

# Optical properties of TiO<sub>2</sub> nanorods modified by electron-donating stabilizers

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**Abstract**—A significant change in the UV-vis absorption of TiO<sub>2</sub> nanorods (NRs) was induced by changing electron-donating stabilizer from oleic acid (OA) to acrylic acid (AcA). When TiO<sub>2</sub> NRs with an average size of 2.5 nm in diameter and 30 nm in length were dispersed in an aqueous AcA solution, a red shift in the optical absorption (0.73 eV at the band edge and 0.55 eV at the onset) was observed. The red shift was attributed to an increase in the electron density inside the TiO<sub>2</sub> NRs. The applicability of the AcA-exchanged TiO<sub>2</sub> NRs for the photocatalyst as well as a UV sensor was evaluated. The AcA-exchanged TiO<sub>2</sub> NRs showed significant photocatalytic activity on the degradation of toluene in the visible light region. Moreover, thin film of the AcA-exchanged TiO<sub>2</sub> NRs on a quartz plate was tested as a UV sensor and it exhibited a good response to a wide range of the UV light.

Key words: Red Shift, Optical Absorption, TiO<sub>2</sub> Nanorod, Photocatalyst, UV Sensor

## INTRODUCTION

Wide band gap semiconductors such as TiO<sub>2</sub> and ZnO have a great potential for applications in many areas [1]. The band gap energy of TiO<sub>2</sub> and ZnO (3.2 eV for bulk anatase TiO<sub>2</sub> and 3.3 eV for bulk ZnO) lies in the UV region, which comprises only a small fraction of the sun's energy (<10%) [1,2]. However, by doping these materials with other elements or by modifying their surface with other photo-sensitive compounds, the optical activity of these semiconductors can be increased and the onset of the optical absorption can be shifted from the UV to the visible light region. This kind of behavior would be beneficial to the optical applications of these semiconductors [1].

To improve the optical activity of semiconductors through surface modification, many scientists have studied the interaction of aromatic compounds with the surface of the semiconductors [1,2]. Among the various semiconductors, TiO<sub>2</sub> has received much attention due to a large red shift observed in the UV-vis absorption spectra. The red shift is caused by the injection of delocalized electrons from hydrocarbon rings in the surface agents to the conduction band of the semiconductors through covalent bonds [1,2]. In contrast to the ring compounds, stabilizers with highly saturated hydrocarbon chains generally do not have a significant impact on the optical absorption of semiconductors because these stabilizers are not effective electron donors [3,4]. Many electron-donating stabilizers can enhance [5-7] or quench [5,8,9] photoluminescence (PL) and affect the PL quantum yield [5,10,11] of semiconductors. Even though the effect of stabilizer was not significant in the case of UV-vis absorption spectra, one of the largest red shifts was 10 nm for CdSe quantum dots modified with dithiocarbamate [4]. Due to the negligible influence of highly saturated hydrocarbon chain stabilizers on the optical absorption of semiconductors, there has been little effort to increase the absorption shift or to interpret these phenomena in

detail. However, from our preliminary experiments, we found that the AcA-exchanged TiO<sub>2</sub> NRs used in the previous investigation [12] might be possible to show a significant change in the optical absorption, which made us investigate further the optical properties of TiO<sub>2</sub> NRs modified by electron-donating stabilizers.

In this work, in order to show the effects of stabilizers on the optical properties of TiO<sub>2</sub> NRs, the changes of the PL spectra as well as the UV-vis absorption spectra have been measured. The TiO<sub>2</sub> NRs modified with acrylic acid were used to show their potential applicabilities in the areas of the photocatalysis and the sensing of UV light.

## EXPERIMENTAL

### 1. Materials

Acrylic acid (AcA, 99%), oleic acid (OA, 90%), titanium (IV) isopropoxide (TTIP, 97%), tetramethylammonium hydroxide (TMAH, 25 wt% in H<sub>2</sub>O), and hexane (mixture of isomers, 98.5%) were obtained from Sigma-Aldrich. High purity water (18 MΩ cm) was made using a Millipore Q-guard 2 purification system, and used in the hydrolysis reaction of TTIP as well as in the ligand exchange. Ethanol (Daejung Company, Korea, 95%) was used as an anti-solvent in recovery and separation of nanocrystals. All chemicals were used as received without further purification.

### 2. Synthesis of Hydrophobic TiO<sub>2</sub> NRs

TiO<sub>2</sub> NRs with an average 2.5 nm diameters and 30 nm lengths (or 3.5 nm diameters and 30 nm lengths) were prepared by using the procedure described by Cozzoli et al. [13] with small modification. Typically, 35 g OA was dried at 100 °C for 1 hr with vigorous stirring in a 100 mL three-neck flask connected to a reflux condenser under nitrogen atmosphere. Four grams of TTIP was then added to the flask and stirred for 5 min to form a Ti-oleic complex. The hydrolysis reaction was initiated by rapid injection of 3 mL of 2 M aqueous TMAH solution into the flask. The solution was maintained at 100 °C and stirred under mild reflux over 48 hrs to promote further hydrolysis and crystallization. After cooling to room

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temperature, TiO<sub>2</sub> NRs were readily precipitated by the addition of excess ethanol to the reaction mixture. The resulting precipitate was isolated by centrifugation and then redispersed in 40 mL hexane.

### 3. Synthesis of Hydrophilic TiO<sub>2</sub> NRs through the Ligand Exchange

The procedure for the synthesis of AcA-exchanged TiO<sub>2</sub> using AcA is described in the previous investigation [12]. For a typical experiment, 3.6 mL of AcA and 0.4 mL of water were first loaded into a 10 mL vessel and stirred for 5 min. Then, 4 mL of TiO<sub>2</sub>-hexane solution (0.1 g of TiO<sub>2</sub>) was loaded into a 5 mL syringe and slowly added to the vessel without stirring. Within 5 min, white precipitate was formed and suspended in the interface. TiO<sub>2</sub> NRs started slowly transferring into the AcA solution side, and the process was completed within 8 hrs. A transparent yellow AcA solution was col-

lected and used for characterization without centrifugation.

### 4. Characterization

Transmission electron microscopy (TEM) images were obtained with a JEM 2011 Hitachi S-4200 operated at 200 kV. Field emission scanning electron microscopy (FE-SEM) was performed with a JEOL JSM-6300F at an accelerating voltage of 10 kV. X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermo VG Scientific Escalab 250 spectrometer. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q50. Ultraviolet-visible (UV-vis) spectra were measured with an Analytikjena Specord S-600. PL measurements were obtained with a Hitachi F-2500 fluorescence spectrophotometer. A gas chromatograph (Agilent Tech., 6890N) equipped with a HP-5 capillary column (0.32 mm ID, 30 m L, and 0.25 mm film thickness) was used to measure the concentration of toluene in the photocatalytic reactions. The resistance response of the TiO<sub>2</sub> thin films under UV light was measured with a Keithley 4200 SCS.

## RESULTS AND DISCUSSION

### 1. Photoluminescence (PL) Properties of TiO<sub>2</sub> NRs

Shown in Fig. 1(a) are the PL emission spectra of the TiO<sub>2</sub> NRs; several sharp bands over a wide wavelength range are evident. The positions of the PL bands were almost identical regardless of the ligand type (OA or AcA). After the ligand exchange, the emission intensity increased to a wavelength greater than 400 nm, especially around 485.2 nm. The enhancement in the emission intensity is an indicator that the presence of AcA improved the surface passivation of the TiO<sub>2</sub> nanocrystals [5,6]. The positions of peaks in the emission spectra of the TiO<sub>2</sub> NRs were different from those of TiO<sub>2</sub> nanoparticles [14] or nanosheets [15,16], but were similar to those of TiO<sub>2</sub> nanotubes [17]. Like the observed emission spectra, the excitation spectra of the OA-coated and AcA-exchanged TiO<sub>2</sub> NRs (Fig. 1(b)) were similar in terms of position. It was also found that

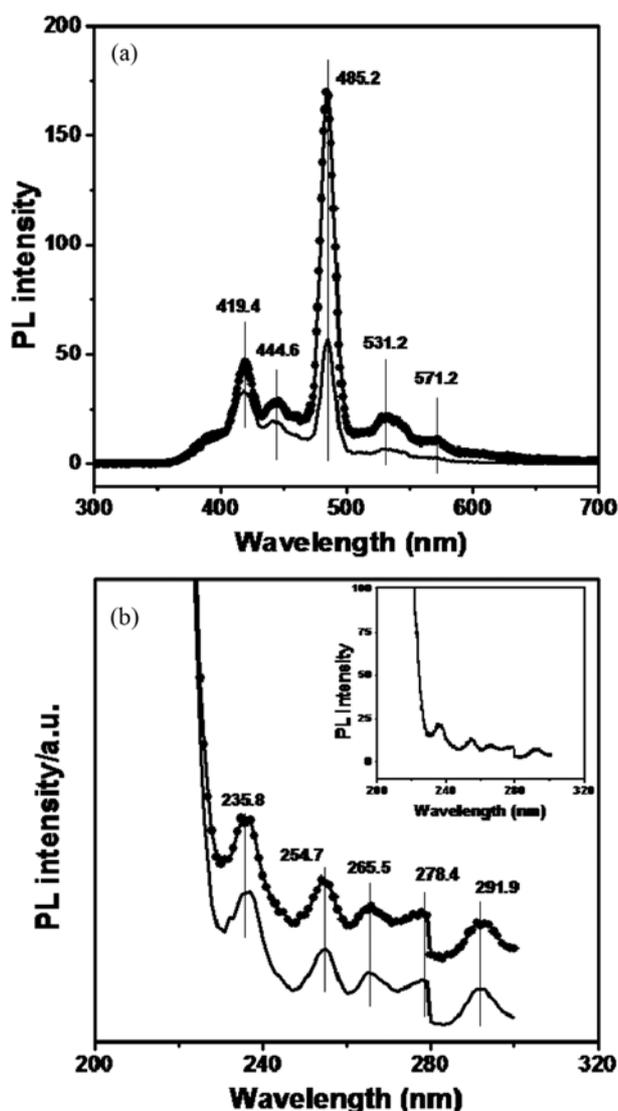


Fig. 1. (a) PL emission and (b) excitation spectra of the OA-coated TiO<sub>2</sub> NRs dispersed in hexane (—) and the AcA-exchanged TiO<sub>2</sub> NRs in aqueous AcA solutions (---). Inset: Excitation spectra of the TiO<sub>2</sub> NRs in absolute intensity. The concentration of TiO<sub>2</sub> in each solution was 35 mmol. The used excitation wavelength and emission wavelength were 237 nm and 400 nm, respectively [17].

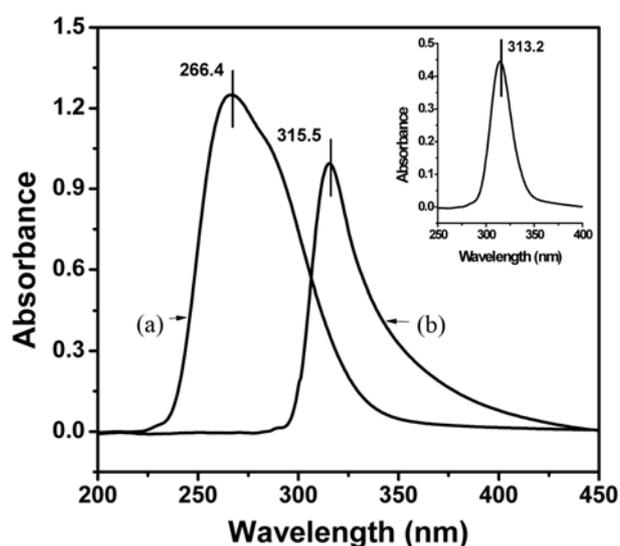


Fig. 2. UV-vis spectra of (a) OA-coated TiO<sub>2</sub> NRs in hexane and (b) AcA-exchanged TiO<sub>2</sub> NRs in aqueous solutions (0.12 mmol TiO<sub>2</sub>). The UV-vis absorption of acrylic-Ti complex (0.12 mmol TiO<sub>2</sub>) is shown in the inset.

**Table 1. Binding energies (eV) of the TiO<sub>2</sub> NRs**

Materials	C1s (C-C)	C1s (C-O)	O1s (O-C)	O1s (O-Ti)	Ti2p (3/2)	Ti2p (1/2)	Ti3p
OA-coated TiO <sub>2</sub>	284.92	288.60	531.46	529.62	458.63	464.33	37.21
AcA-exchanged TiO <sub>2</sub>	284.51	288.43	531.46	529.86	458.39	464.17	36.85

the excitation peaks of the TiO<sub>2</sub> NRs matched well with those of TiO<sub>2</sub> nanotubes [17].

## 2. Absorption Properties of TiO<sub>2</sub> NRs

Fig. 2 shows the UV-vis spectra of OA-coated and AcA-exchanged TiO<sub>2</sub> NRs dispersed in hexane and aqueous AcA solutions, respectively. After the OA on the TiO<sub>2</sub> surface was exchanged with AcA, the optical properties of the TiO<sub>2</sub> changed significantly. For example, the absorption edge band shifted from 266.4 to 315.5 nm (~0.73 eV) and the absorption onset shifted from 350 nm to 415 nm (~0.55 eV). The peak at 315.5 nm for the AcA-exchanged TiO<sub>2</sub> NRs arose from the absorption of the TiO<sub>2</sub> NRs rather than from the absorption of other species (OA, water, AcA, and hexane) in the aqueous AcA solution or from the aggregation of TiO<sub>2</sub> NRs. Therefore, we concluded that the large red shift in the UV-vis spectra was caused only by the change of the ligand from OA to AcA. As explained below, the ligand change resulted in an increase in the electron density inside the TiO<sub>2</sub> NRs.

The binding energies of the TiO<sub>2</sub> NRs obtained from XPS analysis are summarized in Table 1. After the ligand exchange, the binding energy of the carbons in the alkane chain (C-C) varied from 284.92 to 284.51 eV and that of carbons in the carboxylic group (C-O) decreased from 288.60 to 288.43 eV [18]. The intensity ratio of C-O/C-C increased significantly because the ratio of C-O/C-C bonds in AcA was much greater than that in OA. The binding energy of oxygen coordinated with Ti (O-Ti) increased from 529.62 to 529.86 eV, whereas those of Ti decreased. The decreased binding energies of titanium in the AcA-exchanged TiO<sub>2</sub> NRs implies the existence of a lower state of Ti<sup>3+</sup>, which could result in a red shift in the UV-vis absorption of the TiO<sub>2</sub> NRs [19,20].

The elemental surface compositions of the TiO<sub>2</sub> NRs are shown in Table 2. After the ligand exchange, the content of carbon on the TiO<sub>2</sub> surface decreased, while the concentration of O and Ti increased. In a previous report [12] we concluded that OA on the TiO<sub>2</sub> surface was completely replaced by AcA through the ligand exchange. Therefore, if only OA and AcA were present on the TiO<sub>2</sub> surface before and after the surface modification, it could be calculated that the number of AcA molecules was 2.33 times greater than the number of OA molecules.

In addition to the XPS analysis, TGA measurements were also performed to determine the total amount of organic materials on the TiO<sub>2</sub> NR surface. As shown in Table 2, the weight loss of the OA-coated TiO<sub>2</sub> NRs was 38.8% and was caused by the decomposition of OA on the TiO<sub>2</sub> surface. After the ligand exchange with

AcA, the weight loss decreased to 26.6%. Based on the weight losses observed in the TGA, the number of AcA molecules was calculated to be 2.24 times greater than the number of OA molecules, which is in good agreement with the XPS results.

It is well-known that the interaction between stabilizers and colloidal nanocrystals is usually a donor-acceptor interaction [21]. As shown from the XPS and TGA measurements, the number of COO<sup>-</sup> groups attached to the TiO<sub>2</sub> surface increased by more than 2.2 times after the ligand exchange. The increased number of COO<sup>-</sup> groups in the AcA-exchanged TiO<sub>2</sub> NRs resulted in a high electron density comparing to the original OA-coated TiO<sub>2</sub>. Currently, it is believed that no reliable method exists that can directly measure the electron density in nanomaterials. However, theoretical calculations by Diaz et al. [3] showed that a higher electron density in semiconductor materials could shift their optical absorption to a lower energy region. The higher electron density led to an increase in Coulombic interactions between the excited states of electrons in the TiO<sub>2</sub> NRs, which reduced the overall electron localization. This in turn induced a red shift in the UV-vis absorption of the AcA-exchanged TiO<sub>2</sub> [22]. This phenomenon was similar to the red shift in the MoS<sub>4</sub><sup>2-</sup>-CdS nanoparticle system which showed a shift of 0.06 eV when MoS<sub>4</sub><sup>2-</sup> ions were adsorbed on the CdS surface [3].

Braginsky et al. [23] showed that the absorbance intensity of TiO<sub>2</sub> was enhanced with an increase in the electron density inside TiO<sub>2</sub> nanocrystals. However, as shown in Fig. 2, the UV-vis absorbance intensity of the AcA-exchanged TiO<sub>2</sub> NRs decreased even though the electron density inside the TiO<sub>2</sub> was increased. When the TiO<sub>2</sub> surface was covered by AcA, the complex between the AcA and the TiO<sub>2</sub> surface also affected the absorbance intensity [1,23]. The absorbance intensity of the acrylic-Ti complex in solution was low (Fig. 2, inset) and may be similar to the acrylic-Ti complex on the TiO<sub>2</sub> surface [13,24]. Therefore, the decrease in the absorbance intensity in the AcA-exchanged TiO<sub>2</sub> NRs may be explained based on the combination of two competing effects. The increasing factor was the high electron density inside the TiO<sub>2</sub> cores, while the decreasing factor was the presence of the acrylic-Ti complex on the TiO<sub>2</sub> surface. Therefore, the decrease in the absorbance intensity of the AcA-exchanged TiO<sub>2</sub> NRs was thought to be caused by the more dominant decreasing effect of the acrylic-Ti complex on the TiO<sub>2</sub> surface.

## 3. Photocatalytic Activities of TiO<sub>2</sub> NRs in the Visible Region

As mentioned previously, the surface modification of the TiO<sub>2</sub> NRs shifted the UV-vis absorption to the longer wavelength (red

**Table 2. Elemental surface compositions and percentage of organic material in the TiO<sub>2</sub> NRs**

Materials	XPS			TGA		
	Elemental surface composition (atom %)			AcA/OA ratio	Weight loss (%)	AcA/OA ratio
	C	O	Ti			
OA-coated TiO <sub>2</sub>	59.70	26.81	13.49	2.33	38.8	2.24
AcA-exchanged TiO <sub>2</sub>	37.46	40.77	21.77			

shift) and the onset of the light absorption could be observed even at the visible light region. Therefore, it is natural to expect that the surface-modified TiO<sub>2</sub> NRs should show photocatalytic activities in the visible light region. To check the catalytic activities, two kinds of TiO<sub>2</sub> NRs, i.e., the OA-coated TiO<sub>2</sub> NRs and the AcA-exchanged TiO<sub>2</sub> NRs, were used as photocatalysts for the degradation of gaseous toluene. The photocatalysts on the glass slides were prepared by spin-coating the OA-coated TiO<sub>2</sub> solution or the AcA-exchanged TiO<sub>2</sub> aqueous solution (2 wt% TiO<sub>2</sub>) and subsequent drying at 120 °C for 24 hr. For the photocatalytic reactions, the glass slides with catalyst film (200 cm<sup>2</sup>) were placed inside the reactor (1,500 cm<sup>3</sup>) where the initial concentration of gaseous toluene was 0.05 mol/m<sup>3</sup>. Since the presence of water molecules enhanced the oxidation rate of toluene [25], the initial water vapor concentration was kept as 0.3 mol/m<sup>3</sup>. The temperature of the jacketed reactor was maintained at 20 °C with temperature-controlled circulating water. The photocatalytic reactions were promoted by the visible light generated from four tungsten lamps (4 × 100 W) placed around the reactor.

Fig. 3 shows the change of the toluene concentration with reaction time. When the OA-coated TiO<sub>2</sub> NRs were used as catalyst, it clear that the photodegradation of toluene did not occur. The OA-coated TiO<sub>2</sub> NRs did not have any photocatalytic activities in the visible light region. However, in the case of the AcA-exchanged TiO<sub>2</sub> NRs, the degradation of toluene took place and the conversion reached 28% after 24 h irradiation. This conversion was low compared to the photocatalytic activities of the previous investigations [26-28] using doped TiO<sub>2</sub> materials because of a small visible light absorption in the AcA-exchanged TiO<sub>2</sub> NRs and a small free area (not covered by AcA) to adsorb toluene. The decomposition reaction of toluene was induced by absorption of visible light that generates hole (h<sup>+</sup>) and electron (e<sup>-</sup>) inside the AcA-exchanged TiO<sub>2</sub> NRs [1], i.e., the magnitude of the visible light absorption greatly affected the photodegradation rates. The generated charge carriers then migrated to the TiO<sub>2</sub> surface and reacted with toluene adsorbed on the surface. When the photodegradation rate of toluene using the AcA-exchanged TiO<sub>2</sub> NRs is described as first order, the reaction rate constant is calculated to be 0.01384 h<sup>-1</sup>. After the reaction, the catalysts were analyzed again using FT-IR, UV-vis and TGA

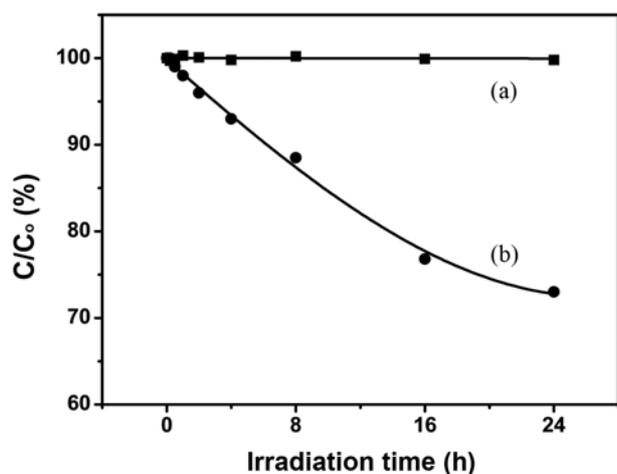


Fig. 3. Photodegradation of toluene under visible light using (a) OA-coated TiO<sub>2</sub> and (b) AcA-exchanged TiO<sub>2</sub> as catalysts.

measurements. The results (not presented in the manuscript) showed that the characteristics of the used catalysts were almost unchanged and were stable during the photodegradation reaction of gaseous toluene.

#### 4. Application of TiO<sub>2</sub> NRs to a UV Sensor

A new composite material was fabricated by combining OA-coated and AcA-exchanged TiO<sub>2</sub> NRs. This composite was expected to exhibit absorption responses in an extremely broad UV range. To see if this was the case, a double-layer thin film of OA-coated and AcA-exchanged TiO<sub>2</sub> NRs on a quartz slide was fabricated by spin-coating each layer at 2,000 rpm for 15 seconds and drying it at 120 °C for 24 h. As shown in Fig. 4A, the double-layer TiO<sub>2</sub> thin film exhibited light absorption in a broad wavelength range from

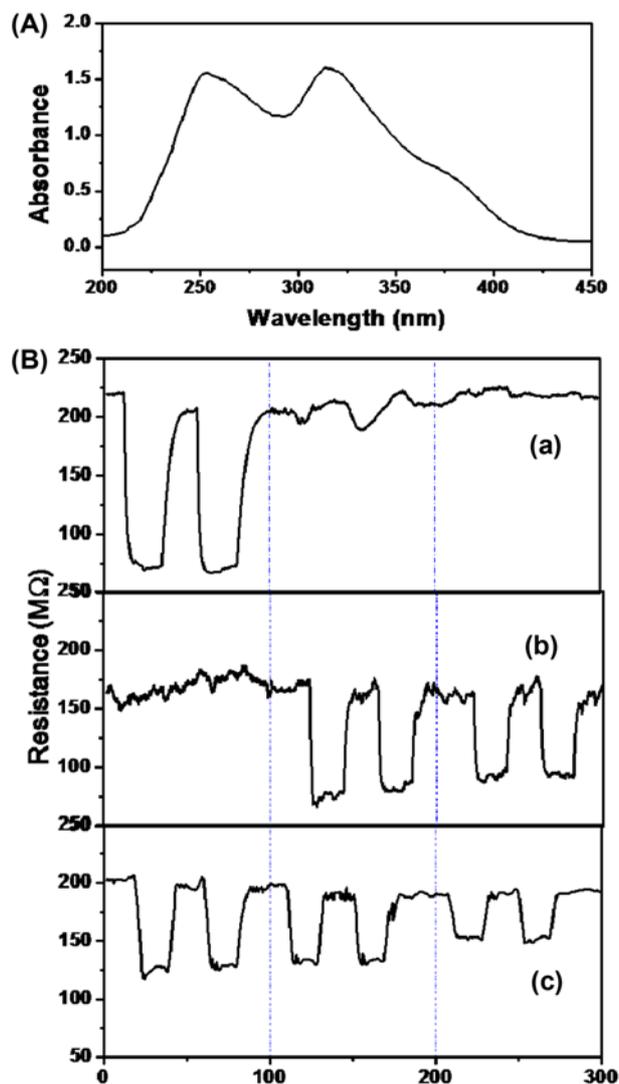


Fig. 4. (A) UV-vis spectrum of a double-layer thin film of OA-coated TiO<sub>2</sub> NRs in hexane (1 wt% TiO<sub>2</sub>) and AcA-exchanged TiO<sub>2</sub> NRs in an aqueous solution (1 wt% TiO<sub>2</sub>) on a quartz slide. (B) Resistance responses of the TiO<sub>2</sub> films upon irradiation with 254-380 nm UV light. The films were made from (a) OA-coated TiO<sub>2</sub> NRs in hexane (10 wt% TiO<sub>2</sub>), (b) AcA-exchanged TiO<sub>2</sub> NRs in an aqueous solution (10 wt% TiO<sub>2</sub>), (c) double-layer of OA-coated TiO<sub>2</sub> NRs and AcA-exchanged TiO<sub>2</sub> NRs.

225 to 400 nm. Therefore, this composite film was thought to be potentially applicable in such areas as UV sensors and photocatalysis.

To show the potential of double-layer TiO<sub>2</sub> NRs, three thin films were fabricated: one film of OA-coated TiO<sub>2</sub> NRs, one film of AcA-exchanged TiO<sub>2</sub> NRs, and one double-layer consisting of each NR. It is well-known that photon absorption by semiconductors can reduce their electrical resistance because electrons in semiconductor materials are excited to the conduction bands [29-31]. In this work, the three films were irradiated with UV light with wavelengths of 254, 365, and 380 nm. As shown in Fig. 4B, at wavelength of 254 nm, the resistances of the OA-coated TiO<sub>2</sub> film decreased to low values after irradiation with UV light for 20 s. The resistance values quickly returned to their initial states when the UV light was turned off. The resistances of the AcA-exchanged TiO<sub>2</sub> film did not show any signals under 254 nm UV light. However, at wavelengths of 365 and 380 nm, the AcA-exchange TiO<sub>2</sub> film exhibited clear signals after irradiation with UV light, while no signal was detected for the OA-coated TiO<sub>2</sub> film. As expected from the UV-vis absorption results for the double-layer TiO<sub>2</sub> NRs (Fig. 4A), the signals persisted from 254 to 380 nm, as shown in Fig. 4B(c). As a result, the double layer of OA-coated and AcA-exchanged TiO<sub>2</sub> NRs exhibited clear signals over a broad UV range. Such behavior is beneficial for UV sensor applications [29-31].

## CONCLUSIONS

The optical properties of TiO<sub>2</sub> NRs have been varied significantly by changing their electron-donating stabilizers from OA to AcA. After the ligand exchange, the PL emission intensity increased at wavelengths greater than 400 nm, whereas the PL excitation intensity remained unchanged. In the UV-vis absorption result for stabilized TiO<sub>2</sub> NRs, the absorption wavelength shifted significantly to a lower energy (red shift) by changing the stabilizer from OA to AcA. It was concluded that the red shift was caused by an increase in the electron density inside the TiO<sub>2</sub> NRs after the ligand exchange. Through XPS and TGA measurements, the increase in the electron density was confirmed by the presence of 2.2 times more COO<sup>-</sup> groups on the TiO<sub>2</sub> surface after the ligand exchange with AcA. A decrease in the absorbance intensity of the TiO<sub>2</sub> was explained as the effect of two competing phenomena, i.e., weak light absorption of the acrylic-Ti complex and the existence of a high electron density inside the TiO<sub>2</sub> cores.

The applicabilities of the AcA-exchanged TiO<sub>2</sub> NRs for the photocatalyst as well as the UV sensor were evaluated. In order to check the photocatalytic activities, two kinds of TiO<sub>2</sub> NRs were used as photocatalysts for the degradation of gaseous toluene. After the ligand exchange, the AcA-exchanged TiO<sub>2</sub> NRs could catalyze the degradation of toluene in the visible region and the conversion reached to 28% after 24 h while the original OA-coated TiO<sub>2</sub> NRs were inactive. Moreover, a double-layer thin film of OA-coated TiO<sub>2</sub> NRs and AcA-exchanged TiO<sub>2</sub> NRs was fabricated and tested as a UV sensor. The double-layer thin film exhibited good characteristics for use as a UV sensor since it yielded clear signals over wide UV range from 254 to 380 nm.

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