

# Controlled growth of TiO<sub>2</sub> nanorods capped with carboxylate groups by the solvothermal process

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**Abstract** A solvothermal method is described for preparing nanomaterials of titanium dioxide (TiO<sub>2</sub>) while controlling the growth of rod-shaped nanomaterials. Titanium (IV) isopropoxide (TTIP) and butyl ether were chosen as the precursor and solvent, respectively. Oleic acid and decanoic acid were used as the surfactant. TiO<sub>2</sub> nanospherical particles and nano-rods were synthesized in mass quantities by adjusting the kind of surfactant, the concentration of the precursor, and the solvothermal reaction temperature. The synthesized TiO<sub>2</sub> nanospherical particles and nanorods were uniform and transparent in the toluene. The TiO<sub>2</sub> nanospherical particles were about 3.5 nm in size. The TiO<sub>2</sub> nanospherical particles and nanorods were of a highly crystalline anatase structure. The direction of growth of the TiO<sub>2</sub> nanorods was [001] and the band gap energy of the TiO<sub>2</sub> nanorods, evaluated by optical absorption, was 3.34 eV.

## Introduction

TiO<sub>2</sub>, an n-type wide band gap semiconductor, has a variety of promising applications, for example in dye sensitized solar cells [1–3], photocatalysts [4, 5], lithium batteries [6–8], and photochromic devices [9, 10], due to its attractive optical, electrical, chemical, and catalytic properties. One-dimensional TiO<sub>2</sub> materials, such as nanotubes, nanowires, nanofibers, and nanorods have attracted particular interest

due to their unique microstructure and promising functions [11–14]. One-dimensional TiO<sub>2</sub> nanocrystals exhibit a high surface to volume ratio, improved charge transport afforded by their dimensional anisotropy and an increased number of delocalized carriers [11, 15, 16]. Depending on these properties and applications, TiO<sub>2</sub> materials must fulfill a wide variety of requirements in terms of particle size, size distribution, morphology, crystallinity, and phase.

Various methods, such as sol–gel processing [17–19], hydrothermal reactions [20–22], and wet-chemical methods [23, 24] have been applied to improve the size and shape of one-dimensional TiO<sub>2</sub> nanomaterials. However, due to the fast reactivity of titanium alkoxides and the forming of large complex molecules upon exposure of titanium alkoxides to ambient humidity, the concentration of titanium alkoxides was so low that only a small quantity of TiO<sub>2</sub> nanocrystals could be made by non-aggregation of TiO<sub>2</sub> nanoparticles. Although these problems in the preparation of TiO<sub>2</sub> nanomaterials are solved through the modification, one of the limitations of these techniques is a low crystallinity. In order to improve this factor, most of the previous researches have been performed employing long reaction time (over 20 h) and additional heat-treatments (over 600 °C).

Recently, a solvothermal process [25–37] has been widely utilized in the synthesis of TiO<sub>2</sub> nanostructures, which makes easier to control the size, crystallinity, morphology, and surface chemistry of TiO<sub>2</sub> compared with other synthetic processes. Since the reaction is performed at an elevated pressure, more crystallized and denser structures have been obtained at a given temperature.

Thus, in this work, we combined the solvothermal process and reverse micelle technique to obtain more crystallized and controlled morphology of titania nanoparticles

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without aggregation. We have chosen TTIP, decanoic acid, oleic acid, and butyl ether as a  $\text{TiO}_2$  precursor, surfactant, and solvents, respectively. The carboxylic acids of long hydrocarbon chain form a stable reverse micelle structure in non-polar ether. During the solvothermal reaction, it has been reported that the application of surface selective surfactants would be finely tune the growth rate of the faces to follow the resulting shape evolution process [14, 38–40]. In particular, carboxylic acids bind very strongly to {001} face of anatase, one of the  $\text{TiO}_2$  crystal phases. This fact suggests that we can synthesize one-dimensional  $\text{TiO}_2$  nanorods bound to carboxylic acids at a low temperature [40]. Various variables (e.g., the amount of concentration of carboxylic acids, the kind of carboxylic acids, the reaction temperature, and the reaction time) have been studied. From the results, we will describe the reaction mechanism of the  $\text{TiO}_2$  formation process.

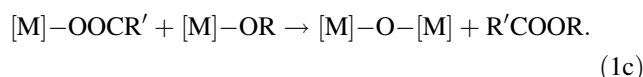
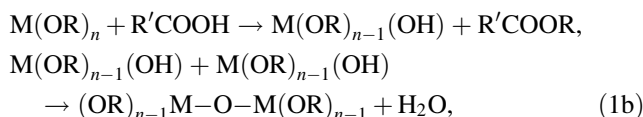
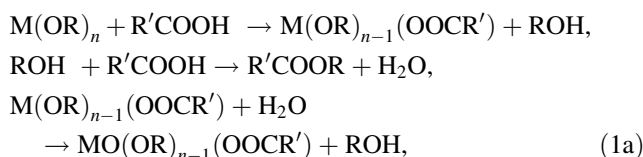
### Experimental procedure

0.015 mol of titanium (IV) tetraisopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , 97%, Aldrich, TTIP) was dissolved in 100 mL of butyl ether ( $\text{C}_4\text{H}_9\text{OC}_4\text{H}_9$ , 99%, Aldrich), and the oleic acid ( $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ , 90%, Aldrich) and decanoic acid ( $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ , 98%, Sigma) with a molar ratio of TTIP:acid = 1:1, 1:2, 1:3, and 1:4 were added dropwise in nitrogen atmosphere. The mixture was stirred for 1 h and then the resulting transparent yellow solution was transferred to an autoclave. For the solvothermal reaction, the temperature of the autoclave was raised to 250, 280, or 300 °C at a rate of 5 °C/min, and held for 2, 4, 6, or 8 h. The reactor pressure was about 30 atm. After the solvothermal reaction, we obtained a deep yellow  $\text{TiO}_2$  colloidal suspension. Excess ethanol was added to  $\text{TiO}_2$  colloidal suspension and the mixture was transferred to round bottom flask, tempered to 40 °C in a water bath, and held under a reduced pressure for 30 min using a vacuum pump to remove surfactant residuals. This step was repeated five times. The resulting white powder could easily be re-dispersed in a non-polar solvent. Synthesized  $\text{TiO}_2$  was then dispersed into toluene resulting in a transparent solution. The synthesized  $\text{TiO}_2$  nanorods were characterized by X-ray diffractometry (XRD, DMAX 2500, Rigaku, Japan) using Cu-K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) and a high resolution transmission electron microscope (TEM, CM200, Philips, Netherlands). Infra-red (IR) and Raman spectra were collected with an FT-IR spectrometer (Presitige-21, Shimadzu, Japan) and an FT-Raman spectrometer (RFS-100/S, Bruker, Germany), respectively. Optical absorption was recorded at room temperature with UV-vis spectroscopy (UV 2450, Shimadzu, Japan).

### Results and discussion

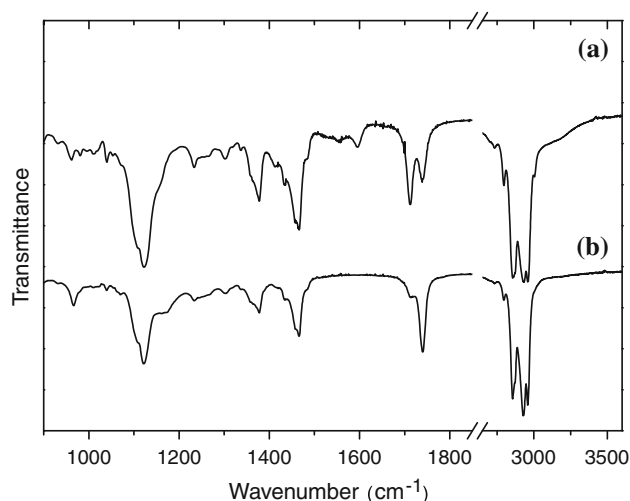
#### Solvothermal reaction of the $\text{TiO}_2$ nanocrystals with carboxylic acid

In this study, we have demonstrated a solvothermal process, controlling the concentration of carboxylic acids, the kind of carboxylic acids, the reaction temperature, and the reaction time. The result was a successful crystallization of  $\text{TiO}_2$  nanoparticles and nanorods. Titanium alkoxides are known to readily react with carboxylic acids by competitive pathways shown below [41]:



Poly nuclear oxo complexes have been produced, depending on experimental conditions.

Figure 1 shows the FT-IR spectra of the  $\text{TiO}_2$  suspension: (a) the mixture of TTIP and oleic acid in dibutyl ether, and (b) as-synthesized  $\text{TiO}_2$  nanorod. In Fig. 1a, two absorption bands are observed at 1,710 and 1,740  $\text{cm}^{-1}$  resulting from the carbonyl group band of the free oleic acid and the ester, which was produced from the mixing of



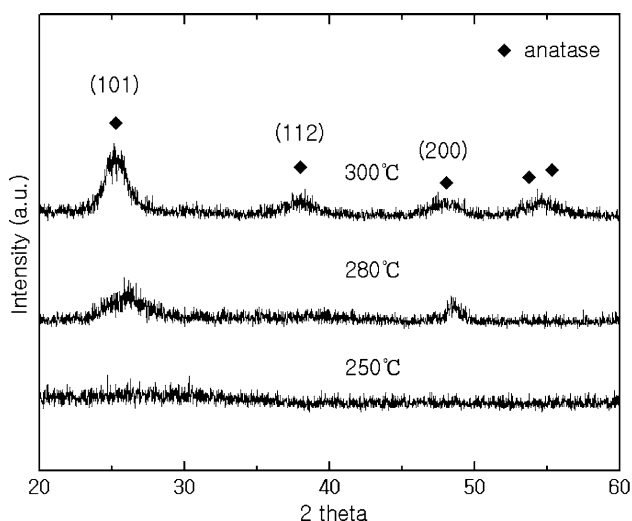
**Fig. 1** FT-IR spectra of the  $\text{TiO}_2$  suspensions: **a** the mixture of TTIP and carboxylic acid in dibutyl ether, and **b** as-synthesized  $\text{TiO}_2$  nanorods in dibutyl ether (at 300 °C for 6 h with 0.045 mol oleic acid)

the materials [33, 42, 43]. After the reaction proceeds for 6 h, the absorption peak resulting from the carbonyl group band of oleic acid at  $1,710\text{ cm}^{-1}$  almost disappeared. On the other hand, the intensity of the carbonyl band originating from the produced ester at  $1,740\text{ cm}^{-1}$  increased sharply as shown in Fig. 1b. This indicates that ester was produced from the carboxyl group of the oleic acid and alkyl group of the TTIP in accordance with Eq. 1b. The medium intensity band at  $1,600\text{ cm}^{-1}$  and the very broad band around  $3,000\text{--}3,300\text{ cm}^{-1}$  in Fig. 1a result from the bending vibration and the stretching vibration of the Ti–OH bonds [14].

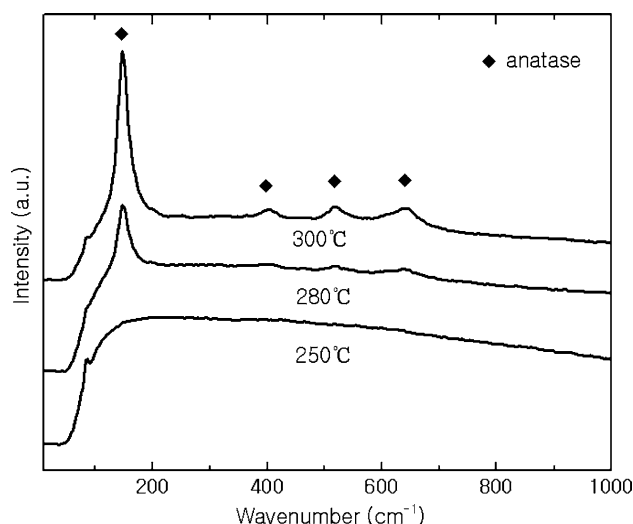
From the FT-IR analysis, we conclude that these hydroxide groups in TiOH forms the  $\text{TiO}_2$  nanocrystals by the condensation reaction at elevated temperature and pressure. We believe that complete disappearance of these peaks from the hydroxide groups in TiOH as shown in Fig. 1b supports above-mentioned mechanism, Eq. 1b.

The crystalline phase, size, and morphology of the  $\text{TiO}_2$  nanocrystals

As indicated by the XRD patterns in Fig. 2, the  $\text{TiO}_2$  particles prepared at  $250\text{ }^\circ\text{C}$  were amorphous at 0.015 mol oleic acid. On the other hand, the  $\text{TiO}_2$  nanoparticles prepared at  $300\text{ }^\circ\text{C}$  were pure anatase phase with lattice constants of  $a = b = 3.785\text{ \AA}$  and  $c = 9.514\text{ \AA}$  (JCPDS card No.: 21-1272), which is in agreement with the result obtained from FT-Raman (Fig. 3). Moreover, when the concentration of the oleic acid was increased, the tendency of the  $\text{TiO}_2$  nanocrystals with regard to reaction temperature was the same, which denotes that the amount of the surfactant is not a parameter that controls the crystalline



**Fig. 2** XRD patterns of  $\text{TiO}_2$  nanoparticles synthesized at different reaction temperature for 6 h with 0.015 mol oleic acid

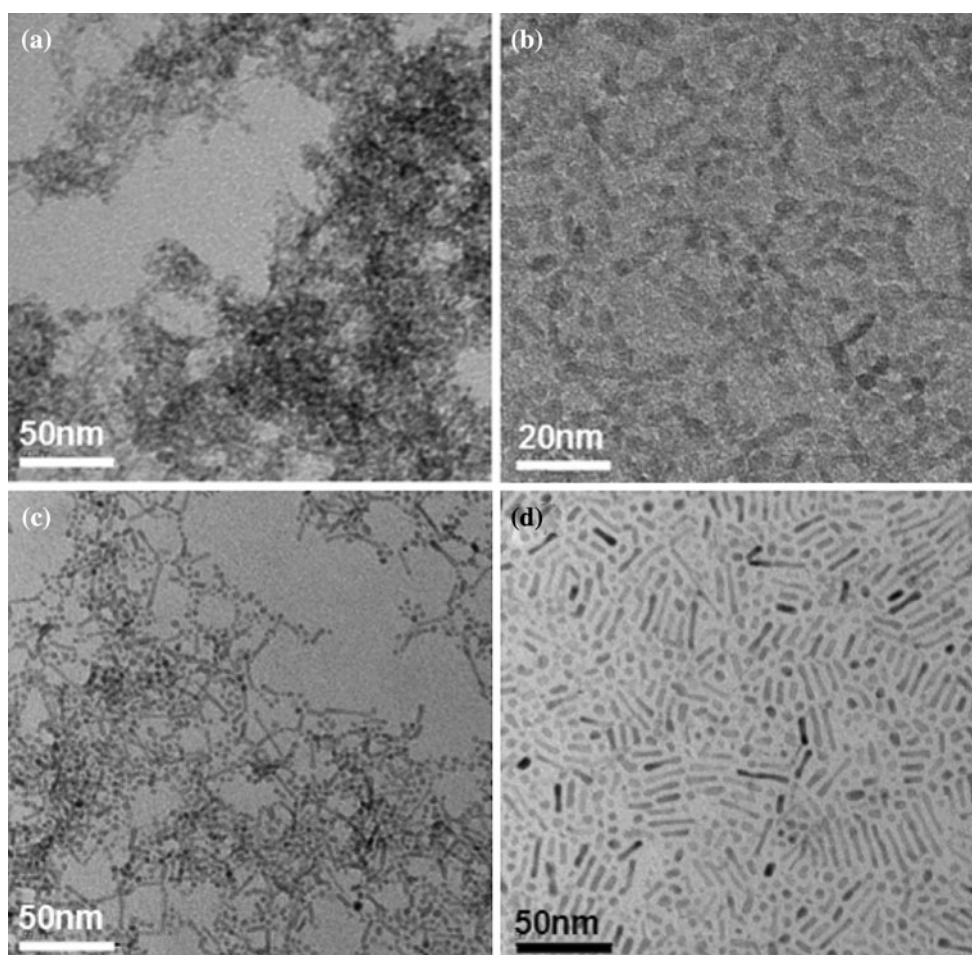


**Fig. 3** FT-Raman spectra of the  $\text{TiO}_2$  nanoparticles synthesized at different temperature for 6 h with 0.015 mol oleic acid

phase of  $\text{TiO}_2$ . The average crystallite sizes of  $\text{TiO}_2$  nanoparticles at  $300\text{ }^\circ\text{C}$  were calculated from the full-width at half-maximum intensity of the (101) peak at  $2\theta = 25.28^\circ$  using the Scherrer equation. The average crystallite size of the  $\text{TiO}_2$  nanoparticles was about 3.5 nm, which was very small as compared with those obtained by other methods. On the other hand, the average crystallite size of the  $\text{TiO}_2$  nanoparticles prepared by decanoic acid was 5.5 nm. This indicated that the chain length of the carboxylic acids is a very important parameter controlling the particle size. This feature is also observed by TEM study.

Figure 4 shows low magnification TEM images of synthesized nanostructures. The concentration of the carboxylic acids greatly influences the morphology of the final product. When the content of decanoic acid was 0.015 mol, synthesized  $\text{TiO}_2$  nanoparticles were aggregated. However, increasing the content of decanoic acid decreased the aggregation of  $\text{TiO}_2$  nanoparticles and increased their dispersibility. Moreover, when the amount of the decanoic acid was 0.045 mol, the synthesized  $\text{TiO}_2$  was rod-shaped. This feature also appeared in the  $\text{TiO}_2$  nanocrystals prepared with the oleic acid. However, when the  $\text{TiO}_2$  samples were synthesized with different amounts of oleic acid, dispersibility improved and the rod shape and anatase phase of the  $\text{TiO}_2$  were distinct compared with that synthesized with decanoic acid. These results indicate that oleic acid is useful for preparing  $\text{TiO}_2$  of uniform rod shape. In Table 1, we have summarized these tendencies of the morphology of  $\text{TiO}_2$  nanocrystals synthesized with different carboxylic acids.

When the content of the oleic acid was 0.06 mol, the average size of the rod-shaped  $\text{TiO}_2$  was about  $3.5 \times 30\text{ nm}$  (Fig. 5a). Figure 5b is an HRTEM image of  $\text{TiO}_2$



**Fig. 4** TEM images of TiO<sub>2</sub> synthesized at 300 °C for 6 h with different amount of carboxylic acid: **a** 0.015 mol of decanoic acid, **b** 0.045 mol of decanoic acid, **c** 0.015 mol of oleic acid, and **d** 0.045 mol of oleic acid

**Table 1** Morphologies of TiO<sub>2</sub> samples obtained under different kind and amount of the surfactants (reaction temperature: 300 °C, reaction time: 6 h)

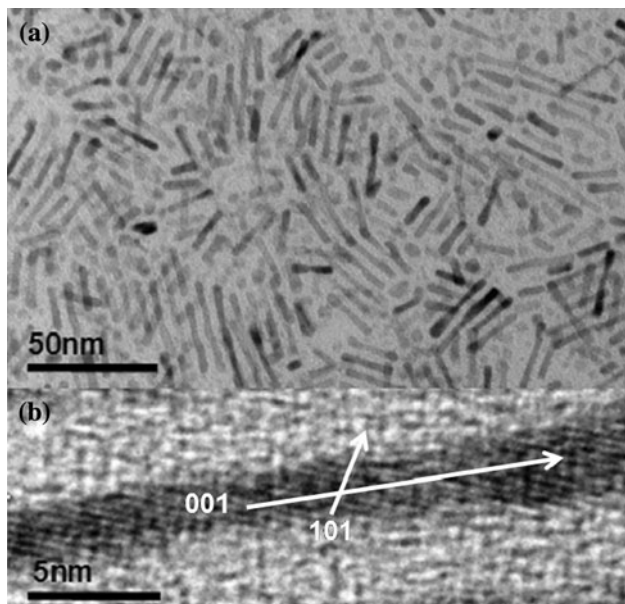
	0.015 mol	0.03 mol	0.045 mol	0.06 mol
Decanoic acid	Aggregated nanoparticles	Dispersed nanoparticles and nanorods	Dispersed nanorods	
Oleic acid	Dispersed nanoparticles	Dispersed nanoparticles and nanorods	Dispersed nanoparticles and nanorods	Dispersed nanorods

nanorods synthesized with 0.06 mol of oleic acid. These nanorods are structurally uniform with an interplanar space of about 3.5 Å, which corresponds to the distance between two (101) planes of anatase phase TiO<sub>2</sub>. In general, the reduction in surface energy is the primary driving force for simple particle growth, and morphology evolution is driven by the further reaction in energy due to minimization of the area of high surface energy faces. According to the Donnay–Hargreaves rules, the surface free energy of the {001} faces is nearly 1.4 times larger than that of the {101} faces

[15, 22, 40, 44–47]. Therefore, these features determine the intrinsic instability of the nucleus; the shape evolution in TiO<sub>2</sub> anatase can be realized by modifying the surface free energy and growth rate of the nucleus with the surface adhesion of the ligands.

Ethanol has been introduced to remove the surfactant residuals. We found out, however, that successive washing of synthesized TiO<sub>2</sub> with ethanol brings about the change in the shape of nanorods as depicted in Fig. 6. It has been observed that the length of the TiO<sub>2</sub> nanocrystals increased





**Fig. 5** **a** TEM image of TiO<sub>2</sub> synthesized at 300 °C for 6 h with 0.06 mol oleic acid, and **b** high-resolution TEM image of **(a)** image

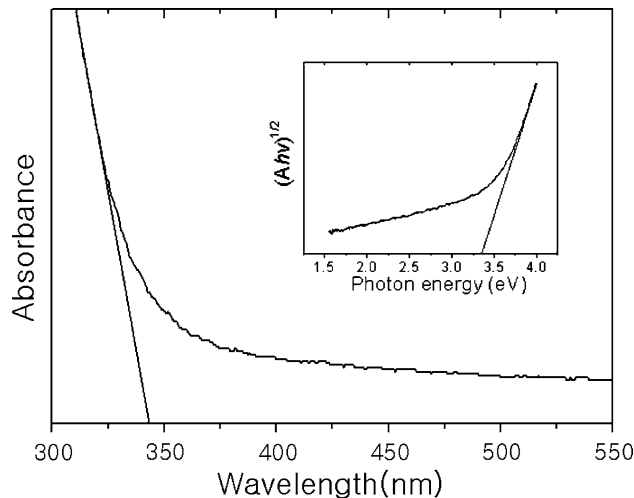
with the number of washings by ethanol. We do not fully understand why the washing away of surfactant residuals causes this very interesting effect. Further studies are needed to explain this result.

The bandgap energy of the TiO<sub>2</sub> nanocrystals

The optical band gaps of the TiO<sub>2</sub> nanorods were studied by the UV–vis spectroscope absorbance spectra displayed in Fig. 7. The absorption coefficient ( $\alpha$ ) and the bandgap ( $E_g$ ) are related through the equation [48].

$$(\alpha h\nu)^s = h\nu - E_g$$

where  $\nu$  is the frequency,  $h$  is Planck’s constant, and  $s = 0.5$  for indirect bandgap material. The Tauc plot is  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$ . As absorbance ( $A$ ) is proportional to the



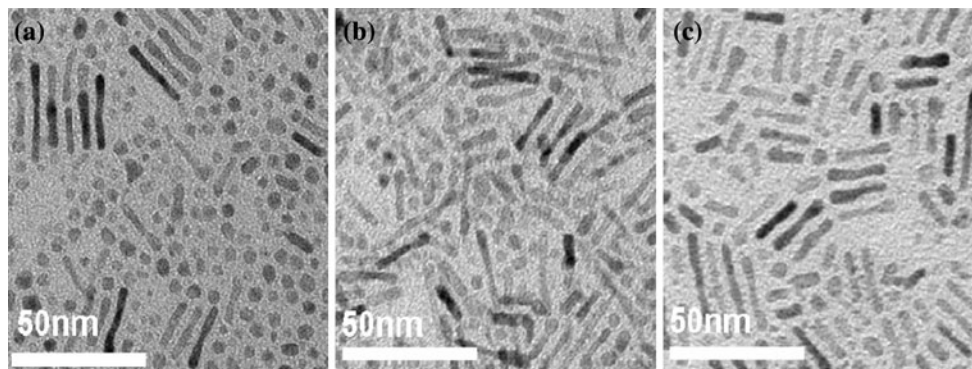
**Fig. 7** UV–vis spectrum of the TiO<sub>2</sub> nanorods synthesized by solvothermal process with 0.06 mol of oleic acid

absorption coefficient ( $\alpha$ ) [20], the Tauc plot,  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  was replaced by  $(Ah\nu)^{1/2}$  vs.  $h\nu$ .

From this spectrum, the optical bandgap, obtained by dropping a line from the slope of the curve, is 3.34 eV. The reported bandgap value of the bulk anatase phase is 3.2 eV. The peak is 40 nm blue shifted from that of bulk anatase. This 40 nm blue shift seems to be the result of quantum size effects.

**Conclusions**

The crystal phase, size, and shape controlled TiO<sub>2</sub> nanorods were synthesized through a solvothermal process. On the basis of the experimental results, a possible reaction mechanism of formation of TiO<sub>2</sub> nanorods has been proposed. This process is very useful and holds several significant advantages for the synthesis of one-dimensional TiO<sub>2</sub> nanocrystals. The prepared TiO<sub>2</sub> nanorods were clear



**Fig. 6** TEM images of TiO<sub>2</sub> synthesized at 300 °C for 6 h with 0.06 mol oleic acid: **a** one time washing, **b** three times washing, and **c** five times washing and evaporation with ethanol

anatase phase. The shape and length of the TiO<sub>2</sub> nanocrystals could be controlled by selecting the concentration and kind of surfactants and with the washing-evaporation procedure. In our future research, we will apply the TiO<sub>2</sub> nanorods to electrodes of dye sensitized solar cells.

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