

Effect of Chelating Agent on Surface Morphology and Electrochemical Properties of TiO₂ Nanotube Arrays

Hlaing Min^{*}, Min Min Thein^{**}, May Thawdar Phoo^{***} and Than Zaw Oo^{****}

Abstract

Titania (TiO₂) nanotubes were developed by electrochemical anodization method. Upon introducing the chelating agent (Na₂EDTA) in the electrochemical growth solution, the changes in surface morphology and size (diameter and length), optical absorption and electrochemical energy levels of TiO₂ nanotubes were determined by using Scanning Electron Microscopy (SEM), UV-Vis spectrophotometry with integrating sphere and cyclic voltammetry. In addition, organic dye (LEG4) was infiltrated into TiO₂ nanotubes and the effect of Na₂EDTA on the dye coverage and dye molecular levels were also investigated.

Key words: Titania nanotubes, Electrochemical anodization, Chelating agent, Optical and Electrochemical Energy Level

Introduction

TiO₂ nanotubes have attracted tremendous attention due to the combination of a wide band gap semiconductive nature with high surface area and high aspect ratio. Their excellent optical and electrical characteristics make them suitable for use in water splitting, dye-sensitized solar cells (DSSCs) and photocatalysis [1]. TiO₂ is a typical transition metal oxide semiconductor with high chemical stability, low-costs, non-toxicity, strong photocatalytic activity and high photoelectric conversion efficiency. These unique physical and chemical properties render it excellent material for solar energy conversion in dye-sensitized solar cells, heterojunction solar cells, photocatalysis, and many other applications [2]. Vertically oriented titania nanotube arrays can be synthesized by electrochemical anodic oxidation or anodization of titanium foil, generally using fluoride-based electrolytes. Well optimization of anodization parameters such as anodization voltage, time and electrolyte composition leads to a precise control of titania nanotube architectures including pore diameter, wall thickness, tube length, and surface roughness [3]. It is well known that the crystal structures of TiO₂ nanotubes can greatly affect their application performances, and in many cases amorphous TiO₂ nanotubes need to be converted to crystalline TiO₂ nanotubes in order to improve their catalytic activity, electronic conductivity or mechanical strength to achieve higher application performances [4].

In this study, we prepared TiO₂ nanotubes by electrochemical anodization of titanium metal foil in two different solutions containing ethylenediaminetetraacetic acid (10 mM and 20 mM) and compared those with anodizations made in blank solutions with no EDTA. EDTA was selected to enhance the solubility of titanium because it is a common chemical and as a strong chelating agent it captures titanium ions from their fluoro complexes formed upon dissolution of titanium metal by fluoride ions [5].

Experimental Details

Titanium sheet (99.7% purity) with a thickness of 0.2 mm was taken for the anodization. Small pieces of Ti-sheet of size 25 mm x 20 mm were ultrasonically cleaned separately in detergent, acetone and ethanol for 10 minutes each and then rinsed in distilled water and finally dried by air blow. The volume ratio of ethylene glycol (EG) to distilled

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water (DW) was fixed at 9:1 and the ammonium fluoride (NH_4F) content was 0.5 wt%. The electrolyte solution was stirred for 30 min with magnetic stirrer before anodization and stirred continuously during the anodization process. Anodization was performed at room temperature in a standard two-electrode electrochemical cell with Ti foil as the working electrode and platinum rod (diameter: 1mm; purity: 99.9%) as the counter electrode connected to a dc power supply.

The present investigation focuses on the effect of Na_2EDTA concentrations on optical and electrochemical properties of TiO_2 nanotubes. In the preparation of Na_2EDTA incorporated TiO_2 nanotubes samples, the different concentrations of chelating agent Na_2EDTA (10 mM and 20 mM) was added to the anodization solutions. The applied voltage between the titanium sample and the platinum cathode (they are 2 cm apart) was 50 V, and the anodization time was 1 hr. After anodization, TiO_2 nanotubes were rinsed with distilled water and dried in air. The anodized samples were annealed at 500°C using a digital muffle furnace (DMF 05) for 3 hr. The LEG4 dye in ethanol (4.49 mg/l) solution was prepared and stirred in ultrasonic bath about 20 min. To prepare the LEG4 dye loaded TiO_2 nanotubes samples, the anodized TiO_2 nanotubes were immersed in LEG4 dye solution for 24 hr for adsorption of dyes.

The changes in surface morphology and size (diameter and length), optical absorption and electrochemical energy levels of TiO_2 nanotubes were determined using Scanning Electron Microscopy (SEM ZEISS EVO 60), UV-Vis spectrophotometry with integrating sphere (Shimazu, UV-2600) and cyclic voltammetry (DigiIvy, DY2000).

Results and discussion

The scanning electron microscopy (SEM) image of TiO_2 nanotube arrays developed at the different concentrations of chelating agent Na_2EDTA (10 mM and 20 mM) is shown in (Fig. 1). It is clearly found that the TiO_2 nanotube arrays were well-defined and uniform morphology over large area in all the images.

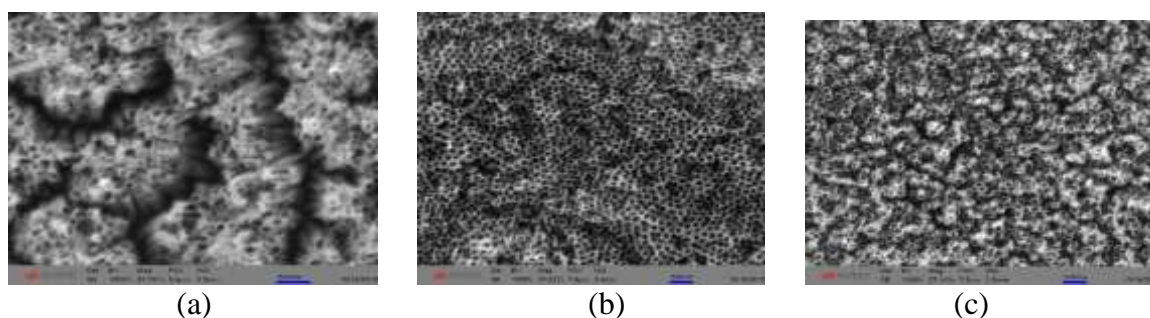


Fig. 1 SEM images (Top View) of TiO_2 nanotube arrays developed at different chelating agent (Na_2EDTA): (a) 0 mM (b) 10 mM and (c) 20 mM.

To carefully examine the diameter of TiO_2 nanotubes, the size distribution histogram were generated (Fig. 2). It is found that average inner diameter of TiO_2 nanotubes spanned from 80 nm up to 160 nm for chelating agent Na_2EDTA concentrations of (0 mM-10mM), from 100 nm up to 170 nm for chelating agent Na_2EDTA concentrations of 20mM. The highest frequency of nanotube sizes are 110 – 120 nm, 120 – 130 nm and 120 – 130 nm for chelating agent Na_2EDTA concentrations of 0 mM, 10mM and 20 mM respectively. It is noteworthy from this study that a change in chelating agent Na_2EDTA concentrations could not enable to change the diameter of nanotubes significantly.

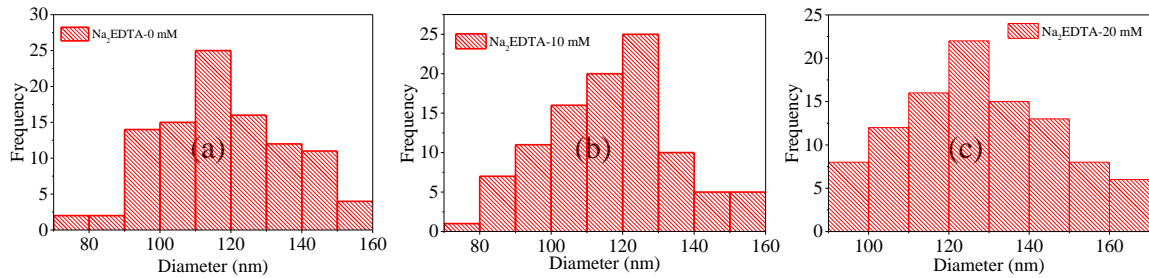


Fig. 2 Size distribution histograms of TiO₂ nanotube arrays developed at different chelating agent (Na₂EDTA): (a) 0 mM (b) 10 mM and (c) 20 mM.

Moreover, the length of TiO₂ nanotube arrays was also determined by scanning the cross-sectional view of TiO₂ nanotubes (Fig.3). From the SEM cross-sectional images of TiO₂ nanotubes, the length of the nanotubes were about 2 μm, 5 μm and 4 μm respectively.

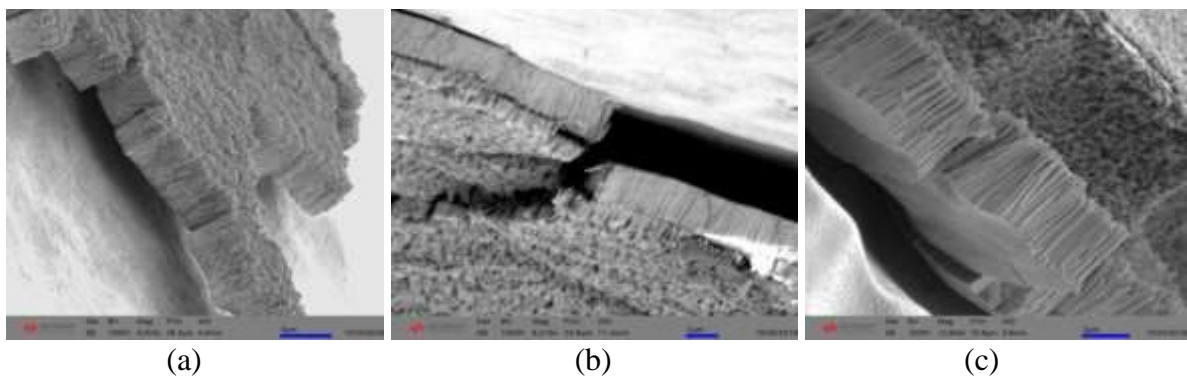


Fig. 3 SEM images (Cross-sectional view) of TiO₂ nanotube arrays developed at different chelating agent (Na₂EDTA): (a) 0 mM (b) 10 mM and (c) 20 mM.

The effect of chelating agent (Na₂EDTA) on the optical absorption of TiO₂ nanotubes and LEG4 dye loaded TiO₂ nanotubes were determined by UV-Vis spectrophotometer (Shimadzu, UV-2600) with integrating sphere. The obtained absorption spectra are shown in Fig.4. As seen in Fig.4. (a) the peak intensity below 400 nm is due to the typical absorption of the TiO₂ nanotubes while the broad peak in the visible region is attributable to the presence of the LEG4 dye on the surface of TiO₂ nanotubes as seen in Fig.4. (b). It is well known that LEG4 dye absorbs light in the visible region. It is clearly seen that upon increasing Na₂EDTA concentrations from 0 mM to 20 mM, absorption peak intensities of TO₂ nanotubes are slightly increased. In comparing the absorption peak intensities with and without chelating agent (Na₂EDTA), the absorption peak intensities of TO₂ nanotubes with chelating agent (Na₂EDTA) are higher than without chelating agent (Na₂EDTA).

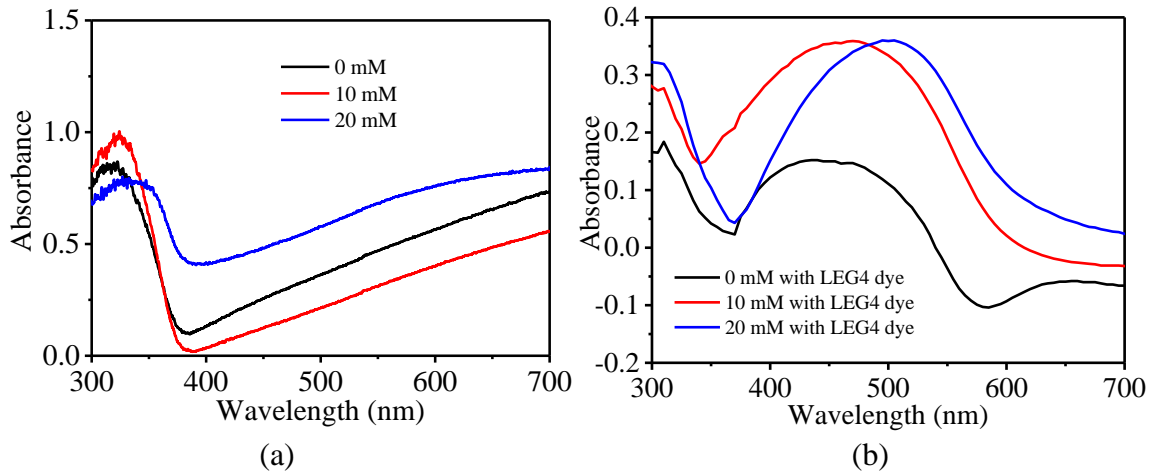


Fig. 4 Optical absorption spectra of (a) TiO_2 nanotubes and (b) LEG4 dye loaded TiO_2 nanotubes as a function of chelating agent (Na_2EDTA) concentrations.

We concentrate on the effects of Na_2EDTA incorporation and UV exposure on electrochemical properties (onset reduction potential and the peak current density) of TiO_2 nanotubes. Onset reduction potentials and the peak current densities of TiO_2 nanotubes with different concentrations of Na_2EDTA were determined from the cyclic voltammograms (Fig.5). It is observed from cyclic voltammograms of Fig.5 (a) that the onset potential for reduction of TiO_2 nanotubes in dark were observed to be -0.63 eV, -0.615 eV and -0.618 eV and onset potential under UV were -0.59 eV, -0.575 eV and -0.58 eV for TiO_2 nanotubes with Na_2EDTA concentration of 0 mM, 10 mM and 20 mM respectively. It is clearly observed that upon increasing Na_2EDTA concentrations, onset potentials of TiO_2 nanotubes slightly increased at 10 mM and decreased at 20 mM in dark and under UV light. It is also seen the effect of UV light, onset potentials of TiO_2 nanotubes are significantly changed to less negative values under UV exposure for TiO_2 nanotubes with all Na_2EDTA concentrations.

In addition, the peak current density for reduction of TiO_2 nanotubes with different Na_2EDTA in dark and under UV light are shown in Fig.5 (b). It is observed that the current densities of TiO_2 nanotubes with Na_2EDTA (0 mM, 10 mM and 20 mM) were 0.81 mA/cm^2 , 0.75 mA/cm^2 and 0.59 mA/cm^2 in dark and increased to 1.61 mA/cm^2 , 1.44 mA/cm^2 and 1.11 mA/cm^2 under UV light. As seen in Fig.5 (b), upon increasing Na_2EDTA concentrations from 0 mM to 20 mM with step interval of 10 mM, peak current densities of TiO_2 nanotubes are slightly decreased. In comparing the current densities of TiO_2 nanotubes in dark and under UV, the peak current densities of TiO_2 nanotubes are higher under UV irradiation.

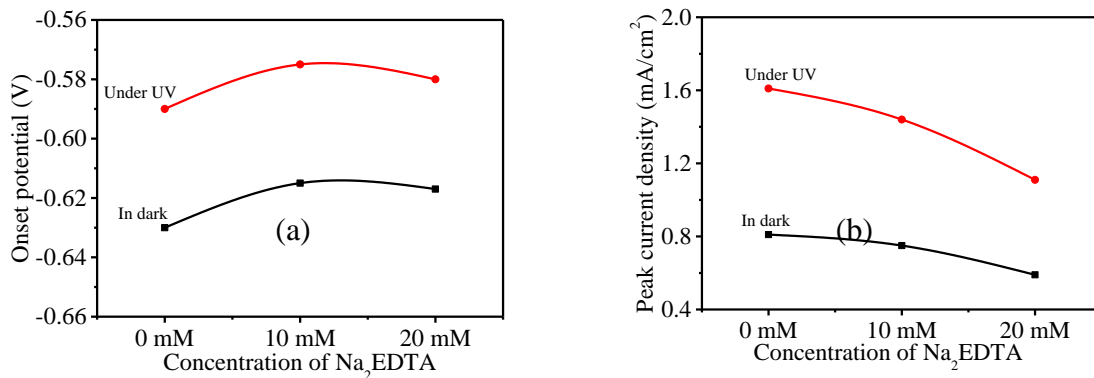


Fig. 5 (a) Onset reduction potential and (b) peak current density of TiO_2 nanotubes in dark and under UV light as a function of Na_2EDTA concentration.

Fig. 6 depicts the onset reduction potentials and peak current densities of LEG4 dye loaded TiO₂ nanotubes in dark and under UV light as a function of Na₂EDTA concentrations. The onset potentials for reduction of TiO₂ nanotubes in dark were observed to be -0.79 eV, -0.78eV and -0.8 eV and onset potentials under UV were observed to be -0.76 eV, -0.75 eV and -0.77 eV for LEG4 dye loaded TiO₂ nanotubes with Na₂EDTA concentrations of 0 mM, 10 mM and 20 mM respectively. It is seen that in dark and under UV light, the onset potentials of LEG4 dye loaded TiO₂ nanotubes are slightly increased for the Na₂EDTA concentration of 10 mM and decreased again at higher Na₂EDTA concentration of 20 mM. It is also seen the effect of UV light, onset potentials of TiO₂ nanotubes are significantly changed to less negative values under UV exposure for all Na₂EDTA concentrations. In addition, the peak current density for reduction of LEG4 dye loaded TiO₂ nanotubes with different Na₂EDTA in dark and under UV light are shown in Fig.6 (b). It is observed that the current densities of LEG4 dye loaded TiO₂ nanotubes with Na₂EDTA (0 mM, 10 mM and 20 mM) were 0.7 mA/cm², 0.68 mA/cm² and 0.78 mA/cm² in dark and 0.8 mA/cm², 0.73 mA/cm² and 0.74 mA/cm² under UV light. As seen in Fig.6 (b), upon increasing Na₂EDTA concentrations from 0 mM to 10 mM, peak current density of LEG4 dye loaded TiO₂ nanotubes in dark are slightly decreased and increased again at higher Na₂EDTA concentration of 20 mM. It is also observed that the peak current densities of LEG4 dye loaded TiO₂ nanotubes under UV light. In comparing the current densities of LEG4 dye loaded TiO₂ nanotubes in dark and under UV light, the peak current densities of LEG4 dye loaded TiO₂ nanotubes are higher under UV at Na₂EDTA concentrations of 0 mM and 10 mM and slightly decreased at Na₂EDTA concentration of 20 mM.

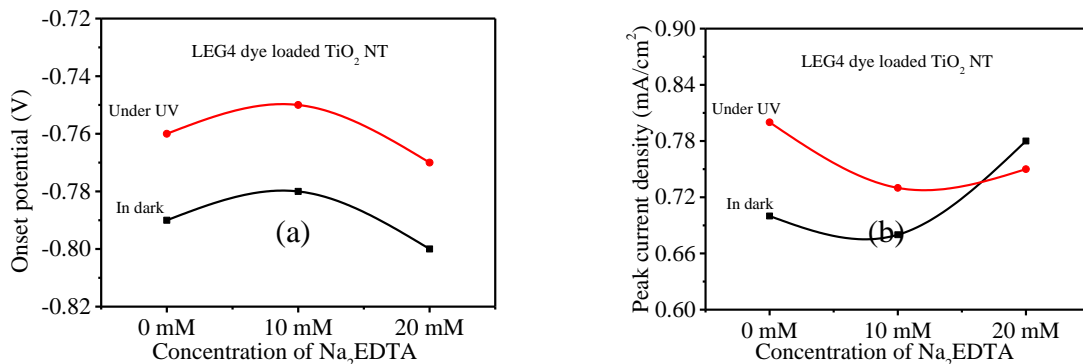


Fig. 6 (a) Onset reduction potential and (b) peak current density of LEG4 dye loaded TiO₂ nanotubes in dark and under UV light as a function of Na₂EDTA concentration.

The energy levels (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of LEG4 dye loaded TiO₂ nanotubes with chelating agent (Na₂EDTA) (0 mM, 10 mM and 20 mM) were estimated using electrochemical cyclic voltammetry (CV) measurement together with UV-Vis absorption measurement. From the onset reduction potentials of LEG4 dye loaded TiO₂ nanotubes, the LUMO levels were calculated using the following equation [6];

$$E_{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} + 4.4 \text{ eV})$$

where, $E_{\text{red}}^{\text{onset}}$ are the onset potentials of reduction. For the calculation of HOMO energy levels of LEG4 dye loaded TiO₂ nanotubes, the following equation was used.

$$E_{\text{HOMO}} = E_{\text{g}} + E_{\text{LUMO}}$$

where E_{g} = optical band gap energy of LEG4 dye which is around 2.15 eV and determined from optical absorption spectra of LEG4 dye solution.

Table 1 represents the calculated HOMO and LUMO energy levels of LEG4 dye loaded TiO₂ nanotubes as a function of Na₂EDTA concentrations in dark and under UV light. It is seen in the Table 1 that the positions of the calculated HOMO and LUMO levels of LEG4 dye loaded TiO₂ nanotubes with Na₂EDTA from 0 mM to 20 mM do not change significantly in dark and under UV light.

Table 1 Calculated HOMO and LUMO energy levels and band gap energies of LEG4 dye loaded TiO₂ nanotubes as a function of Na₂EDTA concentrations in dark and under UV light.

| LEG4 dye loaded TiO ₂ nanotubes | In dark | | Under UV | |
|---|-------------|--------------|-------------|--------------|
| | LUM (eV) | HOMO (eV) | LUM (eV) | HOMO (eV) |
| Na ₂ EDTA (0 mM) | -3.61 | -5.76 | -3.64 | -5.79 |
| Na ₂ EDTA (10mM) | -3.62 | -5.77 | -3.65 | -5.80 |
| Na ₂ EDTA (20mM) | -3.60 | -5.75 | -3.63 | -5.78 |

The energy levels for HOMO and LUMO of LEG4 dye loaded TiO₂ nanotubes with Na₂EDTA concentration of 0 mM, 10 mM and 20 mM in dark and under UV light are illustrated in Fig. 7. The driving force for regeneration is determined by the energy difference between a HOMO level of a dye and the redox potential of a redox couple. Since the HOMO levels of LEG4 dye on TiO₂ nanotubes with and without Na₂EDTA are almost invariant, thus the possibility of electron regeneration from the redox potential of electrolyte to HOMO level of LEG4 dye is almost the same. It seems that the incorporation of chelating agent (Na₂EDTA) do not effect on the electron regeneration efficiency at redox/dye interface.

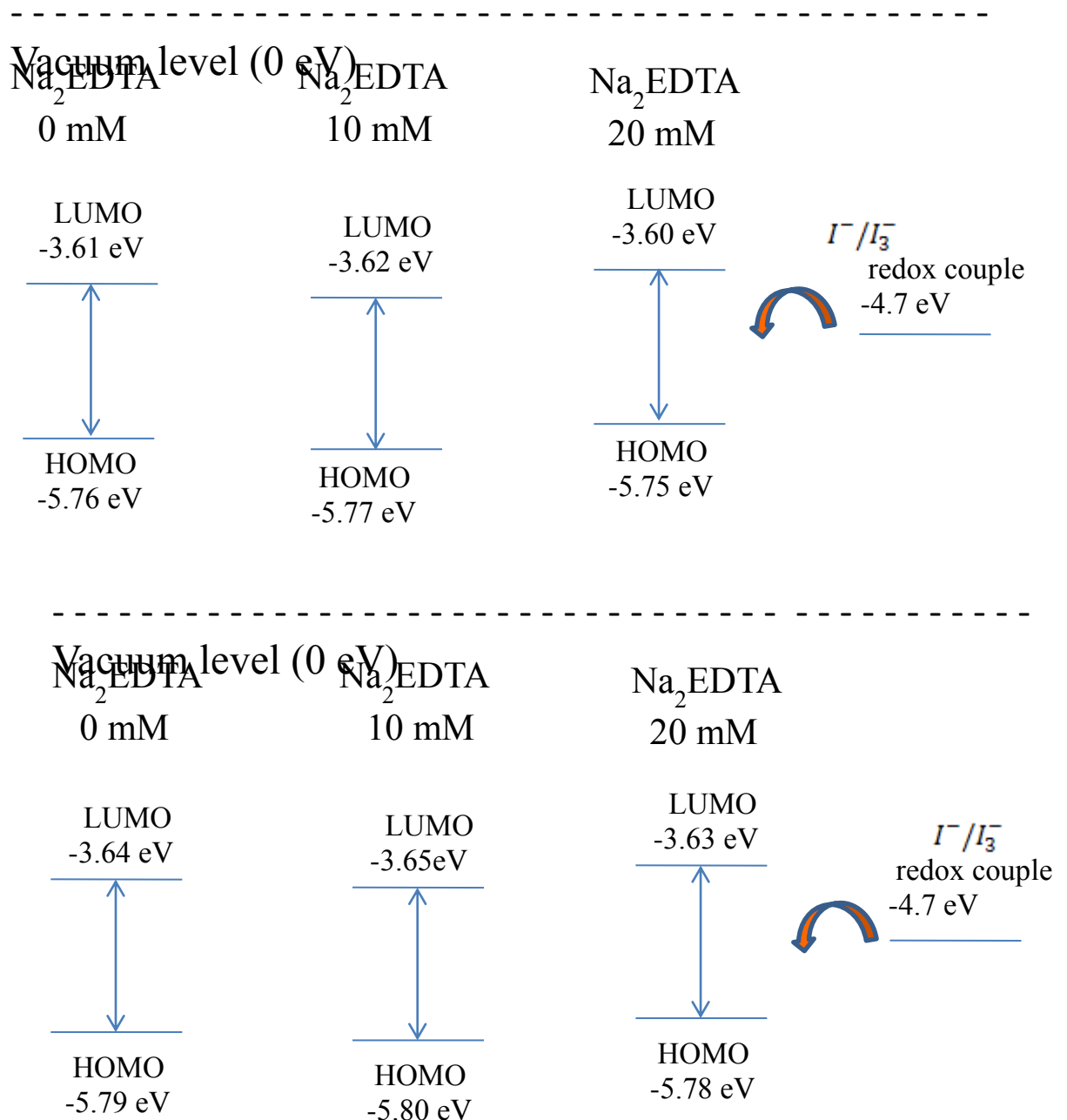


Fig. 7 Energy levels for HOMO and LUMO of LEG4 dye loaded TiO₂ nanotubes with Na₂EDTA concentration of 0 mM, 10 mM and 20 mM (a) in dark and (b) under UV light. The energy level of I⁻/I₃⁻ redox couple is also shown.

Summary and Conclusion

Scanning Electron Microscopy (SEM) investigation shows that an increase in chelating agent Na₂EDTA does not significantly modulate the diameter of TiO₂ nanotubes (around 130 nm), but increases their length up to 5 μm at Na₂EDTA concentration of 10 mM. The optical absorption below 400 nm is due to the typical absorption of the TiO₂ while the broad peak in the visible region is attributable to the presence of the LEG4 dye on the surface of TiO₂ nanotubes. The LEG4 dye loaded TiO₂ nanotubes are intended to be used as photoanode in dye-sensitized solar cells (DSSC). The electrochemical energy levels

(specifically highest occupied molecular orbital) of the LEG4 dye loaded TiO₂ nanotubes are almost unchanged upon introducing chelating agent (Na₂EDTA). The regeneration efficiency of electron from I⁻/I₃⁻ redox couple to LEG4 dye is determined by the energy different between HOMO of dye and redox potential. The HOMO levels of LEG4 dye on TiO₂ nanotubes with and without Na₂EDTA are almost invariant, the possibility of electron regeneration from the redox potential of electrolyte to HOMO level of LEG4 dye is almost the same.

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References

- [1] H. Yin, *et al.*, Nanotechnology **21**, (2010) 1.
- [2] J. Yan, *et al.*, J. Mater. Chem. **21**, (2011) 9406.
- [3] S. Yoriya, *et al.*, J. Chem. Chem. Eng. **6**, (2012) 686.
- [4] Z. Su, *et al.*, Mater. Int. **23**, (2013) 294.
- [5] J. Tupala, *et al.*, J. Electrochem. Soc. **161**, (2014) 61.
- [6] L. Andery, *et al.*, J. Sol. Energy. **135** (2013) 1.