The influence of calcination temperature on (photo)electrochemical property of TiO$_2$ prepared by the sol-gel method

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Abstract. In this work, titanium dioxide (TiO$_2$) was successfully synthesized via the sol-gel method using Titanium (IV) isopropoxide as a precursor. The mixture was heated to 115°C to obtain the solid powder of TiO$_2$. Ti K-edge XANES measurement was performed to determine its structure. Three pre-edge peaks at energy levels between 5460-5480 eV were clearly observed. These features correlated to 1s→d electronic transition in the distorted-octahedral structure of anatase TiO$_2$. The in situ XANES experiment at 700°C revealed no phase transformation from anatase to rutile. There was no characteristic of the rutile phase on the XRD pattern of TiO$_2$ calcined at 700°C. This result confirmed the stability of anatase. SEM images revealed the circular shape of TiO$_2$ particles with a diameter of around 50 nm. The highest (photo)electrochemical activity of TiO$_2$ was obtained at the calcination temperature of 300°C as investigated by a cyclic voltammetry.

1. Introduction
Photochemical processes in heterogeneous systems have been an area of great interest over the past three decades. In 1972, Fujishima and Honda discovered the photoelectrochemical properties of titanium dioxide (TiO$_2$) electrodes on the splitting of water under solar energy [1]. They also extended its application to the area of environmental photocatalysis including self-cleaning [2], photoinduced hydrophilicity [3], and antifogging [4]. More recently, many studies have been published on the photocatalytic applications of TiO$_2$ for the decomposition of organic compounds (pollutants) [5-8]. The important advantages of TiO$_2$ for pollutant treatment are: (i) the process occurs under ambient conditions; (ii) oxidation of the substrates to CO$_2$ is completed; (iii) the photocatalyst (TiO$_2$) is inexpensive and has a high turnover; (iv) TiO$_2$ can be supported on suitable reactor substrates, and (v) the process offers great potential as an industrial technology to detoxify wastewater.
The four polymorphs of TiO$_2$ are found in nature including anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO$_2$ (B) (monoclinic) [9]. Two additional high-pressure forms have been synthesized starting from rutile: TiO$_2$(II) [10]. The structures of rutile and anatase can be discussed in terms of octahedral (TiO$_6$). Anatase can be regarded to be built up from octahedral connected by their vertices; in rutile, the edges are connected. TiO$_2$ can be prepared by the sol gel process. The sol gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) [11]. The precursors for synthesizing this colloid consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they are commercially available in high purity and react readily with water [12-14]. The encapsulated liquid can be removed from a gel by either evaporative drying or drying with supercritical drying. The resulting solid products are known as a xerogel and an aerogel, respectively. Heat treatment is necessary to burn off any residue organics or to oxidize the sample to a catalytically useful form. Heating is usually done in the presence of a reactive gas. The exposure of the sample to a high temperature over an extended period leads to sintering and consequently a decrease in surface area [15]. The process can also cause the material to crystallize into different structural forms. Thus, the physical characteristics of the product depend on parameters such as temperature, heating rate, time, and gaseous environment.

In this work, TiO$_2$ was prepared by sol-gel method. The characteristics of the TiO$_2$ were investigated by transmission electron spectroscopy (TEM), x-ray powder diffraction (XRD), x-ray absorption near edge structure (XANES) and cyclic voltammetry (CV).

2. Experimental

TiO$_2$ was prepared by the sol-gel method. Titanium (IV) isopropoxide was added to the mixture of 2-propanol and acetic acid under magnetic stirring. The suspension was stirred at room temperature for 20 min. Water was then added in the well mixed solution and continuously stirred for 60 min. The gel was then dried at 115°C to obtain the solid powder of TiO$_2$ (TiO$_2$-D). To study the influence of temperature on the TiO$_2$ structure, the samples were calcinated in air at 300°C, 500°C and 700°C for 1 hour. To investigate the morphology of TiO$_2$, TEM analysis of the samples was performed using a Talos Thermoscientific operated at 200 keV. The powders were prepared for TEM analysis by dropping the suspension of the powders in isopropanol on to a copper grid. The structural property of TiO$_2$ was characterized by x-ray powder diffraction (XRD) (Smartlab, Rigaku) and x-ray absorption near edge structure (XANES) (BL2.2, Synchrotron Light Research Institute, Thailand). To record the XRD pattern, the detector scanned the peak position from the sample as a function of 20 to 90 range and a scan speed of 2.42 deg/min. Ti K-edge XANSE spectra was recorded on a transmission mode. The energy dispersive monochromator, Si(111) single crystal and NMOS linear image sensor were employed. The measurement of diffuse reflectance spectra was performed on Lambda 950 UV/Vis/NIR spectrometer (PerkinElmer). The study of TiO$_2$ photocatalytic activity was obtained from cyclic voltammetry (CV). CV was performed in a three-electrode configuration with a Pt rod counter electrode and Ag/AgCl reference electrode. The cyclic voltammograms were recorded by the Autolab electrochemical workstation (PGSTAT302N, Metrohm). Sodium sulfate (1.0 M Na$_2$SO$_4$) was employed as a supporting electrolyte. For photocatalytic reaction, a 200 W Hg arc lamp (LOT) was used for excitation.

3. Results and discussion

The structural property of the prepared catalysts was investigated by XANES. The normalized Ti K-edge XANES spectra of standard anatase TiO$_2$ (TiO$_2$-A), rutile TiO$_2$ (TiO$_2$-R) and TiO$_2$ calcined at various temperatures are shown in Fig. 1. Three pre-edge peaks at energy levels between 4925-4950 eV of TiO$_2$-A indicated the electronic transition of electrons from 1s to 3d orbitals. Although this electron transition in Ti atoms was forbidden by selection rules, the mixing of d and p orbitals of Ti and O atoms in the TiO$_2$ system produced the pseudo-p character in the d orbital which consequently allows 1s→3d
transition. The characteristics of these peaks have been reported by Farges et al. [17]. The quadrupole transition of the 1s electron to the $t_2$ levels of the octahedron structure was denoted as A1. For dipole transition, $1s \rightarrow t_2g$ and $1s \rightarrow e_g$ were denoted as A2 and A3. After calcination, TiO$_2$-300 revealed three pre-edge peaks similar to the anatase. Although the calcination temperature was increased to 700$^\circ$C, there was no indication of the rutile phase of TiO. This result indicated the stability of the anatase phase at this temperature.

![Normalized Ti K-edge XANES](image)

**Figure 1.** Normalized Ti K-edge XANES of anatase TiO$_2$ (TiO$_2$-A), rutile TiO$_2$ (TiO$_2$-R), non-calcined TiO$_2$ (TiO$_2$-D), and TiO$_2$ calcinated at 300$^\circ$C, 400$^\circ$C, 500$^\circ$C, 600$^\circ$C, 700$^\circ$C, respectively

The structure of TiO$_2$ was further determined by means of x-ray diffraction spectroscopy. The diffraction patterns of TiO$_2$ calcined at 300$^\circ$C, 500$^\circ$C and 700$^\circ$C are shown in Fig. 2. The prepared TiO$_2$ film showed the XRD patterns of anatase (JCPDS No. 83-2243). By calcination at 300$^\circ$C, TiO$_2$-300 exhibited broad and not well-defined peaks of the anatase phase, suggesting a small grain size of TiO$_2$. The crystalline structure of anatase could be improved by increasing the calcination temperature. The sharper and higher intensity of XRD peaks of TiO$_2$-500 and TiO$_2$-700 could be clearly observed. The result indicated the improvement in the crystallinity of anatase TiO$_2$. It has been reported that the typical temperature required for the anatase to rutile phase transformation reported by Bastow and Withfield is ca. 600$^\circ$C [16]. However, there was no indication of rutile phases in the XRD pattern although the calcination temperature was increased to 700$^\circ$C.
The morphology and size of the prepared TiO$_2$ were characterized by a transmission electron microscope. TEM images of TiO$_2$ calcined at 300°C, 500°C and 700°C are shown in Fig. 3. By the calcination at 300°C, as seen in Fig. 3A, the TEM image for TiO$_2$ displayed a sphere-like morphology with average particle-size of about 10 nm in diameter. The larger size of the TiO$_2$ particles was observed when the calcination temperature was increased to 500°C and 700°C. The thermal treatment affected the crystal growth, indicating the aggregation of TiO$_2$ nanoparticles when the temperature increases. The smaller size of the TiO$_2$-300 particles was also evident from the broader XRD peaks.

Fig. 4(A) shows the diffuse reflectance spectra of the standard anatase and TiO$_2$ calcinated at 200°C and 700°C. The increasing of reflection was started around 350 nm due to the reduction of photon absorption. For TiO$_2$-200 and TiO$_2$-700, the absorption edge displayed a gradual blue shift. Further analysis of reflectance spectra was performed to determine the energy different between the lowest conduction band the highest valence (band gap). The calculation of band gap can be done by applying the Kubelka–Munk method which based on the following equation: $F(R) = \frac{(1-R)^2}{2R}$, where $R$ is the reflectance and $F(R)$ is proportional to the extinction coefficient ($\alpha$)[18]. For anatase TiO$_2$, the estimated
value of band gap was 3.27 eV (Fig. 4B). However, the smaller values were observed on TiO\textsubscript{2}-200 (3.23 eV) and TiO\textsubscript{2}-700 (3.25 eV).

**Figure 4.** (A) UV-Vis diffuse reflectance spectra and (B) Kubelka-Munk plots and bandgap energy estimation for the standard anatase and TiO\textsubscript{2} calcinated at 200°C and 700°C.

The photoelectrochemical properties of the prepared TiO\textsubscript{2} samples were studied by the photoelectrochemical oxidation of ethanol in water. Photocurrent-voltage curves of TiO\textsubscript{2}-300, TiO\textsubscript{2}-500 and TiO\textsubscript{2}-700 in 1.0 M Na\textsubscript{2}(SO\textsubscript{4}) under chopped irradiation are shown in Fig. 5. When the illumination was exposed on the TiO\textsubscript{2} surface, an anodic polarization coursed in a rapidly rising anodic current (photocurrent). In contrast, this photocurrent immediately disappeared after the light exposure was shut off. For a reverse scan, the experiment was conducted in the dark to provide the background of a cathodic current. The irradiation of the TiO\textsubscript{2} electrode during cathodic polarization also exhibited a similar result. Chopped irradiation on the TiO\textsubscript{2}-300 electrode yielded the average anodic photocurrent of approximately 2 µA. The photocurrent is due to the formation of electron-hole pairs; holes formed in the bulk which are forced to move to the surface (TiO\textsubscript{2}/electrolyte interface), whereas electrons are moving towards the ITO/TiO\textsubscript{2} interface. Under irradiation, the generated photoelectrons may be trapped by the TiO\textsubscript{2} surface groups (TiOH). Once the applied potential is positive for the electron trap potential, a flow of electrons from the trap band to the conducting substrate occurs and an anodic current is generated.

**Figure 5.** Photocurrent-voltages curve of TiO, calcinated at 300°C, 500°C and 700°C in aqueous 1.0 M Na\textsubscript{2}(SO\textsubscript{4}) under chopped irradiation.

Since calcination temperatures affect the structural property of TiO\textsubscript{2}, the photoelectrochemical properties of TiO\textsubscript{2} with different calcination temperatures were investigated. The anodic photocurrent of
TiO$_2$-300 was higher than those of TiO$_2$-500 and TiO$_2$-700. The results suggested that the photocurrent of TiO depends on the crystallinity of anatase. As mentioned before, the generated photoelectrons can be trapped by the TiO$_2$ surface groups (TiOH) $[19]$. Presumably, the photoelectrons of TiO$_2$-300 were trapped by TiOH on the surface, resulting in the delay of the photocurrent. It is clearly seen that TiO$_2$-500 and TiO$_2$-700, with a small amount of TiOH, exhibited a very rapid rise/decay of the photocurrent. Kavan et al. $[20]$ reported the photocurrent of single crystal anatase without any delay of the photocurrent. However, the photocurrent obtained from TiO$_2$-700 was reduced when the calcination temperature was raised to 700°C. The drop in photocurrent might be due to the aggregation of crystalline anatase during the thermal treatment, resulting in the enhancement of charge-transfer resistance of TiO$_2$.

4. Conclusions

The titanium dioxide photocatalyst was successfully prepared by the sol gel method. The average particle size of 10 nm of TiO$_2$-300 was obtained. TEM images revealed the aggregation of TiO$_2$ particles when the calcination temperature was increased to 700°C. XRD patterns as well as the Fe K-edge XANES spectrum confirmed the formation of the anatase phase. There was no indication of a rutile structure in any samples. The photocurrent-voltage curves clearly revealed the influence of anatase crystallinity on the TiO$_2$ photocurrent.

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6. References

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