan
²Department of Physics, National Chung-Hsing University, Taichung 40227, Taiwan
³Graduate Institute of Biomedical Engineering, National Chung-Hsing University, Taichung 40227, Taiwan

Correspondence should be addressed to Gou-Jen Wang; gjwang@dragon.nchu.edu.tw

Received 31 December 2014; Revised 11 March 2015; Accepted 11 March 2015

Academic Editor: Leonardo Palmisano

Copyright © 2015 You-Da Hsieh et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We propose a novel quantum-dot sensitized solar cell (QDSSC) structure that employs a quantum dot/semiconductor silicon (QD/Si) coaxial nanorod array to replace the conventional dye/TiO₂/TCO photoelectrode. We replaced the backlight input mode with top-side illumination and used a quantum dot to replace dye as the light-absorbing material. Photon-excited photoelectrons can be effectively transported to each silicon nanorod and conveyed to the counter electrode. We use two-stage metal-assisted etching (MAE) to fabricate the micro-nano hybrid structure on a silicon substrate. We then use the chemical bath deposition (CBD) method to synthesize a Sb₂S₃ quantum dot on the surface of each silicon nanorod to form the photoelectrode for the quantum dot/semiconductor silicon coaxial nanorod array. We use a xenon lamp to simulate AM 1.5G (1000 W/m²) sunlight. Then, we investigate the influence of different silicon nanorod arrays and CBD deposition times on the photoelectric conversion efficiency. When an NH (N-type with high resistance) silicon substrate is used, the QD/Si coaxial nanorod array synthesized by three runs of Sb₂S₃ deposition shows the highest photoelectric conversion efficiency of 0.253%. The corresponding short-circuit current density, open-circuit voltage, and fill factor are 5.19 mA/cm², 0.24 V, and 20.33%, respectively.

1. Introduction

In general, the dye-sensitized solar cell (DSSC) is categorized, with respect to its components, as an organic compound solar cell. The DSSC is the only organic compound solar cell that utilizes molecules to absorb photons and converts photons into electrons without relying on the intermolecular transfer of the excited electrons. The DSSC is also the only solar cell type that conducts light harvesting and charge-carrier transport functions at different places [1]. Compared to the conventional silicon-based solar cell, the main advantages of the DSSC include its simple manufacturing process, low cost, physical and chemical TiO₂ stability, lack of toxicity, and wider application range. Although the photoelectric conversion efficiency of the DSSC has not reached the level of silicon-based solar cells, a DSSC with an efficiency of 12.3% has been reported [2].

Although the fabrication of DSSCs is relatively simple and cost-effective, mass production of DSSCs is still limited for a number of reasons. The main issue is the aging of the dye during solar cell operation. In addition, most of the available dyes can only absorb photons within the visible light range. Furthermore, the commonly used photoelectrode is based on the coating and the successive sintering of TiO₂ on a fluorine-doped tin oxide (FTO) glass to obtain an anatase type of TiO₂. The sintering of TiO₂ not only degrades the conductivity of the FTO substrate but also limits mass production fabrication. Recently, semiconductor-sensitized solar cells (SSSCs) that use semiconductors to replace the dye have attracted attention. Since the activity of a semiconductor will not degrade during solar cell operation, theoretically, the lifetime of an SSSC should be much longer than that of the conventional DSSC.

The quantum-dot sensitized solar cell (QDSSC) is one kind of DSSC [3–9]. Different semiconductor quantum dots (QDs) are used to replace dye as the light absorber. In addition to the lifetime enhancement of the light absorbers, the photon absorption range can be accurately manipulated
by selecting the type and size of the QD. Hence, the photon absorption range can be greatly expanded by combining several types of QDs that absorb photons of various wavelengths. A QDSSC using a CdS/CdSe hybrid QD with a photoelectric conversion efficiency of 4.22% was reported in 2009 [5]. Later, another QDSSC with a better photoelectric conversion efficiency (6.5%) was developed [8]. Shalom et al. [10] used a DSSC consisting of a photoelectrode by directly depositing QDs onto an FTO glass to quantify the lifetime and density of the photogenerated electrons within the QD layer. The authors verified that the electronic properties in quantum dot-sensitized solar cells are illumination intensity-dependent. Bhubut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent. Buhbut et al. [11] deposited type-II ZnSe/CdS quantum dot-sensitized solar cells are illumination intensity-dependent.

Nanomaterials and nanofabrication techniques have also been incorporated into the fabrication of DSSCs to achieve higher efficiency and lower cost [13–15]. The nanostructured photoelectrode can support the electrolyte and the dyes, as well as the acceptor and the conductor of the photoexcited electrons. A porous nanostructured photoelectrode can provide the electrolyte and the dyes with a sufficient absorption area to achieve a fast charge transfer. Hence, the photoelectric conversion efficiency can be enhanced.

In this study, we propose a novel and simple QDSSC structure using a silicon nanowire array (SNA) as the substrate. We use chemical bath deposition (CBD) [16–18] to grow Sb$_2$S$_3$ QDs between the silicon nanowires to form the QD/Si coaxial nanowire array, replacing the conventional dye/TiO$_2$/TCO photoelectrode. The photon-excited photoelectrons from the Sb$_2$S$_3$ QDs can be effectively transported to each silicon nanorod and then conveyed to the counter electrode. Since the silicon substrate is not fully transparent, we adapted illumination from the counter electrode. We expected that the high-surface-to-volume Si nanowire array would greatly expand the absorption area of the Sb$_2$S$_3$ QDs, hence increasing efficiency. Furthermore, the proposed new DSSC structure can be easily and directly produced in a silicon wafer, making the mass production of the proposed QDSSC highly feasible.

2. Material and Methods

2.1. QD/Si Coaxial Nanowire Array-Based DSSC. Figure 1 schematically illustrates a cross-sectional view of the proposed QD/Si coaxial nanowire array-based QDSSC. Solar light irradiates through the counter electrode and then penetrates the electrolyte to the photoelectrode of the QD/Si coaxial nanowire array to produce photoelectrochemical reactions. The photon-excited electrons are conveyed from the QD shell to the Si nanowire core and then are driven to the counter electrode through the back electrode, finally entering the electrolyte and reducing the ions therein. The QDs that have loose electrons due to photoelectrochemical reactions retrieve the electrons provided by the oxidation reactions in the electrolyte.

2.2. Fabrication of the Silicon Nanowire Photoelectrode Based Sb$_2$S$_3$ QDSSC. The fabrication procedures of the proposed novel QDSSC include (1) Si nanowire array fabrication, (2) Sb$_2$S$_3$ QDs deposition, (3) metal electrode fabrication, (4) counter electrode preparation, (5) electrolyte preparation, and (6) cell packaging as schematically illustrated in Scheme 1.

(i) Wafer cleaning: wash the Si wafer in acetone, ethanol (EtOH), and distilled water sequentially and...
(1) Si nanowire array fabrication

(2) Sb$_2$S$_3$ QDs deposition

(3) Metal electrode fabrication

(4) Counter electrode preparation

(5) Electrolyte preparation

(6) Cell packaging

**Scheme 1: QDSSC fabrication procedures.**

ultrasonically, and then remove the oxide layer on the wafer surface with diluted HF acid. Then, wash the wafer with distilled water.

(ii) Micropyramid array production: wet-etch the cleaned Si wafer using an etchant with a weight ratio of DI water: KOH (40 wt%): IPA = 70: 2:5 to create the micropyramid array on the wafer surface. Then, use more dilute HF acid to remove the oxide layer from the wafer surface.

(iii) Two-stage MAE: for the first MAE stage, use a mixing etchant of AgNO$_3$ (0.34 M) and HF (4.6 M) at 40$^\circ$C for 30 min. Then, for the second MAE stage use AgNO$_3$ (0.03 M) and HF (4.6 M) mixing etchant at 40$^\circ$C for 5 min. Remove the silver conifers that accumulate on the nanowire surface during the MAE process using nitric acid (HNO$_3$). Finally, remove the SiO$_2$ layer produced during the previous silver conifer removal step using an HF and distilled water mixing solution (ratio = 1:3).

(2) Sb$_2$S$_3$ QDs Deposition. We employed the chemical bath deposition (CBD) method to deposit a QD shell of Sb$_2$S$_3$ on each individual Si nanowire, thereby establishing the QD/Si coaxial nanowire array photoelectrode. The steps we followed in this method are detailed below.

(i) Na$_2$S$_2$O$_3$ solution preparation: dissolve the Na$_2$S$_2$O$_3$ ⋅ 5H$_2$O (6.2 g) with 25 mL distilled water, followed by 10 min of ultrasonication to obtain a transparent solution with no precipitate.

(ii) SbCl$_3$ solution preparation: take the SbCl$_3$ (0.65 g) from the nitrogen glove box and dissolve it in 2.5 mL ethanol. Ultrasonicate this solution for 10 min to obtain a transparent solution with no precipitate.

(iii) Sb$_2$S$_3$ QDs deposition: pour the prepared Na$_2$S$_2$O$_3$ and Na$_2$S$_2$O$_3$ solution into a beaker and use distilled water at 5$^\circ$C to increase the total volume of the CBD solution to 100 mL. Observe white suspensions that are the products of the SbCl$_3$-water chemical reactions. Transfer the CBD solution to a specific bottle for CBD. Then shake the bottle to allow uniform chemical reactions, followed by vertically immersing the prepared SNA specimen into the bottle. Keep the CBD bottle at 5$^\circ$C for 2 h per cycle and shake the bottle every half hour to ensure a uniform distribution of the solution. Then take the SNA specimen out of the bottle and rinse it with distilled water to obtain an orange amorphous Sb$_2$S$_3$ layer on the SNA surface. Finally, anneal the QDs-covered SNA specimen at 350$^\circ$C for 30 min, increasing the temperature from room temperature to 350$^\circ$C in 20 min.

(3) Metal Electrode Fabrication. Since the SNA substrate is a semiconductor, it must sputter a 30 nm thick thin gold film electrode on the bottom side of the substrate to reduce the series resistance of the DSSC and form ohmic contact, thereby enhancing the carrier collection capacity of the photodetector.

(4) Counter Electrode Preparation. Platinum thin film was used as the counter electrode material. The preparation procedures of the Pt counter electrode are briefly summarized below.

(i) Punch two small holes in a commercially available FTO substrate. One is used for the injection of the electrolyte, and the other one is used to exhaust the air inside the cell during the electrolyte injection process. Wash the FTO substrate in acetone, ethanol (EtOH),
and distilled water sequentially and ultrasonically, followed by heating at 60°C for 20 min to completely remove residual moisture.

(ii) Prepare a 5 mM H$_2$PtCl$_6$ solution by mixing 0.0515 g of H$_2$PtCl$_6$ with 20 mL ethanol, followed by ultrasonication for 10 min. Spin-coat the H$_2$PtCl$_6$ solution onto the cleaned FTO substrate twice. The rotational speed and duration for each coating are 1000 rpm and 10 min, respectively. Finally, sinter the H$_2$PtCl$_6$ solution-coated FTO at 400°C for 15 min to obtain the Pt thin film counter electrode.

(5) Electrolyte Preparation. The electrolyte used in the DSSCs must have a high diffusion coefficient, a fast oxidation-reduction reaction, and a low intrinsic resistance. The formula for the electrolyte used in this study that satisfies these requirements is

$$0.5 \text{ M LiI} + 0.05 \text{ M I$_2$} + 0.5 \text{ M TBP} + 0.6 \text{ M BMII in Acetonitrile + Valeronitrile (1 : 1).}$$

(6) Cell Packaging. The cell packaging procedures, as illustrated in the schematic in Figure 2, are as follows.

(i) Prepare a 1.5 × 1.5 cm$^2$ rectangular parafilm. Punch a 0.3 × 0.3 cm$^2$ square in the center of the rectangular parafilm as the photoreaction area.

(ii) Prepare a 1.5 × 1.5 cm$^2$ rectangular parafilm. Punch a 0.5 × 0.5 cm$^2$ square in the center of the rectangular parafilm as the buffer for the electrolyte leakage.

(iii) Attach the parafilm with the defined buffer square to the Pt thin film counter electrode, and then attach them both to the photoelectrode.

(iv) Bond the packaged device at 85°C for 7 min. It may be desirable to place an external load on top to ensure solid bonding of the parafilms.

(v) Adhere a silver conductive adhesive foil to the Au thin film electrode beneath the photoelectrode for clamping the measurement fixture.

(vi) Inject the electrolyte into the cell body using a syringe.

3. Results and Discussion

3.1. SNA Fabrication Results. After the fabrication of the SNA on the surface of the pyramid array using the two-stage MAE process, we then deposited Sb$_2$S$_3$ QDs on the surface of each of the SNA nanowires to serve as the photoelectrode. Since the relatively high-concentration AgNO$_3$ etchant used in the first stage contained more silver ions, the reduced silver atoms aggregated at the surface of the Si substrate and were uniformly deposited on the Si substrate. However, the Si substrate could also be oxidized quickly by the highly concentrated silver ions; therefore, the processing time of the first-stage MAE was set to be less than 1 min. The low-concentration AgNO$_3$ etchant used in the second-stage MAE enabled the uniformly deposited silver particles on the substrate surface to etch downward slowly so that a uniform SNA, microscale in height, could be fabricated.

Figure 3 shows SEM images of the fabricated SNA under a constant first-stage processing time of 30 sec and various second-stage processing times. We can observe that Si nanowires with heights of micrometers grew uniformly on the surface of the pyramid array. We also found that the length of the SNA increased with an increased second-stage processing time. The top-view image, as shown in the inset in each image, displays the Si nanowires on the surface of the pyramid array.

In successive experiments, we set the second-stage processing time at 5 min, accompanied by various first-stage processing times (20, 25, 30, 35, 40, and 45 sec). Figure 4 illustrates the fabrication results. The SNAs fabricated under first-stage processing times of 20 and 25 sec (Figures 4(a) and 4(b)) reveal denser but shorter structures. We speculate that the shorter first-stage processing time produced smaller silver particles, resulting in an unevenly distributed redox reaction speed in the second stage of the MAE process. In Figures 4(c) and 4(d), uniform and vertical SNAs with micrometer lengths can be observed. The SNAs fabricated with a relatively longer first-stage processing time (Figures 4(e) and 4(f)) have a relatively looser and more flexible structure. These results can be mainly attributed to the fact that a longer first-stage processing time induces a continuous catalytic reaction on the substrate surface.

3.2. QDs Sb$_2$S$_3$ Characterization. The novelty of this study is the development of the photoelectrode with the QD/Si
Figure 3: SEM images of the fabricated SNA under a constant first-stage processing time of 30 sec and various second-stage processing times: (a) second-stage processing time: 1 min, (b) 2 min, (c) 3 min, and (d) 4 min.

Figure 4: SEM images of the fabricated SNA under a constant second-stage processing time of 5 min and various first-stage processing times: (a) first-stage processing time: 20 sec, (b) 25 sec, (c) 30 sec, (d) 35 sec, (e) 40 sec, and (f) 45 sec.
Figure 5: SEM images for the synthesized QD/Si coaxial nanowire array after various CBD cycles: (a) 1 CBD cycle, (b) 2 CBD cycles, (c) 3 CBD cycles, and (d) 4 CBD cycles. Scale bar = 1 𝜇m.

Figure 6: SEM images after annealing of the QD/Si coaxial nanowire array for various CBD cycles: (a) 1 CBD cycle, (b) 2 CBD cycles, (c) 3 CBD cycles, and (d) 4 CBD cycles. Scale bar = 1 𝜇m.
coaxial nanowire array. The properties of the synthesized Sb$_2$S$_3$ surrounding each nanowire highly affect the performance of the DSSC. Therefore, we used scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM) to characterize the synthesized Sb$_2$S$_3$ QDs.

(1) Topography Analysis. SEM images for the QD/Si coaxial nanowire array for various CBD cycles are shown in Figures 5 and 6. Figure 5 displays the synthesized coaxial nanowire array, while Figure 6 presents array images after annealing. Figures 5(a) and 6(a) are the images before and after annealing of the coaxial nanowire arrays after 1 CBD cycle. We find no apparent difference between these two arrays but for several plush-like structures at the tip of the array after annealing (Figure 6(a)). The array images before and after annealing after 2 CBD cycles are shown in Figures 5(b) and 6(b), respectively. Compared with the images of the 1 CBD cycle arrays, relatively more obvious topographical differences can now be observed. More nanoparticles are attached to the surface of each nanowire in Figure 5(b). After annealing, the attached nanoparticles disappeared and each nanowire was covered by a film which enlarged the size of the nanowire. When the number of CBD cycles was increased to three, each nanowire was fully surrounded by nanoparticles after the CBD process (Figure 5(c)). After annealing, the topography was similar to that shown in Figure 6(b). Besides the tip of the nanowire, the rest of the nanowire either was fully covered by a thin film or adhered to neighboring nanowires, forming the desired photoelectrode with a QD/Si coaxial nanowire array (Figure 6(c)). Figures 5(d) and 6(d) show images of the nanowire arrays after 4 CBD cycles. Each Si nanowire was completely covered by Sb$_2$S$_3$ nanoparticles after the CBD process. After annealing, no obvious shape of the original nanowire can be seen. The photoelectrode with distinct QD/Si coaxial nanowires can be seen in Figure 6(d).

The above SEM analyses indicate that the Sb$_2$S$_3$ nanoparticles started to adhere to the nanowire surface after 2 CBD cycles and fully covered each nanowire when the number of CBD cycles was increased to four. We therefore suggest that the CBD process should be repeated 2–4 times to obtain the desired QD/Si coaxial nanowire array-based photoelectrode.

(2) Components Analysis. To further verify that both the nanoparticles and the thin film covering the Si nanowire after annealing consist of Sb$_2$S$_3$, we conducted an EDS analysis. Table 1 tabulates the components of the coaxial nanowire array fabricated under different CBD cycles. We can observe that the samples contain antimony (Sb) and sulfur (S), which are the components of Sb$_2$S$_3$. The data indicate that
![Image](image_url)

**Figure 8:** Images of the synthesized coaxial nanowire arrays after 3 CBD cycles; (a) cross-sectional SEM image, (b) individual coaxial nanowire TEM (×8,000) image, (c) front end TEM (×40,000) image, and (d) middle TEM (×40,000) image.

| CBD cycles | Si (Weight%) (Atomic%) | S (Weight%) (Atomic%) | Sb (Weight%) (Atomic%) |
|------------|------------------------|-----------------------|------------------------|
| 0          | 88.24 (94.32)          | 4.04 (3.78)           | 7.73 (1.90)            |
| 1          | 45.93 (67.66)          | 14.70 (18.96)         | 39.37 (13.38)          |
| 2          | 32.52 (54.00)          | 18.81 (27.36)         | 48.66 (18.64)          |
| 3          | 14.97 (30.07)          | 23.55 (41.44)         | 61.47 (28.49)          |
| 4          | 9.94 (22.03)           | 22.35 (43.37)         | 67.71 (34.60)          |

**Table 1: Components of the coaxial nanowire array fabricated after different numbers of CBD cycles.**

The percentage of Sb$_2$S$_3$ in the samples increased with an increased number of CBD cycles. In contrast, the percentage of Si gradually decreased.

(3) **Structure Analysis.** Figures 7 and 8 show images of the synthesized coaxial nanowire arrays after 1 and 3 CBD cycles, respectively. The SEM image shown in Figure 7(a) indicates that the length of the coaxial nanowire array is around 2.25 µm. The length of the individual nanowire shown in the TEM image (Figure 7(b)) is 1.5 µm, which is close to the entire array length indicated by the SEM image. Figure 7(c) displays the ×40,000 magnified image. Clear boundaries separating the core Si nanowire and the coated Sb$_2$S$_3$ can be observed. The diameter of the core Si nanowire is estimated to be 50 nm. Similarly, the length of the 3-CBD-cycle-synthesized coaxial nanowire array, as shown in Figure 8(a), is about 3.2 µm. An individual coaxial nanowire, as shown in Figure 8(b), measures 2 µm in length. Boundaries separating the core Si nanowire and the Sb$_2$S$_3$ coating are more apparent in this figure. At the front end, the diameters of the core Si nanowire and the coaxial nanowire are estimated to be 100 and 200 nm, respectively (Figure 8(c)). In the middle, the diameter of the core Si nanowire remained at 100 nm, while that of the coaxial nanowire increased to 275 nm (Figure 8(d)). The cause of the size difference at the front end and the middle can be attributed to the downward flow of the Sb$_2$S$_3$ QDs during annealing.

Table 2 summarizes the TEM analysis results for various QDs/Si coaxial nanowire arrays fabricated with different numbers of CBD cycles. Since the TEM sample was prepared by supersonicating the synthesized photoelectrode sample in
Table 2: TEM analysis results for various QDs/Si coaxial nanowire arrays fabricated with different numbers of CBD cycles.

| CBD cycles | Si nanowire diameter (nm) | Sb$_2$S$_3$ shell thickness (nm) |
|------------|--------------------------|---------------------------------|
| 1          | 50                       | 20                              |
| 2          | 60                       | 30                              |
| 3          | 100                      | 50 (front), 87.5 (middle)       |
| 4          | 80                       | 195 (front), 225 (middle)       |

Figure 9: I-V curves for various DSSCs based on the QDs/Si coaxial nanowire array-based photoelectrodes synthesized with different numbers of CBD cycles.

Table 3: Photoelectric conversion efficiencies for various DSSCs based on the QDs/Si coaxial nanowire array-based photoelectrodes synthesized using different numbers of CBD cycles.

| CBD cycles | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | $\eta$ (%) |
|------------|----------------------|-------------|--------|------------|
| 1          | 2.71                 | 0.20        | 21.56  | 0.116      |
| 2          | 4.51                 | 0.20        | 17.36  | 0.157      |
| 3          | 5.19                 | 0.24        | 20.33  | 0.253      |
| 4          | 2.48                 | 0.20        | 21.38  | 0.106      |
| 5          | 1.29                 | 0.21        | 20.80  | 0.056      |

increased. However, when the number of CBD cycles was increased to four, an excessive amount of QDs was deposited on the surface of the Si nanowires. This excessively thick shell of QDs degraded the photon absorption and photoelectron migration.

Although the proposed QDs/Si coaxial nanowire array-based DSSC has the advantages of simplicity, low cost, and high mass production feasibility, the convex IV curve results in a small FF, about 20% in this work. Possible explanations for this include the following.

(1) Large Resistance. The resistance of the proposed DSSC was measured by impedance spectroscopy analysis to be 20 k–25 k$\Omega$. Hence the current density could only reach 5.19 mA/cm$^2$, resulting in a relatively lower photoelectric conversion efficiency. Furthermore, the fill factor was not as good as that of a conventional TiO$_2$-based DSSC. The leakage of the electrolyte due to less than fully tight packaging may be the major cause.

(2) Reduced Illumination. Sunlight irradiates through both the counter electrode and the electrolyte to reach the photoelectrode, resulting in a degraded illumination of the DQs, which then affects the photoelectric conversion efficiency.

In our future work, we will use a thinner Si wafer or increasing the doping concentration to reduce the resistance of the photoelectrode and a gelatinous electrolyte to avoid possible electrolyte leakage.

4. Conclusion

The DSSC is considered to be a highly promising technology for low cost renewable energy. However, the mass production of DSSC is still limited by a number of factors, including the aging of dye during operation and the relatively narrow light spectrum of the photon absorption. In this study, we proposed a novel and simple QDSSC structure based on a QDs/Si coaxial nanowire array-based photoelectrode. We use two-stage MAE to fabricate the micro-nano hybrid structure on a silicon substrate. We then used CBD to deposit Sb$_2$S$_3$ QDs on the surface of each silicon nanowire to form the QD/Si coaxial nanowire array to replace the conventional dye/TiO$_2$/TCO photoelectrode. The quantum dot replaces dye as the light-absorbing material. Since the Si-based photoelectrode is opaque, we obtain illumination from the counter electrode. Experimental results illustrate
that the QD/Si coaxial nanorod array-based photoelectrode synthesized by three runs of Sb$_2$S$_3$ deposition provides the highest photoelectric conversion efficiency of 0.253%. The corresponding short-circuit current density, open-circuit voltage, and fill factor are 5.19 mA/cm$^2$, 0.24 V, and 20.33%, respectively.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**Acknowledgment**

The authors would like to offer their thanks to the National Science Council of Taiwan for their financial support of this research under Grant no. NSC-101-2212-E-005-022-MY3.

**References**

[1] M. Grätzel, “Recent advances in sensitized mesoscopic solar cells,” *Accounts of Chemical Research*, vol. 42, no. 11, pp. 1788–1798, 2009.

[2] A. Yella, H.-W. Lee, H. N. Tsao et al., “Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency,” *Science*, vol. 334, no. 6056, pp. 629–634, 2011.

[3] C. H. Chang and Y. L. Lee, “Chemical bath deposition of CdS quantum dots onto mesoscopic TiO$_2$ films for application in quantum-dot-sensitized solar cells,” *Applied Physics Letters*, vol. 91, no. 5, Article ID 053503, 2007.

[4] D. R. Baker and P. V. Kamat, “Photosensitization of TiO$_2$ nanostructures with CdS quantum dots: particulate versus tubular support architectures,” *Advanced Functional Materials*, vol. 19, no. 5, pp. 805–811, 2009.

[5] Y.-L. Lee and Y.-S. Lo, “Highly efficient quantum-dot-sensitized solar cell based on co-sensitization of CdS/CdSe,” *Advanced Functional Materials*, vol. 19, no. 4, pp. 604–609, 2009.

[6] A. Tubtimtae, K.-L. Wu, H.-Y. Tung, M.-W. Lee, and G. J. Wang, “Ag$_3$S quantum dot-sensitized solar cells,” *Electrochemistry Communications*, vol. 12, no. 9, pp. 1158–1160, 2010.

[7] A. Tubtimtae, M.-W. Lee, and G.-J. Wang, “Ag$_3$Se quantum-dot sensitized solar cells for full solar spectrum light harvesting,” *Journal of Power Sources*, vol. 196, no. 15, pp. 6603–6608, 2011.

[8] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, and N.-G. Park, “6.5% efficient perovskite quantum-dot-sensitized solar cell,” *Nanoscale*, vol. 3, no. 10, pp. 4088–4093, 2011.

[9] A. Tubtimtae and M.-W. Lee, “Effects of passivation treatment on performance of CdS/CdSe quantum-dot co-sensitized solar cells,” *Thin Solid Films*, vol. 526, pp. 225–230, 2012.

[10] M. Shalom, Z. Tachan, Y. Bouhadana, H.-N. Barad, and A. Zaban, “Illumination intensity-dependent electronic properties in quantum dot sensitized solar cells,” *Journal of Physical Chemistry Letters*, vol. 2, no. 16, pp. 1998–2003, 2011.

[11] S. Buhbut, S. Itzhakov, I. Hod, D. Oron, and A. Zaban, “Photo-induced dipoles: a new method to convert photons into photovoltage in quantum dot sensitized solar cells,” *Nano Letters*, vol. 13, no. 9, pp. 4456–4461, 2013.

[12] P. N. Kumar, S. Mandal, M. Deepa, A. K. Srivastava, and A. G. Joshi, “Functionalyzed graphite platelets and lead sulfide quantum dots enhance solar conversion capability of a titanium dioxide/cadmium sulfide assembly,” *The Journal of Physical Chemistry C*, vol. 118, no. 33, pp. 18924–18937, 2014.

[13] V. Amoli, R. Tiwari, A. Dutta, A. Bhaumik, and A. K. Sinha, “Structurally stabilized organosilane-templated thermostable mesoporous titania,” *ChemPhysChem*, vol. 15, no. 1, pp. 187–194, 2014.

[14] S.-P. Ng, X. Q. Lu, N. Ding, C.-M. L. Wu, and C.-S. Lee, “Plasmonic enhanced dye-sensitized solar cells with self-assembly gold-TiO$_2$@core-shell nanoislands,” *Solar Energy*, vol. 99, pp. 115–125, 2014.

[15] C. M. Yang, M. H. Hon, and I. C. Leu, “Hierarchical ZnO nanostructures growth by aqueous solution process for dye-sensitized solar cells,” *Journal of the Electrochemical Society*, vol. 159, no. 7, pp. H638–H643, 2012.

[16] W. Lee, S. K. Min, V. Dhas, S. B. Ogale, and S. H. Han, “Chemical bath deposition of CdS quantum dots on vertically aligned ZnO nanorods for quantum dots-sensitized solar cells,” *Electrochemistry Communications*, vol. 11, no. 1, pp. 103–106, 2009.

[17] W.-S. Chang, C.-C. Wu, M.-S. Jeng, K.-W. Cheng, C.-M. Huang, and T.-C. Lee, “Ternary Ag-In-S polycrystalline films deposited using chemical bath deposition for photoelectrochemical applications,” *Materials Chemistry and Physics*, vol. 120, no. 2-3, pp. 307–312, 2010.

[18] Q. Guo, G. M. Ford, W.-C. Yang et al., “Fabrication of 7.2% efficient CZTSSe solar cells using CZTS nanocrystals,” *Journal of the American Chemical Society*, vol. 132, no. 49, pp. 17384–17386, 2010.

[19] H. Morinaga, M. Suyama, and T. Ohmi, “Mechanism of metallic particle growth and metal-induced pitting on Si wafer surface in wet chemical processing,” *Journal of the Electrochemical Society*, vol. 141, no. 10, pp. 2834–2841, 1994.

[20] J. S. Kim, H. Morita, J. D. Joo, and T. Ohmi, “The role of metal induced oxidation for copper deposition on silicon surface,” *Journal of the Electrochemical Society*, vol. 144, no. 9, pp. 3275–3283, 1997.

[21] K. Peng and J. Zhu, “Morphological selection of electroless metal deposits on silicon in aqueous fluoride solution,” *Electrochimica Acta*, vol. 49, no. 16, pp. 2563–2568, 2004.

[22] H. C. Liu and G. J. Wang, “Superior antireflection coating for a silicon cell with a micronanohybrid structure,” *International Journal of Photoenergy*, vol. 2014, Article ID 807812, 8 pages, 2014.

[23] H. C. Liu and G. J. Wang, “Fabrication of high anti-reflection nanowires on silicon using two-stage metal-assisted etching,” *Journal of Renewable and Sustainable Energy*, vol. 5, no. 5, Article ID 053115, 2013.
