In-situ hydrogenation synthesis of Ti^{3+} self-doped TiO_2 hollow spheres with enhanced visible light photoactivity

He-Yi Du [a], Ya-Hsuan Liou [b], Chin-Jung Lin [a,*]

[a] *Department of Environmental Engineering, National Ilan University, Ilan, 260, Taiwan*

b Department of Geosciences, National Taiwan University, Taipei, 106, Taiwan

** E-mail: lincj@niu.edu.tw*

Abstract:

A hydrothermal synthetic process has been developed to prepare Ti^{3+} self-doped titanium dioxide (TiO_2). The freshly formed TiO_2 was in situ surface hydrogenated during the condensation stage by introducing $NaBH_4$, and Ti^{3+} ions were created near the surface of TiO_2. Using ESCA spectrum, the relative content of Ti^{3+} ions near the surface of TiO_2 is estimated to be 10%. The decomposition of paracetamol under visible light irradiation was significantly enhanced, contributing to the high absorption of visible light and suppression of charge recombination. This study demonstrates a simple and low-cost method to produce Ti^{3+} self-doped TiO_2 hollow spheres with effective photoactivity in visible light.

Keywords: hydrogenation synthesis, TiO_2, hollow sphere.

1. Introduction

Because of the chemical stability and low toxicity of titanium dioxide, much attention has been paid to the application of materials. However, the wide bandgap (3.2eV) of its own relationship is more limited by ultraviolet light under photocatalysis.[1] So far, there have been many studies[2,3] on the photocatalysis of titanium dioxide which has been coupled with a narrow bandgap metal oxide, doped with different metals or non-metal ions on titanium dioxide, caused defects on the surface of titanium dioxide, and even modified titanium dioxide activity, and the reduction of Ti^{3+} -containing titanium dioxide to improve its activity on visible light. They are more environmentally friendly and effective methods.

2. Experimental

Firstly, adding ethanol, ether, glycerin and $TiOSO_4$ into a stainless steel autoclave to solvothermal-hydrothermal method to prepare organotitanium microparticles. After the reaction is completed, the solid in the autoclave is filtered out with ethanol and dried in the oven. A fixed amount of organic titanium microspheres and $NaBH_4$ are added into a stainless steel autoclave to heating for hydrolysis reaction. Conducting an internal hollowing reaction and sodium borohydride turn appearance of organic titanium microspheres to the sea urchin-shaped surface.The preparation of the finished sea urchin-shaped hollow titanium dioxide microspheres and the concentration of paracetamol aqueous solution has been configured under full-wavelength light source 300 minutes of continuous degradation of acetaminophen photocatalytic reaction and sampling at a predetermined time. The determination of acetaminophen concentration was carried on using HPLC.

3. Results and discussion

Figure 1(a) and (b) are appearance of Ti^{3+} self-doped sea urchin-shaped hollow TiO_2 microspheres by SEM (Scanning Electron Microscope) and TEM (Transmission electron microscope) under the proper conditions of hydrothermal synthetic method.

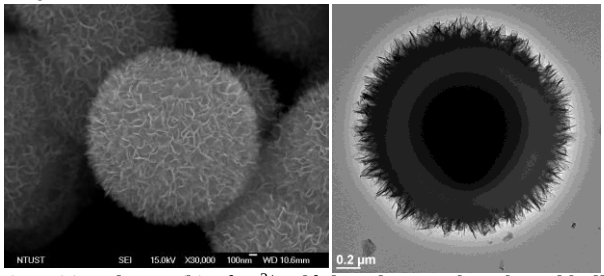

Figure 1. SEM(a) and TEM(b) of Ti^{3+} self-doped sea urchin-shaped hollow TiO_2 microspheres.

We used XAS and XANES to analysis Ti^{3+} self-doped sea urchin-shaped hollow TiO_2 microspheres. Fig. 2 (A) shows that the Ti L3-edge electronic structure of the experimental material of this study has changed. It can be seen that the intensity of the peak rises, which is the phenomenon of octahedral distortion. Usually in the appearance of defects are caused by oxygen vacancies. And Fig. 2 (B) shows that Ti^{3+} ratio of the experimental material of this study is better than other experimental material with Fig. 2(B)(c)

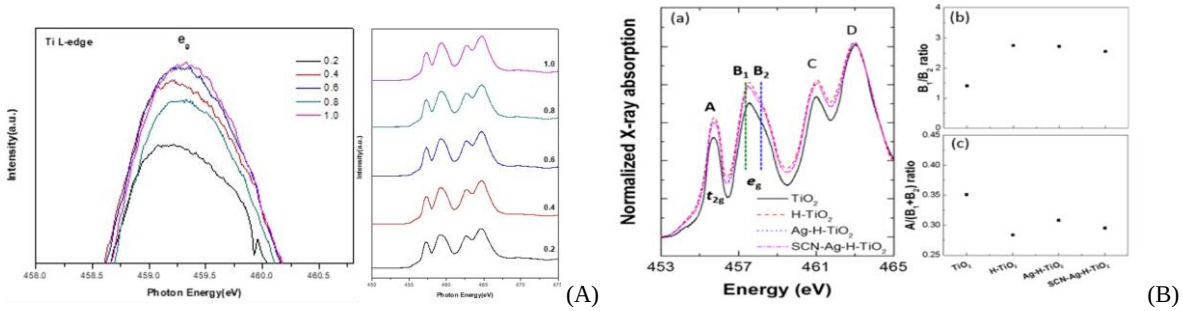

Figure 2. (A)The Ti L-edge of XAS with different concentrations of sodium borohydride on Ti^{3+} self-doped sea urchin-shaped hollow TiO_2 microspheres. (B) Ti L3,2-edge XANES spectra of various TiO2. (b)The ratio of B_1/B_2 and (c) $A/(B_1+B_2)$ integrated intensities with various TiO_2.

The different $NaBH_4$ dosage of the experimental materials of this study have been configured under full-wavelength light source 300 minutes of continuous degradation of acetaminophen photocatalytic reaction and sampling at a predetermined time. For acetaminophen concentration detection by HPLC. Fig. 4 shows that the $NaBH_4$ dosage of 1.0g is the best degradation. Acetaminophen concentration about can be degraded to 15% or less.

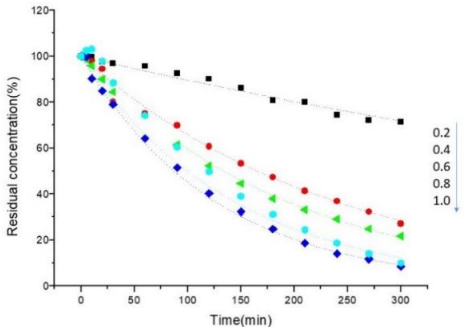

Figure 4. Different sodium borohydride dosage of sea urchin-shaped titanium dioxide hollow microspheres degradation of acetaminophen results data

4. Conclusions

In summary, we synthesized Ti^{3+} form the appearance of sea urchin-shaped hollow TiO_2 microspheres. The material of this study is effectively enhanced its photocatalytic properties by the structure of defects reduces the energy gap of itself. The results show that when the dosage of $NaBH_4$ is 1.0g, the reaction temperature is 110 ℃ and the reaction time is 16 hours, the synthesized sea urchin-shaped hollow TiO_2 microspheres have the best morphologies and defects, and the reduction of Ti^{3+}. It is in the degradation of acetaminophen effect compared to the amount of sodium borohydride added 0.2g increase of about 4 times stronger.

References

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