Improved conversion efficiency of Ag$_2$S quantum dot-sensitized solar cells based on TiO$_2$ nanotubes with a ZnO recombination barrier layer

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Abstract
We improve the conversion efficiency of Ag$_2$S quantum dot (QD)-sensitized TiO$_2$ nanotube-array electrodes by chemically depositing ZnO recombination barrier layer on plain TiO$_2$ nanotube-array electrodes. The optical properties, structural properties, compositional analysis, and photoelectrochemistry properties of prepared electrodes have been investigated. It is found that for the prepared electrodes, with increasing the cycles of Ag$_2$S deposition, the photocurrent density and the conversion efficiency increase. In addition, as compared to the Ag$_2$S QD-sensitized TiO$_2$ nanotube-array electrode without the ZnO layers, the conversion efficiency of the electrode with the ZnO layers increases significantly due to the formation of efficient recombination layer between the TiO$_2$ nanotube array and electrolyte.

Keywords: quantum dots, TiO$_2$ nanotube, Ag$_2$S, solar cells

Introduction
In recent years, dye-sensitized solar cells (DSSCs) have attracted much attention as a promising alternative to conventional p-n junction photovoltaic devices because of their low cost and ease of production [1-4]. A high power conversion efficiency of 11.3% was achieved [5]. The conventional DSSCs consist of dye-sensitized nanocrystalline TiO$_2$ film as working electrode, electrolyte, and opposite electrode. In DSSCs, the organic dyes act as light absorbers and usually have a strong absorption band in the visible. Various organic dyes such as N719 and black dye have been applied for improving the efficiency, light absorption coverage, stability, and reducing the cost. However, the organic dyes have a weak absorbance at shorter wavelengths. Materials that have high absorption coefficients over the whole spectral region from NIR to UV are needed for high power conversion efficiency. During the last few years, instead of organic dyes, the narrow band gap semiconductor quantum dots (QDs) such as CdS [6,7], CdSe [7-9], PbS [10,11], InAs [12], and InP [13] have been used as sensitizers. The unique characteristics of QDs over the organic dyes are their stronger photoresponse in the visible region, tunable optical properties, and band gaps simply by controlling the sizes. The QD-sensitized solar cells (QDSSCs) have been considered the next-generation sensitizers [14]. In either DSSCs or QDSSCs, the nanoparticle porous film electrode plays a key role in the improvement of power conversion efficiency. Recently, to improve the properties of TiO$_2$ film electrode, one-dimensional nanostructure arrays as working electrodes, including nanowires and nanotubes, have been proposed and studied. Compared with the nanoparticle porous films, aligned one-dimensional nanostructure arrays can provide a direct pathway for charge transport and superior optical absorption properties. Therefore, more and more studies focus on QDSSCs based on one-dimensional nanomaterials, such as the TiO$_2$ nanotubes (TNTs) [15-17].

Among QDs, Ag$_2$S is an important material for photocatalysis [18-20] and electronic devices [21-24]. Ag$_2$S has a large absorption coefficient and a direct band gap of 0.9 to 1.05 eV, which makes Ag$_2$S an effective semiconductor material for photovoltaic application. In the past several years, although there are some reports on the photovoltaic application of Ag$_2$S [10,25], few studies on Ag$_2$S QDSSCs based on TNTs are reported. In this work, we...
report on the synthesis of Ag$_2$S QD-sensitized TNT photoelectrode combining the excellent charge transport property of the TNTs and absorption property of Ag$_2$S. Besides, to improve the efficiency of as-prepared photoelectrodes, we interpose a ZnO recombination barrier layer between TNTs and Ag$_2$S QDs to reduce the charge recombination in Ag$_2$S QDSSCs because the ZnO layer can block the recombination of photoinjected electrons with redox ions from the electrolyte. Recently, we have reported the improved conversion efficiency of CdS QD-sensitized TiO$_2$ nanotube array using ZnO energy barrier layer [26]. Similar method has been used by Lee et al. to enhance the efficiency of CdSe QDSSCs by interposing a ZnO layer between CdSe QDs and TNT [27]. Our results show that Ag$_2$S QD-sensitized TiO$_2$ nanotube-array photoelectrodes were successfully achieved. The more important thing is that the conversion efficiency of the Ag$_2$S-sensitized TNTs is significantly enhanced due to the formation of ZnO on the TNTs.

**Experimental section**

**Materials**

Titanium foil (99.6% purity, 0.1 mm thick) was purchased from Goodfellow (Huntingdon, England). Silver nitrate (AgNO$_3$, 99.5%) and glycerol were from Junsei Chemical Co. (Tokyo, Japan). Ammonium fluoride (NH$_4$F), sodium sulfide nonahydrate (Na$_2$S, 98.0%), and zinc chloride (ZnCl$_2$, 99.995+) were available from Sigma-Aldrich (St. Louis, MO, USA).

**Synthesis of TNTs**

Vertically oriented TNTs were fabricated by anodic oxidation of Ti foil, which is similar to that described by Paulose et al. [28]. Briefly, the Ti foils were first treated with acetone, isopropanol, methanol, and ethanol, followed by distilled (DI) water and finally drying in a N$_2$ stream. Then, the dried Ti foils were immersed in high-purity glycerol (90.0 wt.%) solution with 0.5 wt.% of NH$_4$F and 9.5 wt.% DI water and anodic oxidized at 60 V in a two-electrode configuration with a cathode of flag-shaped platinum (Pt) foil at 20°C for 25 h. After oxidation, the samples were washed in DI water to remove precipitation atop the nanotube film and dried in a N$_2$ stream. The obtained titania nanotube film was annealed at 450°C in an air environment for 2 h.

**Synthesis of Ag$_2$S-sensitized plain TNT and ZnO/TNT electrodes**

The ZnO thin films on TNTs were prepared by using the successive ionic layer adsorption and reaction method, as described elsewhere [27,29]. Briefly, the annealed TNT electrodes were immersed in 0.01 M ZnCl$_2$ solution complexed with an ammonia solution for 15 s and then in DI water at 92°C for 30 s, with the formation of solid ZnO layer. Finally, the as-prepared TNT electrodes were dried in air and annealed at 450°C for 30 min in air for better electrical continuity. Ag$_2$S QDs were assembled on the crystallized TNT and ZnO/TNT electrodes by sequential chemical bath deposition (CBD) [25,30]. Typically, one CBD process was performed by dipping the plain TNT and ZnO/TNT electrodes in a 0.1 M AgNO$_3$ ethanol solution at 25°C for 2 min, rinsing it with ethanol, and then dipped in a 0.1 M Na$_2$S methanol solution for 2 min, followed by rinsing it again with methanol. The two-step dipping procedure is considered one CBD cycle. After several cycles, the sample became dark. In this study, 2, 4, and 8 cycles of Ag$_2$S deposition were performed (denoted as Ag$_2$S(2), Ag$_2$S(4), and Ag$_2$S(8), respectively). Finally, the as-prepared samples were dried in a N$_2$ stream. The preparation process of as Ag$_2$S-sensitized ZnO/TNT electrode is shown in Figure 1. For comparison, Ag$_2$S-sensitized TNT electrodes without ZnO films were also fabricated by the same process.

**Materials characterization**

The surface morphology of the as-prepared electrodes was monitored using a scanning electron microscope (SEM) (Nova230, FEI Company, Eindhoven, Netherlands). The mapping and crystal distribution of the samples were done using a scanning transmission electron microscope (TEM) (Tecnai G2 F30, FEI Company Eindhoven, Netherlands) to which an Oxford Instruments (Abingdon, Oxfordshire, UK) energy dispersive X-ray spectroscopy (EDS) detector was coupled. The surface compositions of the samples were analyzed using EDS. The crystalline phase and structure were confirmed by using X-ray diffraction (XRD) (Rigaku D/MAX 2500 V diffractor; Rigaku Corporation, Tokyo, Japan). The UV-visible (UV-vis) absorbance spectroscopy was obtained from a S-4100 spectrometer with a SA-13.1 diffuse reflector (Scinco Co., Ltd, Seoul, South Korea).

**Photoelectrochemical measurements**

The photoelectrochemical measurements were performed in a 300-mL rectangular quartz cell using a three-electrode configuration with a Pt foil counter electrode and a saturated SCE reference electrode, and the electrolyte was 1.0 M Na$_2$S. The working electrode, including the TNTs, ZnO/TNTs, Ag$_2$S(n)/TNTs, and Ag$_2$S(n)/ZnO/TNTs ($n = 2, 4,$ and 8), with a surface area of 0.5 cm$^2$ was illuminated under UV-vis light ($I = 100$ mW cm$^{-2}$) with a simulated solar light during a voltage sweep from -1.4 to 0 V. The simulated solar light was produced by a solar simulator equipped with a 150-W Xe lamp. The light intensity was measured with a digital power meter.
Results and discussion

Morphology of the TNTs

Figure 2a shows the SEM image of the plain TNT film fabricated by anodization of Ti foil before coating with ZnO and Ag$_2$S, which reveals a regularly arranged pore structure of the film. The average diameter of these pores is found to be approximately 200 nm and the thickness of the wall of the TNTs approximately 30 nm.

Characterization of the Ag$_2$S QD-sensitized ZnO/TNT (and TNTs) electrodes

Figure 2a shows the surface SEM image of the Ag$_2$S(4)/TNT film. It can be clearly seen from Figure 2b that Ag$_2$S is deposited as spherical nanoparticles on the TNTs and the wall thickness of the Ag$_2$S(4)/TNTs is similar to that of the plain TNTs. In addition, a uniform distribution of the Ag$_2$S nanoparticles with diameters of approximately 10 nm is also observed.

For a comparison, the surface SEM image of the ZnO/TNTs covered by Ag$_2$S after four CBD cycles (i.e., the Ag$_2$S/ZnO/TNT electrode) is shown in Figure 2c. It is found that after the formation of the ZnO thin layer on the TNTs, the diameter and distribution of Ag$_2$S nanoparticles did not change much. However, the diameter of the ZnO-coated TNTs increased slightly compared to that of the plain TNTs shown in Figure 2b. These results are similar to previous reports [26,27].

The detailed microscopic structure of the Ag$_2$S(4)/ZnO/TNTs was further investigated by a high-resolution transmission electron microscope (HR-TEM). Figure 3a shows the low-magnification TEM image of the Ag$_2$S(4)/ZnO/TNTs. It can be clearly seen that many Ag$_2$S nanoparticles with diameters of approximately 10 nm were deposited into the TNTs. This is supported by our earlier observation in the SEM measurement (Figure 2c). Figure 3b shows the high-magnification image of the Ag$_2$S(4)/ZnO/TNTs. It is observed that the crystalline Ag$_2$S nanoparticles were grown on crystalline TNTs. In addition, the HR-TEM image in Figure 3b reveals clear lattice fringes, the observed lattice fringe spacing of 0.268 nm is consistent with the unique separation (0.266 nm) between (120) planes in bulk acanthite Ag$_2$S crystallites.

To determine the composition of the nanoparticles, the corresponding energy dispersive x-ray (EDX) spectrum of the Ag$_2$S(4)/ZnO/TNTs was carried out in the HR-TEM as seen in Figure 3c. The characteristics peaks in the spectrum are associated with Ag, Ti, O, Zn, and S. The quantitative analysis reveals the atomic ratio of Ag and S is close to 2:1, indicating the deposited materials are possible Ag$_2$S.

In order to determine the structure of the Ag$_2$S(4)/ZnO/TNTs, the crystalline phases of the Ag$_2$S(4)/ZnO/TNTs and the corresponding TNTs were characterized by XRD, as shown in Figure 3d. The XRD pattern shows peaks corresponding to TiO$_2$ (anatase), ZnO (hexagon), and Ag$_2$S (acanthite). The observed peaks indicate high crystallinities in the TNTs, ZnO, and Ag$_2$S nanoparticles, consistent with the SEM results shown in Figure 2. The results further confirm that the obtained films are composed of TiO$_2$, ZnO, and Ag$_2$S.

Optical and photoelectrochemistry properties of Ag$_2$S QD-sensitized TNT electrodes in the presence of ZnO layers

Figure 4 shows optical absorption of annealed TNTs, ZnO/TNTs, and Ag$_2$S(n)/ZnO/TNTs (n = 2, 4, and 8). It can be seen from Figure 4 that both plain TNTs and ZnO/TNTs absorb mainly UV light with wavelengths smaller than 400 nm. However, for the ZnO/TNT film, the absorbance of the spectra slightly increases compared to that for plain TNTs, suggesting the formation of ZnO thin film on TNTs. This result is similar to that for ZnO-coated TiO$_2$ films in DSSCs [29], which can be attributed to the absorption of the ZnO layers coated on TNTs.
After Ag$_2$S deposition, the absorbance of the Ag$_2$S($n$)/ZnO/TNT films increases with the cycles of Ag$_2$S chemical bath deposition process. Moreover, a significant shift of the spectral photoresponse is observed in the Ag$_2$S($n$)/ZnO/TNT films, indicating that the Ag$_2$S deposits can be used to sensitize TiO$_2$ nanotube arrays with respect to lower energy (longer wavelength) region of the sunlight. In addition, the absorbance increases with the increase in the cycles of Ag$_2$S deposition, resulting from an increased amount of Ag$_2$S nanoparticles.

For the performance comparison of as-prepared Ag$_2$S-sensitized TNT and ZnO/TNT electrodes, the curves of photocurrent density vs. the applied potential for the Ag$_2$S($n$)/TNT and Ag$_2$S($n$)/ZnO/TNT ($n = 2, 4, \text{ and } 8$) electrodes in the dark and under simulated AM 1.5 G sunlight irradiation (100 mW cm$^{-2}$) are shown in Figure 5.

It is clearly seen from Figure 5 that for a chemical bath deposition (CBD) cycle $n$ and an applied potential, the photocurrent density of the Ag$_2$S($n$)/ZnO/TNT electrode is higher than that of the Ag$_2$S($n$)/TNTs without ZnO layer. This can be explained from the increased absorbance of the Ag$_2$S($n$)/ZnO/TNT electrode shown in Figure 4 and the energy diagram of Ag$_2$S-sensitized ZnO/TNT solar cells presented in Figure 6a. Due to the formation of ZnO energy barrier layer over TNTs, the charge recombination with either oxidized Ag$_2$S quantum dots or the electrolyte in the Ag$_2$S-sensitized ZnO/TNT electrode is suppressed compared to the Ag$_2$S-sensitized TNTs. This explanation can be supported by the dark current density-applied potential characteristics of the Ag$_2$S($n$)/ZnO/TNTs and Ag$_2$S($n$)/TNTs because the dark current represented the recombination between the electrons in the conduction band and the redox ions of the electrolyte. As an example, Figure 6b shows the curves of dark density vs. the applied potential for the Ag$_2$S(4)/ZnO/TNTs and Ag$_2$S(4)/TNTs. Apparently, for the Ag$_2$S-sensitized TNTs with ZnO-coated layers, the dark current density decreases significantly. In addition, it is found that for both Ag$_2$S-sensitized ZnO/TNT and TNT electrodes, the photocurrent density at an applied potential increases with increasing CBD cycles, which can be attributed to a higher incorporated amount of Ag$_2$S that can induce a higher photocurrent density. This result is consistent with the observed UV-vis absorption spectra shown in Figure 4. Similar results have been obtained in CdS-sensitized QDSSCs [31]. Moreover, it should be noted that although the conduction band (CB) level of ZnO is slightly higher than that of TiO$_2$ (Figure 6a), it seems that the electron transfer efficiency from Ag$_2$S to ZnO is not much lower than that from Ag$_2$S to ZnO because the photocurrent density of the Ag$_2$S/ZnO/TNTs is more higher than that of the Ag$_2$S/TNTs. This phenomenon can be explained as follows. According to Marcus and Gerischer’s theory [32-34], the rate of electron transfer from electron donor to electron acceptor depends on the energetic overlap of electron donor and acceptor which are related to the density of states (DOS) at energy $E$ relative to the conductor band edge, reorganization energy, and temperature. Therefore, in our case, even though the CB level of electron donor (Ag$_2$S) is
lower than that of electron acceptor (TiO$_2$ or ZnO), the electron transfer may also happen if there is an overlap of the DOS of Ag$_2$S and TiO$_2$ (or ZnO), which may be the reason for the photocurrent generation in Ag$_2$S-sensitized TNT electrodes. The more important thing is that for semiconductor nanoparticles, the DOS may be strongly influenced by the doped impurity [35], the size of the nanoparticles [36], and the presence of surrounding media such as liquid electrolyte (i.e., Na$_2$Se electrolyte in our case) [37]. This means that the DOS of semiconductor nanoparticles may distribute in a wide energy range. Recently, the calculation results [38] showed that the DOS of Ag$_2$S can distribute in a wide energy range from about -14 to 5 eV, indicating that the electron can probably transfer from Ag$_2$S to TiO$_2$ or ZnO due to the overlap of the electric states of Ag$_2$S and TiO$_2$ or ZnO. Besides, considering that the difference between the CB level of TiO$_2$ and that of ZnO is not so large, it may be possible that the electron transfer rate from Ag$_2$S to ZnO is not much lower than that from Ag$_2$S to TiO$_2$. The photocurrent and photovoltage of Ag$_2$S QD-sensitized TiO$_2$ electrode have been experimentally found not only by us but also by others [10,25].

Figure 3 The low- and high-magnification TEM images, EDX spectrum, and XRD pattern (a) TEM image of the Ag$_2$S(4)/ZnO/TNT electrode showing the formation of ZnO on the TNTs and the Ag$_2$S nanoparticles inside the TNTs, (b) an HR-TEM image of a deposited Ag$_2$S quantum dot, (c) the EDX spectrum, and (d) XRD pattern of the Ag$_2$S(4)/ZnO/TNTs.

Figure 4 UV-vis absorption spectrum of the plain TNT, ZnO/TNT, Ag$_2$S(4)/TNT, and Ag$_2$S(n)/ZnO/TNT films. $n = 2, 4$ and 8.
Figure 5 $J$-$V$ characteristics of the plain TNT, $Ag_2S(n)/TNT$, and $Ag_2S(n)/ZnO/TNT$ electrodes. $n = 2, 4,$ and $8$.

Figure 6 Energy diagram and dark current. (a) Energy diagram of $Ag_2S$-sensitized $ZnO$/TNT solar cells and (b) the dark current of the $Ag_2S(4)/ZnO$/TNT and $Ag_2S(4)/TNT$ electrodes.
Figure 7 shows the photoconversion efficiency $\eta$ as a function of applied potential (vs. Ag/AgCl) for the Ag$_2$S(8)/ZnO/TNT and Ag$_2$S(8)/TNT electrodes under UV-vis light irradiation. The efficiency $\eta$ is calculated as [39], $\eta \ (%) = [(\text{total power output} - \text{electric power input})/\text{light power input}] \times 100 = j_p \times (E_{\text{rev}} - E_{\text{app}})/I_0 \times 100$, where $j_p$ is the photocurrent density (milliamperes per square centimeter), $j_p \times E_{\text{app}}$ is the total power output, $j_p \times E_{\text{rev}}$ is the electrical power input, and $I_0$ is the power density of incident light (milliwatts per square centimeter). $E_{\text{rev}}$ is the standard state-reversible potential, which is 1.23 V/NHE. The applied potential is $E_{\text{app}} = E_{\text{means}} - E_{\text{aoc}}$, where $E_{\text{means}}$ is the electrode potential (vs. Ag/AgCl) of the working electrode at which photocurrent was measured under illumination and $E_{\text{aoc}}$ is the electrode potential (vs. Ag/AgCl) of the same working electrode under open circuit conditions, under the same illumination, and in the same electrolyte. It can be clearly seen from Figure 7 that the Ag$_2$S(8)/ZnO/TNT electrode shows a higher photoconversion efficiency compared to the Ag$_2$S(8)/TNT electrode with a ZnO layer for an applied potential. In particular, a maximum photoconversion efficiency of 0.28% was obtained at an applied potential of -0.67 V vs. Ag/AgCl for the Ag$_2$S(8)/ZnO/TNT electrode, while it was 0.22% for the Ag$_2$S(8)/TNT electrode at an applied potential of -0.67 V.

The maximum photoconversion efficiency of the Ag$_2$S(8)/ZnO/TNT electrode is about 1.3 times that of the Ag$_2$S(8)/TNT electrode. However, it should be noted that the efficiency of the Ag$_2$S-sensitized TNT electrode is worse than that of TiO$_2$ as shown in Figure 6a[40], but the CB level of CdS is higher than that of TiO$_2$. Therefore, the electron transfer is more efficient in CdS/TNT solar cells. The comparison of our experimental results with those by Tubtimtae et al. indicates that there is still much scope for improving the performance of the Ag$_2$S-sensitized ZnO/TNT electrode. Nevertheless, our results show that the ZnO layer leads to an increased $\eta$.

Conclusions

In conclusion, Ag$_2$S quantum dot-sensitized TiO$_2$ nanotube array photoelectrodes were successfully achieved using a simple sequential chemical bath deposition (CBD) method. In order to improve the efficiencies of as-prepared Ag$_2$S quantum dot-sensitized solar cells, the
Ag2S quantum dot-sensitized ZnO/TNT electrodes were prepared by the interposition of a ZnO energy barrier between the TNTs and Ag2S quantum dots. The ZnO thin layers were formed using wet-chemical process. The formed ZnO energy barrier layers over TNTs significantly increase the power conversion efficiencies of the Ag2S(n)/ZnO/TNTs due to a reduced recombination.

Acknowledgements
This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea Ministry of Education, Science and Technology (MEST) (no. 2010-0026150).

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Authors’ contributions
CC carried out the experiments, participated in the sequence alignment and drafted the manuscript. YA participated in the design of the study and performed the statistical analysis GA and SHY participated in the device preparation. SOC conceived of the study, and participated in its design and coordination. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

Received: 5 April 2011 Accepted: 21 July 2011 Published: 21 July 2011

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Cite this article as: Chen et al. Improved conversion efficiency of Ag2S quantum dot-sensitized solar cells based on TiO2 nanotubes with a ZnO recombination barrier layer. *Nanoscale Research Letters* 2011 6:462.