Electro-Optics and Band Gap Energies of Nanosilver-Coated TiO₂ Nanotubes on Titanium Metal

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Abstract TiO₂ nanotubes on Ti metal surface were prepared by the electrochemical anodization method. Then, nanosilver was deposited onto the nanotubes by the electroless dip coating and the anodization. The obtained TiO₂ nanotubes were examined by using scanning electron microscopy, atomic force microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, cyclic voltammetry, and UV–Vis. The electrochemical band gap (E_g^{CV}) of the nanosilver-coated TiO₂ nanotubes prepared by the anodization was found as 1.54 eV. Using the UV–Vis measurements, the optical band gap energy (E_g^{op}) was calculated as 1.51 eV for the Ag/TiO₂ nanotubes obtained by electroless dip coating. The electrical conductivity of the TiO₂ nanotubes also increased from 3.0×10^{-4} to 34.7 S/cm after nano Ag deposition by the anodization method. These Ag/TiO₂ nanotubes with low band gap and high electrical conductivity are desirable for the applications in electronics, Li-ion batteries, and solar cells.

KEY WORDS: Electrochemical anodization; TiO₂ nanotubes; Nano Ag deposition; Band gap energy; Electrical conductivity

1 Introduction

Titanium dioxide (TiO₂) is an excellent corrosion resistant, low cost, and non-toxic material, and it has a broad range of technological applications in the industry. Generally, it is used in photocatalysis, dye-sensitized solar cells, and other semiconductive applications. TiO₂ has a wide band gap energy with stable physical and chemical properties [1–5]. The optical band gap energies of TiO₂ are 3.2 eV for anatase, 3.0 eV for rutile, and about 3.2–3.5 eV for the

amorphous phase [6]. For the synthesis of TiO₂ nanomaterials, various approaches have been investigated in the literature. For example, TiO₂ nanotubes have been synthesized due to the better properties as compared to the other forms of TiO₂ for the applications in photocatalysis, photoelectrolysis, and photovoltaics [1, 3, 7]. A large surface to volume ratio, high porosity, and uniformity are the exceptional properties of TiO₂ nanotubes. These advantages drive researchers to investigate the interesting material properties of TiO₂ nanotubes prepared by using the different methods [1, 8].

In order to synthesize TiO₂ nanotubes, hydrothermal synthesis, electrochemical anodization (oxidation), and template methods can be used [7, 9]. In the anodization method, the use of aqueous HF electrolyte leads to the formation of TiO₂ nanotubes due to the high chemical dissolution rate of the anodized TiO₂ layer [10, 11]. In this study, the TiO₂ nanotube surfaces were obtained on Ti metal using HF electrolyte solution by the electrochemical anodization method.

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Additionally, the nanotubular TiO_2 structures are often doped with metal ions to increase their functional properties. Particularly, the noble metals have been deposited onto the TiO_2 structures to modify their surface properties. Paramasivam *et al.* [12] investigated the photocatalytic activities of Ag and Au nanoparticle loaded TiO_2 nanotube layers. Among the noble metals, Ag is the most attracting choice to obtain the functional TiO_2 nanotubes [2]. The relative low cost, the strong bactericidal property, and the special oxygen adsorption behavior made silver a preferred choice for the modification of TiO_2 nanotube materials [7, 13–15]. In recent years, different methods have been applied to obtain the nano Ag-coated TiO_2 nanotubes in the literature. For instance, the thermal decomposition [16], the UV illumination [1, 7, 17], the wetting–thermal decomposition [18], the sputter deposition [19, 20], the photochemical deposition [21], the sunlight reduction [22], the photo reduction [23, 24], the electrophoretic deposition [25], and the ultrasound-aided photochemical deposition [26] methods have been studied for the preparation of Ag/ TiO_2 nanotubes.

In the present work, we have prepared TiO_2 nanotubes on Ti metal surface by the electrochemical anodization

method. They were coated with nano Ag particles by using the electroless dip coating and the anodization methods. The morphological, optical, electronic, and spectroscopic properties of TiO_2 and Ag/ TiO_2 nanotubes were examined by scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), cyclic voltammetry (CV), and UV–Vis methods. The electrochemical (E_g^{CV}) and optical (E_g^{op}) band gap energies of the prepared nano Ag/ TiO_2 nanotubes were calculated from the CV voltammograms and UV–Vis spectra, respectively. The electrical conductivities of the prepared Ag/ TiO_2 nanotubes were measured and compared with each other.

2 Materials and Methods

2.1 Preparation of TiO_2 Nanotubes on Ti Metal Surface

TiO_2 nanotube surfaces were prepared by using the electrochemical anodization process. The anodization process was applied to the Ti metal electrode for producing the

Fig. 1 Nano Ag coating methods of TiO_2 nanotube surfaces: **a** dip coating during the anodization of Ti, **b** electroless dip coating after the anodization of Ti

Fig. 2 SEM images of TiO_2 , Ag/ TiO_2 nanotubes

TiO₂ nanotube structures on the surface of Ti. The electrochemical anodization of the polished Ti metal was performed under different voltages. In order to provide the formation of the uniform TiO₂ nanotube structures on the surface, a voltage of 20 V was used for 30 min in 0.5% HF electrolyte solution.

2.2 Deposition of Nano Ag on TiO₂ Nanotubes

The deposition of silver nanoparticles on TiO₂ nanotubes was performed using two different procedures. The schematic diagrams of these deposition methods are given in Fig. 1. The anodization dip coating of nano Ag was performed as the first method. In this anodization process shown in Fig. 1a, 0.5% HF electrolyte solution containing Ag⁺ ions (0.25 g/L AgNO₃) and Tween 20 (5 mL/L) were used for the simultaneous silver deposition during the growth of TiO₂ nanotubes. As the second method, the electroless dip coating of nano Ag on TiO₂ nanotubes was studied. In this process, the nano Ag coating was carried out on previously prepared TiO₂ nanotubes. The nano Ag dip coating of TiO₂ nanotubes was performed for 30 min by mixing the Ag⁺ solution containing 0.025 g AgNO₃, 1 mL H₂O, 25 mL acetone, and 1 mL poly(dimethylsiloxane) as the reducing agent (Fig. 1b) [14].

2.3 Experimental Measurements

The SEM microscopy analyses of TiO₂ nanotubes and nano Ag-coated TiO₂ nanotube samples were carried out by using a TESCAN VEGA3 instrument. The AFM surface images were examined on a NTEGRA P9 (NTEGRA Prima) model atomic force microscope. The crystallographic structures of the TiO₂ and Ag/TiO₂ nanotubes were detected by using a Rigaku D/MAX 2000 X-ray diffractometer (XRD) with CuK_α radiation in the range of $10 < 2\theta < 90^\circ$. The FT-IR spectra of the samples were recorded between 400 and 4000 cm⁻¹ on a Perkin Elmer Spectrum Two model spectrophotometer with ATR attachment. The CV measurements of the TiO₂ and Ag/TiO₂ nanotube samples were performed on a Gamry 750 EQCM model potentiostat at the scanning rate of 25 mV/s and 100 mV/s. The measurements were carried out by using Ag/AgCl reference electrode ($E = +0.197$ V) and a platinum electrode as the counter electrode. The prepared TiO₂ nanotube samples were used as the working electrode. In the CV measurements, 0.05 M LiClO₄ solution in CH₃CN or 0.1 M KNO₃ in H₂O was used to provide the electrolytic conductivity of the cell. The UV–Vis spectra of the prepared TiO₂ nanotube samples were measured on a Shimadzu UV–Vis 2600 PC model double beam spectrophotometer by using ISR attachment between 200 and 1400 nm. The electrical conductivity of the TiO₂ nanotube

samples was studied before and after nano Ag deposition. The electrical conductivities of the samples were measured by using a four-point measurement system (Lucas Pro4).

3 Results and Discussion

3.1 Preparation of TiO₂ and Nano Ag/TiO₂ Nanotubes

Ti metal surfaces have been oxidized by the anodization in fluoride-containing electrolyte to obtain TiO₂ nanotube surfaces. Then, the TiO₂ nanotube surfaces were coated with the nano Ag particles using firstly the dip coating method during the anodization of Ti and secondly, the electroless dip coating method after the anodization of Ti (Fig. 1). The uniform TiO₂ nanotubes on the surface of Ti metal were obtained and they were coated with the nano Ag. The properties of the prepared TiO₂ and nano Ag/TiO₂ nanotubes were examined by SEM, AFM, XRD, FT-IR, CV, UV–Vis, and the electrical conductivity measurements.

Fig. 3 EDS spectra of nano Ag/TiO₂ nanotube surfaces

3.2 SEM Analysis

The SEM images of the TiO₂ nanotubes and the nano Ag-coated TiO₂ nanotubes were examined. Figure 2a shows the SEM image of TiO₂ nanotubes prepared by anodization with the voltage at 20 V for 30 min. From the SEM image in Fig. 2a, it can be seen that all the surface of Ti metal could be converted to the uniform and vertical TiO₂ nanotubes during the anodization. It was estimated that the inner diameters of the TiO₂ nanotube holes were between 50 and 100 nm with the nanotube wall thicknesses of about 25 nm. The nano Ag/TiO₂ nanotubes were examined by SEM analysis method. The SEM images after the nano Ag deposition of the TiO₂ nanotube surfaces are given in Fig. 2b for the anodization deep coating and Fig. 2c for the electroless deep coating. In the anodization deep coating, nano Ag particles were generally deposited in the nanotube wall surfaces, and the holes of the TiO₂ nanotubes remained open. In the second deposition method, the use of the electroless dip coating process resulted in Ag/TiO₂ nanotubes with different surface morphologies. It was observed that some parts of the TiO₂ nanotube surfaces have been covered by nano Ag particles. Furthermore, the EDS analyses of prepared TiO₂ and nano Ag/TiO₂ nanotubes were measured and the obtained spectra are shown in Fig. 3. The Ag contents of the Ag/TiO₂ nanotubes were

measured about $1.1 \pm 0.2\%$ on TiO₂ surfaces. In addition, the Ag contents of the prepared Ag/TiO₂ samples were analyzed by using the ICP-OES measurements after the leaching of silver in 10% HNO₃ solutions. The amounts of silver were obtained as 0.65 $\mu\text{g}/\text{cm}^2$ for the sample prepared by the anodization coating process and 0.63 $\mu\text{g}/\text{cm}^2$ for the sample prepared by the electroless dip coating process. The SEM elemental mappings of Ag and Ti elements are also shown in Fig. 4. The silver nanoparticles were deposited mostly on the wall surfaces of the nanotubes, and there were less Ag nanoparticles inside the nanotubes. Both the elemental mappings and the EDS measurements are in agreement with the presence of nano Ag particles on TiO₂ nanotubes.

3.3 AFM Analysis

The surface morphology of the TiO₂ nanotubes has been further investigated by AFM before and after nano Ag deposition process. The results are given in Fig. 5 showing the 3-D AFM images of the surfaces of TiO₂ and nano Ag/TiO₂ nanotubes. The AFM results demonstrated that the surface roughness of TiO₂ nanotubes changed after the nano Ag deposition. The TiO₂ surfaces were covered by nano Ag particles.

Fig. 4 Elemental mappings of Ag and Ti on nano Ag/TiO₂ nanotube surfaces

Fig. 5 AFM surface images of TiO_2 , Ag/ TiO_2 nanotubes

3.4 XRD Analysis

The prepared TiO_2 and nano Ag/ TiO_2 nanotubes were also examined by XRD analysis. The XRD patterns of the TiO_2 and nano Ag/ TiO_2 nanotubes are shown in Fig. 6. According to the XRD patterns of the TiO_2 nanotubes, Ti metal and Ti_3O crystalline structures were detected

[27–29]. The peaks of Ti metal come from Ti substrate as the starting material. Ti_3O phase forms during the anodization process. TiO_2 phase was not detected in crystalline form. It was concluded that the prepared TiO_2 nanotubes are in amorphous form, and this result is in agreement with the previous literature [29]. As compared to the XRD patterns of TiO_2 nanotubes, two new peaks

Fig. 6 XRD patterns of TiO₂ and Ag/TiO₂ nanotubes

Fig. 7 FT-IR spectra of Ti, TiO₂, Ag/TiO₂ nanotubes

corresponding to Ag(101) and Ag(220) of nano Ag particles were observed after nano Ag deposition by using both the deposition methods (Fig. 6) [30]. The other Ag peaks of Ag/TiO₂ nanotubes could not be identified, since they were

over placed on Ti metal peaks. The results of the XRD measurements also confirmed the deposition of the Ag nanoparticles.

3.5 FT-IR Spectroscopy

The formation of TiO₂ nanotubes during the oxidation of Ti metal surface and the nano Ag coating of the prepared TiO₂ nanotubes were investigated by FT-IR. The FT-IR measurements were taken from the TiO₂ nanotube surfaces with the ATR attachment. The obtained FT-IR spectra are compared in Fig. 7. There is no absorption band in the FT-IR spectrum of the Ti metal surface. This indicates that Ti metal surface does not include any organic and oxide covalent bonds and it is well cleaned before the TiO₂ nanotube preparation process. The FT-IR spectrum of the TiO₂ nanotubes showed a broad absorption peak at 571 cm⁻¹. This absorption peak can be attributed to the Ti–O bond. The FT-IR measurements of nano Ag/TiO₂ nanotubes resulted in different maximum absorption vibration frequencies. The broad absorption maximums of the nano Ag/TiO₂ deposited by the electroless dip coating and the anodization dip coating methods were noted at 579 and 559 cm⁻¹, respectively. These shifts are probably due to the bonding of nano Ag particles to the TiO₂.

3.6 Cyclic Voltammetry

The prepared Ti, TiO₂ nanotube, and nano Ag/TiO₂ nanotube surfaces were examined by CV method. The obtained CV voltammograms are given in Figs. 8 and 9. Firstly, the CV measurements of the Ti metal, TiO₂ nanotubes, and nano Ag/TiO₂ nanotubes were taken in 0.05 M LiClO₄ electrolyte in CH₃CN (Fig. 8a, c, e). Then, the samples were measured in 0.1 M KNO₃ electrolyte in H₂O (Fig. 8b, d, f). In the LiClO₄ electrolyte in CH₃CN, the voltammogram of the Ti metal resulted in both anodic and cathodic peaks as reversible electrochemical behaviors (Fig. 8a). However, in the KNO₃ electrolyte, only anodic peaks of Ti metal were observed (Fig. 8b). In the voltammograms of the TiO₂ nanotubes, it was seen that the anodic peaks of Ti metal disappeared (Fig. 8c, d). This means that Ti metal surface is oxidized during the preparation of the TiO₂ nanotubes. The voltammogram of the nano Ag-coated TiO₂ nanotubes in LiClO₄ electrolyte did not show any nano Ag anodic peak (Fig. 8e). LiClO₄ is a high oxidative electrolyte material. The expected anodic peak of nano Ag may not be obtained due to the probable oxidation and dissolution of Ag nanoparticles in LiClO₄ electrolyte. We have repeated the measurements in KNO₃ aqueous electrolyte. The CV voltammograms of the TiO₂ and nano Ag/TiO₂ nanotube samples in KNO₃ electrolyte at 25 mV/s were compared in separate figures (Fig. 9b, d, f). The CV

Fig. 8 CV voltammograms of Ti metal (a LiClO₄, b KNO₃), TiO₂ nanotubes (c LiClO₄, d KNO₃), nano Ag/TiO₂ nanotubes (e LiClO₄, f KNO₃)

measurements shown in Figs. 8 and 9 exhibited only anodic oxidation peaks in KNO₃ electrolyte. Thus, there is Ag⁰ and no Ag⁺ presence in nano Ag-coated nanotube samples. The use of LiClO₄ electrolyte in CH₃CN led to the partial oxidation of the Ag⁰ to Ag⁺ during the CV measurements, and we observed the presence of Ag⁺ cathodic reduction peaks in Fig. 8. It is demonstrated that the anodic peak of nano Ag at 0.94 V and another peak of residual Ti metal at 2.20 V could be detected at about 20–150 μ A current intensity by using a low scan rate of 25 mV/s (Fig. 9d, f). According to the CV results, the anodic peaks of the nano Ag deposited samples prepared by the electroless dip

coating and the anodization methods were observed at 1.30 and 0.94 V potential values, respectively (Fig. 9d, f). These decreases in the anodic peak potentials are the indications of the lower band gap values of TiO₂ nanotubes after the nano Ag deposition.

The band gap, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) energy levels of the semiconductor TiO₂ materials are important parameters in solar cells [31]. Here, the electrochemical band gap energies (E_g^{CV}) of the TiO₂ nanotubes and nano Ag/TiO₂ nanotubes were obtained from the obtained CV voltammograms (Figs. 8, 9). The

Fig. 9 CV voltammograms of TiO₂ nanotubes (**a** 100 mV/s, **b** 25 mV/s), nano Ag/TiO₂ nanotubes (**c** electroless dip coating, 100 mV/s, **d** electroless dip coating, 25 mV/s, **e** dip coating during anodization, 100 mV/s, **f** dip coating during anodization, 25 mV/s) in 0.1 M KNO₃ electrolyte

HOMO and LUMO energy levels were calculated from the oxidation and reduction potential values ($E_{1/2}$), respectively, by using Eqs. (1) and (2). The E_g^{CV} values were found from the difference of the HOMO and LUMO energies by using Eq. (3) [31–36].

$$E_{HOMO} = -(E_{1/2}^{Ox} + 4.34) \text{ eV}, \quad (1)$$

$$E_{LUMO} = -(E_{1/2}^{Red} + 4.34) \text{ eV}, \quad (2)$$

$$E_g^{CV} = -(E_{HOMO} - E_{LUMO}) \text{ eV}. \quad (3)$$

The calculated E_{HOMO} , E_{LUMO} , and E_g^{CV} of the TiO₂ and nano Ag/TiO₂ nanotubes are given in Table 1. Both the nano Ag deposition methods have resulted in the decrease of the electrochemical band gap energies.

3.7 UV-Vis Spectroscopy

Titanium dioxide, a wide band gap semiconductor, is widely used in solar cell devices as a light absorbing and an

Table 1 Electrochemical band gap energies

Energy	TiO ₂ nanotubes	Nano Ag/TiO ₂ nanotubes (anodization dip coating)	Nano Ag/TiO ₂ nanotubes (electroless dip coating)
E_{HOMO} (eV)	− 6.36	− 4.89	− 5.59
E_{LUMO} (eV)	− 3.34	− 3.34	− 3.22
E_{g}^{cv} (eV)	3.02	1.54	2.37

electron transporting material. The optical band gap energy of TiO₂ can be improved to better absorption values for the harvesting of sunlight [31–37]. The UV–Vis absorption spectroscopy is often used to determine the absorptivity coefficient of the light absorbing materials. Therefore, in this study, the UV–Vis absorption spectroscopy of Ti metal, TiO₂, and nano Ag/TiO₂ nanotubes were investigated.

The UV–Vis absorption spectra of the prepared samples are given in Fig. 10. It was found that the nano Ag deposition has improved the light absorbing property of TiO₂ nanotubes between 380 and 820 nm wavelengths. The surface of TiO₂ nanotubes absorbs the photons mostly in the UV region. The UV–Vis results showed that the nano Ag deposition increased the light absorption intensity in the visible region. Especially, the electroless dip coating method resulted in more increase of absorbance in the visible region. This means that the nano Ag/TiO₂ nanotubes are more efficient materials than the uncoated TiO₂ nanotubes for the harvesting of the sunlight.

The optical band gap energy of TiO₂ is observed between 3.0 and 3.5 eV depending on its structure [6, 38, 39]. Here, the optical band gap energy (E_{g}^{op}) of the TiO₂ nanotube sample was found as 3.26 eV from the onset of their absorption bands. Similarly, the E_{g}^{op} energies were calculated as 1.51 eV for the electroless dip-coated Ag/TiO₂ nanotubes and 2.07 eV for the anodization-coated Ag/TiO₂ nanotubes. The electroless dip coating method showed lower optical band gap energy (E_{g}^{op}).

3.8 Electrical Conductivity

The electrical conductivities of obtained TiO₂ nanotubes were measured before and after nano Ag particle depositions using the two different coating methods. The electrical conductivity results are given in Fig. 11. It was observed that both the nano Ag deposition methods improved the electrical conductivity of the TiO₂ nanotubes. The electroless nano Ag coating method has slightly increased the electrical conductivity of the TiO₂ nanotubes from 3.0×10^{-4} to 4.7×10^{-4} S/cm. The electroless deposition showed a little effect on the increase in the electrical conductivity of the TiO₂ nanotubes. However, very significant increase in the electrical conductivity was

Fig. 10 UV–Vis spectra of Ti metal, TiO₂ nanotubes, nano Ag/TiO₂ nanotubes

observed for the Ag/TiO₂ nanotubes prepared by the anodization method. The electrical conductivity of TiO₂ nanotubes increased from 3.0×10^{-4} to 34.7 S/cm after the Ag anodization deposition process. According to the literature, TiO₂ films have electrical conductivity values in the range of 10^{-4} – 10^{-7} S/cm [6]. The electrical conductivity measurements in this study showed that the Ag/TiO₂ nanotubes have higher electrical conductivity than the other TiO₂ films. As a result, the obtained nano Ag/TiO₂ nanotubes on Ti metal can be utilized as the electrode material in electronics, solar cells, and Li-ion batteries.

Nano Ag/TiO₂ nanotube surfaces on Ti can be prepared by the anodization or the electroless dip coating methods and they are both low cost and practical processes. The experimental measurements performed on nano Ag/TiO₂

Fig. 11 Electrical conductivities of TiO₂, Ag/TiO₂ nanotubes

nanotube samples demonstrated that there are significant changes in the photophysical properties of TiO₂ nanotubes. The UV–Vis, FT-IR, CV, and the band gap values were evaluated after the nanosilver coating of TiO₂ nanotubes. In this study, it has been shown that the optical and the electronic properties of TiO₂ nanotubes can be enhanced using the nanosilver particle deposition process.

4 Conclusion

In this study, we have prepared the TiO₂ nanotubes on Ti metal surfaces by the electrochemical anodization method. The prepared TiO₂ nanotubes were coated with the nano Ag particles by using the anodization dip coating and the electroless dip coating methods. The morphology, the FT-IR, the cyclic voltammetry, the UV–Vis absorption spectroscopy, the electrical conductivity, and the band gap energies of nano Ag/TiO₂ nanotubes have been investigated. The results showed that the inner diameters of TiO₂ nanotube holes are about 50–100 nm with the 25 nm wall thicknesses. It was seen that the nano Ag coating decreased the band gap energy of the TiO₂ nanotubes. The electrochemical (E_g^{CV}) and optical (E_g^{opt}) band gap energies of the nano Ag/TiO₂ nanotubes have been found as 1.54 and 1.51 eV, respectively. It was also found that the electrical conductivity of TiO₂ nanotubes increased from 3.0×10^{-4} to 4.7×10^{-4} S/cm for the electroless dip coating and to 34.7 S/cm for the anodization coating methods. The electrochemical and optical properties of the TiO₂ nanotube surfaces have been affected differently depending on the deposition method. The obtained nano Ag/TiO₂ nanotubes exhibited low band gap energy, the improved light absorption behavior, and the good electrical conductivity. In conclusion, compared to the uncoated TiO₂ nanotubes, the nano Ag/TiO₂ nanotubes are more suitable electrode materials in electronics, solar cells, photocatalysis, and Li-ion batteries.

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