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Synergistic Nanostructured Electrochemically Reduced Graphene Oxide/Molybdenum Trioxide Photoelectrodes For Enhanced Photoresponse

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Abstract: Photovoltaic systems that convert solar energy into electrical energy are one of the promising solutions for clean and renewable energy resources to meet the rapidly increasing energy need in the world. For this purpose, investigation of new photovoltaics with high conversion efficiency has gained importance for alternative strategies. Goal of this research is to present electrochemical synthesis and photoresponse of synergistic nanostructured electrochemically reduced graphene oxide/molybdenum trioxide photoelectrodes for proposing an alternative photovoltaic material. With this work, the obtained results indicate that electrochemically synthesized photoelectrodes are utilizable as new alternative materials for various energy production devices, such as solar cells. These interpretations can later be verified by subsequent solar cell applications.

Gelişmiş Fototepki İçin Sinerjistik Nanoyapılı Elektrokimyasal İndirgenmiş Grafen Oksit/Molibden Üçoksit Fotoelektrotlar

Anahtar Kelimeler
Fototepki, Elektrokimyasal indirgenmiş grafen oksit, Molibden trioksit, Sinerjistik nanoyapılı

Öz: Güneş enerjisini elektrik enerjisine dönüştüren fotovoltaik sistemler, dünyada hızla artan enerji ihtiyacının karşılanmasında temiz ve yenilenebilir enerji kaynakları için umut verici çözümlerden biridir. Bu amaç doğrultusunda yüksek dönüşüm verimliliğine sahip yeni fotovoltaiklerin araştırılması alternatif stratejiler açısından önem kazanmıştır. Bu araştırmanın amacı, alternatif bir fotovoltaik malzeme olarak sinerjistik nanoyapılı elektrokimyasal indirgenmiş grafen oksit/molibden trioksit fotoelektrotların elektrokimyasal sentezini ve fototepkisini sunmaktır. Bu çalışma kapsamında elde edilen bulgular, elektrokimyasal sentezlenen fotoelektrotların, güneş pilleri gibi çeşitli enerji üretim cihazlarında yeni alternatif malzemeler olarak kullanılabileceğini göstermektedir. Bu bulgular ileride yapılacak güneş pili uygulamalarında kullanılabilir.

1. INTRODUCTION

The demand for energy in the world is increasing day by day, but the energy resources that meet this demand are also rapidly depleting [1-3]. Statistical studies show that existing fossil resources such as coal, oil and natural gas will be insufficient after a few decades [4]. In addition, the energy produced by traditional methods using these fossil fuels negatively affects nature due to negative consequences such as global warming and environmental pollution [5,6]. Due to this situation, researchers have focused on innovative and environmentally friendly energy production studies. These studies are centered on direct electrical energy production with wind and solar energy, which are renewable energy sources. Solar energy can be easily converted into electrical energy using semiconductor-based photovoltaics [7-9]. Titanium dioxide (TiO_2) and zinc oxide (ZnO) are the metal oxides with the best photovoltaic properties among these semiconductors, and scientific studies on alternative materials continue.

Molybdenum trioxide (MoO_3) has a variety of interesting chemical, structural, optical and electrical properties among metal oxides. Its superior properties have been researched in different application areas such as gas sensor [10, 11], photocatalysis [12-14] and ion batteries [15,16]. MoO_3 can be a strong competitor to ZnO and TiO_2 in metal oxide-based photovoltaics with its improvable properties. These improvements can be achieved by composites with materials such as graphene, which have a large specific surface area and excellent electrical conductivity [17].

Herein, we present synthesis route and characterization of synergistic nanostructured electrochemically reduced graphene oxide/molybdenum trioxide (ERGO/MoO_3) photoelectrodes and their enhanced photoresponses. Structurally and morphologically characterized FTO-ERGO/MoO_3 photoelectrodes were analyzed electrochemically and optically to indicate their photoelectric properties.

2. MATERIAL AND METHOD

A three-electrode cell (fluorine-doped tin oxide (FTO) coated glass as working electrode, Pt wire (approximately 99.95% purity) as counter electrode, and Ag/AgCl (3M KCl) as reference electrode) was used for electrochemical synthesis and measurements. X-ray diffractometer (Cu-Kα (λ=15.405 Å) (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and UV-VIS spectroscopies were used for structural, morphological and optical analyzes.

The FTO coated glass working electrodes were cleaned by using an ultrasonic bath before all electrochemical synthesis processes with pure ethanol and distilled water. We used a mixture solution containing 10 mM MoO_3, 50 mM HCl and 2 mg mL^{-1} graphene oxide (GO) dispersion for electrochemical synthesis of ERGO/MoO_3. HCl was used to provide acidic media to increase the solubility of MoO_3 in water. MoO_3 was used as Mo^{6+} source and GO was used as ERGO precursor. Electrodeposition was carried out at -1.15 V (vs. Ag/AgCl) to reduce Mo^{+6} and GO, simultaneously, for 5 min in the presence of oxygen gas passing through the mixture solution. Then, deposited electrodes were rinsed with deionized water and dried with Ar gas. After all, the as-prepared electrodes were treated by thermal annealing at 400°C for 1 h for the formation of FTO-ERGO/MoO_3 photoelectrodes. The experimental procedure is shown in Figure 1.

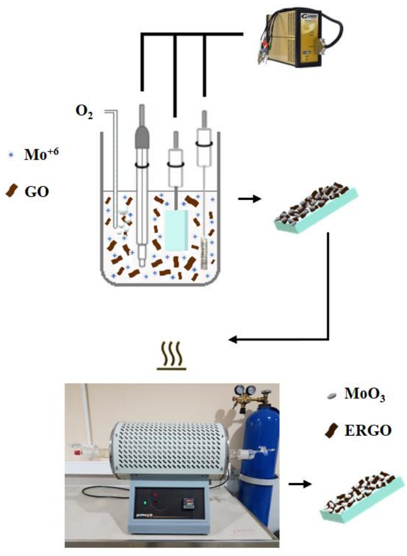

Figure 1. The schematic illustration of the experimental procedure.

3. RESULTS

Morphological properties of FTO-ERGO/MoO_3 photoelectrodes were analyzed by using SEM. SEM images of FTO-ERGO/MoO_3 photoelectrodes were given in Figure 2a. The images show the formation of MoO_3 clusters covered by ERGO on FTO electrode surface homogeneously. The elemental composition of FTO-ERGO/MoO_3 photoelectrodes was investigated by using EDS attached with SEM (Figure 2b). The detected peaks demonstrate the existence of O, Mo, and C which are forming the elemental composition of FTO-ERGO/MoO_3 photoelectrodes.

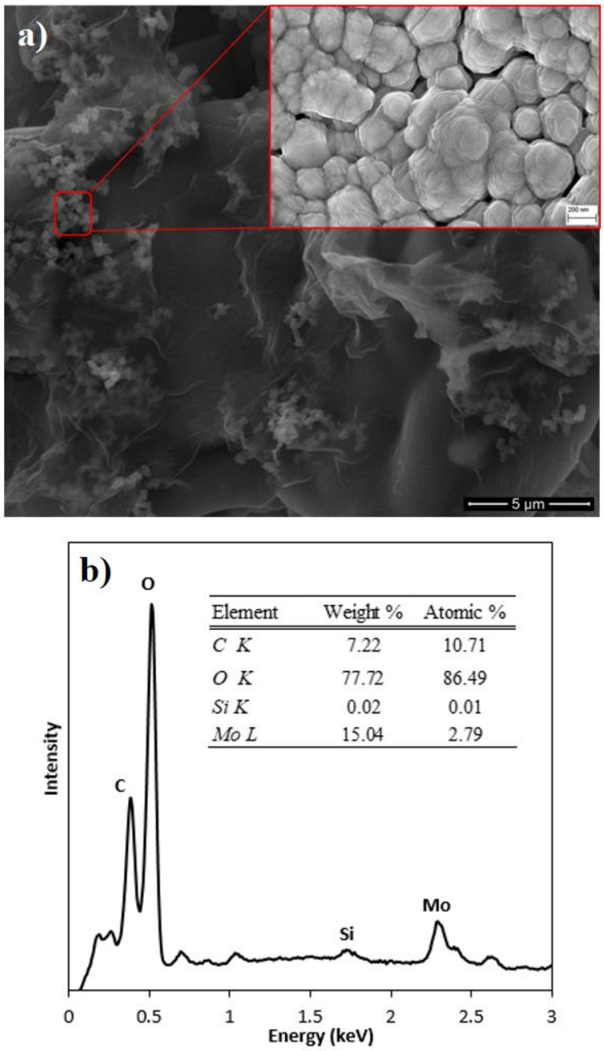

Figure 2. SEM images (a) and EDS spectra (b) of FTO-ERGO/MoO_3 photoelectrodes.

Rigaku Miniflex X-ray diffractometer (Cu-Kα (λ=15.405 Å) was utilized to investigate the crystal structure of FTO-ERGO/MoO_3. The determined peaks at 12.7°, 25.7°, 27.3°, 30.1°, and 38.9° in diffractogram (Figure 3) corresponds to (020), (040), (021), (130), and (060) planes, respectively, and promote the existence of MoO_3 with crystalline form (JCPDS No.05-0508). Additionally, the diffraction peak of ERGO at 25° was not detected in the diffractogram. This situation is related to the loss of layer stacking regularity after the composite of ERGO layers with MoO_3 particles. This phenomenon was observed in various previous studies [18,19].

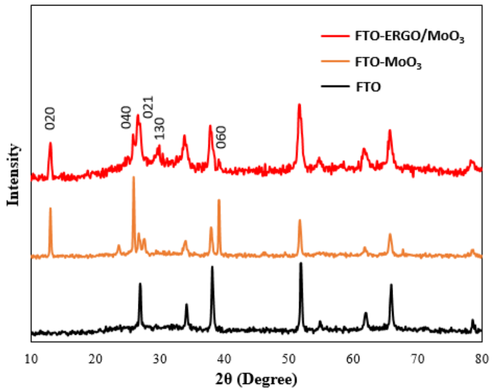

Figure 3. XRD diffractograms of FTO, FTO-MoO_3 and FTO-ERGO/MoO_3 photoelectrode.

UV-VIS spectroscopy was used to record the optical absorbance spectras for identifying and comparing the optical band-gap energies of FTO-MoO_3 and FTO-ERGO/MoO_3 photoelectrodes (Figure 4a). With the usage of Tauc plot, the band-gap value of the FTO-ERGO/MoO_3 photoelectrodes calculated as 3.03 eV whereas FTO-MoO_3 photoelectrode is 3.95 eV (Figure 4b). This decrease in the band-gap value can be attributed to the strong interaction and synergistic effect between ERGO and MoO_3 in the light of the literature [20,21].

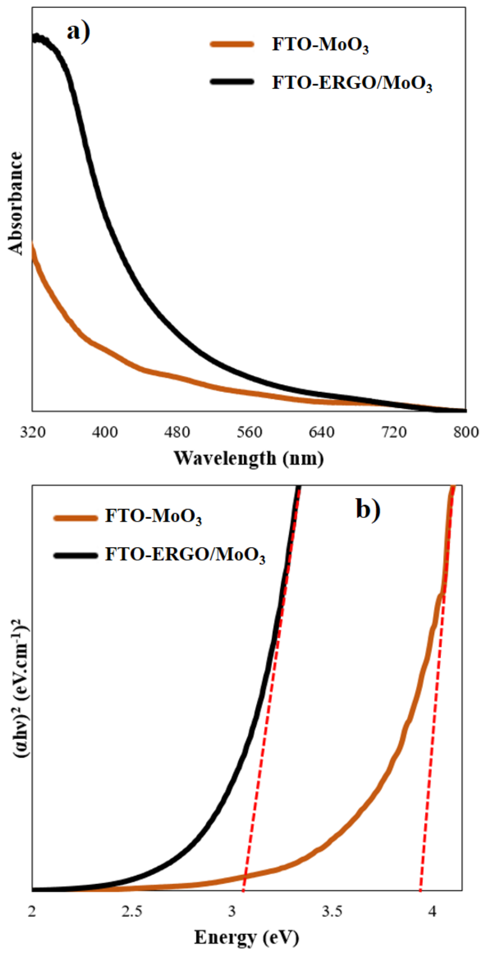

Figure 4. UV–VIS absorbance spectras (a) and Tauc plots (b) for the FTO-MoO_3 and FTO-ERGO/MoO_3 photoelectrodes.

Figure 5 shows the photocurrent–time diagrams of the FTO-MoO_3 and FTO-ERGO/MoO_3 photoelectrodes saved at 0 V for 90 s in 0.1 M Na_2SO_4 aqueous electrolyte. When the sunlight illumination is switched on, the photoresponse increases swiftly to ~24.7 µA.cm^{-2}. Further, with the light illumination switching on and off, the photoresponse rise and fall immediately.

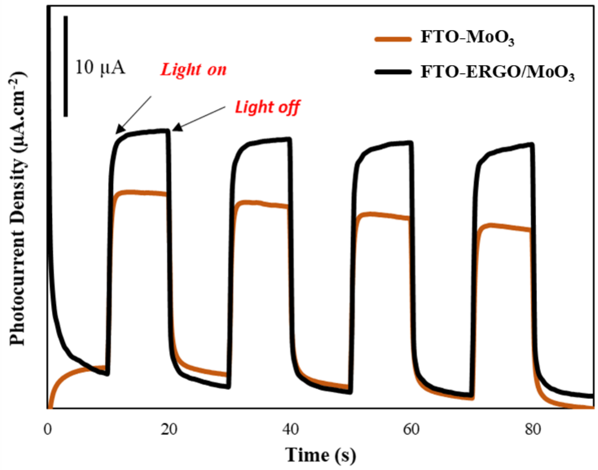

Figure 5. The photoresponse of the FTO-ERGO/MoO_3 and FTO-MoO_3 photoelectrodes in 0.1 M Na_2SO_4 aqueous electrolyte.

4. DISCUSSION AND CONCLUSION

Herein, FTO-ERGO/MoO_3 photoelectrodes were synthesized successfully by using electrochemical method. The photoelectrodes were explored with SEM, EDS, XRD and UV-VIS spectroscopic techniques for morphological, structural and optical characterization, successfully. A photocurrent density of ~24.7 µA.cm^{-2} was obtained for FTO-ERGO/MoO_3 photoelectrode which is attributed to enhanced photoresponse compared to FTO-MoO_3. The results indicate that electrochemically synthesized FTO-ERGO/MoO_3 photoelectrodes are utilizable as new alternative materials for various energy production devices, such as solar cells.

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