Prepare heterostructure of MoS2/TiO2 solar cell via simple two-steps by hydrothermal method

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Abstract:

Organic dyes employ in traditional Dye-sensitized solar cells (DSSC) results in both high cost and low stability under light exposure. In this study, we present an inorganic semiconductor heterostructure solar cell based in ordered thin film of MoS2 deposited on one-dimensional nanorods array of TiO2 which were produced via simple two-steps by hydrothermal method. The solar cell MoS2/TiO2 heterostructure exhibit a good fill factor, and a greatly enhanced power conversion efficiency. The research presented here will provide a path for creating heterostructure inorganic materials for highly efficient solar cells.

Keywords: inorganic semiconductor, TiO2, MoS2, nanorods, solar cells, hydrothermal method.

1-Introduction

In recent decades, a significant increase in research literature has focus in the solar energy conversion for generate solar cells [1,2]. Titanium Dioxide TiO2 semiconductor nanomaterials exhibiting various morphologies are considered the most favorable candidates for photoanode in solar cells [3, 4]. Among the numerous TiO2 nanostructures including nanotubes, nanowires, and nanorods arranged in ordered to one-dimension array, that have demonstrated great potential for use in DSSC. This is due to their potential to offer direct pathways for efficient charge transfer and also collection [5,6]. Furthermore, light harvesting is facilitated by the vertical alignment and ordered arrangement of nanostructures due to many internal reflections between neighboring construction blocks [7,8]. Also, the 1D TiO2 nanostructures might also provide a special three-dimensional (3D) architecture that would facilitate the simple entry and diffusion of the electrolyte [8]. Many
researchers focusing on TiO₂ due to unique features which include chemical and thermal stability, low toxicity, and environmental safety, as well as its affordability[9]. The hydrothermal method is an inexpensive, safe method, and simple technique for TiO₂ growth on fluorine-doped tin oxide (FTO) coated glass substrate without the requirement for seed layers. This due to the similar crystal structures and low lattice mismatch between FTO and TiO₂[10]. In the fact, the TiO₂ semiconductor exhibits light absorption in the ultraviolet (UV) range due to its high band gap energy of (~ 3.2) eV which reduce the utilization of sunlight [11-13]. One of the promising approaches to address these issues is to develop inorganic sensitizers with good optical absorption and good chemical stability. Molybdenum Disulfide (MoS₂) a two-dimensional semiconductor similar to Graphene with fascinating electrical and optical features [14]. Bulk MoS₂ is composed of several S-Mo-S stacking layers that are weakly bound together by weakly Van der Waals forces, While few-layer MoS₂ showed promise in optical and electrical applications [15]. The single-layer MoS₂ exhibits a sandwich structure where two S atoms are hexagonally packed around Mo atoms in the center [16,17]. MoS₂ in bulk was typically utilized as a mechanical lubricant, although single- MoS₂ has a narrow band gap of (1.2-1.9) eV having the proper band structure to promotes high photo – response within the visible light spectrum [18,19].

In this study, we grew single-layer MoS₂ in the one-dimension nanorods of TiO₂ using a simple two-step hydrothermal method. MoS₂ demonstrated that is an good inorganic sensitizer, significantly enhancing the light-harvesting and charge separation capabilities of the TiO₂ photoanode.

2- Experimental

TiO₂ nanorods array were grown using a hydrothermal method on a Conductive FTO substrate (1cm*1.5 cm). To achieve this, the FTO substrate was placed inside a sealed Teflon-lined stainless steel autoclave along with a solution containing Titanium butoxide (0.5 ml), Deionized water (15 ml), and Hydrochloric acid (15 ml). The autoclave was then heated to 150°C at different time periods 5, 10, 15, 20, and 25 hours. After allowing the autoclave to cool naturally. The rutile TiO₂ NRs films were deposited on FTO substrate and subsequently washed twice with water is consistent with previous research [19]. The procedure to preparing the MoS₂/TiO₂ composite thin film is described as follows: Thioacetamide (C₅H₅NS) 0.12 g and Sodium molybdate (Na₂MoO₄.2H₂O) 0.06 g were dissolved in 40 mL of DI water and stirred magnetically for 40 minutes until a transparent solution was formed. The resulting mixture was then transferred into a 75 mL Teflon-lined stainless steel autoclave containing vertically placed TiO₂ NRs. The autoclave was heated at 200°C for 24 hours to obtain the MoS₂/TiO₂ composite thin film. Finally, the product was washed with DI water and dried at 80°C for 10 hours.

The Grätzel model was used to assemble the solar cells, which utilized the MoS₂/TiO₂/FTO prepared earlier as the photoanode, and an Ag-modified FTO glass as the counter electrode. The solution of electrolyte (Iodoite Z – 100) prepared by combining (0.1 M) LiI, (0.05 M) I₂, and (0.5 M) 4-tert-butylpyridine in acetonitrile. The surface morphology for samples was show by Scanning Electron Microscopy SEM (Supra 55 VP), but the crystal structure of samples was evaluated through XRD technique (land X’ Pert Pro MPD- Philips Nether). The Raman
spectra were recorded using Raman microscopy (Renishaw Invia). The UV-Vis spectrophotometer (Shimadzu UV2100) was used to measure the absorption spectra of the samples. The Current density – Voltage (J-V) curve were measured using a Keithley digital source at 25°C, that simulated sunlight under AM 1.5 G was illumination using Xe- lamp. The active area of solar cells was controlled to be (0.8 cm²).

3- Results and discussions:

Fig. (1) displays the typical Scanning Electron Microscope (SEM) images of the top - view of TiO₂ NRs films synthesized via hydrothermal method. It can be noticed that densely aligned TiO₂ NRs is covered with uniform on the FTO surface. The shape of the nanorods structure is tetragonal and the top surfaces of all nanorods are square or rectangle [20]. The rate diameter of the nanorods can be seen increased with longer the deposition periods as shown in Table (1). Experiments have shown that TiO₂ NRs do not grow when growth time is less than 3 hours and at 150°C. But when the growth time extends to 30 hours, the TiO₂ NRs membrane begins to peel off from the FTO surface because of the competition between crystal growth and decomposition of the crystals themselves. Fig. (2a) shows the (SEM) images of MoS₂ nanoflowers grown on FTO substrate via hydrothermal method. The high-magnification SEM images revel that MoS₂ randomly grow on FTO substrate with self-assembly nanoflowers ornamented on the surface. The mean length (250 - 260) nm and thickness (18-20) nm of the nanoflowers were determined [21]. Fig. (2b) shows numerous small MoS₂ were present on both the top and side surfaces of TiO₂ nanorods [22].

Table (1): values of rate diameter of the nanorods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Period of deposition h</th>
<th>Temp. of deposition °C</th>
<th>Rate diameter of rod nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₅</td>
<td>5</td>
<td>150°C</td>
<td>37.3</td>
</tr>
<tr>
<td>T₁₀</td>
<td>10</td>
<td>150°C</td>
<td>112.8</td>
</tr>
<tr>
<td>T₁₅</td>
<td>15</td>
<td>150°C</td>
<td>123.6</td>
</tr>
<tr>
<td>T₂₀</td>
<td>20</td>
<td>150°C</td>
<td>148.7</td>
</tr>
<tr>
<td>T₂₅</td>
<td>25</td>
<td>150°C</td>
<td>188.9</td>
</tr>
</tbody>
</table>
Fig. (1): SEM images of TiO$_2$ synthesized at 150°C with different reaction times (a) 5 hour, (b) 10 hour, (c) 15 hour, (d) 20 hour, (e) 25 hour.
The X-ray diffraction (XRD) patterns of TiO$_2$ nanorods array fabricated on an FTO substrate using the hydrothermal method are shown in Figure (3a). The patterns reveal that the films fabricated are matching well with the tetragonal rutile TiO$_2$ peaks (JCPDS no. 21-1276). The minor lattice mismatch between the rutile phase of TiO$_2$ and FTO substrate is the reason for the rutile TiO$_2$ nanorods are generated instead of other phases such as anatase and brookite. The lattice parameters of both the rutile phase and FTO are very similar with $a=b=0.4594$ nm and $c=0.2958$ nm for TiO$_2$, and $a=b=0.4737$ nm and $c=0.3185$ nm for FTO. The thin films synthesized with different growth period observed four rutile peaks (110), (101), (002) and (112) at ($2\theta = 26.86^\circ$, $36.08^\circ$, $62.74^\circ$ and $65.92^\circ$), respectively. The intensity of the (101) and

Fig. (2): SEM images of (a) MoS$_2$ nanoflowers (b) MoS$_2$/TiO$_2$. 

The intensity of the (101) and
(002) peaks increases significantly with an increase in reaction time from 5 to 20 hour, where the growth density of the nanorods is high enough to cover the entire surface of the FTO substrate [21]. However, when the reaction time is extended to 25, the diameter and length of the nanorods are growing at angle on the FTO surface and increased them led to collide with each other. This collision leads to the breakage of some of the rods and the filling of the space between them. As a result, the intensity of the (101) and (002) peaks decreases. High intensity of the (101) peak indicated that TiO$_2$ NRs have a good crystallization and highly oriented against the FTO substrate in the (001) direction. These results supported by other workers[22]. Fig. (3b) displays the XRD pattern of MoS$_2$ nanoflowers grown through the hydrothermal method on an FTO substrate. The pattern exhibits prominent diffraction peaks originating from the FTO substrate. Furthermore, weak peaks located at 2$\theta$ = 14.52$^\circ$ and 33.88$^\circ$ can be observed, which correspond the (002) and (101) planes, respectively, to the standard 2H-MoS$_2$ (PDF card NO. 37-1492). The strong intensity of the (002) diffraction peak in the sample XRD pattern suggests the formation of a stacked layered structure of MoS$_2$ [23].

Fig. (4) shows XRD pattern when MoS$_2$ is deposited on TiO$_2$ NRs film prepared at a reaction time of 20 hours (M/T$_{20}$) and it is noted that the characteristic peaks appear for each of the two compounds. In this figure, it is noted that the intensity of the diffraction peaks due to TiO$_2$ is higher and this is due to recrystallization in the second stage from hydrothermal treatment [24].
Fig. (3): XRD patterns of (a) TiO$_2$ at 150°C for different reaction times (b) MoS$_2$ at 200°C.
Fig. (4): XRD patterns of MoS$_2$/TiO$_2$ (M/T$_{20}$).

Fig. (5a) shows the Raman spectra of TiO$_2$ NRs and MoS$_2$ nanoflowers that was grown on FTO. The Raman curve of TiO$_2$ NRs displays two resonance peaks centered at 458 and 625 cm$^{-1}$ which correspond to the E$_g$ and A$_{1g}$ vibrational modes of TiO$_2$ rutile phase, respectively [25]. Fig. (5b) can be well ascribed to the MoS$_2$ grown on FTO substrate. The Raman scattering peak located at 407 cm$^{-1}$ can be which may be ascribed to $E_{2g}^1$ modes of 2H-MoS$_2$ [26].
Fig. (5): Raman spectra of (a) TiO$_2$ nanorods (b) MoS$_2$ nanoflowers.

Fig. (6) displays the UV-Visible absorption spectra of TiO$_2$ NRs and MoS$_2$. The Fig. (6a) represents the absorbance as function to the wavelength for the TiO$_2$ NRs, that it has evident a sharp absorption edge at around 400 nm and significant absorption in (UV) region when the period of time increase [27]. Fig. (6b) shows the absorption spectrum of MoS$_2$ where the absorption spectrum within the visible region (400-750) nm and the edge absorption is approximately at 750 nm. Fig. (6c) shows the absorption spectrum obtained when MoS$_2$ nanoflowers is deposited on the surface of TiO$_2$ nanorods prepared with a time of 20 hours (M/T$_{20}$). The intensity of the absorption spectrum is observed to be in the visible region, which can be attributed to the absorption of visible light by MoS$_2$ nanoflowers. The fig(6c) shows a reduction in the absorbance intensity, which could be attributed to the excessive
stacking of MoS$_2$. This stacking may lead to a decrease in the material's specific surface area, ultimately causing a decline in its optical performance.

The optical band gap directly allowed transmission which was calculated using the following equation:

$$a h \nu = \text{const} \ (h \nu - E_g)^{1/2}$$

Where $\alpha$ represent the absorption coefficient, $h \nu$ represent photon energy, and $E_g$ is the band gap.

Fig. (7) depicts a plot of $(a h \nu)^2$ versus energy $(h \nu)$, which was utilized to determine the optical band gap. The energy gap was observed to be 3.1, 3.06, 3.02, 2.99, and 2.93 eV for reaction times of 5, 10, 15, 20, and 25 hours, respectively [28]. The decrease in the energy gap value with increasing reaction time can be attributed to the variation in rod length and diameter. As the reaction time increases, the resulting rods are longer and wider suggesting reduced quantum confinement at longer reaction times. The Fig. (7M) displays the direct energy gap of MoS$_2$ which is approximately 1.7 eV. The results showed that compared to the energy gap of the T$_{20}$ sample, which is around 2.99eV. It will decrease when a MoS$_2$ is deposited on TiO$_2$ and the energy gap of the (M/T20) becomes 2.78 eV as shown in the Fig. 8 [12].
Fig. (6): UV-vis absorbance spectra of the samples (a) TiO$_2$ NRs (b) MoS$_2$ (c) M/T$_{20}$. 
Fig. (7): $(ahv)^2$ as a function of $(hv)$ of TiO$_2$ NRs (T5) 5 hour (T10) 10 hour (T15) 15 hour (T20) 20 hour (T25) 25 hour (M) MoS$_2$. 

- $E_g = 3.1$ eV for T5.
- $E_g = 3.06$ eV for T10.
- $E_g = 3.02$ eV for T15.
- $E_g = 2.99$ eV for T20.
- $E_g = 2.93$ eV for T25.
- $E_g = 1.7$ eV for MoS$_2$. 

$Y$-axis: $(ahv^2 \text{ (eVcm}^{-1}\text{)})^2$

X-axis: Energy (eV)
The energy level diagram of MoS$_2$/TiO$_2$ heterostructure solar cells is illustrated in Figure (9). For effective sensitization, the photo-generated electrons in MoS$_2$ must migrate to the MoS$_2$/TiO$_2$ interface and inject into the conduction band of TiO$_2$ where they can be extracted to the FTO. Meanwhile, the remaining holes in the valence band of MoS$_2$ are anticipated to be transported to the electrolyte or any other hole-conductive material. However, significant recombination of electrons and holes transpires at the interface of MoS$_2$/TiO$_2$ structure, owing to the presence of a large number of defects in that region. This constitutes the primary reason for the limited efficiency of inorganic semiconductor-sensitized solar cells [29].
efficiency($\eta$). The efficiency initially rises to ($\eta = 0.94\%$) at the time of preparation of the nanorods reaches 20h but decreases again to ($\eta = 0.82\%$) when time of preparation of TiO$_2$ reaches 25hour. As the height of the nanorods increases the growth time from (5-20) hour, a greater amount of MoS$_2$ can adhere to the surface due to the increased surface area leading to improved light absorption and short circuit current density [29]. However, longer growth times 25hour lead to longer nanorods lengths and diameter widths, as shown in fig(1) resulting in a lower effective internal surface area available for MoS$_2$ adsorption and therefore a reduction in conversion efficiency [30].

**Table (2): Cell parameters of solar cells based on MoS$_2$/TiO$_2$.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{SC}$</th>
<th>$V_{OC}$</th>
<th>$P_{MAX}$</th>
<th>FF</th>
<th>$\eta$</th>
<th>$R_S$</th>
<th>$R_{SH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mA/cm$^2$</td>
<td>V</td>
<td>mW/cm$^2$</td>
<td>%</td>
<td>%</td>
<td>$\Omega$</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>M/T$_5$</td>
<td>2.42</td>
<td>0.328</td>
<td>0.323</td>
<td>40</td>
<td>0.43</td>
<td>508.67</td>
<td>1069.43</td>
</tr>
<tr>
<td>M/T$_{10}$</td>
<td>2.56</td>
<td>0.433</td>
<td>0.421</td>
<td>38</td>
<td>0.56</td>
<td>1260.7</td>
<td>173.33</td>
</tr>
<tr>
<td>M/T$_{15}$</td>
<td>3.22</td>
<td>0.397</td>
<td>0.585</td>
<td>45</td>
<td>0.78</td>
<td>4532.24</td>
<td>122.08</td>
</tr>
<tr>
<td>M/T$_{20}$</td>
<td>4.76</td>
<td>0.379</td>
<td>0.706</td>
<td>39</td>
<td>0.94</td>
<td>1773.09</td>
<td>139.99</td>
</tr>
<tr>
<td>M/T$_{25}$</td>
<td>4.89</td>
<td>0.329</td>
<td>0.613</td>
<td>38</td>
<td>0.82</td>
<td>178.40</td>
<td>34.18</td>
</tr>
</tbody>
</table>

**Fig. (10): (J-V) curves of solar cells based MoS$_2$/TiO$_2$.**

**4- Conclusions:**

In brief, this study presents approach of integrating low-cost and environmentally friendly semiconductors into 1D nanostructure array to create high performance photovoltaic devices. A
simple hydrothermal method was used to successfully grow of MoS$_2$/TiO$_2$ heterostructure and Rutile TiO$_2$ nanorods were prepared on FTO substrate using various growth durations (5, 10, 15, 20, and 25 hours). The morphology, structure, optical, and electrical properties of the TiO$_2$ nanorods were observed to be influenced by the duration of growth. The MoS$_2$ nanosheets has a suitable band gap, which acts as an effective inorganic dye that aids in light absorption and electron transfer in the TiO$_2$ photoanode. Consequently, the MoS2/TiO$_2$-based solar cells exhibit a significantly improved power conversion efficiency (PCE) to 0.94%. The improved photo conversion efficiency was linked to the vertically aligned nanorods which were densely arranged and created efficient pathways for the charge carriers generated by light.

REFERENCES


