UV Raman Spectroscopic Studies on Surface Phase Transformation and Photocatalytic Performance of TiO_2

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Introduction

TiO_2-based photocatalysts have recently attracted much interest for their potential applications to detoxification of environmental pollutants and solar-energy conversion [1]. As a strategy for enhancing the photoactivity of TiO_2, coupling of different phases in the surface was proposed [2], meaning the effect of the surface-phase structure. On the other hand, the phase transformation, particularly the surface phase transformation, is one of the most important issues in the practical application of TiO_2. The particle size greatly influences the surface and bulk phase transformation of TiO_2 particles [3].

It is worth noting that whether the photoactivity or phase transformation of TiO_2 is associated with the surface properties. UV Raman spectroscopy has been found to be more sensitive to the surface phase of the samples with strong-absorption in ultraviolet [4]. This advantage of UV Raman spectroscopy makes it possible to correlate the surface crystalline phase with photocatalytic performance.

Materials and Methods

The anatase TiO_2 with different particle sizes were prepared at this laboratory [3, 4]; Preparation of anatase deposited on rutile sample (denoted as $TiO_2(A)/TiO_2(R)$) [2]: The rutile TiO_2 (Alfa Aesar, 99.8% rutile phase) was used as the support. $TiO_2(A)/TiO_2(R)$ sample was prepared by a wet impregnation method.

Results and Discussion

The rutile content in the surface and bulk during the phase transformation can be estimated by UV Raman spectroscopy and XRD, respectively. The proposed model of agglomerated TiO_2 particles is shown in Figure 1. The transformation temperature is decreased with the decrease of the initial particle size. Rutile mainly nucleates at the interfaces of the contacting anatase grain (<60 nm) and the free surface, interface and bulk are all likely to work as rutile nucleation sites for particles larger than 60 nm.

A correlation (Figure 2) has been found between the surface phase of TiO_2 and its photoactivity for hydrogen evolution via the catalytic methanol reforming. It is found that the photoactivity is sensitive to the surface phase and the TiO_2 samples with surface anatase-rutile mixed phase exhibit maximum photoactivity. The effect could be attributed to the formation of surface-phase junction between anatase and rutile, which essentially enhances the charge separation. The junction formed between MoS_2 and CdS is supposed to be responsible for the enhanced photocatalytic activity of MoS_2/ CdS. [5], the result further confirms the effect of the surface junction on photocatalytic activity.

Significance

The surface sensitivity of UV Raman spectroscopy can be widely applied in the investigation of surface properties and catalytic performance of catalysts. The importance of surface-phase junction provides a possible strategy to develop high-activity photocatalysts for both environmental protection and solar energy utilization.

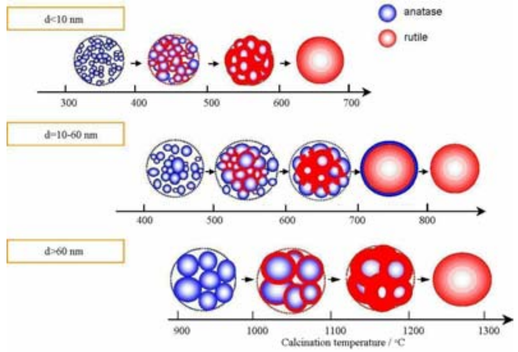

Figure 1. A proposed scheme for phase transformation of TiO_2 with different particle sizes.

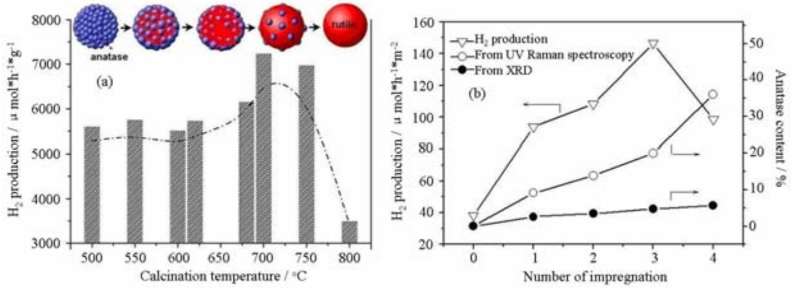

Figure 2. Photoactivity for hydrogen evolution of (a) TiO_2 calcined at different temperatures and (b) anatase deposited on rutile (denoted as $TiO_2(A)/TiO_2(R)$-n, where n is the number of impregnation).

References

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