In-situ hydrogenation synthesis of Ti$^{3+}$ self-doped TiO$_2$ hollow spheres with enhanced visible light photoactivity

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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. So far, there have been many studies 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.](image)
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)

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.

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 $^\circ$C 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