

# Dependence of quenching process on Ti<sup>3+</sup> defect sites and photocatalytic activity of solvothermal-derived nano titanium (IV) oxide

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## Introduction

Nowadays as the concerns with global environmental issue increase, the application of TiO<sub>2</sub> to the treatment of polluted air and wastewater has become more and more widespread because of its promising photocatalytic performance [1]. The photocatalytic activity of TiO<sub>2</sub> is greatly influenced by its crystal structure, particle size, surface area, incident light intensity and porosity. With the decrease in particle size of powder to the nanometer scale, the catalytic activity is enhanced because the optical band gap is widened due to surface defect [2], combined with the increased surface area [3]. Among these factors, the crystal structure and crystallinity of titania are considered as important factors. Amorphous titania has negligible photocatalytic activity because of the recombination between the pair of photoexcited electron and hole in the amorphous structure. Titania is known to have three natural polymorphs: rutile, anatase, and brookite. Rutile is thermodynamically stable polymorph, but anatase is more suitable form for catalytic applications and for crystalline titania, only anatase is generally accepted to have significant photocatalytic activity [4].

In the present work, crystallite sizes of TiO<sub>2</sub> powders were prepared by the solvothermal method using titanium butoxide as the precursor and quenched in air or hydrogen peroxide at different temperatures. The quenching processes were applied in order to modify surface properties and photocatalytic activities of the TiO<sub>2</sub>. The modified-TiO<sub>2</sub> particles were characterized by X-ray diffraction, N<sub>2</sub> physisorption, CO<sub>2</sub>-temperature programmed desorption, and ESR spectroscopy. Photocatalytic activity of the TiO<sub>2</sub> was tested in a gas-phase decomposition of ethylene under UV irradiation.

## Experimental

### 1. Preparation of TiO<sub>2</sub>

Nanocrystalline TiO<sub>2</sub> was prepared using the solvothermal method according to that of Payakgul et al. [5] using titanium (IV) *n*-butoxide (TNB) as starting material. In general, an amount of 15-25 g of TNB was suspended in 100 cm<sup>3</sup> of toluene in a test tube, which was then placed in a 300 cm<sup>3</sup> autoclave. The gap between the test tube and the autoclave wall was filled with 30 cm<sup>3</sup> of the same solvent used in the test tube. The autoclave was purged completely by nitrogen before heating up to the desired temperature, in the range of 573-593 K at a rate of 2.5 K/min. Autogenously pressure during the reaction gradually increased as the temperature was raised. Once the prescribed temperature was reached, the temperature was held constant for 0.5-6 h. After the system was cooled down, the resulting powders were repeatedly washed with methanol and dried in air.

### 2. Quenching processes

Prior to quenching, the synthesized TiO<sub>2</sub> was dried in air atmosphere at 573 K with a heating rate of 10 K/min for 1 h and then it was taken out and immediately quenched in various quenching media. In this study, both liquid phase and gas phase media were used. For quenching in gas phase media, air at room temperature and 373 K (sample A and B) were selected. For quenching in liquid phase media, hydrogen peroxide at room temperature and 373 K (sample C and D) and water at room temperature and 373 K (sample E and F) were selected. After the samples were quenched in the media for 30 min, all samples were dried in air at room temperature and stored in a desiccator.

### 3. Catalyst characterization

3.1. *X-ray powder diffraction.* The XRD spectra were measured using a SIEMENS D5000 X-ray diffractometer using CuK<sub>α</sub> radiation with a Ni filter in the range of 20–80 two theta. The crystallite size of TiO<sub>2</sub> was determined from half-height width of the 101 diffraction peak of anatase using the Scherrer equation.

3.2. *BET surface area.* The specific surface area (S<sub>BET</sub>) was calculated using BET single-point method on the basis of nitrogen (N<sub>2</sub>) uptake measured at 77 K in a Micromeritics ASAP 2000.

3.3. *Temperature programmed desorption,* Temperature programmed desorption using CO<sub>2</sub> as a probe molecule (CO<sub>2</sub>-TPD) was performed to determine the Ti<sup>3+</sup> site existing on the surface of TiO<sub>2</sub> particle. It was carried out using 0.05 g of a TiO<sub>2</sub> sample. TiO<sub>2</sub> was dosed by 1 vol. % CO<sub>2</sub> in helium for 1 h and then desorbed from 143 K to 273 K with the rate of 21.5 K/min.

3.4. Electron spin resonance spectroscopy (ESR) was conducted using a JEOL, JES-RE2X electron spin resonance spectrometer. It was performed to monitor the surface Ti<sup>3+</sup> on surface titania.

### 4. Photocatalytic activity measurement

Catalytic decomposition of ethylene was carried out in order to determine photocatalytic activity of TiO<sub>2</sub> using a horizontal quartz fixed bed reactor. High purity grade air containing 0.1 vol. % ethylene was continuously fed at a constant flow rate with GHSV of 120 h<sup>-1</sup>. An air stream with 0.1 vol. % ethylene was first passed through the reactor without irradiation until reaching gas–solid adsorption equilibrium. Then, UV light was irradiated on the surface of the catalyst using 500W mercury lamp (Philips, HPL-N). The outlet gas was taken every 30 minutes. Its composition was analyzed using a SHIMADZU GC-14B gas chromatograph equipped with the flame-ionized detector until the reaction reached steady state.

## Results and Discussion

### 1. Structure and surface properties of TiO<sub>2</sub> quenched in different media

In order to modify their surface properties, the crystallite sizes of TiO<sub>2</sub> powders were subjected to quenching processes using various media and quenching conditions. Air, hydrogen peroxide and water at different temperatures are chosen as the quenching media for this study.

The surface area and crystallite size of the solvothermal derived titania amounts of TNB are shown in Table 1. XRD patterns shown anatase titania catalyst. Thermal desorption profiles of CO<sub>2</sub> from a titania surface are shown in Figure 1. The titania samples exhibited two main desorption peaks at temperatures ca. 183 K and 213 K. As reported, surface of titania have two structures which is similar to the results found by Tracy et al. [6]. Based on their study, it was suggested that the peak at ca. 183 K is attributed to CO<sub>2</sub> molecules bounding to regular five-coordinate Ti<sup>4+</sup> site which was considered as the perfected titania structure. The second peak at ca. 213 K has been considered as desorption of CO<sub>2</sub> molecules bounding to Ti<sup>3+</sup> defect/surface area of titania. From TPD results, it was observed that the CO<sub>2</sub> desorption peak areas at ca. 213 K apparently increased with quenching by air at 373 K, air at room temperature, water at 373 K, water at room temperature, hydrogen peroxide at 373 K and hydrogen peroxide at room temperature, respectively. That results were insisted by ESR.

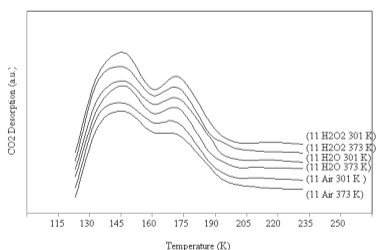
### 2. Photocatalytic activity of the TiO<sub>2</sub> quenched in different media

The photocatalytic activities for the decomposition of ethylene of the various titania were evaluated. The results are shown in figure 2. The conversions of anatase titania prepared with different quenching media were found to be in the order: hydrogen peroxide at room temperature > hydrogen peroxide at 373 K > water at room temperature > water at 373 K > air at room temperature > air at 373 K. The results suggest that photocatalytic activity of anatase titania increases with increasing amount of Ti<sup>3+</sup> defect in the titania or temperature of media have effect on Ti<sup>3+</sup> defect, that titania quenching in media at low temperature better than quenching in media at high temperature. Some differences between the quenching media can be observed from the results of oxygen in quenching media, that the surface defect of titania support was increased by increasing the oxygen percent in feed during the calcination process [7]. Which will be further studied.

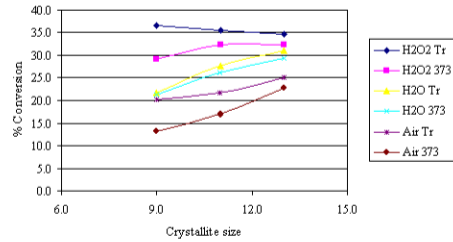
**Table 1** Phase compositions and structural properties of TiO<sub>2</sub> synthesized by solvothermal method after quenching in various media

Sample	Quenching medium	TiO <sub>2</sub> phase	Crystallite size (nm)	S <sub>BET</sub> (m <sup>2</sup> /g)
9A	Air at RT*	Anatase	9.4	93.9
9B	Air at 377 K	Anatase	8.6	96.0
9C	H <sub>2</sub> O <sub>2</sub> at RT	Anatase	10.5	91.1
9D	H <sub>2</sub> O <sub>2</sub> at 373 K	Anatase	10.0	92.3
9E	H <sub>2</sub> O at RT	Anatase	8.9	104.0
9F	H <sub>2</sub> O at 373 K	Anatase	9.0	99.0
11A	Air at RT	Anatase	10.6	93.0
11B	Air at 377 K	Anatase	9.6	85.2
11C	H <sub>2</sub> O <sub>2</sub> at RT	Anatase	13.3	94.0
11D	H <sub>2</sub> O <sub>2</sub> at 373 K	Anatase	13.2	90.0
11E	H <sub>2</sub> O at RT	Anatase	10.5	111.6
11F	H <sub>2</sub> O at 373 K	Anatase	10.4	94.5
13A	Air at RT	Anatase	13.4	66.9
13B	Air at 377 K	Anatase	10.4	60.0
13C	H <sub>2</sub> O <sub>2</sub> at RT	Anatase	14.7	62.5
13D	H <sub>2</sub> O <sub>2</sub> at 373 K	Anatase	14.6	61.1
13E	H <sub>2</sub> O at RT	Anatase	13.2	69.1
13F	H <sub>2</sub> O at 373 K	Anatase	13.4	66.9

\* RT is room temperature



**Figure 1.** Thermal desorption spectra for CO<sub>2</sub> adsorbed on titania.



**Figure 2.** Results of photocatalytic testing comparing the activities of Different TiO<sub>2</sub> samples.

## References

1. Mills, A., Hunte Le, S., *J. Photochem. Photobiol. A: Chem* 108,1 (1997).
2. Suriye, K., Praserttham, P., Jongsomjit, B., *Ind. Eng. Chem. Res* 44, 6599 (2005).
3. Reddy, K.M., Reddy, C.V.G., Manorama, S.V., *J. Solid State Chem* 158, 180 (2001).
4. Tanaka, K., Hisanaga, T., Rivera, A.P., in “Photocatalytic Purification and Treatment of Water and Air” (D.F. Ollis, H. Al-Ekabi Eds.) p. 169. Elsevier, Amsterdam, 1993.
5. W. Payakgul, O. Mekasuwandumrong, V. Pavarajarn, P. Praserttham, *Ceram. Int.* 31 (2005) 391.
6. Thompson, T.L., Diwald, O., Yates, J.T., *J. Phys. Chem. B* 107, 11700 (2003).
7. Suriye, K., Praserttham, P., Jongsomjit, B., *Ind. Eng. Chem. Res.* 44, 6599 (2005)