

Surface Phase Transformation and Photocatalysis of TiO₂ Studied by UV Raman Spectroscopy

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Introduction

Titania (TiO₂) has drawn much research attention in recent years due to its possible applications to environmental purification and solar energy conversion [1]. Anatase and rutile phase are the two major phases of TiO₂. Many studies suggested that the photoactivity of TiO₂ was governed by its crystalline phase [2]. The surface phase of TiO₂ should be responsible for its photoactivity because the photocatalytic reaction takes place on the surface. However, the surface phase of TiO₂, particularly during the phase transformation has not been well investigated. Additionally, the phase transformation from anatase to rutile is influenced by particle size [3], but is the mechanism of the phase transformation of small TiO₂ particle the same as that of big one? The correlation between the surface phases of TiO₂ and its photocatalytic performance is of great significance, but has remained unclear. The difficulty in answering the above questions was mainly due to lacking suitable techniques that can sensitively detect the surface phase of TiO₂.

UV Raman spectroscopy is found to be more sensitive to the surface phase of a solid sample when the sample absorbs UV light [4]. This finding leads us to study the crystalline phase in the surface region of TiO₂ by UV Raman spectroscopy as TiO₂ strongly absorbs UV light and further try to correlate the surface phase of TiO₂ and its photoactivity.

Materials and Methods

A mixture solution of titanium (IV) n-butoxide (Ti(OBu)₄) and anhydrous ethanol was added to a mixture solution of deionised water and anhydrous ethanol. The molar ratio of the H₂O/Ti(OBu)₄ was 75. After the formed white precipitate was filtered, washed and dried, it was calcined at temperatures from 500 °C to 800 °C, then cooled down to room temperature.

Results and Discussion

To understand the mechanism of the phase change of TiO₂ with different particle sizes, the rutile content in surface and bulk region during the phase transformation are studied by UV Raman spectroscopy and XRD, respectively. The mechanisms of the phase transformation of TiO₂ with different particle sizes are proposed (Figure 1). The rutile phase starts to form at the interfaces between the anatase particles of the agglomerated TiO₂ particles when the TiO₂ particle size is in the range of 10-60 nm [5]. However, for anatase TiO₂ with particle sizes below 10 nm and larger than 60 nm, both the surface of anatase particles and interfaces of the contacting anatase particles may provide the nucleation sites of rutile phase.

A direct correlation has been proposed between the surface phase of TiO₂ and its photoactivity of water splitting (Figure 2a) and photodegradation methylene blue (MB) (Figure 2c). It is found that the presence the surface anatase phase is important for the photocatalytic

performance of TiO₂ and the photoactivity is sensitive to the surface phase of TiO₂. Although the bulk region is gradually transformed into the rutile phase with elevated calcination temperature, the samples with surface anatase phase still exhibit the similar photoactivities (Figure 2a, 2c). When the anatase phase in the surface region was transformed into the rutile phase, the photoactivity decreases dramatically. The synthetic effect between the surface anatase phase and bulk rutile phase is significantly responsible for the high photocatalytic activity of sample. The synergistic effect could be interpreted in terms of a semiconductor heterojunction between anatase and rutile, which essentially enhances the charge separation efficiency between excited holes and electrons.

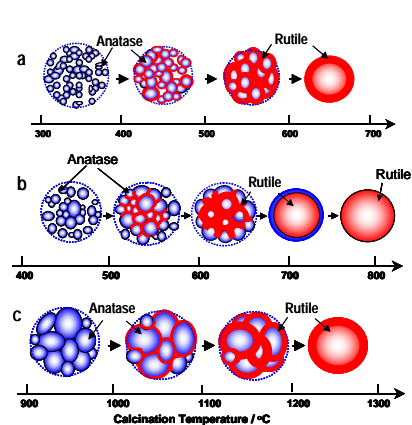


Figure 1. A proposed scheme for the phase transformation of TiO₂ with different particle sizes, particle size <10 nm (a), 10 nm <particle size <60 nm (b), and particle size >60 nm (c).

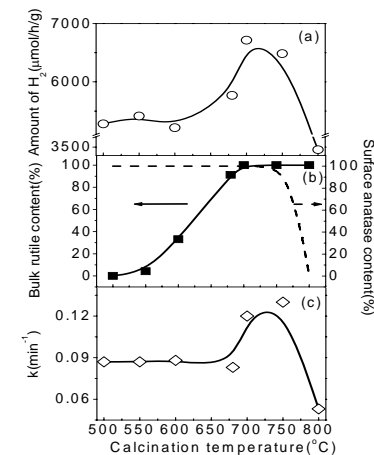


Figure 2 The overall amount of H₂ production for the photocatalytic water splitting (a) and the apparent rate constants (min⁻¹) of the photocatalytic degradation of MB (c) on TiO₂ sample calcined at different temperatures

Significance

The synergistic effect between the tightly contact surface anatase and bulk rutile phase is mainly responsible for enhancing the photoactivity. This work actually reveals a general essence that the surface phase structure of catalysts usually plays the crucial role in catalytic performance, particularly in a photocatalytic reaction.

References

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