Direct fabrication of Au/ TiO$_2$ hollow spheres with enhanced visible light photoactivity

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Abstract:
A simple method for the fabrication of mesoporous Au/TiO$_2$ hollow microspheres was proposed, using hydrothermal reactions. The resulted nanocomposites were Au located in the core of TiO$_2$ spheres. The samples were characterized by SEM, TEM, XRD, XPS, BET, and UV−vis DRS. The visible-light photodegradation rate of 90% for paracetamol was achieved within 24 h illumination, which exhibited an significant increase compared to Degussa P25 TiO$_2$. Furthermore, no deactivation occurred during catalytic reaction for three times, exhibiting superior photocatalytic stability.

Keywords: Photocatalyst, titanium dioxide, hollow spheres

1. Introduction
Titanium dioxide mainly absorbs ultraviolet light (λ <387nm). When titanium dioxide was excited by light whose energy is greater than the energy gap, and the electrons and holes inside the titanium dioxide react with target pollutants without moving to the surface of the semiconductor material. So the inside of the material electrons and holes combined again, and it will reduce the photocatalytic reaction efficiency. The solution of this limitation is to modify titanium dioxide to increase the efficiency of shortening or migrating electrons and holes to the surface by reducing the size of the semiconductor material, increasing its crystallinity or depositing cocatalysts, which are electron carriers or electron acceptors to improve this disadvantage. Herein, we design a general hydrothermal method for the fabrication of mesoporous Au/TiO$_2$ hollow microspheres. The samples were characterized by SEM, TEM, XRD, XPS, BET, and UV−vis DRS. Paracetamol was chosen as the target organic compound for the visible-light photocatalytic oxidation reactions. Repeated experiments on the photocatalytic degradation of paracetamol were also carried out to evaluate the durability of the prepared photocatalytic samples.

2. Experimental
Weighing accurately the appropriate amount of TiF$_4$ configured TiF$_4$ solution as a titanium source. The anhydrous ethanol and water are mixed in an appropriate proportion, and then the TiF$_4$ solution is added. Finally, HAuCl$_4$ solution is added according to the weight ratio of Au/Ti, and the mixture is stirred for 10 minutes by a magnetic stirrer at 400 rpm to be sealed into the Teflon container to high-performance microwave reactor hydrothermal method at 140 °C for two hours to reflect the conditions. After several hours of microwave heating, removing the Teflon container to be allowed to fall to room temperature, and then the solution was centrifuged 3000rpm 15 minutes. Removing the supernatant to remove the lower layer of the solid solution containing solids by a pore size of 0.2μm the filter paper which is filtered and dried. Obtaining titanium dioxide hollow microspheres with nano-gold particles located inside the shell, and then storing in a bottle for use.

3. Results and discussion
This study used hydrothermal method to complete the gold doped TiO$_2$ hollow microspheres. Fixed four kind of gold doping ratio of 1wt%, 0.5wt%, 0.25wt%, 0.1wt% were prepared. The obtained materials were characterized by a series of characterizations and their photocatalytic properties which were identified. The morphology and the structure of the spherical shell were observed by SEM and TEM (Fig.1). The XRD (Fig.2) analyses the materials of crystal structures, and the XPS analyses the materials of the surface chemical composition. Then, the photocatalytic degradation ability of the photocatalyst was evaluated.
Photocatalysts with containing different ratio of gold make photocatalytic degradation of acetaminophen. During the photocatalytic degradation, monitoring by HPLC (Fig.3), identifying intermediates and concentration profiles, and understanding of the degradation pathway.

Figure 1. TEM image of Au-TMS-I (a) 0 Au-TMS-I (b) 0.5 Au-TMS-I

Figure 2. Doping with different Au concentrations of XRD

Figure 3. The HPLC analysis diagram about degradation of paracetamol by using different Au content titanium dioxide with visible light

4. Conclusions
   In summary, we used a one-step hydrothermal synthesis to form titanium dioxide microparticles. In order to make titanium dioxide work in the visible light condition and know what’s the percentages of Au is the best for degradation, which means the efficiency will reach the highest, we respectively use 0.1wt%, 0.25wt%, 0.5wt%, and 1.0wt% gold ratio to mix with the titanium dioxide and make sure the gold will be attached on its interior. Then we used acetaminophen as a pollution source and analyze its efficiency to select the best one. And the result of the analysis showed that the 0.25wt% of Au addition are the best. Therefore, our study provides a simple method and new direction to synthesize titanium dioxide and make it more useful.

References