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A control of TiO_2 nanostructures by hydrothermal condition and their application: a short review

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Abstract. TiO_2 (titanium dioxide) is an inorganic material that has many uses in various fields such as environment, sensor devices and solar energy conversion. Various method approaches have been developed for the synthesis of nanostructured TiO_2, but the hydrothermal method is still considered the most effective method and provides many advantages in nanostructure formation because the methods can be controlled. In the present study, we will discuss the formation of TiO_2 with various conditions on hydrothermal methods in TiO_2 nanostructure formation. Generally, TiO_2 nanoparticles can be obtained by hydrothermal methods. TiO_2 precursors, pH, reaction time and also temperature are factors that influence the formation of TiO_2 structures. The methods are commonly used because hydrothermal methods can easily control conditions to obtain a homogenous structure. The difference of TiO_2 structure is very influential in its properties and activity performance.

1. Introduction

Titanium dioxide (TiO_2) is an inorganic material which have high stability, low cost and safety for humans and the environment. Because of its properties, the materials has many uses in various fields such as for photocatalysis process, solar energy conversation and sensor devices. TiO_2 as a semiconductor is able to absorb photons to produce electrons so the material can be widely used in various fields. However, the limitation of the system shows that TiO_2 requires high-energy for producing an electron. Therefore, this material is often modified to reach the nanostructure. So far, there are many approach ways to the synthesis of TiO_2 nanostructured, i.e. via templating, chemical vapor deposition, solvothermal methods, direct oxidation, microwave methods and hydrothermal synthesis methods. However, hydrothermal synthesis is a common method widely used to prepare TiO_2 nanostructure because the methods have a simple route for synthesis.

Hydrothermal methods were firstly introduced in the 1990s by controlling morphology and shape of materials. Hydrothermal method is one of synthesizing nanoparticle materials that are easy to use. The Hydrothermal method can be used to obtain 0D, 1D, 2D and 3D nanostructures TiO_2. These methods are usually used at high temperature (>100 ^oC), a high pressure and an aqueous medium with a presence of catalyst [1]. Some literature reported that this method showed effective methods for synthesized nanomaterials with high crystallinity, purity and also a homogenous structure [2].

Currently, the development of hydrothermal methods for synthesized nanostructures is still an interisting topic to discuss. Some kinds of literature have reported that the development of these methods not only focusing to obtain a homogenous nanoparticle but also but also to produce nanocomposites or nano-hybrid materials [3-5].

Wahyuningsih et al. (2016) firstly reported that TiO_2 powder could be synthesized by mixing a TiO_2 powder and NaOH solution at high temperature [28]. The results showed that the structure of TiO_2 was strongly influenced by several factors which previously explained [6]. In this study, we focused on discussing the production of hydrothermal TiO_2 nanostructures with regard to several factors such as time, precursor, pH condition, also temperature and its application.

2. Experimental

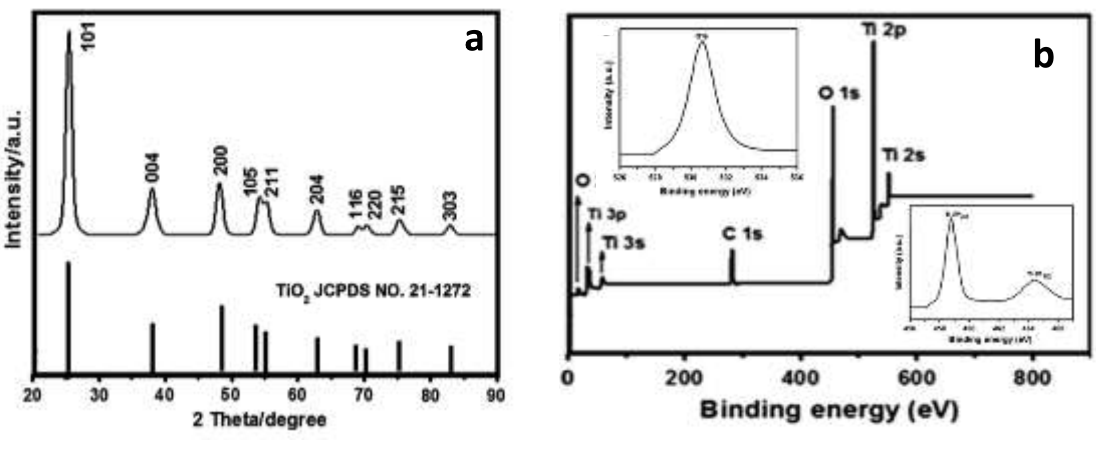
2.1 Synthesis of TiO_2 nanostructures

Some kinds of literature have reported that the TiO_2 nanostructures could be synthesized by hydrothermal methods in various conditions such as precursors, time and temperatures during the reaction process, and pH solution. Huang et al. (2016) reported that TiO_2 nanorods have been successfully synthesized from titanium oxalate as precursors in NaOH solution. Generally, titanium tetraisopropoxide (TTIP) was selected and reacted with oxalate. The reaction would produce a titanium oxalate which used as precursors for the synthesis of TiO_2 nanostructures. Beside, Wahyuningsih et al. (2016) reported that TiO_2 nanorods could be synthesized from TiO_2 powder. TiO_2 that was used in the hydrothermal reaction was brookite phase that resulted from mechanical milling of anatase TiO_2. TiO_2 was reacted in basic solution (NaOH) with various concentration of NaOH. TiO_2 nanostructures was not only reacted in basic solution but also in acidic solution like chloric acid or fluroric acid. Nanoparticles were characterized by spectroscopy techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and EDX (Energy Dispersive X-Ray).

3. Results and discussions

3.1. Precursor Effect

TiO_2 nanostructures could be synthesized in various conditions. The difference of hydrothermal condition gives different result especially for homogeneity and crytanillity of materials. As mentioned earlier, these methods can produce nanostructures, however, all of these are influenced by the selected precursors. Huang et al (2016) reported that TiO_2 nanorods (1D) could be synthesized from titanium oxalate in basic solution [7]. Beside, Fadillah et al. (2017) also reported that TiO_2 1D can be synthesized as directly using TiO_2 powder at a high base concentration [8]. However, the use of TiO_2 powder as a precursor resulted in poor homogeneous crystals. Generally, to ensure the shape of the structure, the material was characterized by X-ray photoelectron spectroscopy (XPS), EDX (Energy Dispersive X-Ray) and X-ray diffraction (XRD). The characterization result as shown on Figure 1.



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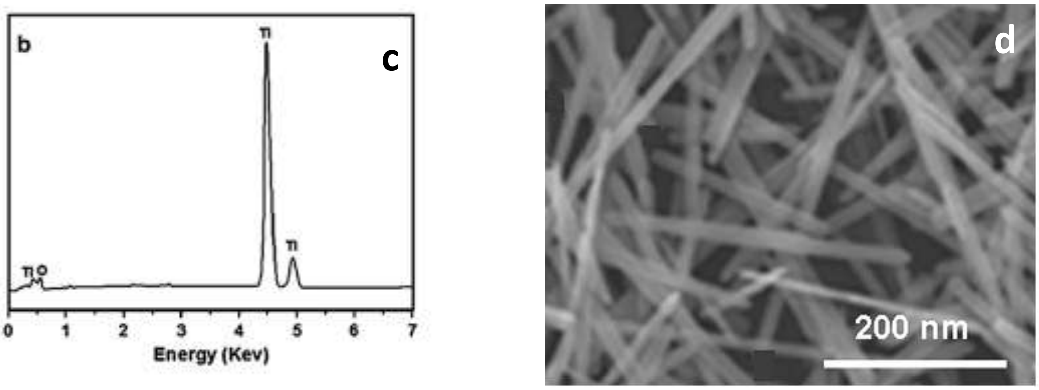

Figure 1. Characterization of TiO_2 nanostructures (a) XRD, (b) XPS, (c) EDX and (d) SEM [7].

Based on The XRD spectra (Figure 1a) shows that TiO_2 has a good crytallinity because the diffractogram shows a clear and sharp shape. The pattern of diffraction matches as well with the standard (following Number of JCPDS 21-1272). To ensure the materials have been successfully formed, the XPS data was used to support the data. XPS spectra in Figure 1b shows not only the elemental compositions but also the chemical status of TiO_2. The results indicated that the composition of materials only contains Ti and O. In addition, the TiO_2 was also confirmed using EDX data. The data reported that the sample contains only Ti and O elements like XPS results.

The SEM characterization showed that the TiO_2 nanorods have been successfully synthesized with average diameters between 10-20 nm. The results confirmed that the 1D materials could be synthesized from TTIP as precursors [9]. The other studies reported that TiO_2 nanoparticles could be formed by hydrothermal methods using TTIP as a precursor in ethanolic HNO_3 solution [10, 11]. The XRD characterizations results the XRD patterns of synthesized TiO_2 nanorods using hydrothermal methods. The results indicated that the diffraction of TiO_2 has changed to rutile phase (101 and 002).
The surface morphology characterization both SEM and TEM show that TiO_2 nanorods have a distinctive shape that is rod-shape. The TiO_2 nanorods grows up regularly on the surface of FTO substrate. Whereas the image shows a single crystalline of TiO_2 nanorods and it has [001] growth direction based on SAD (selected area diffraction) pattern. The obtained TiO_2 nanorods have a uniform diameter that is around 50 nm. Tan et al. (2015) have synthesized layered nanostructured TiO_2 by using $TiCl_4$ as a precursor and tetramethylammonium hydroxide (TMAH) [12]. The 3D TiO_2 nanostructures can be obtained from TTIP in HNO_3 solution hydrothermally. TEM characterization of two TiO_2 nanoparticles as shown in Figure 2.

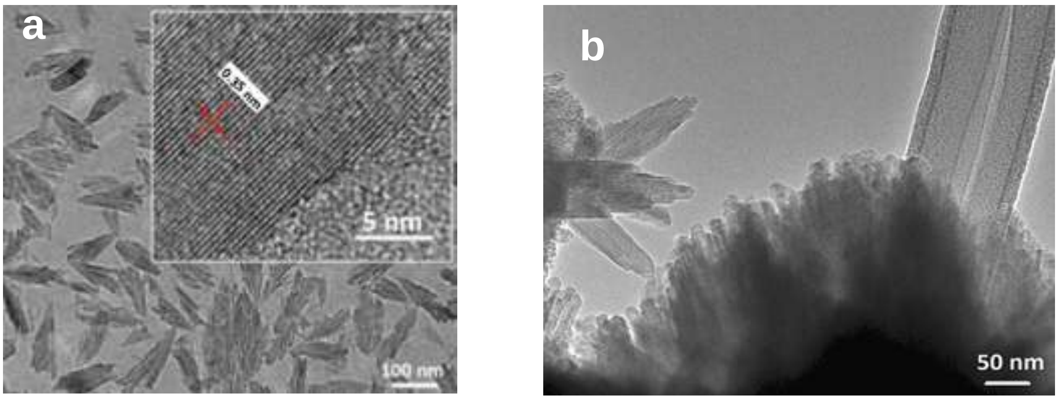

Figure 2. TEM images of TiO_2 nanoparticles (a) 2D [12] and (b) 3D respectively [13].

3.2. Temperature and Time

The effect of time and temperature during the reaction process show a significant influence on the formation of TiO_2 nanostructure. Erdogan et al. (2016) reported that the increasing temperature affected to intensity of the peak as shown in Figure 3 because of the change of TiO_2 crystallinity [13,14].

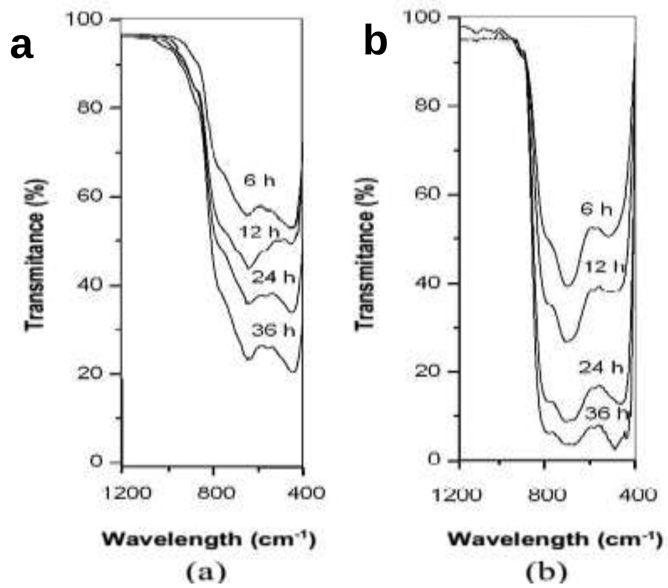

Figure 3. FT-IR spectra of TiO_2 in different temperatures (a) 150 ^oC and (b) 200 ^oC at different times [15].

Based on Figure 3, a reaction time of hydrothermal effects on crystal formation of TiO_2. It can be known from XRD patterns of TiO_2 nanorods in Figure 4. There is a different ratio of Rutile (101) and (002) that indicates in lower temperature, the nanorods have a random orientation then a higher temperature occurs well-aligned arrays of the vertical nanorods [15-18]. The orientation change is supported by morphology data from SEM analysis. It revealed that the difference of a time reaction is not only effects on a dimensional size but also a orientation of crystal growth on the surface of the substrate [19]. The rate of TiO_2 nanorods growth in the other literature is shown in Figure 5a.

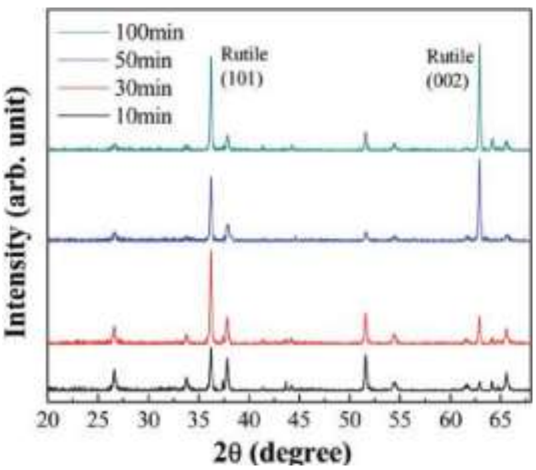

Figure 4. The effect of reaction time of hydrothermal on TiO_2 nanorods diffractogram [10].

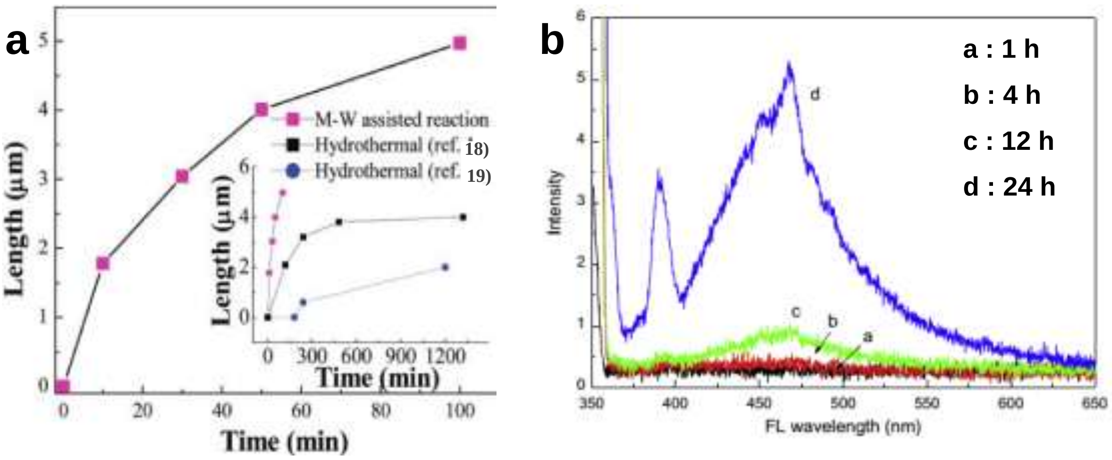

Figure 5. (a) The rate of TiO_2 nanorods growth during a microwave-assisted hydrothermal reaction compare with a conventional hydrothermal and (b) Luminescence spectra of TiO_2 influenced by reaction time duration [12].

The influence of reaction time to an optical characteristic of TiO_2 nanoparticles is shown in Figure 5b. This spectroscopy technique is used for knowing the crystalline TiO_2 formation [23]. TiO_2 nanoparticles are radiated with UV-Visible lamp so it caused excite TiO_2 molecules. The 1 h reaction time does not show emission peak, it is a different result in the 4 h treated that it shows a very weak emission at 470 nm. The maximum emission peak is obtained for 24 h. The result indicates that anatase TiO_2 nanoparticles are produced in a large amount during a long time reaction.

3.3. pH Condition
The pH is one of the factors to the formation of TiO_2 nanostructure. Nian et al. (2006) reported that different pH values give a different resulted shape of TiO_2 nanorods. The pH during reaction could be controlled by adding base solution such as NaOH into TiO_2, then by adding acid solution such as HNO_3 until pH values were achieved [20]. Some literatures reported that TiO_2 ID like nanotubes is a good precursor for the synthesis of TiO_2 nanorods due to it has a specific shape. So, the hydrothermal reaction for these nanotubes under acidic or basic condition impacts on bond cleavage and then the destruction of its [21]. The results of TiO_2 nanorods synthesized from nanotubes mention in Figure 6.

Figure 6a shows the influence of pH condition on XRD pattern of TiO_2 nanorods. There is a reduction of XRD peak intensity for TiO_2 anatase phase. It means that the higher pH values effect in the stability of TiO_2 anatase phase. This is confirmed by a morphology showed of TiO_2 nanorods in Figure 6b. The measurement of TiO_2 nanorods average size under highly acidic condition (pH 2.2) are about 10 nm. The pH condition has an effect on the crystalline sizes of TiO_2 nanostructure [22,23]. The average thickness of crystal face can be known from XRD data while the true lengths of the long and short particles can be determined from TEM images. Because of a high hydrothermal temperature, nucleation and crystallization of TiO_2 occur fastly after the nanotube destruction. Based on this phenomenon, the TiO_2 growth is controlled by kinetics, not thermodynamics, so there is obtained metastable anatase [24,25].

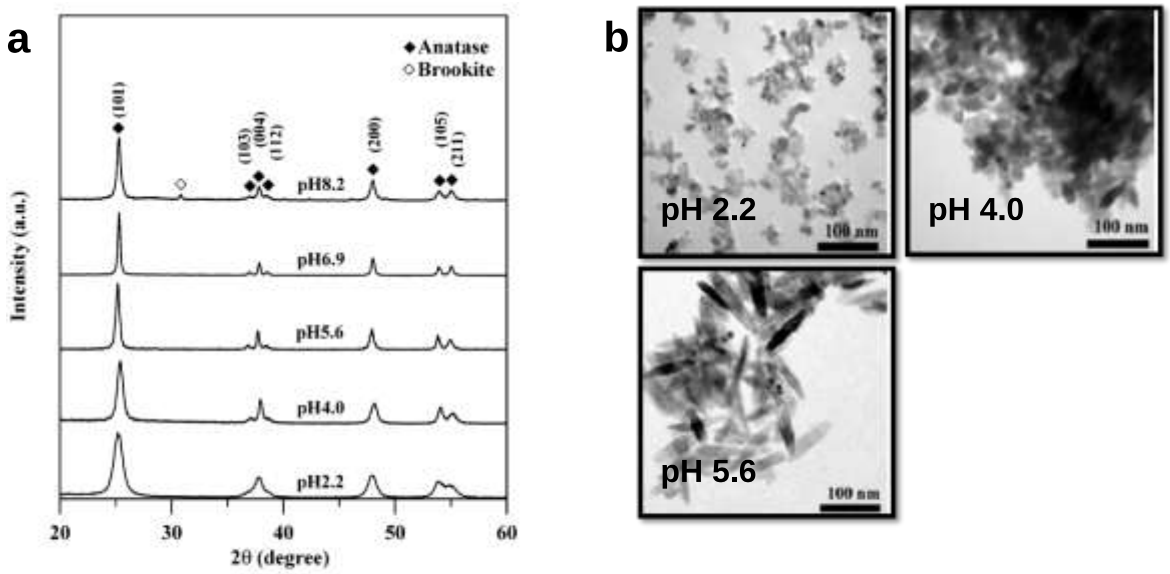

Figure 6. pH values dependence of TiO_2 nanorods (a) XRD spectra and (b) TEM images [21].

3.4. *Energy application*

The one of huge applications of TiO_2 nanoparticles is dye sensitized solar cells (DSSC). TiO_2 is commonly used as a semiconductor in photovoltaics. The materials are worked as harvesting light so the materials have an important function. Tacchini et al. (2012) reported that TiO_2 nanostructure have successfully synthesized by hydrothermal for DSSC semiconductor [26,28]. The results were obtained with the highest lighting conversion (3.2%). The determination of DSSC efficiency uses I-V measurement and IPCE analyzer as in Figure 7a.

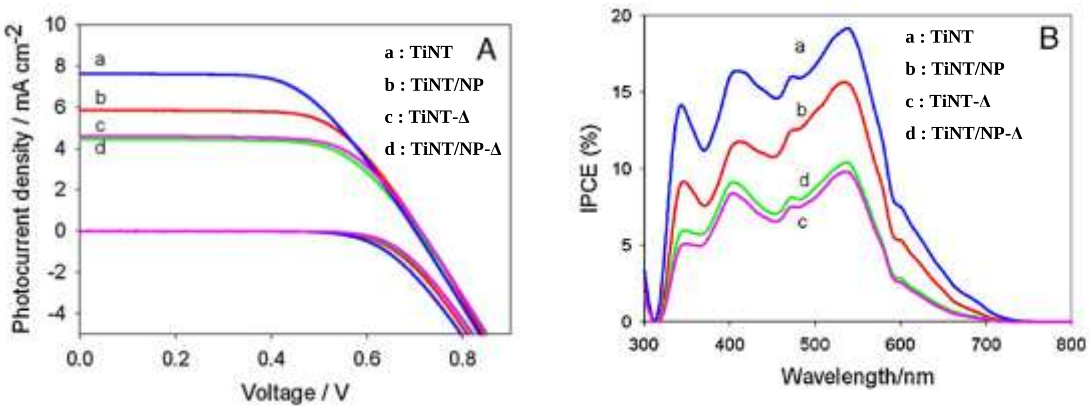

Figure 7. (a) I-V curves and (b) IPCE analysis of TiO_2 nanostructures [26].

Based on Figure 7b, The results revealed that the highest %IPCE is showed by TiO_2 nanotubes. The IPCE spectra confirm that TiO_2 nanotubes give the highest efficiency. Another research, TiO_2 nanorods can be synthesized with TiO_2 powder as precursor via the hydrothermal process for DSSC material [27]. The efficiency test shows that TiO_2 nanotubes have a higher efficiency that commercial TiO_2. It shows that the shape of nanostructures is one of the factors for electron mobility on the system.

3.5. Environmental application

The another application of TiO_2 nanoparticles as a semiconductor is used widely for wastewater treatment such as photochemical reaction for degradation of synthetic dye. Huang et al. (2016) reported that a photocatalytic performance of TiO_2 nanorods for Rhodamine-B (RhB) degradation [24]. Figure 8a shows the absorption spectra of RhB after treated with TiO_2 nanoparticles as catalyst. The results show that the presence of TiO_2 as photocatalyst could decrease a dye color as well. The optimum results were found at maximum degradation of dye more than 90%. The comparison study for 3 types of TiO_2 has reported in Figure 8b. The results show that TiO_2 nanorods showed significantly performance for decreasing a dye color. TiO_2 nanorods have a rod-shape and it makes electron mobility become more effective for producing hydroxyl radical to react with dye molecules.

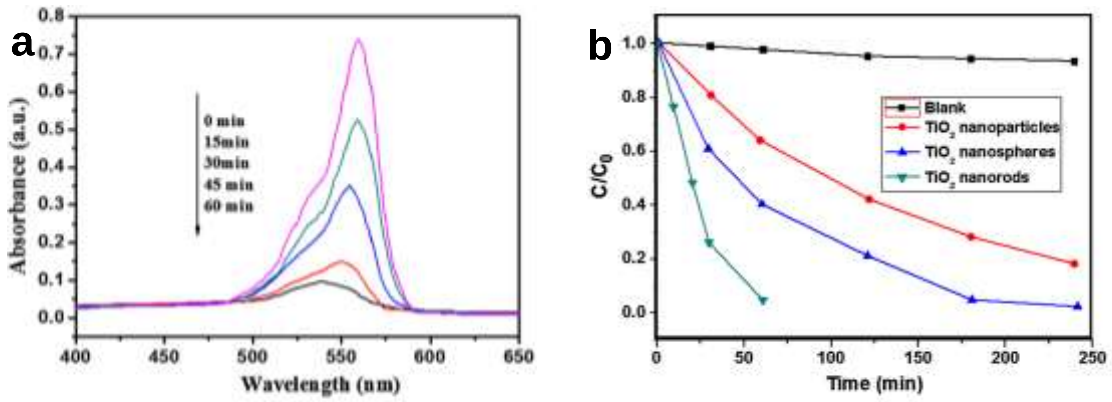

Figure 8. Photocatalytic activity of TiO_2 nanostructures (a) UV-Vis absorption spectra of RhB and (b) photodegradation rate of RhB [7].

4. Conclusion

Hydrothermal is one of methods for producing a TiO_2 nanostructure. The structure TiO_2 depends on several factors that are pH, time and temperature during the hydrothermal reaction and also precursors. Controlling the shape and size of the structure of TiO_2 greatly influences its chemical properties so that it can be widely used in several applications. In addition, the nanorods and nanotubes structure of TiO_2 shows a good performance both as a seminconductor and photocatalyst.

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