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# Hydrothermal synthesis, characterization, and photocatalytic performance of silica-modified titanium dioxide nanoparticles

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## Abstract

Silica-modified titanium dioxides were prepared by a hydrothermal method and then characterized by XRD, FT-IR, XPS, TEM, and UV–visible spectroscopy. The silica-modified titanium dioxides were in anatase phase and had large surface areas. There was strong interaction between $SiO_2$ and $TiO_2$, and Ti–O–Si bonds formed during the hydrothermal process. The addition of silica in $TiO_2$ particles could effectively suppress the formation of the rutile phase and the growth of titanium dioxide crystals. DRS spectra proved an increase in the band-gap transition with the increase of silica. The silica-modified $TiO_2$ nanoparticles exhibited better photocatalytic activity, which increased with the silica amount, in comparison with pure $TiO_2$ nanoparticles. Due to better thermal stability, the photocatalytic activity of the silica-modified $TiO_2$ sample held good photocatalytic activity even after calcined at 1273 K.

*Keywords:* Titanium dioxide; Silica; Hydrothermal; Anatase; Photocatalytic

## 1. Introduction

It is well known that the photocatalytic activity of titanium dioxide strongly relies on its crystallinity and specific surface area, and the anatase phase with large surface area is desired in photocatalytic applications [1,2]. Thus, efforts have been put into formation of anatase phases with large surface area. The addition of $LaO_2$, $CeO_2$, $Fe_2O_3$, $Nb_2O_3$, $SiO_2$, or other oxides was found to improve the thermal stability and photocatalytic activity of titanium dioxide [3–8], although these effects were shown to be sensitive to the preparation methods, and the mechanisms for the stabilization effects of these dopants were not yet fully elucidated. Among them, the titanium dioxide–silica system was considered as a potential candidate for photocatalysts [7,9]. Silica-modified titanium dioxide was reported to exhibit a better photocatalytic performance than titanium dioxide itself. This was partially explained in terms of the interaction between titanium dioxide and silica, as well as the different structure from bulk titanium dioxide.

In general, silica-modified titanium dioxide is synthesized by chemical vapor deposition [10] and sol–gel methods [7,11–13], but the transformation of the amorphous phase to anatase on calcination in air always resulted in serious particle agglomeration, larger crystal grain, less surface area, and thus lower photocatalytic activity of $TiO_2$. To avoid those defects, the glycothermal method was applied to prepare silica-modified titanium dioxide nanoparticles, and it was found that these materials had quite large surface areas and exhibited high thermal stabilities [8]. But the glycothermal method usually required butanediol as solvent and high reaction temperature (473–573 K). Hydrothermal synthesis represented an alternative way to provide a facile route to prepare uniform, unaggregated, well-crystalline titanium dioxide nanoparticles [14–20]. However, the preparation of silica-modified titanium dioxide through a hydrothermal method seems not to have been reported until now. In the present work, the hydrothermal preparation of silica-

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modified titanium dioxide nanoparticles is therefore developed, and the resultant nanoparticles exhibit high thermal stabilities and better photocatalytic activity due to the interaction between $SiO_2$ and $TiO_2$.

## 2. Experimental

### 2.1. Synthesis of samples

Tetraethylorthosilicate (TEOS) was added to concentrated nitric acid solution at 313–323 K with magnetic stirring and a clear solution was formed. Titanium $n$-butoxide (TB) was then added dropwise to the above solution under magnetic stirring within 0.5 h. The molar composition of the mixtures was 1 titanium $n$-butoxide:2 $HNO_3$:50 water. After being stirred for 20 min, the mixture was transferred to a Teflon-lined autoclave, and the hydrothermal reaction was carried at 313 K for 10 h. The resulted sample was dried at 393 K. According to the silicon amounts of 3.5, 7.0, 15.0, and 40 wt%, the samples were labeled as ST1, ST2, ST3, and ST4, respectively. Then they were calcined at 673, 873, 1073, and 1273 K for 2 h in each case.

### 2.2. Characterization of samples

The crystalline phase and the phase transformation of titanium dioxide particles were determined using X-ray diffraction (XRD) performed on a D/max2500 diffractometer (40 kV, 30 mA, Cu$K\alpha$ radiation). The crystallite size was estimated using the Scherrer formula, $L = K\lambda/(\beta\cos\theta)$; here, $\lambda$, $\beta$, and $2\theta$ were the wavelength of the X-ray radiation, the half-height width of the diffractive peak, and the diffractive angle, respectively. The morphologies of $TiO_2$ particles were observed on a transmission electron microscope (TEM, Hitachi-600-2). The BET surface area was determined by nitrogen adsorption at 77 K on a Tristar3000 (Micromeritics, Co.). The thermal gravimetry (TG) analysis was carried out in a Perkin–Elmer TGA-2 thermal gravimeter in air at a heating rate of 10 K/min. The element composition and the chemical state of particle surface were determined by X-ray photoelectron spectroscopy (XPS, PHI5300X, Perkin–Elmer Physics Electronics, Mg$K\alpha$ as radiation source). FT-IR spectra were measured on a Nicolet 560 spectrometer. UV–vis diffuse reflectance spectra (DRS) were measured on Shimadzu UV-2101 apparatus, equipped with an integrating sphere, using $BaSO_4$ as reference.

### 2.3. Photodecomposition of methylene blue (MB)

The photochemical reactor consisted of a cylindrical jacketed quartz tube 5.0 cm in diameter and 27 cm in length. A high-pressure mercury vapor lamp of 300 W was placed inside the reactor. To maintain the temperature of the solution during the reaction, water was circulated through the annulus of the jacket quartz tube. The light source assembly was placed concentrically inside the 300-ml Pyrex glass container 6.0 cm in diameter and 28.5 cm in height filled with 250 ml of MB solution. The distance between the source and bottom of the vessel was 1.5 cm for better stirring using a magnetic stirrer. The lamp radiated predominantly at wavelength 365 nm. The MB concentration employed was 100 ppm with a catalyst loading of 0.5 $kg/m^3$ ($TiO_2$). In all experiments, prior to irradiation, the aqueous solution was stirred continuously in the dark for 30 min to ensure adsorption/desorption equilibrium. The concentration of substrate in solution at this point was used as the initial value for the further kinetic treatment of the photodecomposition processes. Samples were collected from the mixture solution at regular intervals and centrifuged to analyze by spectrophotometer to determine the concentration of MB.

## 3. Results and discussion

### 3.1. Thermal stability

Fig. 1 shows XRD patterns of the pure and silica-modified $TiO_2$. It could be seen that all silica-modified $TiO_2$ samples was anatase phase, which was greatly different from pure titanium dioxide. Generally, the rutile structure was directly produced without the additives in the present synthesis. According to Scherrer formula, the crystalline grain size of $TiO_2$ decreased from 13.8 to 7.0 nm when the silica content increased from 3.5 to 40 wt%. These results implied that their crystallinity and sizes strongly depend on the silica content in the samples, and that small silica content (even at 3.5 wt%) could effectively suppress the formation of rutile phase and the growth of titanium dioxide crystals. Fig. 2 shows the XRD patterns of samples thus produced calcined at different temperatures. When the temperature reached 1273 K, most of the anatase phase transformed into rutile for ST1, and a little rutile phase appeared for ST2 and ST3. For ST4 there was no phase transformation from anatase to rutile. Generally, the phase transformation of anatase to rutile took place at 573–873 K for pure titanium dioxide [21]. Thus, the presence of silica effectively suppressed the phase transformation of anatase to rutile in titanium dioxide during

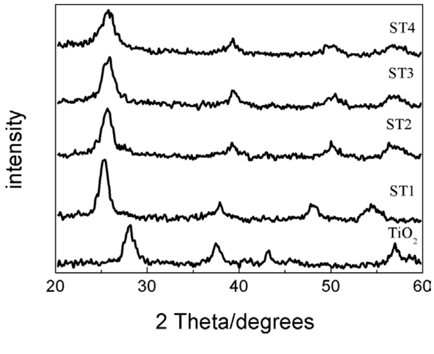

Fig. 1. XRD patterns of the pure $TiO_2$ and silica-modified $TiO_2$.