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Electrochemical performance of decorated reduced graphene oxide by MoO$_3$ nanoparticles as a counter electrode

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Abstract

We present an efficient electrocatalytic material based on anchored MoO$_3$ nanoparticles on reduced graphene oxide nanosheets (RGM). After preparation of graphene oxide (GO), the MoO$_3$ nanoparticles anchored on GO nanosheet by using the arc-discharge method. FTIR and Raman spectroscopy results show that GO nanosheets are reduced due to arc-discharge and decorated by MoO$_3$ nanoparticles. X-ray diffraction patterns confirm that the MoO$_3$ nanoparticles are well crystallized on reduced GO (RGO) in the orthorhombic crystalline phase with a crystallite size of 83 nm. The surface energy of the electrode based on RGM was measured as 44.56 mJ m$^{-2}$, which shows the desirable spreading ability of the electrolyte on the electrode. Finally, electrochemical performance was studied in the symmetrical dummy cell by impedance spectroscopy and cyclic voltammetry. Our results show that the electrochemical performance of the RGM electrode (with the charge transfer and series cell resistance of 64.96 and 5.88 $\Omega$cm$^2$, respectively) is better than the RGO electrode and is comparable with the Pt electrode. In addition, the photochemical tests show that the efficiency of the cell by RGM counter electrode in a dye-sensitized solar cell is 5.55% with a fill factor of 63%.

1. Introduction

Enhancing the performance of electrochemical and electrocatalytic is important for energy storage and conversion in various devices such as batteries, capacitors, fuel cells, and solar cells [1–3]. In recent years, organic solar cells, which are based on electrochemical reactions, have attracted remarkable attention of researchers due to the facile and inexpensive production process with an average efficiency of about 12%–14% [4–6]. The main effort of the researchers is to reduce production costs, increase efficiency and raise the stability of these type of solar cells [7, 8].

Use of organic compounds instead of current costly materials is a challenge towards achieving these three aims [9–12]. In a solar cell, the counter electrode is one of the deterministic components, which affects the performance of the cell. For instance, in a dye-sensitized solar cell, by light radiation on the dye molecules, electrons excite and flow into the circuit and then collect via a counter electrode from the external circuit and finally inject into the electrolyte to reduce dye molecules again [8, 13–15]. In such a system, the counter electrode plays a crucial role to complete this cycle in order to produce a photocurrent. To improve this electrode, researchers have conducted a wide range of their studies on carbonaceous materials for energy conversion and storage, due to its low-cost availability, high chemical stability, and proper electrical conductivity as an alternative for Pt [16].

Among carbonaceous materials, graphene has drawn extensive attention as a promising material because of high surface area (2630 m$^2$ g$^{-1}$) and fast charged carrier mobility (200,000 cm$^2$ V$^{-1}$ s$^{-1}$) [17–20]. In electrochemical devices, the number of active sites determines the rate of electrochemical reactions and this site typically located in defects and crystal edges [21]. Enhancing defects and functional groups in graphene allows us to increase the active sites for improving electrocatalytic activity. These factors can be controlled by heating the...
GO, and results show that by proper heat treatment of GO, the electron transfer resistance can be reduced to less than 1.20 ohm.cm² [22]. On the other hand, reducing GO causes to eliminate the functional groups in graphene sheets and their active sites in porous structure [23]. The counter electrode can be improved by embedded catalytic nanoparticles between graphene sheets, which maintain the electrical conductivity while improving the porous catalytic sites [24].

The MoO₃ nanoparticle as an n-type semiconductor [25] with multiple valence states and high chemical and thermal stability, is an efficient material for this purpose, which previously used in organic LED, Li-ion batteries applications and electrocatalyst for hydrogen evolution reaction [26–31]. RGM can be used as an electrochemical catalyst for I⁻/I₃⁻ redox couple reaction in dye-sensitized solar cells. Triiodide/iodide redox is a common electrolyte in dye-sensitized solar cells and lithium-iodine batteries [12, 32]. Nanostructured MoO₃ in proximity to graphene can be used as a counter electrode for application in organic photovoltaic cells. At the interface of graphene and MoO₃ nanoparticles, high work function and ionization energy of MoO₃ nanoparticles cause to flow down the electrons to MoO₃ nanoparticles in order to maintain the thermodynamic equilibrium. This creates a large dipole and increases the hole concentration in the interface of graphene and MoO₃ nanoparticles and led to the band bending in MoO₃ below to the Fermi level of graphene. As a result, the electron transfer barrier is almost zero and this junction treats similar to a usual metal, and n-type semiconductor junction [33–36]. However, its reaction as an electrocatalyst material with triiodide/iodide redox has not been studied yet.

In the following, we introduce a facile method of synthesis of RGM and characterize it. Then we compare the performance of three electrodes including RGM as a proposed electrode and RGO and Pt as references in dye-sensitized solar cell. The electrochemical impedance spectroscopy and cycle voltammetry were used to study the prepared cells. Finally, the efficiency of the prepared solar cell were measured by the J-V curve measurement and results show similar performance for RGM and Pt electrodes.

2. Experimental

2.1. GO synthesis

GO synthesized by improved Hummers and Offeman method [37] that have been reported previously by us [38]. In brief, 15 ml sulfuric acid added to 1.0 g graphite powder from Sigma Aldrich (45 μm powder) and stirred at 27 °C for 15 min. Then in the ice bath, the 3.0 g of potassium permanganate was added slowly to the solution. The mixture stirred for 2 h at 40 °C with speed of 1200 rpm. Afterward 300 ml deionized water was added to the solution. Using DI water and centrifuge successively, the remaining acid was removed from the solution. To exfoliate graphite oxide to GO, the solution was exposed in ultrasound bath for 1.5 h and finally was centrifuged to achieve a homogenous dark brown solution.

2.2. RGM preparation

To prepare RGM, we used the arc-discharge method by semi-auto arc discharge device [39]. Two molybdenum electrodes with 3 mm diameter and 99.8% purity were placed in GO aqueous solution. Arc current with a value of 10 A were stabilized between these two electrodes for 15 min. A micrometer screw was used to adjust the separation distance between the electrodes (figure 1(a)). As a result, MoO₃ nanoparticles were ablated from the anode due to arc current, and then condensed on the nano-sheets.

2.3. Fabrication of electrodes

The RGM electrode was fabricated from the prepared solution by coating on a clean fluorine-doped tin oxide glass (FTO) using drop casting method. After drying the prepared samples at 75 °C in air, it was annealed at 400 °C for 2 h (figure 1(b)). To fabricate the RGO electrode, we reduced the coated GO on FTO by placing in hydrazine hydrate space for 15 min and then annealed at 250 °C for 1 h. The Pt electrode was purchased from solar Sharif Company. The TiO₂ paste (9 gr TiO₂ powder, 1.5 ml acetic acid, 0.2 ml surfactant) coated on clean FTO glass by the doctor blade method. The prepared photoanodes annealed at 325 °C, 375 °C, 450 °C, 500 °C for 5, 5, 15, 15 min, respectively.

2.4. Symmetrical dummy cell fabrication

To investigate the electrochemical activity of the prepared electrodes, a symmetrical dummy cell was fabricated by two identical electrodes (figure 1(c)). The prepared electrodes were separated by 60 μm thick tape as a spacer and sealing with an active area of 0.1962 cm² and finally, the electrolyte was injected between them.
2.5. Dye-sensitized solar cell fabrication

To fabricate dye-sensitized solar cell we sensitized the TiO$_2$ nanoparticles on photoanode. The prepared photoanodes were soaked overnight in N719 dye solution (0.3 mM in a mixed solvent of acetonitrile and tart-butanol with a volume ratio of 1:1). The solar cells were assembled using the prepared electrodes and same photoanode. A spacer with 60 $\mu$m thick and 0.1962 cm$^2$ active area was applied between the cathode and photoanode. Finally, the electrolyte (10 ml ethylene glycol, 830 mg potassium iodide, and 127 mg iodine crystals) was injected to the cell and then closed by tape.

2.6. Characterization

Fourier transform infrared (FTIR) spectra were measured with a Thermo Scientific Nicolet iS10 FTIR spectrometer. The x-ray Diffraction (XRD) experiments were performed using a Philips x-ray diffractometer (PW 1730) by a Cu $\alpha$ radiation source with a wavelength of 1.54 Å. Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM) was carried out using a TESCAN VEGA-II and TESCAN MIRA-III, respectively. Raman spectroscopy was recorded by FirstGuard Handheld Raman Analyzer (Rigaku) with an excitation wavelength of 1064 nm. Electrochemical measurements was performed by using the OGFOIA and OGEFIS multi-channel system from Electrochem Origalys Company. Impedance spectra were measured at the modulation amplitude of 10 mV, in the frequency range from 100 mHz to 65 kHz. The data of impedance spectra were fitted using Zplot/Zview software. J-V curves and cyclic voltammetry were measured at AM 1.5 G with a radiation power of 100 mW cm$^{-2}$ by IV100 from Safir Soraya Sepahan Company. The cyclic voltammetry curves were measured at a scan rate of 10 mV s$^{-1}$ in $-600$ to $+600$ mV voltage range.

3. Results and discussion

3.1. GO, RGO and RGM characterization

Using Fourier transform spectroscopy, we studied the reduction process of GO. Figure 2 shows the comparison between the synthesized GO, RGO (reducing GO by hydrazine hydrate), and RGM (reducing and decorating GO by arc discharge). The peak at 3415 cm$^{-1}$ is the characteristic of the O–H bonds due to adsorbed water molecules. The C–H vibrations appear at 2922 cm$^{-1}$ and the peaks at 1730 and 1398 cm$^{-1}$ are correspond to C=O and C–O bonds, respectively. As shown in figure 2 these peaks have completely disappeared in the RGO and RGM, showing well reduction of GO. The peak at 1622 cm$^{-1}$ corresponds to the carbonic bond in graphene, which is observed for all spectra. The C–O–C bond appears at 1077 cm$^{-1}$ and its intensity slightly decreases in both reduction methods [40, 41]. The 400–1000 cm$^{-1}$ peak in RGM corresponds to the vibrations of metal–oxygen characteristic bonds. The peak at 615 cm$^{-1}$ is oxygen bonding with three molybdenum atoms. The peaks at 991 and 877 cm$^{-1}$ are due to the formation of Mo$^{6+}$ atoms bonding with oxygen in the Mo=O and Mo–O–Mo forms, respectively showing crystallization in the orthorhombic phase [25].

To investigate surface morphology, the FESEM images were taken from the prepared GO, RGO and RGM powder. As seen in figures 3(a) and (b), the GO and RGO nanosheets which are crumpled and loosely packed
together. In figure 3(c), one can see RGM morphology showing anchored MoO$_3$ nanoparticles with the average size of about 20 nm on the curved nanosheets.

In figure 4, the x-ray diffraction spectra of the annealed MoO$_3$ and RGM samples have been presented. In MoO$_3$, the highest intensity of the x-ray diffraction spectrum is due to the (021) plane, which indicates the crystallization of MoO$_3$ in the orthorhombic crystalline phase ($\alpha$-MoO$_3$) ($a = 3.96$ Å, $b = 13.85$ Å, $c = 3.69$ Å).

To calculate the crystallite size, we used the Scherrer’s equation as follows:

$$\tau = \frac{K\lambda}{\beta \cos(\theta)}$$

Where $K$ is the shape factor ($=0.9$), $\lambda$ is the x-ray wavelength ($=0.154$ nm), $\beta$ is the line broadening at the half maximum intensity and $\theta$ is the Bragg angle. According to XRD results, the crystallite size of the MoO$_3$ obtained about 83 nm. In the RGM spectrum, in addition to the MoO$_3$ peaks, three sharp diffraction peaks are seen at 12.94°, 25.85° and 39.15°, which related to the GO and RGO nanosheets [42–44]. By using Bragg’s diffraction law, the spacing of the nanosheets was estimated and the distance between nanosheets for a peak at 12.94° and 25.85° is 6.83, and 3.44 Å, respectively. The high intensity of the RGO peak indicates a significant reduction of GO. The peak at 39.1° with a spacing of nanosheets is equal to 2.3 Å is probably due to a short range order and incomplete oxidation cause them to accumulate [42]. The average crystallite size of the RGM by Scherrer’s equation is calculated about 331 nm, which shows anchoring of the MoO$_3$ nanoparticles on the RGO.

Raman spectroscopy was used to investigate the structure of the prepared samples (figure 5). In a typical Raman spectrum of GO, the D peak at 1290 cm$^{-1}$ is breathing mode which is related to the defects and disorders.
of GO and the G peak at 1599 cm$^{-1}$ represents the graphitized structure and coplanar vibration of sp$^2$-bonded carbon atoms in the two-dimensional hexagonal lattice [45]. In comparison with GO, the intensity of D band relative to G band in the RGM spectrum increases to 1.22, which shows more defects in the structure and high porosity of RGM [46, 47]. According to the empirical equation $L_a (\text{nm}) = (2.4 \times 10^{-10}) \lambda^4 (I_G/I_D)$, the crystallite size of the graphitic carbon is about 252 nm that $\lambda$ is laser excitation wavelength (1064 nm) [48]. In addition, by comparing the G peak for GO and RGM, the peak has a blue shift indicating the strong bond of nanoparticles to the RGO nanosheets. The peaks at 816 and 976 cm$^{-1}$ are related to the symmetrical and asymmetrical Mo=O stretching vibrations. The peaks at 656 cm$^{-1}$ are assigned to the stretching vibration of O-Mo-O bonds and peaks below 600 cm$^{-1}$ are related to the bending vibrations of the $\alpha$-MoO$_3$ crystal [15, 46, 49].

3.2. Characterization of the electrodes
Morphologies, surface porosity and cross thickness of the RGM electrode were examined by SEM. Figure 6(a) shows the SEM image from the as-prepared electrode before heat treatment and figure 6(b) exhibits the electrode surface after annealing at 400 °C. As shown after heat treatment the nanoparticles are crystallized in a
larger size with proper porosity. Figure 6(c) exhibit the cross-section of the prepared electrode showing a layer with a thickness of about 4.5 μm.

In this part, we study the diffusion rate of electrolyte in the RGM electrode. For this purpose, the surface energy by Neumann method was measured. Using the contact angle of five different fluids on the electrode surface (as presented in table 1) and Neumann’s equation of state we obtained the surface energy according to the equation [50]:

$$\cos(\theta) = -1 + \frac{2(\gamma_L - \gamma_S)}{\gamma_L} e^{-\beta(\gamma_L - \gamma_S)^2}$$ (2)

In equation (2), $\theta$ is the contact angle of the applied liquid, $\gamma_S$ is the surface energy of the substrate, $\gamma_L$ is the surface energy of the liquid and $\beta$ is a constant. According to the fitted curve in figure 7 and data in table 1, the surface energy of the RGM electrode was calculated as 44.56 mJ m$^{-2}$. These results indicate that the RGM electrode is suitable for diffusion of organic electrolytes which can rapidly spread over the electrode surface where ions can react with the electrons [51].

To characterize the electrochemical activity, the electrochemical impedance spectroscopy and cyclic voltammetry were carried out in a symmetrical dummy cell configuration. By electrochemical impedance spectroscopy, the electrochemical performance parameters such as charge transfer resistance at the cathode/electrolyte interface ($R_{CT}$), and serial resistance ($R_s$), can be obtained. In figure 8 Nyquist plot of the symmetrical dummy cell based on Pt, RGO, and RGM electrodes are presented. A traditional equivalent circuit used to interpret the Nyquist plot of Pt electrodes as shown in inset of figure 8. The high-frequency intercept on the real axis is attributed to the $R_s$. The first semicircle (0.1–100 kHz) is related to the $R_{CT}$ and double layer capacitance (C) of the electrode. The second semicircle ($<10$ Hz) as Nernstian diffusion element ($Z_{WT}$) describes diffusion of electrolyte species. It is known that the traditional equivalent circuit is not appropriate for porous materials [9]. The proper equivalent circuit for porous electrodes is shown in figure 8 with CPE and $Z_{WT,\text{pore}}$ elements. According to this model the first semicircle (2.5–100 kHz) represents the second Nernst diffusion impedance in the high-frequency region due to charge diffusion through the electrode pores ($Z_{WT,\text{pore}}$). The second semicircle (25–2500 Hz) is related to the $R_{CT}$ and the CPE. The CPE element is the capacitance of the porous electrode and electrolyte interface, which arises from the roughness of the electrodes, which models the behavior of a double layer that is an imperfect capacitor.

The Nyquist plots of RGO and RGM in figure 8, exhibit the high-frequency semicircle that resulting from $Z_{WT,\text{pore}}$. The slight increase in the $Z_{WT,\text{pore}}$ of RGM compared with RGO is probably due to the increase in porosity,
thus resists against the electrolyte species diffusion in porous structures. In the higher frequency region, the onset value of the real axes indicates the $R_S$ of each sample. In the middle-frequency region, second large semicircle in the RGO and RGM Nyquist plot is determined as $R_{CT}$ and corresponding CPE at the interface of electrode and electrolyte. The $R_{CT}$ of RGM is extremely decrease compared to RGO. This is due to an increase in the surface area of RGM compared to RGO, therefore enhance the electrocatalyst activity and fill factor (FF) in

Figure 7. (a) Images of five various liquid droplets on the RGM surface and (b) the contact angle of each of them.

Figure 8. The Nyquist plots of symmetrical dummy cells fabricated with the RGO, RGM and Pt. Left inset: magnified curves in the high-frequency region. Right inset: Equivalent circuit diagram for porous materials (up) and nonporous materials (down) in order to fit the impedance spectra.
the solar cell. These results are summarized in table 2. The third semicircle in the low-frequency region due to diffusion impedance of the triiodide/iodide redox couple in the electrolyte is not observed probably because of overlapping with the second semicircle.

We also carried out the cyclic voltammogram test from symmetrical dummy cells with Pt, RGM, and RGO electrodes. The voltage range was applied between −600 and 600 mV with a scan rate of 10 mV s\(^{-1}\). As shown in figure 9, the maximum current is related to the Pt, RGM, and RGO, respectively. From the slope of voltammogram curve at zero voltage one can obtain the overall cell resistance \([58, 59]\). The resistance values for Pt, RGM, and RGO are 0.25, 0.36, and 0.41 \(\Omega\), respectively.

### Table 2: Photovoltaic parameters of RGM and Pt counter electrodes.

| Parameters | \(I_{SC}\) (mA) | \(V_{OC}\) (mV) | FF (%) | Efficiency (%) | \(R_s\) (\(\Omega\)cm\(^2\)) | \(R_{CT}\) (\(\Omega\)cm\(^2\)) |
|------------|-----------------|----------------|--------|----------------|-----------------|-----------------|
| RGO        | 2.16            | 708            | 55.4   | 4.32           | 8.41            | 248.86          |
| RGM        | 2.3             | 752            | 63     | 5.55           | 5.88            | 64.96           |
| Pt         | 2.27            | 696            | 72.4   | 5.83           | 5.22            | 12.22           |

Figure 9. Cyclic voltammetry plot of the symmetrical dummy cells for RGO, RGM, and Pt.

3.3. Performance in a solar cell

To characterization the performance of the RGM electrode (as counter electrode) in an applicable device, we used it in a dye-sensitized solar cell and measured the J-V curve as presented in figure 10. The experiments were repeated for at least five samples and photovoltaic parameters are presented in table 2 for the most repeatable cell. The open circuit voltage \((V_{OC})\) is the maximum voltage generated by a solar cell. As shown in the schematic of energy levels in figure 11, in dye-sensitized solar cells, \(V_{OC}\) is the voltage difference between the oxidation in photoanode and reduction in RGM electrode of the dye molecules. The short-circuit current \((I_{SC})\) is the current through the solar cell when the voltage across the solar cell is zero. By decreasing the overall series resistance of the cell, the \(I_{SC}\) increases. FF is an interpreter of a deviation from an ideal solar cell that defined as the ratio of the maximum power from the solar cell to the product of \(V_{OC}\) and \(I_{SC}\). A solar cell with less \(R_{CT}\) and \(R_s\) shows better FF which is attributed to the increased electrocatalytic performance of the prepared counter electrodes.

To compare the performance of RGM electrode we used the Pt electrode as a reference and the RGO electrode as a base carbon material, with the same photoanode. According to table 2, the \(V_{OC}\) by the RGM electrode enhances compared with Pt and RGO electrodes. Increasing the porosity in the RGM electrode provides a sufficient number of catalytic sites for electrolyte ions to reduce. \(R_s\) reduction leads to increasing
ISC of the Pt and RGM electrodes in comparison with the RGO. As we expected, FF enhanced due to the decrease of RCT in RGM electrode in comparison with RGO, and these results lead to the close efficiency of the cost-effective, prose, and facile-prepared RGM electrode to the Pt electrode (Table 3).

![Figure 10](image1.png)

Figure 10. J-V plot of the photoelectrochemical cell by RGO, RGM, and Pt as counter electrodes. The photoanode is identical for all cells.

![Figure 11](image2.png)

Figure 11. Schematic of energy levels in different layers of a photovoltaic cell [60].

| Counter electrode                      | Jsc (mA cm⁻²) | Voc (mV) | FF (%) | Efficiency (%) |
|----------------------------------------|----------------|----------|--------|----------------|
| functionalized graphene sheets [9]     | 7.77           | 710      | 70     | 3.83           |
| Graphene Nanosheets [52]               | 13.42          | 690      | 71     | 6.45           |
| Nitrogen-doped porous carbon [53]      | 15.58          | 702      | 63     | 7.01           |
| MoS₂/Graphene [54]                     | 17.24          | 714      | 63.83  | 7.86           |
| Mesoporous carbon [55]                 | 14.32          | 733      | 58     | 6.06           |
| Sub-micrometer-sized Graphite [56]     | 12.7           | 794      | 62     | 6.2            |
| Nickel selenide/RGO [57]               | 19.94          | 751      | 65     | 9.75           |
| Current work (RGM)                     | 11.72          | 752      | 63     | 5.55           |

Isc of the Pt and RGM electrodes in comparison with the RGO. As we expected, FF enhanced due to the decrease of Rct in RGM electrode in comparison with RGO, and these results lead to the close efficiency of the cost-effective, prose, and facile-prepared RGM electrode to the Pt electrode (Table 3).
4. Conclusions

In this study, we introduced decorated RGO with MoO$_3$ nanoparticles as a cost-effective counter electrode with good chemical stability and catalytic performance for I$_3^-$ reduction. We presented a facile method to anchor the MoO$_3$ nanoparticles on the GO nanosheets using the arc-discharge method and our results exhibit that anchored MoO$_3$ nanoparticles are well crystalized on RGO. In addition, FTIR and Raman spectra confirm that the GO reduced and the MoO$_3$ nanoparticles anchored as well on RGO during the arc-discharge process. The low surface energy of the electrode shows easy spreading and diffusion of electrolytes in it. Finally, the characterization of electrochemical activity by impedance measurements and cyclic voltammogram results showed that incorporation of MoO$_3$ nanoparticles with RGO nanosheets improve porous structure without degradation electrical conductivity of RGO, so that have a significant impact on the electrochemical efficiency. The performance of the dye-sensitized solar cell assembled by RGM electrode indicates that this low-cost and facile-prepared electrode with higher porosity can be an appropriate alternative to the Pt electrode in electrochemical cells with acceptable efficiency and greater $V_{OC}$.

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