

Enhanced Photocurrent of Titania Nanotube Photoelectrode Decorated with CdS Nanoparticles

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Abstract:

In this work, CdS/TiO₂ nanotubes composite nanofilms were successfully synthesized via electrodeposition technique. TiO₂ titania nanotube arrays (NTAs) are commonly used in photoelectrochemical cells as the photoelectrode due to their high surface area, excellent charge transfer between interfaces and fewer interfacial grain boundaries. The anodization technique of titanium foil was used to prepare TiO₂ NTAs photoelectrode. The concentration of CdCl₂ played an important role in the formation of CdS nanoparticles. Field emission scanning electron microscopy (FESEM) shows that the CdS nanoparticles were well deposited onto the outer and inner of nanotube at 40 mM of CdCl₂. X-ray diffraction (XRD) and energy dispersive X-ray (EDX) analyses were executed for the determination of the composition and crystalline structure of the synthesized samples. Furthermore, the data of EDX confirms the formation of titanium and oxygen for TiO₂ nanotubes and cadmium and sulfide for CdS deposits. UV-visible diffuse reflectance spectroscopy (UV-DRS) displayed that CdS nanoparticle which deposited onto TiO₂ NTAs causes a red-shift into the visible region. CdS/TiO₂ NTAs sample prepared at 40 mM of CdCl₂ showed maximum photocurrent of 1.745 mA cm⁻² while the bare TiO₂ NTAs showed 0.026 mA cm⁻¹.

Keywords: Electrochemical deposition, CdS/TiO₂ nanotube, Photoelectrochemical, anodizing.

Introduction:

Metal oxides such as Fe₂O₃, CuO₂, ZnO, TiO₂ and are commonly used as Photoelectrochemical cells (PEC) (1)(2)(3)(4). Nanostructured metal oxides have been improved the absorption of light and photocurrent of PEC. Currently, TiO₂ nanotubes arrays (NTAs) have received increased attention in PEC due to its high surface area, high corrosion resistance, good chemical stabilities, and open end nanotube, which would be appropriate for electron transport to avoid the recombination of electron-hole when applied in PECs (5)(6). Several methods have been developed to prepare TiO₂ films such as sol-gel synthesis, magnetron sputtering deposition, chemical vapor deposition (CVD), hydrothermal treatment, and anodization method, etc (7)(8)(9)(10)(11). Through these methods, anodization technique is considered as a relatively simple method to prepare TiO₂ nanotubes with considerable surface area (12)(13). Furthermore, TiO₂ only absorbs ultraviolet light less than 400 nm, (14)(15).

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In order to solve the mentioned problems, the photoresponse of TiO₂ can be shifted to the visible region via coupling narrow band gap semiconductors such as CdSe (16) (17) (18) (19), CdS (20) (21) and CdTe (22) (23). Moreover, nanostructured metal chalcogenides such as CdTe (23), CdSe (24), CdS (25), PbS (26), Ag₂S (27), ZnS (28), and co-sensitized CdS/CdSe (29)(30) have attracted significant interest due to their applications in electronics, semiconductor and optical devices. CdS is confirmed to be a good sensitizer because its favorable band gap to absorb more light in order to improve optical properties of TiO₂. Various techniques have been carried out for the preparation of CdS include successive ionic layer adsorption and reaction (SILAR) (31), chemical bath deposition (CBD) (32)(33), sputtering (34), and electrochemical deposition (20)(35).

In this work, The CdS/TiO₂ NTAs was synthesized via anodizing Ti foil followed by deposition CdS nanoparticles through electrochemical deposition technique. The electrochemical deposition technique offers a convenient way to deposit CdS nanoparticles onto titania nanotubes in a shorter time frame.

Materials and Methods:

1. Preparation of TiO₂ NTAs

Titania nanotubes were prepared according to the following steps. First of all, Ti foil (99.7 % purity, 0.127 mm) was cut into pieces of 2 x 1 cm². Then, the Ti pieces were displayed to sonicating in isopropanol, acetone, and deionized water (DI) followed by etching in 5 M HNO₃. After that, they were washed with DI and put in the air to dry. Oxidation method of Ti foil was carried out in a two-electrode cell with the high-density graphite as the counter electrode while Ti foil acts as the working electrode, and 0.5 wt% NH₄F dissolved in 25 vol% water with anhydrous ethylene glycol. The two electrodes were connected to a DC power supply and subjected to a constant 20 V anodic potential for 2 h. Then, the samples were washed with DI water. The products were annealed at 500 °C for 2 h (2°C/min).

2. Deposition of CdS nanoparticles on TiO₂ NTAs

Deposition of CdS nanoparticles was executed onto the NTAs via electrodeposition using a potentiostat system in which the NTAs were used as the working electrode, Pt wire as the counter electrode and saturated Ag/AgCl as the reference electrode. The deposition was carried out at different concentration (10, 20, 30, 40, and 50 mM) of CdCl₂ and 10 mM Na₂S₂O₃. The chosen potential was -0.65 V versus Ag/AgCl and the films were deposited for 20 mins at room temperature. The pH was kept at approximately 2.0 by gradual addition of HCl.

3. Materials characterization of TiO₂ NTAs and CdS/TiO₂ NTAs

The field emission scanning electron microscopy (FESEM, JOEL JSM-7600F, Japan) was used to study the surface morphologies of the as-prepared electrodes (CdS/TiO₂ NTAs) while the energy dispersive X-ray (EDX) spectrometer was carried

out to elemental analysis. The x-ray diffractometry (XRD) (Panalytical X, Pert Pro MPD diffractometer with CuK α radiation, $k = 1.5406 \text{ \AA}$) was used in order to determine the structures of NTAs and CdS. The absorption spectra of CdS/TiO₂ NTAs were measured via UV-visible diffuse reflectance spectrophotometer (UV-DRS, Vary 300, USA).

4. Photoelectrochemical response of TiO₂ NTAs and CdS/TiO₂ NTAs

The photoelectrochemical measurements of the as-prepared electrodes TiO₂ NTAs and CdS/TiO₂ NTAs were performed in a 50 mL 0.01 M Na₂S electrolyte under halogen lamp as the light source by using a three-electrode photoelectrochemical cell with CdS/TiO₂ NTAs as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode.

Results and Discussion:

1. Characterization of CdS/TiO₂ NTAs

The self-organized TiO₂ NTAs was produced on titanium substrate via anodization technique at 20 V as shown in Figure 1a. The diameters of the TiO₂ NTAs are in the range of 20–35 nm which grow vertically from the titanium substrate. Figure 1b shows that the pores of the TiO₂ NTAs are not covered by CdS nanoparticles and the surface of the TiO₂ NTAs is not destroyed by the deposition of CdS nanoparticles. Figure 1c and 1d show that particle size and amount of CdS nanoparticles increased with increasing concentration of CdCl₂ to 20 and 30 mM. At 40 mM of CdCl₂, CdS nanoparticles were uniformly distributed on the inner and outer of TiO₂ NTAs as shown in Figure 1e. Moreover, further raise the concentration of CdCl₂ to 50 mM has resulted in the cover of the mouth of the TiO₂ NTAs by CdS nanoparticles as shown in Figure 1f.

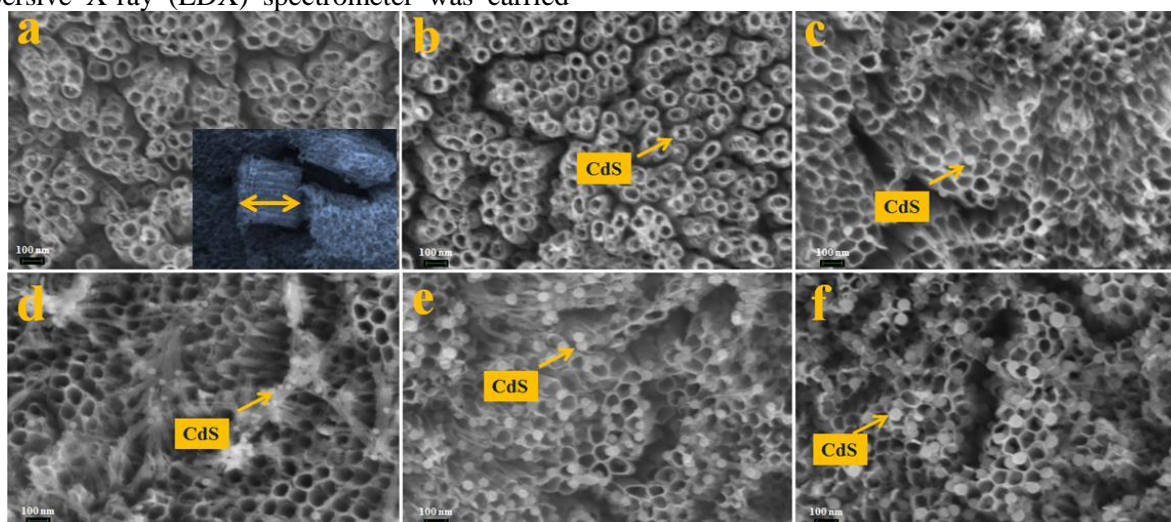


Figure 1. FESEM images: (a) TiO₂ NTAs with cross sectional of TiO₂ NTAs; and CdS/TiO₂ NTAs prepared at various concentration of CdCl₂: (b) 10 mM, (c) 20 mM, (d) 30 mM, (e) 40 mM and (f) 50 mM

The composition of the sample was identified by EDX analysis as shown in Figure 2. The spectrum of EDX confirms the presence of O, Ti, S, and Cd peaks which confirmed forming TiO_2 , and CdS.

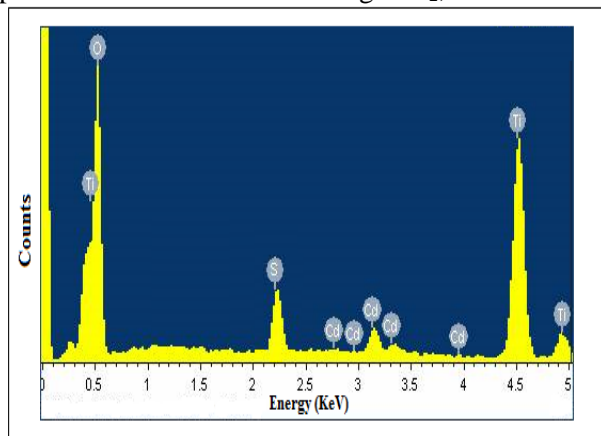


Figure 2. EDX spectra of CdS/ TiO_2 NTAs prepared at 40 mM CdCl_2 and 10 mM $\text{Na}_2\text{S}_2\text{O}_3$

X-ray diffraction experiments were used to examine the crystal structure of the deposited CdS onto TiO_2 NTAs. The X-ray diffraction pattern for the bare TiO_2 NTAs sample is also given for comparison after deposition CdS nanoparticles. As shown in Figure 3a, all diffraction peaks of TiO_2 were indexed with anatase phase (JCPDS: 00-002-0406) and (JCPDS: 00-001-1197) for titanium metal phase. Furthermore, titanium and TiO_2 diffraction peaks, also CdS peaks (JCPDS: 01-077-2306) are presented in Figure 3 (b, c, d, e, and f), and these peaks detect that the CdS nanoparticles are the hexagonal structure.

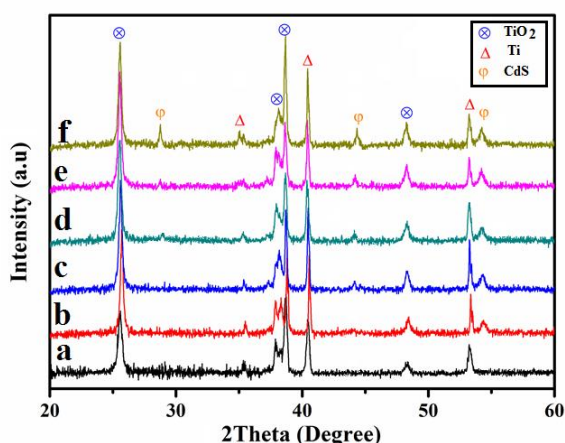


Figure 3. XRD patterns: (a) TiO_2 NTAs; and CdS/ TiO_2 NTAs prepared at various concentration of CdCl_2 : (b) 10 mM, (c) 20 mM, (d) 30 mM, (e) 40 mM and (f) 50 mM

UV-Vis diffuse reflectance analysis (DRS) was carried out to study optical properties of the prepared samples. Due to the intrinsic optical absorption of TiO_2 , the bare TiO_2 NTAs absorb at the wavelengths less than 400 nm (36). The CdS

nanoparticles deposited onto TiO_2 NTAs exhibits a significant absorption more than 400 nm due to more visible light that has been absorbed by CdS nanoparticles. It is consequently able to produce the better amount of charge carriers.

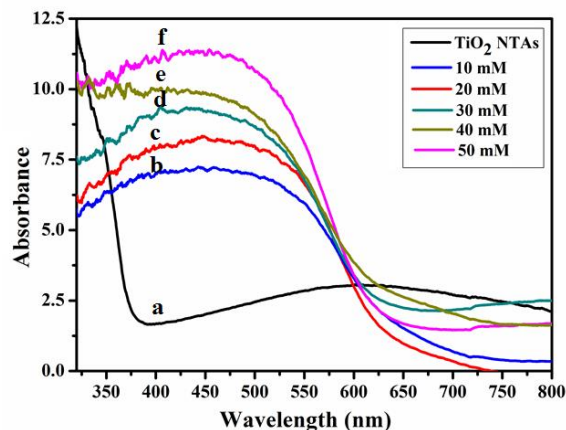


Figure 4. UV-Vis absorption curves: (a) TiO_2 NTAs; and CdS/ TiO_2 NTAs prepared at various concentration of CdCl_2 : (b) 10 mM, (c) 20 mM, (d) 30 mM, (e) 40 mM and (f) 50 mM

2. Photoelectrochemical (PEC) performance

To enhance absorption of the light, the nanostructure of a CdS/ TiO_2 NTAs also modifies separation of the electrons and holes (37). The Photoelectrochemical (PEC) measurement was carried out to estimate the photoresponse of CdS/ TiO_2 NTAs photoelectrode is shown in Figure 5. As CdS/ TiO_2 NTAs nanostructure was predictable to be semiconductors; therefore, it should be sensitive to the light, with energy higher than their band gap (38). For a comparison, the photoresponse of as-prepared plain TiO_2 NTAs and CdS/ TiO_2 NTAs electrodes, the curves of photocurrent density versus the applied potential under intermittent illumination were shown in Figure 5. Good photoresponse was observed at 40 mM CdCl_2 due to more nanoparticles that were deposited on the outer and inner of nanotubes; thus, they would absorb more light. However, the PEC performance decreased when the concentration of CdCl_2 was increased to 50 mM. At these concentrations, the nanoparticles size were larger, therefore; forming a thicker film and cause hindering of light and affected the formation charge carriers at the interface of the electrode solution.

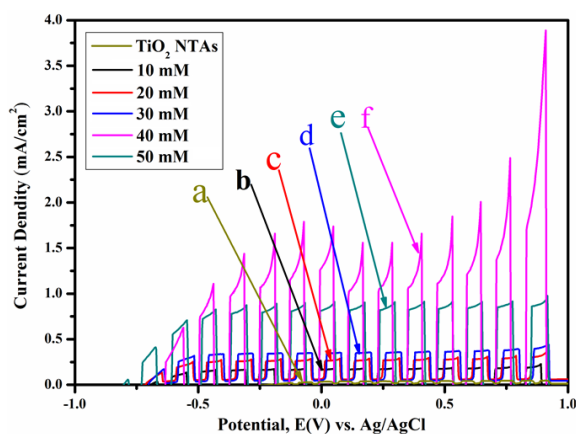


Figure 5. Photocurrent density, (intermittent lighting) in 0.01 M Na₂S: (a) TiO₂ NTAs NTAs; and CdS/TiO₂ NTAs prepared at various concentration of CdCl₂: (b) 10 mM, (c) 20 mM, (d) 30 mM, (e) 40 mM and (f) 50 mM

Conclusion:

Uniform and well-ordered TiO₂ NTAs films were successfully prepared via applied electrochemical anodization technique. The annealing temperature at 500 °C contributes the transformation of the TiO₂ NTAs to the anatase phase. CdS nanoparticles were excellently covered on the inner and outer walls of the TiO₂ nanotubes. The distribution and size of CdS nanoparticles were orderly through the variation of CdCl₂ concentration. Composite film was shifted Light absorption to the visible region more than 400 nm, also CdS nanoparticles were considerably raised of the photocurrent intensity. The highest photocurrent value was 1.745 mA cm⁻² which obtained under the illumination of halogen lamp when prepared CdS/TiO₂ NTAs from 40 mm CdCl₂ with 10 mm Na₂S₂O₃. Thus, it is a perspective that synthesized CdS/TiO₂ NTAs films are highly pertinent materials for photoelectrochemical cells application.

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تحسين التيار الضوئي لقطب التيتانيا النانوي المزين بالدقائق النانوية من CdS

أسماء كاظم عيال

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الخلاصة:

في هذا العمل تم تصنيع الأنابيب النانوية المركبة بنجاح CdS/ TiO₂ عن طريق تقنية الترسيب الكهربائي. صفائف الأنابيب النانوية للتيتانيا تستخدم بصورة واسعة في الخلايا الكهروضوئية كألكترود ضوئي بسبب المساحة السطحية العالية، ونقل الشحنة ممتاز بين الاسطح البينية والحدود البينية للحبوب أقل. استخدمت تقنية الأنودة لرقائق التيتانيوم لإعداد الألكترود الضوئي (TiO₂ NTAs). لعب تركيز CdCl₂ دورا هاما في تشكيل الدقائق النانوية CdS. يظهر ال FESEM أن الدقائق النانوية CdS ترسبت بشكل جيد خارج وداخل الأنابيب النانوية في 40 ملي مولر من CdCl₂. (XRD) و (EDX) نفذت لتحديد التركيب والهيكل البلوري للعينات المحضرة. وعلاوة على ذلك، فإن (EDX) تؤكد تشكيل التيتانيوم والأكسجين للأنابيب النانوية TiO₂ والكادميوم والبريتيد لل CdS. أظهر (UV-DRS) أن الدقائق النانوية ل CdS المترسبة على TiO₂ تؤدي إلى ازاحة حمراء إلى المنطقة المرئية. وأظهرت عينة CdS /TiO₂ المعدة في 40 ملي مولر CdCl₂ أعلى تيار ضوئي وهو 1.745 mA/cm² بينما TiO₂ الخالية أظهرت 0.026 mA/cm².

الكلمات المفتاحية: الترسيب الكهروكيميائي، CdS /TiO₂ الأنبوب النانوي، الكهروكيميائية الضوئية، الأنودة.