One-dimensional WO₃ nanorods as photoelectrodes for dye-sensitized solar cells

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Tungsten oxide (WO₃) nanorods were applied for the first time as photoelectrodes in dye-sensitized solar cells (DSSCs). The DSSC based on WO₃ nanorods showed a short-circuit current, an open-circuit voltage, fill factor, and a conversion efficiency of 4.66 mA/cm², 0.383 V, 0.22, and 0.75%, respectively. The WO₃ nanorod photoelectrode was treated with TiCl₄ aqueous solution to improve the dye absorption and open-circuit voltage by coating the thin TiO₂ layer on the WO₃ nanorod surface. The TiCl₄ treatment resulted in the enhanced performance of the short-circuit current of 6.75 mA/cm², the open-circuit voltage of 0.457 V, the fill factor of 0.489, and the conversion efficiency of 1.51%. These values can be compared with 5.55 mA/cm², 0.447 V, 0.423, and 1.05% for the photoelectrode based on the TiCl₄-treated WO₃ nanoparticles. The higher short-circuit current and fill factor for the nanorods compared with the nanoparticles can be attributed to the high charge transport property of the 1-D nanostructure.

1. Introduction

Since O’Regan and Grätzel firstly reported in 1991 [1], dye-sensitized solar cells (DSSCs) have attracted considerable interest as potential candidates to replace conventional Si-based solar cells in specialized applications because of low manufacturing cost and easy fabrication [2,3]. A DSSC is composed as follows (Fig. 1): transparent conducting substrate, mesoporous semiconductor oxide film (photoelectrode), dye molecules absorbed on the surface of oxide surface, electrolyte (iodide/tri-iodide couple), and Pt-coated transparent conducting substrate (counter electrode). When a photon is absorbed by a dye, the excited dye transfers an electron to the conduction band of semiconductor oxide. The oxidized dye is reduced by iodide. The electron in the photoelectrode passes through the external load and reduces tri-iodide to iodide at the counter electrode [2].

TiO₂ are typically used as the photoelectrode and gives the highest efficiency of about 11% [4]. ZnO and SnO₂ have been widely studied as possible alternatives of the TiO₂. ZnO and SnO₂-based DSSCs have been achieved 6.6% [5] and 6.3% [6] efficiencies, respectively. Besides these oxides, Nb₂O₅ [7] and SrTiO₃ [8] have been also investigated.

Tungsten oxide (WO₃) is a semiconductor oxide material with a band-gap of 2.6–3.0 eV [9], and it is becoming the focus of research attention due to its unique electronic properties. In particular, various WO₃ nanostructures (nanoparticles, nanoplatelets, nanorods, and nanowires) are of special interest as promising candidates for photocatalyst [9], electrochromic devices [10–12], and gas sensors [13,14] because of their high surface area and novel properties [15]. Recently, Zheng et al. [16] reported for the first time that WO₃ nanomaterials have the potential to be used as alternative photo-electrode materials in dye-sensitized solar cells. They used commercial WO₃ nanoparticles with a size of approximately 40 nm as the photoelectrode in DSSC and investigated the effect of various parameters on the cell performance. DSSCs based on WO₃ nanoparticles exhibited a conversion efficiency of 0.75%, which was enhanced up to 1.46% by the surface modification. However, the problem is that the efficiency is relatively lower than that of DSSCs based on the other semiconducting metal oxides, such as TiO₂, SnO₂, and ZnO.

In the last decade, numerous approaches to improving the performance of DSSCs have been considered. Among many possible approaches, introducing a one-dimensional (1-D) nanostructure (nanowires, nanorods, and nanotubes) as the photoelectrode is one of the most promising candidates. In the operational process of DSSC, some electrons in conduction band of the photoelectrode travel back to the electrolyte, which results in a loss of efficiency in the DSSC [2,17]. Therefore, it is important to suppress this recombination reaction and to improve the collection of photo-injected electrons for enhancing the cell performance. The 1-D nanostructures can help to provide a rapid collection of photo-injected electrons because of their outstanding electron transport property [18–20]. Law et al. [21] first introduced a dense array of oriented, crystalline ZnO nanowire instead of the traditional nanoparticle film. Myakhostupov et al. [22] fabricated the DSSCs using hydrothermally prepared TiO₂ nanotubes. Mor et al. [23] prepared highly ordered transparent TiO₂ nanotubes arrays and applied them to the photoelectrode for DSSCs.

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In this study, we present for the first time a DSSC based on WO$_3$ nanorods and investigated the influence of 1-D WO$_3$ nanostructures on the conversion efficiency enhancement of DSSCs. The effect of surface modification by the TiCl$_4$ treatment was also studied. To the best of our knowledge, this is the first report on the use of 1-D WO$_3$ nanorods as a photoelectrode for DSSCs.

2. Experimental

The source material of the W$_{18}$O$_{49}$ nanorods was synthesized following the experimental procedure reported in our group [24]. Initially, the starting solution was prepared by dissolving 8.1 g of tungsten hexachloride in 200 mL of ethanol. Next, 10 mL of starting solution was mixed with 60 mL of ethanol under mild magnetic stirring at room temperature. The final solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 200 °C for 10 h in a preheated electric oven and then allowed to cool to room temperature. The products were collected and washed repeatedly with deionized water and ethanol and then dried at 60 °C for 12 h.

Fig. 1. Schematic diagram of a dye-sensitized solar cell.

The details of the electrode fabrication and DSSC assembly are described elsewhere [25]. A fluoride-doped tin oxide (FTO)-coated glass (7 Ω/cm$^2$) was sequentially cleaned in acetone, in 0.1 M HCl ethanolic solution, in deionized water, and in ethanol. After cleaning, a W$_{18}$O$_{49}$ nanorod paste was coated on the FTO glass by the doctor-blade method. The paste was prepared by mixing W$_{18}$O$_{49}$ nanorods with terpineol and ethyl cellulose ethanol solution. This mixture was then sonicated and stirred for 24 h. Ethanol was removed from this mixture solution by a rotary evaporator. The final paste contained 18 wt.% W$_{18}$O$_{49}$, 9 wt.% ethyl cellulose, and 73 wt.% terpineol. Finally, the coated film was sintered at 500 °C for 30 min in air; through this sintering process, the phase of W$_{18}$O$_{49}$ changed to WO$_3$. Additionally, a TiCl$_4$ treatment was conducted to coat a TiO$_2$ layer on the WO$_3$ nanorods. The sintered WO$_3$ nanorod electrodes were immersed in 40 mM aqueous TiCl$_4$ solution at 70 °C for 1 h, then rinsed with water and ethanol and resintered at 500 °C for 30 min. The thickness of the coated film was measured to be approximately 13 μm.

For the dye coating, the photoelectrodes were dipped in a 0.5 mM N719 dye solution in a mixture of acetonitrile and tert-butyl alcohol (1:1 volume ratio) for 24 h. After the sensitizer uptake, the photoelectrodes were washed with acetonitrile. A platinum-coated FTO glass was used as a counter electrode. A Platinum coating was produced by thermal decomposition of H$_2$PtCl$_6$. The counter- and photoelectrodes were assembled into the sandwich-type cell and sealed with an ionomer film (Meltonix 1170-60). The internal space of the cell was filled with a liquid electrolyte by capillary action. The commercially available electrolyte AN-50 (Solaronix) was used. The active area of the fabricated cells was varied from 0.14 to 0.16 cm$^2$.

Fig. 2. (a) XRD pattern, (b) and, (c) TEM, and (d) HR-TEM micrographs of the as-synthesized W$_{18}$O$_{49}$ nanorods. Inset in (b) shows the electron diffraction pattern.
photodiode (PV Measurements Inc., USA). The current density–voltage curves were recorded by applying an external bias to the solar cell and measuring the photocurrent with a photovoltaic power meter (Polaronix K101/LAB20, McScience, Korea). The incident photon-to-electron conversion efficiency (IPCE) spectra were recorded with a commercial measurement system (QEX7, PV Measurements Inc., USA). The measurements were carried out in an ambient environment.

3. Results and discussion

Fig. 2 displays the XRD pattern, TEM, HR-TEM micrographs, and electron diffraction pattern of the as-synthesized products. Fig. 2(a) shows the XRD pattern of the as-synthesized product, which matched monoclinic \( \text{W}_{18}\text{O}_{49} \) (JCPDS No. 05-0392). As shown in Fig. 2(b) and (c), TEM images show that the as-prepared \( \text{W}_{18}\text{O}_{49} \) sample is assembled in an urchin-like structure consisting of the individual nanorods. The inset indicates an electron diffraction pattern in which all rings could be indexed to the monoclinic phase of \( \text{W}_{18}\text{O}_{49} \). A typical HR-TEM image is shown in Fig. 2(d), which makes it obvious that the individual \( \text{W}_{18}\text{O}_{49} \) nanorods have an average diameter of 7.4 nm and a length of 143 nm. A clearly observed lattice fringe confirms the nanorod is a well-crystallized single crystal. The calculated distance of the interplane perpendicular to the axis direction of the nanorod is 0.381 nm, corresponding to the \( (010) \) lattice spacing of monoclinic \( \text{W}_{18}\text{O}_{49} \). These results are in good agreement with the reported paper [24].

In the process of the DSSC fabrication, sintering of the coated photoelectrode film should be required to improve the interconnection between the nanoparticles and adhesion between the coated films and the FTO glass substrate. The sintering condition was 500 °C for 30 min in air [16,25]. The change of the phase and morphology of \( \text{W}_{18}\text{O}_{49} \) nanorods after the heat treatment was investigated. Fig. 3 displays the XRD pattern, TEM, HRTEM micrographs, and electron diffraction pattern of the \( \text{W}_{18}\text{O}_{49} \) sample.
The effect of the 1-D WO3 morphology on the cell performance was also investigated. A DSSC based on TiCl4-treated WO3 nanoparticles (Aldrich, size ~ 40 nm) was fabricated, and the cell performance was tested. The DSSC based on TiCl4-treated WO3 nanorods and nanoparticles. The value of the open circuit voltage ($V_{oc}$), the short-circuit current density ($J_{sc}$), the fill factor (FF), and the conversion efficiency ($\eta$) are also summarized in Table 1. Each data was the average of five cells. A DSSC based on WO3 nanorods showed $J_{sc} = 4.66 \text{ mA/cm}^2$, $V_{oc} = 0.383 \text{ V}$, $FF = 0.422$, and $\eta = 0.75\%$ (dotted line). All values are relatively lower than those of conventional DSSCs based on TiO2 nanoparticles. The $V_{oc}$ of a DSSC is determined by the difference between the Fermi level of the photoelectrode and the redox potential of the electrolyte [2]. WO3 has $-0.4 \text{ V}$ versus NHE for $I_3^-/I_2^-$ electrolyte [16]; thus, it could be predicted that the $V_{oc}$ of the WO3-based DSSC is on the order of 0.4 V, which is in good agreement with our $V_{oc}$ result (0.383 V). The lower $J_{sc}$ and $FF$ are mainly attributed to a low isoelectric point (ISP) of WO3. The ISP is simply the pH value at which the metal oxide surface carries no net electric charge [26]. The ISP of WO3 is pH = 0.4–1 [27], which means that the WO3 surface is negatively charged in the dye solution. Therefore, dye absorption on the WO3 surface is poor because the anchoring ligand of the N719 dye is the negatively charged carboxylic group [2,16]. The low dye loading results in the restriction of excited electron quantities and an increase of the dark current by the direct contact between the electrolyte and the WO3 photoelectrode.

Meanwhile, it has been reported that TiO2 coating on the SnO2 improved the cell performance by minimizing the problems of insufficient dye attachment and low $V_{oc}$ [5]. Similarly, to enhance the performance of WO3-based DSSCs, ultrathin TiO2 layer coating on the WO3 surface was deposited by a TiCl4 treatment, as mentioned in the Section 2. As shown in Fig. 5 (straight line) and Table 1, the DSSC based on the TiCl4-treated WO3 nanorods exhibited the cell performance of $J_{sc} = 6.75 \text{ mA/cm}^2$, $V_{oc} = 0.457 \text{ V}$, $FF = 0.489$, and $\eta = 1.51\%$, all higher than the values of the DSSC based on WO3 nanorods. Several factors could contribute to performance enhancement. First, the dye absorption on the WO3 surface increases because the TiO2 has the higher ISP of pH = 5.9–6.0 [16,28], resulting in the improvement of $J_{sc}$ and $FF$. Second, TiO2 acts as a barrier layer to suppress the electron interception by the electrolyte, which enhances the $J_{sc}$, $V_{oc}$, and $FF$. Third, the conduction band of WO3 is negatively shifted by the TiO2 layer because the TiO2 has the higher conduction band than WO3, which provides the enhancement of $V_{oc}$ [3,17].

The incident photon-to-electron conversion efficiency (IPCE) of the fabricated cells based on WO3 nanorods (dotted line), TiCl4-treated WO3 nanorods (straight line), and TiCl4-treated WO3 nanoparticles (dashed line).
nанокристаллической фазы, показавшей эффективность Jsc = 5.55 mA/cm², VOC = 0.447 V, FF = 0.423, и η = 1.05% (рис. 5, пунктирная линия). Это означает, что DSSC на основе TiCl4-обработанной WO3 нанородной фазы показала более высокую эффективность Jsc и FF, чем DSSC на основе TiCl4-обработанной WO3 наночастиц. Это свидетельствует о том, что транспорт электронов в 1-D нанородах происходит быстрее, что приводит к уменьшению джорданского процесса.

Рис. 6 показывает, что фотонно-электронную конверсию эффективность (IPCE), или "квантовую эффективность (QE)" для фотокатода с высоко развитой поверхностью, что позволяет увеличить загрузку красителя и свет."

4. Conclusion

Титановый оксид (WO3) нанороды были введены в качестве фотоэлектрода в DSSCs. WO3 фотоэлектрод был получен с помощью осаждения процесса на нанородах WO3. Во время осаждения процесса, WO3 нанороды были оксидированы до WO3 и диаметр нанородов увеличился от 7.4 до 43 нм. Обращение DSCC на основе WO3 нанородов показало короткое время срабатывания (Jsc) 4.66 mA/cm², открытий к.п.д. (VOC) 0.383 V, коэффициент заполнения (FF) 0.422, а эффективность (η) 0.75%. Нанороды TiCl4 на основе фотоэлектрода WO3 были предложены к использованию для преодоления проблем низкой загрузки красителя и VOC. Как результат, этот подход позволил увеличить загрузку красителя и VOC на поверхности WO3 нанород, что привело к улучшению эффективности DSSC в 1-D нанородной структуре.

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