Modified Sol-Gel Method in TiO$_2$ Fabrication for Conversion of Glucose to High-Value Chemicals

Orousa Panatta$^1$, Jiraporn Payormhorm$^1$, Siriluk Chiarakorn$^3$, Navadol Laosiripojana$^4$, and Surawut Chuangchote$^{1*}$

$^1$The Joint Graduate School of Energy and Environment, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand
$^2$School of Energy Environment and Materials, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand

Abstract. Glucose was successfully converted to be high-value products (acidic compounds) via photocatalytic oxidation with TiO$_2$. This is a new route for chemical production of high-value chemicals. The development of TiO$_2$ synthesis is interesting to improve the properties of photocatalysts. In this research, TiO$_2$ synthesized by modified sol-gel method with microwave (MW) irradiation resulted in small particles and a mixed-crystalline structure of anatase and rutile phases (28.7:65.2). The small particle sizes of TiO$_2$ (MW) (400 nm) influenced high glucose conversion (i.e. 67.7 % at 120 min) because of higher adsorption site of glucose. The mineralization of organic products was occurred after 15 min since pH value of solution trended to increase with increasing time.

Keywords: biomass, sugar, titanium dioxide, sol-gel synthesis, photocatalytic oxidation.

1. Introduction

Conversion of biomass to renewable chemicals has received significant attention as one of the key technologies for the sustainable society [1]. In recent years, many researchers have attempted to find ways to utilize biomass as feedstock for the production of chemicals and fuels because of its abundance and renewability [2]. In the basis of biomass, it is consisted of hydrocarbon compounds (carbon, hydrogen, and oxygen are mainly elements) like fossil fuels, but its chemical compositions are different. Cellulose, hemicelluloses, and lignin are polymeric hydrocarbon which their structures are linear homopolysaccharide, branched heteropolysaccharide and complex three-dimensional polymer of polyphenolic substance, respectively [3]. To consider the glucose, it is abundant and is an important sugar monomer in the structure of cellulose. Recently, various processes have already been developed for biomass conversion including steam gasification, fast pyrolysis, and super critical conversion [4]-[6]. Nevertheless, these processes also require high temperature, high pressure, and high system cost to produce chemicals and fuels. Photocatalysis is one of promising process because it can be performed under solar irradiation at room temperature and mild condition [7].

Titanium dioxide (TiO$_2$) has been considered to be the most attractive heterogeneous photocatalyst due to it presents the excellent photocatalytic activity, low level of toxicity, and strong oxidizing power [8]. It has been widely used for degradation of organic species in waste water, H$_2$ production, and dye sensitized solar cells [9]-[11]. TiO$_2$ can be fabricated by sol-gel method that it is easy to operate and inexpensive [12]. In addition, the photocatalytic activity of TiO$_2$ is depended on morphological appearances and properties such as surface area, particle distribution, crystallinity, etc. Thus, the aim of the present article focused on simplify modification technique to improve the properties of TiO$_2$ that can enhance the photocatalytic conversion of...
glucose to acidic compound products, *i.e.* glucaric acid and gluconic acid, which are high-valued organic compounds that are usually used as platform and building block molecules. The characterizations of TiO$_2$, photocatalytic conversion were carried out and reported.

2. Experimental

2.1. Preparation of TiO$_2$

Titanium (IV) butoxide (Fluka) was mixed with the same mole of acetylacetone (ACA, Sigma Aldrich). Subsequently, 80 mL of distilled water was added drop wise into the solution under stirring at room temperature follow by adding 60 mL of isopropyl alcohol. The mixed solution was kept at room temperature for 24 h to gel formation followed by drying at 80°C for 24 h. The synthesized TiO$_2$ was pulverized into small particles, then it was calcined at 500 °C for 5 h. Ultrasonic assisted TiO$_2$ (US) was synthesized in the same manner, but the mixture solution was treated with ultrasonic (35 kHz, 320 W, Sonorex Digitec, Bandelin) for 1 h in 5 and 10 min per cycles (2 min ultrasound off between cycles) before aging at room temperature for 1 h. Similarly, the microwave assisted TiO$_2$ (MW) was fabricated with the same method and the mixture solution was treated under microwave irradiation (Whirlpool, 2.45 GHz, 970W) for 4 min before drying at 80°C for 24 h.

2.2. Photocatalytic reaction

The 500 mL of glucose solution (1 g/L) was prepared in a mixture of distilled water and acetonitrile (10:90 v/v) and a concentration of 1 g/L of photocatalyst were transferred into borosilicate cylindrical double-walled reactor followed by continuous stirring for 30 min in dark condition for complete adsorption of glucose on photocatalyst surface. A 400 W of mercury lamp (λ$_{\text{max}}$ = 365 nm) was used as a light source to irradiate the sample that located beside the reactor and reaction temperature was maintained by cooling water system. The 10 mL of samples were taken from the photoreactor at specified times, then it was filtrated through 0.45 µm of nylon filter to remove the photocatalyst particles before analysis. The glucose conversion was monitored by high-performance liquid chromatography (HPLC, Shimadzu, LC-20AD pump) equipped with a refractive index detector (Shimadzu RID-10A). Separation was performed on an Aminex HPX-87H column (300 x 7.8 mm) (Bio-Rad). The mobile phase was 5 mM sulfuric acid at a flow rate of 0.5mL/min and injection volume was 20 µL. The organic acid as products in this research was monitored by pH meter (Metrohm).

2.3. Characterizations of photocatalyst

The microstructure of the TiO$_2$ particles was analysed by scanning electron microscopy (SEM; JEOL JSM-6500FE). The constituent phases were determined by X-ray diffraction (XRD; RIGAKU RINT 2100) with Cu-Kα radiation (λ=0.15418 nm) at 40 kV and 30 mA. The average crystal sizes were estimated from the line broadening of X-ray diffraction reflections using Sherrer equation (1):

$$D = \frac{K\lambda}{\beta\cos\theta},$$

where D is crystallite size, K is a coefficient (0.89), λ the wavelength of the X-ray radiation and β is the full-width at half-maximum (FWHM) intensity of peak, and θ is the diffraction angle.

3. Results and Discussion

3.1. Photocatalyst characterizations

XRD patterns of calcined photocatalysts are showed in Fig. 1. All of TiO$_2$ photocatalysts presented 3 main peaks of anatase at 2θ of 25.4°, 37.8, and 48.1°. The TiO$_2$ (US) and TiO$_2$ (SG) photocatalysts exhibited only anatase phase and same crystal size of 25.1 nm (see Table 1). It indicated that ultrasonic treatment did not significantly affect the crystal size of anatase because it was low frequency (35 kHz) of ultrasonic radiation. Interestingly, TiO$_2$ (MW) showed the mixture of anatase and rutile (2θ = 27.5°), but the diffraction line of anatase is lower than that of TiO$_2$ (US) and TiO$_2$ (SG). There were 87% and 14% of anatase and rutile, respectively, with crystal sizes of 28.7 and 65.2 nm, respectively. This result implied that heat treatment under microwave radiation facilitated the transformation of anatase to rutile phase. However, TiO$_2$ (MW) had
larger anatase-crystallite size than that of TiO$_2$ (US) and TiO$_2$ (SG). SEM images of TiO$_2$ (SG), TiO$_2$ (US), and TiO$_2$ (MW) are represented in Fig. 2. The particles size of TiO$_2$ was spherical shape and monodispersion. It is clearly observed that particle size of TiO$_2$ that was treated with microwave radiation (0.4 µm) was smaller than other TiO$_2$. The particle size of TiO$_2$ (SG) (3.0 µm) is larger than that of TiO$_2$ (US) (2.2 µm) (see Table 1).

![X-ray diffraction patterns](image)

Fig. 1: X-ray diffraction patterns of TiO$_2$ (SG), TiO$_2$ (US), and TiO$_2$ (MW).

Table 1: Summary of XRD characterizations of the synthesized TiO$_2$.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Crystal phase$^a$ (%)</th>
<th>Crystallite size(nm)</th>
<th>Particle size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (SG)</td>
<td>A(100)</td>
<td>25.1</td>
<td>3.0</td>
</tr>
<tr>
<td>TiO$_2$ (US)</td>
<td>A(100)</td>
<td>25.1</td>
<td>2.2</td>
</tr>
<tr>
<td>TiO$_2$ (MW)</td>
<td>A(86)/R(14)</td>
<td>28.7/65.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

$^a$A and R denote anatase and rutile, respectively.

![SEM images](image)

Fig. 2: SEM images (10000x) of TiO$_2$(SG) (A), TiO$_2$(US) (B), and TiO$_2$(MW) (C).

3.2. Photocatalytic reactions

The photocatalytic conversion of glucose is showed in Fig. 3. The photocatalytic conversion of glucose increased with long irradiation time. It also indicated that TiO$_2$ (MW) shows higher conversion of glucose (67.7%) than TiO$_2$ (SG) and TiO$_2$ (US) at 120 min. It could be implied that smaller particles of TiO$_2$ and well dispersion of particles of TiO$_2$ (MW) led the larger photoactive area. Therefore, its photocatalytic conversion was high.

The organic acid products were obtained from photocatalytic oxidation of glucose with synthesized TiO$_2$ is shown in term of pH (see Fig. 4). It was indicated that the increasing irradiation time influenced to the reduction of pH. The pH value of product solution of TiO$_2$ (MW) is lower than TiO$_2$ (SG) and TiO$_2$ (US). These results also correspond to the photocatalytic conversion of glucose. Interestingly, pH value of products solution of TiO$_2$ (MW) was lowest at 15 min (pH=2.5) after that it trended to increase. This phenomenon was explained that some organic acid products might be converted to CO$_2$ and H$_2$O via mineralization [13].
Fig. 3: Photocatalytic conversions of 1g/L of glucose in 10/90(v/v) water and acetronitrile with TiO$_2$ (various modified synthesis technique) for 120 min irradiation time.

Fig. 4: Effect of modified technique of TiO$_2$ synthesis on pH of product solution in 120 min of irradiation time.

4. Conclusion

The synthesized TiO$_2$ was obtained from different modification techniques of sol-gel methods. These particles are in spherical shape. Experiments on TiO$_2$ (MW) showed the largest crystalline size of anatase crystal, but its particle size is smallest. It also showed mixture phase of anatase and rutile due to transformation of anatase to rutile phase by heat from the microwave irradiation. The small particles of photocatalysts affect high photocatalytic conversion of glucose to organic acids because high surface area of glucose adsorption site.

5. Acknowledgements

The authors would like to acknowledge financial support for this research from the Joint Graduate School of Energy and Environment. The authors would like to thanks for the research collaborations from Rajamangala University of Technology Thanyaburi and National Center for Genetic Engineering and Biotechnology (BIOTEC).

6. References


