



# Morphology Study of anatase nano-TiO<sub>2</sub> for Self-cleaning Coating

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## ABSTRACT

Titanium dioxide (TiO<sub>2</sub>) has been widely used in the field of pollutant degradation, virus killer and environment protection. In this paper, the 8 nm TiO<sub>2</sub> nanoparticles are first synthesized by TiOSO<sub>4</sub>·2H<sub>2</sub>O precursor. The samples were then characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis and Raman scattering after heat treatments. The XRD results show the sharp picks of the samples after annealing. The SEM results show that the size of nanoparticles is about 8 nm in diameter. Finally Raman scattering pattern of the as-prepared TiO<sub>2</sub> indicates the anatase phase.

**Keywords:** Titanium dioxide, self-cleaning, nanoparticles, synthesis

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## INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) has been widely used as a photocatalyst for solar energy conversion and environmental applications and building materials such as tiles, concrete, paints and glasses because of its low cost, non-toxicity and excellent photoactivity. TiO<sub>2</sub> exists in amorphous and crystalline forms. The amorphous form is photocatalytically inactive. There are three natural crystalline forms of TiO<sub>2</sub>: anatase, rutile and brookite. Anatase and rutile have a tetragonal structure, while the structure of brookite is orthorhombic. Brookite is less common than the former two crystal polymorphs and is far more difficult to obtain. Anatase and rutile photocatalytically are active, while brookite has never been tested for photocatalytic activity. Pure anatase is more active as a photocatalyst than rutile, probably because it has more negative potential on the edge of the conductive band, which means higher potential energy of photogenerated electrons and also because of a larger number of OH groups on its surface. However, it is interesting that the coupling of different crystalline phases of TiO<sub>2</sub> results in the increase in photocatalytic activity. The mechanism of oxidation and reduction of molecular species involves the generation of superoxide anions and hydroxyl radicals. The conduction band e<sup>-</sup> reacts with adsorbed oxygen

leading to formation of superoxide anions (Senić et al., 2011). The holes in the valence band react with water and generate hydroxyl radicals, or react directly with adsorbed organic molecules. Also, hydroxyl radicals can oxidize wide a variety of organic molecules. This process in large excess of photocatalyst finally leads to the complete mineralization of organic molecules.

Recently large number of studies appeared based on the photocatalytic activity of TiO<sub>2</sub> for oxidation of organic chemicals, obviously the most potential environmental process. Many different ways of Preparation of TiO<sub>2</sub> have been emerged, such hydrothermal and solvothermal methods (Andersson, Österlund, Ljungstroem, & Palmqvist, 2002; Li, Peng, Yi, Wang, & Li, 2006) direct oxidation methods (Jin-Ming Wu, 2004) chemical and physical vapor deposition (Jyh-Ming Wu, Shih, & Wu, 2005) micelle and inverse micelle methods (Hong, Lee, Park, & Lee, 2003) and also sonochemical (Blešić, Šaponjić, Nedeljković, & Uskoković, 2002) sol-gel (Blešić et al., 2002) electrodeposition (Lei, Zhang, & Fan, 2001) and microwave deposition methods (Corradi et al., 2005). The sol-gel synthesis is the most promising alternative for the TiO<sub>2</sub> nanoparticles preparation, since it has numerous advantages: low temperatures, versatility of performance, and the homogeneity of products

at the molecular level. The sol-gel method (Anderson & Bard, 1995) is performed by the hydrolysis of a titanium precursor, usually titanium (IV) chloride in a mixture of water and alcohol in acidic conditions. It involves the reaction of hydrolysis of a corresponding Ti precursor and a subsequent polymerization reaction leading to the formation of the liquid sol phase.

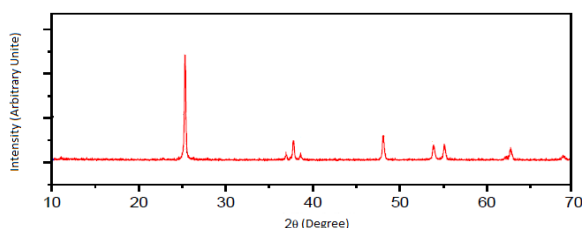
The sol-gel method usually gives amorphous nanoparticles, which are converted to crystalline TiO<sub>2</sub> by heating at temperatures above 400°C. However, this process usually induces agglomeration of nanoparticles, decreasing the number of surface hydroxyl groups, and the surface area-properties that are important for a photocatalytic activity. In this article, the TiO<sub>2</sub> nanoparticles are first synthesized by sol-gel method under given conditions with TiOSO<sub>4</sub>·2H<sub>2</sub>O. Then, the self-cleaning TiO<sub>2</sub> superhydrophobic layers are fabricated on glass. The characterization of the samples is studied by TEM, XRD analyses and Raman scattering after annealing.

## MATERIALS AND METHODS

The synthesis of TiO<sub>2</sub> nanoparticles was carried out by chemical method. The sol-gel process of the nanoparticles is as follow: In the preparation of titanium precursor sol, 20 ml of Titanyl Sulfate (TiOSO<sub>4</sub>·2H<sub>2</sub>O) was added to 40 ml of distilled water while stirring at room temperature. The precipitate was then dispersed in distilled water. This solution was stirred for 10 hours at 1000 rpm. The precipitated gel was separated by centrifugation at 10000 rpm and washed several times with distilled water. Then precipitated gel was dispersed in 80 ml distilled water and refluxed for 4 hours at 80°C to obtain TiO<sub>2</sub> nanoparticles. The reaction was transferred to a preheated furnace and calculated for 2 hours at 800 °C, where the reaction was accompanied by release of a large amount of gases. The morphology and structure of the prepared nanoparticles were characterized by TEM and XRD. The specification of the size and shape of the nanoparticles were examined by TEM analysis using a Philips EM 208. To determine the nanoparticles' structure, the XRD measurement was performed using a Seifert with Cu-K $\alpha$  radiation (wavelength = 1.54 Å). The Raman spectrum of the as-prepared TiO<sub>2</sub> nanoparticles were collected by using a Thermo Nicolet Almega dispersive micro-Raman scattering spectrometer operating by a 532 nm laser line as the second harmonic of a Nd:YLF laser.

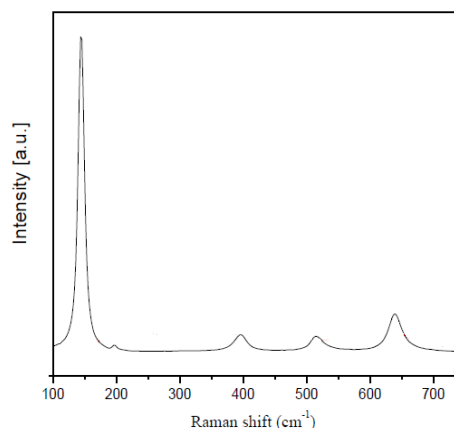
## RESULTS AND DISCUSSION

X-ray diffraction (XRD) measurements were carried out as shown in Fig. 1.



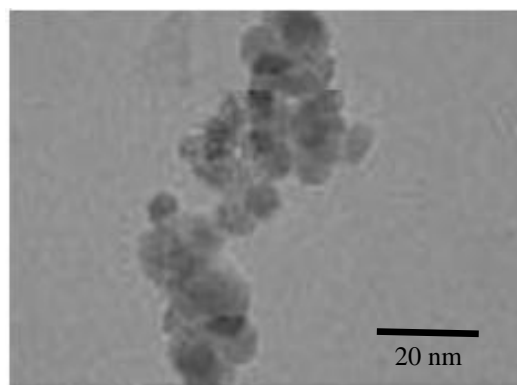
**Figure.1** X-ray diffraction pattern of the annealed TiO<sub>2</sub> nanoparticles.

The pattern of the sample showed peaks, which is regarded as an anatase phase TiO<sub>2</sub> crystallites. The TiO<sub>2</sub> nanoparticles were annealed at 800°C for 2 hours. As you can see the sharp picks reveal the crystalline nanoparticles after heat treatment.



**Figure.2** Raman spectrum of the as-prepared TiO<sub>2</sub>

The Figure2 shows the Raman scattering pattern of the as-prepared TiO<sub>2</sub>. As you can see from Raman spectrum, there are five peaks which indicate the anatase phase. The anatase phase is not stable and tends to be stable at annealed states. In Figure3 also we see the TEM images of the as-prepared TiO<sub>2</sub> nanoparticles. As you can see from the figure3, the size of TiO<sub>2</sub> nanoparticles is about 8nm in diameter after centrifugation and purification.



**Figure.3** TEM images of the TiO<sub>2</sub> nanoparticles

## CONCLUSION

In conclusion, the 8nm self-cleaning TiO<sub>2</sub> superhydrophobic layers were fabricated by sol-gel method. The XRD pattern of annealed TiO<sub>2</sub> nanoparticles shows the sharp picks that reveals the crystalline nanoparticles. TEM images of the TiO<sub>2</sub> show the uniform nanoparticles to use for the self-cleaning processing. Finally, the peaks appeared in Raman scattering of the as-prepared sample is ascribed to the anatase phase TiO<sub>2</sub>.

## ACKNOWLEDGMENTS

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