Synthesis of Mo-doped TiO$_2$/reduced graphene oxide nanocomposite for photoelectrocatalytic applications

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**ABSTRACT**

This study was carried out with the goal of lowering the band gap and electron recombination of the titanium dioxide through doping with Mo, and hybridizing with reduced graphene oxide, respectively, for photoelectrocatalytic applications. Mo with various atomic percentages (0.5, 1, 2, and 3 at%) was doped with TiO$_2$ using the mechanical alloying technique. The results of the ultraviolet diffuse reflectance spectroscopy analysis revealed that the TiO$_2$ doped with 1 at% Mo possessed the lowest band gap energy. Also, to further improve the photoelectrocatalytic efficiency, the 1 at% Mo-doped TiO$_2$ powder was hybridized with the reduced graphene oxide (RGO) through UV-assisted photocatalytic reduction of the graphene oxide. The XRD, FESEM, EDX, and FTIR analyses were implemented for characterization of the TiO$_2$, 1 at% Mo-doped TiO$_2$, and 1 at% Mo-doped TiO$_2$/RGO powders. The superior integration of the TiO$_2$ and RGO was achieved as a result of the photocatalytic reduction method. After coating the powders on the fluorine-doped tin oxide (FTO) glass using the doctor blade technique, linear sweep voltammetry, amperometry, and electrochemical impedance spectroscopy tests were used to study the photoelectrocatalytic behavior of the samples. The results of the electrochemical tests showed that the photoelectrocatalytic activity of the TiO$_2$ was significantly enhanced as doped with Mo, and hybridized with the RGO. The mechanisms affecting the photoelectrocatalytic response in the Mo-doped TiO$_2$/RGO composite are discussed, as well.

1. Introduction

Titanium dioxide (TiO$_2$) is of great interest among the all semiconductors due to its electro-optic properties, which make it suitable for renewable energy and photocatalytic applications [1–3]. However, the wide band-gap energy ($E_g$) of the TiO$_2$ diminishes its photocatalytic efficiency [4]. Among the most promising methods used for reducing the band-gap energy and improving the photocatalytic performance of TiO$_2$, the doping with a number of elements and compounds has attracted a great deal of attention from the researchers [5–7]. By decreasing the band-gap energy of the TiO$_2$ through doping, a wider range of solar spectrum can excite and jump the electrons from the valence band to the conduction band [8,9]. It has been reported that doping with transition metals such as Fe [10], Cu [11], W [12], Zn [13], and Mo [14] could reduce the band-gap energy of TiO$_2$ particles. Lu et al. [10] synthesized the Fe-doped TiO$_2$ nanoparticles by using the sol-gel technique, and decreased the band gap energy of TiO$_2$ (doped with 2 mol% of Fe) from 3.2 eV to 2.76 eV. Colon et al. [11] reported that the band gap energy of TiO$_2$ nanoparticles was reduced from 3.99 eV to 3.00 eV through doping with 0.5 mol% of Cu using the sol-gel method. Shen et al. [12] also reported a decrease in the band gap energy of the TiO$_2$ from 2.95 eV to 2.67 eV after doping with 0.5 mol% of W. Aware et al. [13] used the sol-gel technique to synthesize the TiO$_2$ particles doped with various amounts of Zn, and they could decrease the band gap energy of the TiO$_2$ from 2.96 eV to 2.83 eV after doping with 5 mol% of Zn. Khan et al. [14] evaluated the band gap of the Mo-doped TiO$_2$, and reported a reduction in the band gap energy from 2.95 eV to 2.67 eV after doping with 5 at% of Mo.

The sol-gel and hydrothermal/solvothermal methods are typically used for doping of TiO$_2$ particles with the transition metals [15]. Although the sol-gel technique is widely utilized for doping of the TiO$_2$ with various compounds and elements, there are some restrictions on mass production owing to the high price of the raw materials used in this technique, as well as the need for precise systematic control during the synthesis [16–18]. Similarly, the hydrothermal/solvothermal process is greatly affected by several parameters such as temperature, pressure, pH, and concentration of reactants, and these parameters should be controlled precisely to achieve the appropriate final product
Among the various fabrication techniques, mechanical alloying is of a great interest for producing semiconductor materials due to its low cost, simplicity, and high potential for the mass production [19,20]. Some investigations carried out on the doping of the TiO2 with metal ions by using the mechanical alloying process have indicated that the band-gap energy of TiO2 was significantly reduced [23–26]. For instance, Kim et al. [26] have stated that the band-gap energy of TiO2 was lowered from 3 eV to 2.5 eV after doping with 4.57 wt% Fe using the mechanical alloying technique. The red shift caused by placing the dopant level near the valence band of TiO2, enhanced the photoefficiency of Fe-doped TiO2.

It should be noted that although the narrower band-gap can improve the possibility of producing electron-hole pairs, not all of them are stable and able to react with the surrounding environment [27]. Indeed, a remarkable quantity of electron-hole pairs produced on the surfaces of a photocatalytic material is recombined and thereby, the efficiency of photocatalytic reactions is degraded [28,29]. In order to diminish the electron-hole recombination, semiconductor materials can be hybridized with carbonaceous nanomaterials [30,31]. Over the last decade, a great number of studies were conducted to improve the photocatalytic performance of the TiO2 through hybridizing with the carbon nanotube [32], carbon nanohorn [33], carbon nanowalls [34], graphene [35], etc. Among the various kinds of carbonaceous nanomaterials, graphene has attracted much attention owing to its high specific surface area, electron mobility, and transparency [36]. Fan et al. [37] prepared TiO2 (P25)/reduced graphene oxide (RGO) nanocomposites using several techniques including UV-assisted photocatalytic reduction, hydrazine reduction, and hydrothermal method as photocatalysts for the evolution of hydrogen from alcohol under UV–Visible irradiation. It was shown that the incorporation of RGO into P25 significantly enhanced the photocatalytic activity for hydrogen evolution.

This study is fundamentally aimed at hybridizing Mo-doped TiO2 nanoparticles with RGO. In this regard, first, TiO2 nanoparticles were doped with various amounts of Mo using mechanical alloying to reduce the band-gap width of TiO2. Then, the powder with the lowest band-gap energy was hybridized with RGO using photocatalytic reduction technique. It should be noted that the photocatalytic reduction of graphene oxide (GO) sheets on TiO2 in ethanol solution developed by Williams et al. [38] is a promising method of hybridizing graphene with TiO2. In this method, a TiO2/GO suspension is exposed to radiation in which electron-hole pairs are created. The photogenerated electrons reduce the GO sheets on TiO2 particles resulting in RGO, since the remaining holes are consumed by a hole-scavenger agent, i.e. ethanol [39]. The creation of an efficient interface between RGO and TiO2, removing the hazardous reducing agents, high production rate, and very low processing temperature are some of the advantages of this protocol [40,41]. The effects of doping with the Mo and hybridizing with the RGO on the chemical composition, morphology, structure, and molecular bonds of the TiO2 nanoparticles were examined. The photoelectrocatalytic behavior of the composite powder was studied by linear sweep voltammetry and amperometry techniques under the UV light irradiation.

2. Material and methods

2.1. Doping of TiO2 nanoparticles with Mo

TiO2 and Mo powders with an average particle size of 50 nm provided by Merck (Germany) were used as the starting materials. TiO2 nanoparticles were doped with 0.5, 1, 2, and 3 at% Mo by means of mechanical alloying. TiO2 and Mo powder mixtures were placed in a planetary ball mill (RETSCH-PM 400, Germany) and loaded with tungsten carbide milling balls with a ball-to-powder weight ratio (BPR) of 15:1. Mechanical alloying was performed for 15 h with a rotational speed of 250 rpm under Ar atmosphere. After the milling process, the powders were heated at 400 °C for 2 h in a tube furnace under Ar atmosphere.

2.2. Hybridizing Mo-doped TiO2 nanoparticles with RGO

The Mo-doped TiO2 powder was hybridized with RGO by using the photocatalytic reduction method. To this end, 1 g of Mo-doped TiO2 and 0.025 g of GO (API Technology Pioneers Co., Iran) were mixed in 25 mL distilled water by using an ultrasonic agitator for 2.5 h. The suspension was later placed in an oven at the temperature of 80 °C to vaporize the water. Then, 25 mL absolute ethanol (Merck) was added to the powder mixture and mixed by using ultrasonic agitation for 2 h. Afterwards, the suspension was exposed to UV radiation with a wavelength of 350 nm for 2 h. Finally, the suspension was dried to achieve Mo-doped TiO2/RGO powder.

2.3. Characterization

The band-gap energies of Mo-doped TiO2 powders were measured by UV–Visible Diffuse Reflectance Spectrophotometer (UV–Vis/DRS, Pekin-Elmer Co., USA). In order to analyze the molecular bonds of the powders, Fourier transform infrared spectroscopy (FTIR) analysis (Unicam 4600) was employed. The structure of the powders was investigated using X-ray diffraction (XRD) with CuKα radiation (Bruker, D8 Advance). The morphology and chemical composition of the powders were characterized by a field emission scanning electron microscope (FESEM, MIRA3 model, TESCAN Co., Czech Republic) equipped with energy-dispersive X-ray (EDX) spectroscope.

2.4. Photoelectrocatalytic behavior

The photoelectrocatalytic response of the powders was evaluated in a three-electrode cell by an Autolab PGSTAT30 potentiostat/galvanostat (Metrohm Co., Netherlands). To prepare the working electrode, first the TiO2 or TiO2/RGO powders were mixed with 30 wt% ethylene glycol and 10 wt% acetic acid. Then, a thin layer of the ceramic with a thickness of ~20 μm was coated on a fluorine-doped tin oxide (FTO) glass with a surface area of 1 × 2 cm² using the doctor blade coating technique. After coating, the samples were heated at 400 °C for 1 h under Ar atmosphere. A platinum plate was used as the counter electrode and a saturated calomel electrode (SCE, Ag/AgCl) was used as the reference electrode. The electrolyte used in this experiment was 0.1 M Na2SO4 solution. A PHILIPS PL-S9W lamp with a radiation wavelength of 375 nm was utilized as the UV light source. To investigate the photocatalytic behavior and light sensitivity of the samples, linear sweep voltammetry and amperometry tests were employed. The linear sweep voltammetry was recorded under the UV-light in a positive direction with the scan rate of 0.1 V s⁻¹ within the potential window ranging from ~0.4 V to 0.6 V (vs. SCE). Amperometric measurements were conducted with an applied potential of 1.1 V (vs. SCE) and the current density was measured by switching the UV radiation from an on- to an off-state.

The electrochemical impedance spectroscopy (EIS) measurements were conducted at the open-circuit potential over a frequency ranging from 100 kHz to 10 mHz, the amplitude of 5 mV, in the 0.1 M Na2SO4 solution under the UV radiation.

To ensure the repeatability of the photoelectrocatalytic measurements, each test was repeated three times and the average values were reported.

3. Results and discussion

Fig. 1 demonstrates the absorption spectra obtained from UV–Vis/DRS test for TiO2 powders doped with various amounts of Mo. As seen in Fig. 1, doping with Mo has shifted the absorption edge of the TiO2 to higher wavelengths. The band-gap energy (Eg) was calculated by...
The creation of this interior band between the valence band and the conduction band of TiO$_2$ decreases the required energy for the electron excitation, giving rise to the red shift and the band-gap energy reduction of TiO$_2$. According to Table 1, doping with Mo by up to 1 at% has significantly decreased the band-gap energy of TiO$_2$, yet further doping has proven to have an adverse effect on the band-gap energy; As the atomic percentage of dopant exceeds 1%, the band-gap energy of Mo-doped TiO$_2$ powders is increased. Similar results have been previously reported for Mo-doped TiO$_2$ nanoparticles and thin films [44]. The band-gap broadening at high levels of dopant can be related to the confined movement of the electrons and the changes occurred at the Fermi level [45]. When the electron carrier concentration exceeds the conduction band edge density of states, the absorption edge is pushed to higher energies as a result of some states in close proximity to the conduction band being populated [46]. This phenomenon is called Moss-Burstein effect, which results in increasing the band-gap energy at a high concentration of dopant. Thus, 1 at% Mo-doped TiO$_2$ sample with the lowest band-gap energy was chosen as the optimum sample to be hybridized with RGO.

The XRD patterns of TiO$_2$, 1 at% Mo-doped TiO$_2$, and 1 at% Mo-doped TiO$_2$/RGO powders are summarized in Table 1. The band-gap energy values of TiO$_2$ doped with various amounts of Mo are shown in Fig. 2 and Fig. 3. Mo by up to 1 at% has significantly decreased the band-gap energy of TiO$_2$, yet further doping has proven to have an adverse effect on the band-gap energy; As the atomic percentage of dopant exceeds 1%, the band-gap energy of Mo-doped TiO$_2$ powders is increased. Similar results have been previously reported for Mo-doped TiO$_2$ nanoparticles and thin films [44]. The band-gap broadening at high levels of dopant can be related to the confined movement of the electrons and the changes occurred at the Fermi level [45]. When the electron carrier concentration exceeds the conduction band edge density of states, the absorption edge is pushed to higher energies as a result of some states in close proximity to the conduction band being populated [46]. This phenomenon is called Moss-Burstein effect, which results in increasing the band-gap energy at a high concentration of dopant. Thus, 1 at% Mo-doped TiO$_2$ sample with the lowest band-gap energy was chosen as the optimum sample to be hybridized with RGO.

The XRD patterns of TiO$_2$, 1 at% Mo-doped TiO$_2$, and 1 at% Mo-doped TiO$_2$/RGO powders are demonstrated in Fig. 2. The XRD pattern of TiO$_2$ powder corresponds to the rutile phase, and no peaks analogous to the anatase phase were detected. Nevertheless, in the XRD pattern of Mo-doped TiO$_2$ powder, the main (101) and (002) peaks of anatase phase were observed at 25.4° and 48.2°, respectively, indicating the rutile to anatase phase transformation. It is known that rutile is the stable phase of TiO$_2$, while anatase is metastable. Thus, although the phase transition from metastable anatase to stable rutile has been frequently reported [47], the inverse transformation is less common. The irradiation of rutile single crystal by infrared femtosecond laser pulses [48], reactive r.f. magnetron sputtering process on a glass substrate in Ar/O$_2$ at a high total gas pressure [49], doping of Ce and Nb at low concentrations by r.f. sputtering method [50], and contacting ultrafine rutile particles with strongly negatively charged colloid particles such as V$_2$O$_5$.nH$_2$O [51] are some of the techniques in which rutile to anatase phase transition has been observed. In this study, doping of Mo element in the TiO$_2$ structure and the high pressure resulted from the consecutive strikes of milling balls on the TiO$_2$ particles can induce the rutile to anatase phase transformation. On the other hand, it has been shown that the stability of TiO$_2$ polymorphs is size dependent. For instance, Zhang and Banfield [52] have shown that the anatase is the most thermodynamically stable phase in smaller particles (< 11 nm) while at larger particles (> 35 nm), rutile is the most stable phase. Here, since fragmentation of rutile particles has occurred during high-energy ball milling, the particle size was significantly reduced (as shown in Fig. 4) which can affect the TiO$_2$ phase transformation as well. As can be seen in Fig. 2, a significant peak-line broadening has occurred in the XRD pattern of Mo-doped TiO$_2$ powder, which can be attributed to the grain refinement, accumulation of lattice strain, and substitution of the doped element in the TiO$_2$ structure during mechanical alloying.

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.12</td>
</tr>
<tr>
<td>0.5 at% Mo-doped TiO$_2$</td>
<td>2.28</td>
</tr>
<tr>
<td>1.0 at% Mo-doped TiO$_2$</td>
<td>2.22</td>
</tr>
<tr>
<td>2.0 at% Mo-doped TiO$_2$</td>
<td>2.31</td>
</tr>
<tr>
<td>3.0 at% Mo-doped TiO$_2$</td>
<td>2.40</td>
</tr>
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$E_g$(eV) = 1240/\lambda$(nm) [42], where $\lambda$ is the wavelength of the absorption edge in the spectrum and obtained from extrapolating the absorption edge onto the wavelength axis. The $E_g$ values of Mo-doped TiO$_2$ are summarized in Table 1. The band-gap energies of Mo-doped TiO$_2$ nanoparticles were in the range of 2.22–2.40 eV, much less than the band-gap energy of pure TiO$_2$ powder (3.12 eV). This can be explained by the changes in the band-gap of TiO$_2$; In the photocatalytic process of TiO$_2$, after receiving a radiation with sufficient energy ($E \geq E_g$), electrons jump from the valence band (the O 2p orbital) to the conduction band (the Ti 3d orbital). By doping TiO$_2$ with Mo, an interior band is created below the conduction band due to the presence of the Mo 4d orbital [43]. The creation of this interior band between the valence band and the conduction band of TiO$_2$ decreases the required energy for the electron excitation, giving rise to the red shift and the band-gap energy reduction of TiO$_2$. According to Table 1, doping with Mo by up to 1 at% has significantly decreased the band-gap energy of TiO$_2$, yet further doping has proven to have an adverse effect on the band-gap energy; As the atomic percentage of dopant exceeds 1%, the band-gap energy of Mo-doped TiO$_2$ powders is increased. Similar results have been previously reported for Mo-doped TiO$_2$ nanoparticles and thin films [44]. The band-gap broadening at high levels of dopant can be related to the confined movement of the electrons and the changes occurred at the Fermi level [45]. When the electron carrier concentration exceeds the conduction band edge density of states, the absorption edge is pushed to higher energies as a result of some states in close proximity to the conduction band being populated [46]. This phenomenon is called Moss-Burstein effect, which results in increasing the band-gap energy at a high concentration of dopant. Thus, 1 at% Mo-doped TiO$_2$ sample with the lowest band-gap energy was chosen as the optimum sample to be hybridized with RGO.

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The XRD pattern of the 1 at% Mo-doped TiO$_2$/RGO is similar to that of the 1 at% Mo-doped TiO$_2$, and the RGO peak was not detected due to the low intensity of the RGO diffraction peak and dispersion of the TiO$_2$ particles between the RGO sheets [54].

Fig. 3 illustrates the FTIR spectra of the powders. The FTIR spectrum of the TiO$_2$ powder indicates a strong and broad band below 1000 cm$^{-1}$, which is related to the stretching and bending vibration modes of Ti-O-Ti [55–57]. The peak at 2350 cm$^{-1}$ is related to the O=C=O stretching band and originates from the adsorption of CO$_2$ from the air [58]. The peaks at 2850 cm$^{-1}$, 2920 cm$^{-1}$, and 2960 cm$^{-1}$ correspond to the stretching vibration modes of C–H bonds [59]. All the absorption peaks of TiO$_2$ are present in the FTIR spectrum of Mo-doped TiO$_2$. However, the intensity of C–H bond was reduced. In addition, two new peaks were detected in the FTIR spectrum of Mo-doped TiO$_2$. The peak at 1227 cm$^{-1}$ corresponds to the Mo-O bond [60], revealing the doping of Mo in the TiO$_2$ nanoparticles. The other peak which appeared at 1052 cm$^{-1}$ is attributed to the stretching vibration of C–O bonds [61]. The FTIR spectrum TiO$_2$-1% Mo/RGO composite is similar to that of Mo-doped TiO$_2$ except the higher intensities of C–H and O=C=O bonds in the former as a result of the incorporation of RGO into the TiO$_2$ nanoparticles.

Fig. 4 shows FESEM images of the powders. TiO$_2$ particles are rather...
spherical in shape, and their size ranges from 20 nm to 55 nm. The morphology of Mo-doped TiO$_2$ is still spherical, but more irregular than TiO$_2$ particles. Meanwhile, the size of TiO$_2$ particles was reduced to 6–20 nm during mechanical alloying. As seen in the FESEM image of 1 at% Mo-doped TiO$_2$/RGO powder, the surface of TiO$_2$ particles was covered by thin layers of RGO sheets due to the photocatalytic reduction process.

The EDX spectra of the TiO$_2$, Mo-doped TiO$_2$, and Mo-doped TiO$_2$/RGO powders are displayed in Fig. 5. It is clear that after doping of the TiO$_2$ powder with Mo, the peak corresponding to this element has appeared in the EDX spectrum. Quantitative EDX analysis measurements indicate that the atomic percentage of Mo in the TiO$_2$ powder is roughly $1 \pm 0.03$ at%, which confirms the appropriate doping of Mo in the TiO$_2$ powder during the mechanical alloying process. In the EDX
spectrum of the 1 at% Mo-doped TiO$_2$/RGO, in addition to Ti, O, and Mo peaks, the carbon peak was also detected which could be attributed to the RGO hybridized with the TiO$_2$ nanoparticles. The results of EDX mapping analysis for Mo-doped TiO$_2$ powder without and with RGO are presented in Figs. 6 and 7, respectively. The EDX elemental map obtained from 1 at% Mo-doped TiO$_2$ powder (Fig. 6) indicates the homogeneous distribution of Mo in TiO$_2$ powder after mechanical alloying. On the other hand, EDX mapping analysis showed a uniform distribution of carbon corresponding to the presence of RGO sheets in the Mo-doped TiO$_2$/RGO powder (Fig. 7).

![Fig. 7. EDX mapping analysis of 1 at% Mo-doped TiO$_2$/RGO powder.](image)

Fig. 7. EDX mapping analysis of 1 at% Mo-doped TiO$_2$/RGO powder.

![Fig. 8. Linear sweep voltammograms of TiO$_2$, Mo-doped TiO$_2$, and Mo-doped TiO$_2$/RGO photoanodes obtained in 0.1 M Na$_2$SO$_4$ solution under the UV irradiation.](image)

Fig. 8. Linear sweep voltammograms of TiO$_2$, Mo-doped TiO$_2$, and Mo-doped TiO$_2$/RGO photoanodes obtained in 0.1 M Na$_2$SO$_4$ solution under the UV irradiation.

![Fig. 9. Amperometric current-time curves of the samples obtained in 0.1 M Na$_2$SO$_4$ solution under the UV irradiation.](image)

Fig. 9. Amperometric current-time curves of the samples obtained in 0.1 M Na$_2$SO$_4$ solution under the UV irradiation.

Fig. 8 represents the linear sweep voltammograms of the TiO$_2$, 1 at% Mo-doped TiO$_2$, and 1 at% Mo-doped TiO$_2$/RGO samples conducted in the 1 M Na$_2$SO$_4$ solution under the illumination of monochromatic light with the wavelength of 375 nm. The onset of the photo-induced current occurred at potentials of $-0.263$, $-0.309$, and $-0.367$ V vs. SCE for TiO$_2$, Mo-doped TiO$_2$, and Mo-doped TiO$_2$/RGO photoanodes, respectively. The lower potential at the zero photocurrent density, i.e., flat-band potential (FBP), points out the easier movement of electrons and reaction with ions located on the surface of a catalyst [62]. Thus,
the 1 at% Mo-doped TiO2/RGO sample represents a better electro-
photocatalytic behavior in comparison to the other samples. It should
be noted that the negative FBP values signify the easy separation of
electron-hole pairs on the surface of a semiconductor with exposure to
radiation [62]. As seen in Fig. 8, as the potential increases, the photo-
current increases as well and thus, more photo-generated charges can
be transferred due to the larger potential difference between the photo-

to anode and the counter electrode [63]. However, the photocurrent
did not change significantly as the applied potential increased
[64,65]. Thus, it can be deduced that doping of TiO2 with Mo, and more
specifically hybridizing with RGO sheets has significantly increased the
number of generated electrons.

Fig. 10 demonstrates the EIS Nyquist plot of TiO2, Mo-doped TiO2,
and Mo-doped TiO2/RGO under the UV light irradiation. The Nyquist
plot of all the specimens consisted of a circular arc which its radius
varied with the following sequence: \( R_{Mo\text{-TiO}2/RGO} < R_{Mo\text{-TiO}2} < R_{TiO2} \). The smaller the circular arc diameter of the Nyquist plot indicates the effective separation of the electron-hole pairs induced by the radiation, resulting in a fast charge transfer to the electron donor/acceptor at the interface between the catalyst and the reactant environment [67,68]. In fact, as the semicircular radius of the Nyquist plot decreases, the rate of the reactions occur on the surface of the photocatalyst increases [69]. The Mo-doped TiO2/RGO possessed the highest charge transfer in the Na2SO4 solution and thus the best separation efficiency of the electron-
hole pairs, which corresponded to the photoelectrocatalytic experiment results.

The mechanisms affecting the photocatalytic behavior of Mo-
doped TiO2/RGO is similar to that of TiO2, with the exception of the
initial photocurrent spike being higher and subsequently decaying to a
higher steady-state photocurrent, as shown in Fig. 9. The photocurrent
of Mo-doped TiO2 and Mo-doped TiO2/RGO has been significantly
improved in comparison to the bare TiO2 as much as 4.5 and 6.5 orders
of magnitude, respectively. The amount of photocurrent generated
during the amperometry test when the lamp is turned on, is influenced
by the number of electrons exchanged on the photocatalyst surface
[66]. Thus, it can be deduced that doping of TiO2 with Mo, and more
specifically hybridizing with RGO sheets has significantly increased the
number of generated electrons.

To examine the photoresponse over time, amperometric I-t mea-
surements were performed under UV-light irradiation with a wave-
length of 375 nm (on) and without radiation (off) in the 1 M Na2SO4
solution. It is clear from Fig. 9 that a great photocurrent is created at the
early stage of the illumination due to the rapid generation of electron-
hole pairs. Nevertheless, the photocurrent deteriorates over time owing
to the recombination of electron-hole pairs. Finally, the photocurrent
reaches a steady state current when the rates of photocharge generation
and recombination reach an equilibrium [63]. The variation of the
photocurrent as a function of irradiation time for Mo-doped TiO2 and
Mo-doped TiO2/RGO is similar to that of TiO2, with the exception of the

4. Conclusions

The TiO2 nanoparticles doped with the various Mo content ranging
from 0.5 at% to 3 at% with the appreciation of the mechanical alloying
technique. The results showed that doping with the 1 at% Mo decreased
the band gap energy of the TiO2 powder from 3.12 eV to 2.22 eV. The
1 at% Mo-doped TiO2 particles were hybridized with RGO using UV-
assisted photocatalytic reduction of GO. The surfaces of TiO2 nano-
particles were covered by thin layers of RGO nanosheets due to the
photocatalytic reduction process. The doping of TiO2 with Mo together
with the good integration of TiO2 and RGO led to the fabrication of
composite photocatalyst which exhibit ~ 7.8 times enhancement

Fig. 10. Nyquist plots of TiO2, Mo-doped TiO2 and Mo-doped TiO2/RGO spe-
cimens under the UV light irradiation.

Fig. 11. The schematic illustration of the photocatalytic behavior of Mo-doped
TiO2 hybridized with RGO.
in the photogenerated current compared to the bare TiO$_2$. The significant enhancement in the photoelectrocatalytic response of the Mo-doped TiO$_2$/RGO composite was mainly attributed to the reduction of the band-gap energy of the TiO$_2$, as well as the efficient separation and prolonged recombination time of the charge carriers.

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