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Synthesis, Characterization and Photoelectrochemical Properties of MoS_2 decorated TiO_2 Nanotubes Electrodes

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Abstract: In this research, TiO_2/MoS_2 nanocomposite electrodes were synthesized to investigate the photoelectrochemical performances. Firstly, TiO_2 nanotubes were fabricated by anodic oxidation on Ti foil. Then, MoS_2 nanostructures were synthesis by hydrothermal method on TiO_2 nanotubes. The prepared nanocomposite films were characterized by using X-Ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The transient photocurrent response was analyzed to investigate photoelectrochemical activity of electrodes. The results show that TiO_2 nanotube arrays coated with MoS_2 nanostructure homogeneously. Furthermore, TiO_2/MoS_2 nanocomposite electrode were shown better photoelectrochemical activity then bare TiO_2 electrode.

Key words: TiO_2 nanotubes, Anodization, Photocurrent, Hydrothermal

MoS_2 ile dekore edilmiş TiO_2 Nanotüp Elektrotların Sentezi, Karakterizasyonu ve Fotoelektrokimyasal Özellikleri

Özet: Bu araştırmada, TiO_2/MoS_2 nanokompozit elektrotlar fotoelektrokimyasal performanslarını araştırmak için sentezlenmiştir. İlk olarak, Ti folyo üzerinde anodik oksidasyonla TiO_2 nanotüp dizileri üretilmiştir. Daha sonra; MoS_2 nano yapıları, TiO_2 nanotüpler üzerinde hidrotermal yöntemle sentezlenmiştir. Hazırlanan nanokompozit elektrotlar, X-Ray kırınımı (XRD) ve alan emisyonu taramalı elektron mikroskobu (FESEM) kullanılarak karakterize edilmiştir. Geçici foto-akım tepkisi, elektrotların fotoelektrokimyasal aktivitesini araştırmak için analiz edilmiştir. Elde edilen sonuçlar, TiO_2 nanotüp dizileri etrafına MoS_2 nanoyapılar ile homojen bir şekilde kaplandığı belirlenmiştir. Ayrıca, TiO_2/MoS_2 yapıların TiO_2 elektrota göre daha iyi fotoelektrokimyal aktivite gösterdiği belirlenmiştir.

Anahtar kelimeler: TiO_2 nanotüp, Anodizasyon, Foto-akım, Hidrotermal

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1. Introduction

Because of their excellent physical and chemical properties, nanostructures with specific morphologies have been received tremendous interest in many branches of science and technology in recent years. Numerous studies have been conducted in order to fabricate efficient, stable and cost effective electrodes for device fabrication, photocatalysis, and power storage and conversion studies [1,2]. The catalytic activities in many electrochemical reactions are caused by composite metal oxides, which show stoichiometric/non-stoichiometric compositions and the transition metal mixed valences within this structure. Besides that, due to the synergetic effect of the composite material, enhanced catalytic activities can be achieved by combining with metallic materials or metal oxides [3].

The most commonly used semiconductor for electro/photocatalytic applications is titanium dioxide (TiO_2) nanostructures because of its superior physical and chemical stability, non-toxicity, low cost, high-level UV-based photocatalytic performance [4–9]. However, the board range divide and high rate of recombination of nanostructured TiO_2 materials with the electron hole limit their catalytic activities in visible light or sunlight. The use of metal chalcogenides that have a band gap close to TiO_2 is very common route, for achieving higher photoelectrochemical performance [10,11]. To enhance the lower quantum yield of the photo catalytic efficiency of pure TiO_2 many nanomaterials such as; carbon based materials graphene, graphene oxide (GO), carbon nanotubes, etc., metal chalcogenides ZnO, WO_3, CdS, MoS_2, Bi_2S_3, CdSe, CdTe [12–17]. Among them, many studies show that MoS_2/TiO_2 composites show superior catalytic effect in comparison with bare MoS_2 and TiO_2, which together increase the photoelectric electron-hole pairs, the charge transfer to adsorbed substrates and photostability [3,18–20].

In this study, MoS_2 nanostructures were decorated onto TiO_2 nanotubes arrays to analyze the photochemical behavior for the first time. TiO_2/MoS_2 nanocomposite structures were obtained by two step synthesis routes as anodic oxidation and hydrothermal methods, respectively. The XRD and SEM analysis were performed to characterize the as prepared TiO_2/MoS_2 nanocomposites. Photochemical activities of nanocomposite electrodes were tested using the photocurrent responses under UVA light. The results showed that improved photoelectrochemical activity were achieved through MoS_2 decoration.

2. Material and Method

2.1 Reagents

Ti foil (99.99 %), ethylene glycol, ammonium fluoride, and sodium molybdate and thiourea were purchased from Sigma Aldrich and of analytical grade. Ti foil was freshly washed with acetone, methanol and water for 15 min. with the aid of ultrasonic agitation. All solutions were prepared freshly with the ultrapure water (18.2 Ω) prior to each use.

2.2 Preparation of TiO_2 nanotube arrays

TiO_2 nanotube arrays (TNA) was fabricated by using electrochemical anodization method as described in literature [21]. The 1.0 x 2.5 cm pieces of Ti foils were inserted into the electrochemical cell as an anode where the platinum mesh was the cathode

electrode. The cell was filled with the electrolyte solution containing ethylene glycol, 0.4% (w/w) NH_4F and 5% (w/w) deionized water. A 40 V DC potential was applied for 4 hours under hydrodynamic conditions at room temperature. Then, the anode was removed from the electrochemical cell and cleaned with methanol and water. Finally, the TiO_2 nanotube arrays were dried in a oven at 110 ^oC and kept at 450^oC for 1 h for phase transition from amorphous to anatase.

2.3 Preparation of TiO_2/MoS_2 composite

The decoration of TNA with MoS_2 was performed under hydrothermal conditions according to the literature [22]. Briefly, 20 mL aqueous solutions of 80 mM thiourea and sodium molybdate (10, 20 and 30 mM) were prepared by ultrapure water and stirred for 30 min at room temperature. Then, the solutions transferred in the Teflon autoclave and TNA was placed into autoclave. Hydrothermal growth of MoS_2 layer was achieved after 6 hours at 120 ^oC. The electrode then, rinsed with methanol and dried in a oven at 80 ^oC.

2.4 Characterization of TiO_2/MoS_2 Electrode

The crystalline structure of TNA composite was identified by X-Ray diffractometer (PANanalytical, Empyrean), using Cu Kα radiation (λ=1.5406 Å, 45 mV and 40 mA) in the 2ϴ range of 10 – 70^o. The morphology of composite electrode was investigated FEI Quanta 450 field emission scanning electron microscope and the chemical composition of the surface was identified energy dispersive spectroscopy (EDS). The transient photocurrent response was recorded by using gamry reference 1000 potentiostat and UV lamp supplied from TED PELLA, INC. A three electrodes system was used for electrochemical measurements where TNA samples were used as working electrode, Pt mesh used as counter electrode and Ag/AgCl electrode was the reference electrode. 0.5 V bias voltage was applied between reference and working electrode while the current was recorded in chronoamperometry mode.

3. Results

Initial studies were devoted to characterize the TiO_2/MoS_2 composite photoelectrode material. Crystalline structure of TiO_2/MoS_2 photoelectrode modified with different concentrations of sodium molybdate and thiourea was shown in Fig 1. The diffractions at 25.3, 37.1, 48.1, 54.2 and 55.2 (2θ) can be assigned to the (101), (004), (200), (105) and (211) planes of the TiO_2 anatase phase and it is in good agreement with JCPDS card No.02-1272. In addition, the spectrum indicated that no diffraction peak associated with the rutile and brookite phases of TiO_2 were not observed. The characteristic (004), (100), (103), (110) diffractions MoS_2 were observed at 30.3, 34.2, 40.1 and 74.2 2θ angles (JCPDS card no: 37-1492). The modification of TNA with increasing concentration of MoS_2 has resulted from the decrease in the TiO_2 anatase diffraction peaks while the MoS_2 peaks were increased with increasing concentration 10 to 30 mM.

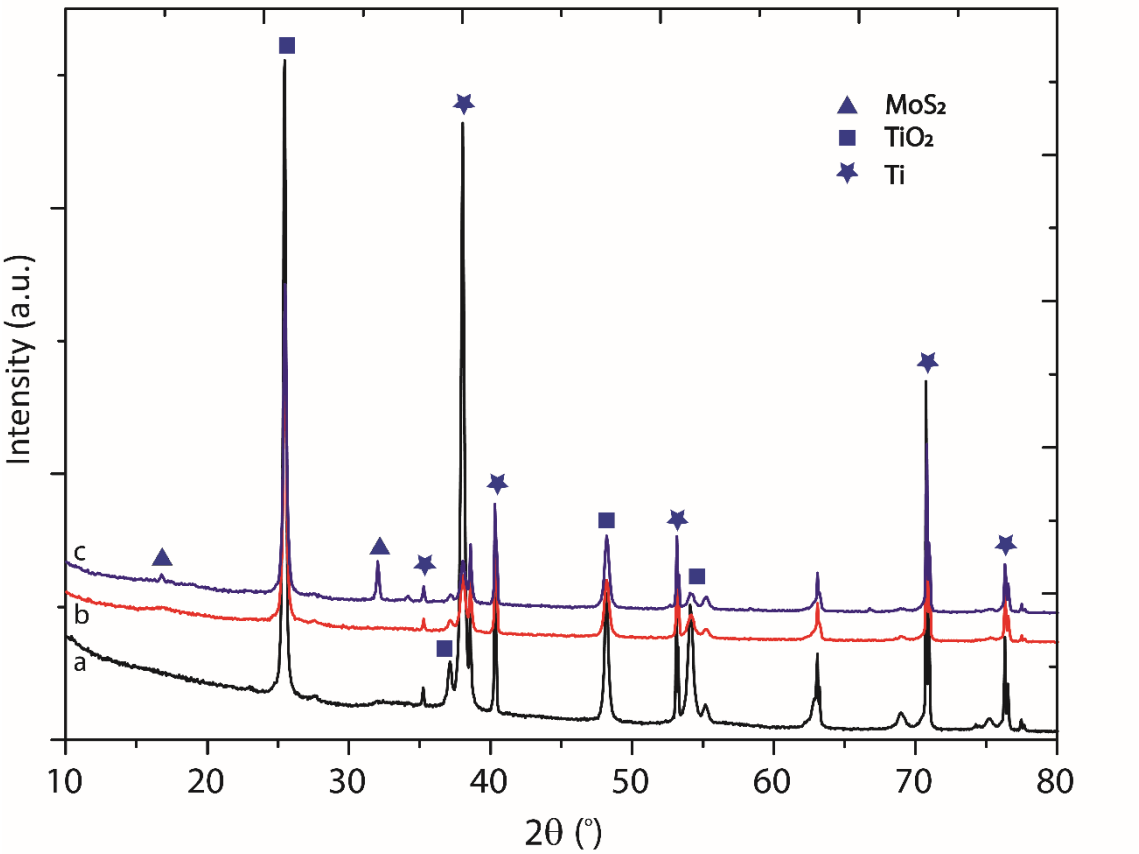

Figure 1. XRD patterns of TiO_2/MoS_2 nanocomposite electrodes (a) 10 mM, (b) 20 mM, (c) 30 mM concentration of MoS_2 precursor.

The morphology of the composite electrode was examined with the SEM technique and given in Fig. 2. According to Fig. 2a vertical orientation TiO_2 nanotube array without any observable damage was observed. As can be followed from Fig. 2b, after the modification with 10 mM sodium molybdate and thiourea the MoS_2 was started the grow on the edges of TiO_2 nanotubes and the atomic ratios of Mo:S was calculated as 1.95 from the EDS spectrum which is very close to identical value. Fig. 2c clearly shown the MoS_2 layers were cover the edges of TiO_2 nanotubes however, hole in the TiO_2 nanotube was still open. The atomic ratio of Mo:S was calculated as 2.05 (Fig.2d). It can be concluded from the SEM images that MoS_2 layer deposited on the edges of TiO_2 nanotube and the increasing concentration of MoS_2 has been almost closed the TiO_2 nanotubes hole. These findings were in good agreement with XRD pattern.

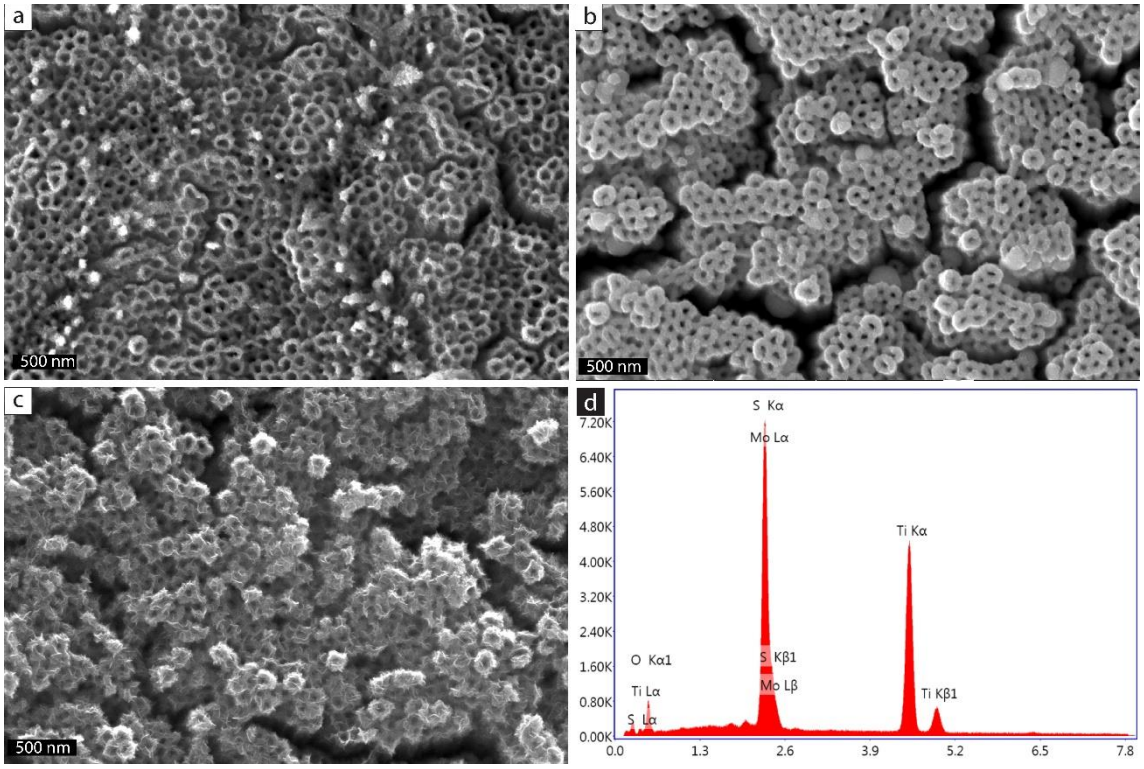

Figure 2. SEM images of TiO_2/MoS_2 nanocomposite electrodes (a) 10 mM, (b) 20 mM, (c) 30 mM concentration of MoS_2 precursor (d) EDX spectra of electrode (20 mM)

Transient photocurrent response of the bare TNA and MoS_2 modified TNA electrodes were given in Fig 3. TNA and modified electrodes were exhibited photocurrent response under the UV illumination on – off cycles. A rapid current increase was observed when the UV illumination was on, probably due to the photo-induced charge transfer. Bare TNA gave a photocurrent response of about 0.5 mA while applying 0.5 V bias voltages. The current response was dramatically increased with the modification of MoS_2 probably due to the enhanced light absorption on the electrode surface and lower charge transfer resistance, as well. The modification of TNA surfaces with 10 mM MoS_2 enhances the photocurrent response to 1.1 mA. The maximum photocurrent was observed as 2.6 mA while 20 mM MoS_2 was used. Further enhancement in MoS_2 concentration has led decline in photocurrent response probably due to the surface coverage.

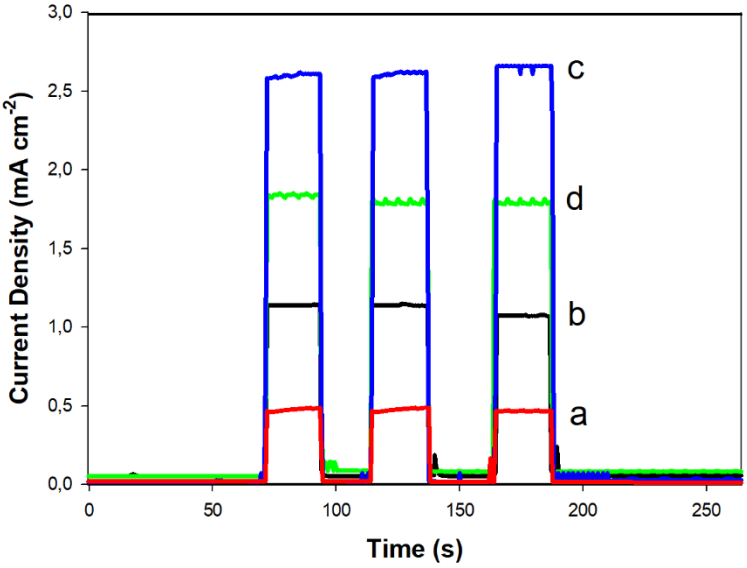

Figure 3. The transient photocurrent responses of TiO_2/MoS_2 nanocomposite electrodes (a) Bare TNA, (b) 10 mM, (c) 20 mM, (d) 30 mM MoS_2 decorated TNA electrodes.

4. Conclusions

TiO_2/MoS_2 nanocomposites were successfully manufactured at different concentrations of the MoS_2 precursor and their photoelectrochemical activities were investigated by transient photocurrent response measurements under UVA irradiation. Two step synthesis method was used to fabricate the TiO_2/MoS_2 nanocomposite as anodic oxidation and hydrothermal method, respectively. As prepared and MoS_2 decorated TiO_2 nanotubes were characterized by FESEM, XRD and XPS techniques. The SEM analyses proved that the all surface of TiO_2 nanotube arrays was coated with MoS_2 nanoparticles. Increasing the concentration of precursor was resulted the covering of TiO_2 nanotube surface. The best photocurrent response of 2.6 mA was obtained by nanocomposite electrode which was synthesized by 20 mM MoS_2 precursor due to synergetic effect of TiO_2 nanotubes and MoS_2 nanoparticles. The photocurrent response decreased in higher MoS_2 precursor concentration because of TiO_2 nanotube array surface completely covered by MoS_2 nanoparticles.

Author Statement

Burcu Bozkurt Çırak: Conceptualization, Methodology, Writing, Data curation, Supervision, Reviewing and Editing
Çiğdem Eden: Investigation

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Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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