Plasmonic enhancement of Au nanoparticle—embedded TiO$_2$ hollow spheres for enhanced visible-light photocatalytic activity

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Abstract:
In this study we fabricated a surface plasmon resonance (SPR) promoted photocatalyst taking advantage of visible light by tailoring Au nanoparticles doping over TiO$_2$ hollow spheres to enhance the catalytic degradation of paracetamol. The Au nanoparticle is used to provide the SPR effect utilizing visible light to enhance the catalytic activity. Regarding different Au loading with the range of 0.0% to 1.0%, the 0.25% and 0.5wt% samples outperformed with highest degradation rate. These results provide a novel design of photocatalyst based on the SPR effect.

Keywords: Photocatalyst, Surface Plasmon Resonance Effect, Titanium Dioxide

1. Introduction
In recent years, newly-developed photocatalyst technology with titanium dioxide is a widely-used method to decompose the harmful chemicals by surface plasmon resonance effect of titanium dioxide. Titanium dioxide is a N-type semiconductor, due to its chemical stability, low cost, non-toxicity and low solubility and can react at room temperature, titanium dioxide is widely used in photocatalysis, such as water degradation of organic pollutants, hydrogen production and air purification. Titanium dioxide is only excited by UV radiation due to its wide bandgap. Despite well-efficient of the titanium dioxide, there are some disadvantages such as it required the particular light wavelength.

When the size of the material is getting to the nanometer scale, it will have different physicochemical property from the bulk material. Taking the nanogold particles as an example, it has special optical properties. When the nanogold with a diameter about 20 nm are suspended in water, the colloidal solution absorbs and scatters light to presents bright red color. This particular optical property results from the interaction of free electrons and electromagnetic waves on the surface after the photoelectromagnetic waves pass through the nanogold and generate the surface plasmon, When the frequency of incident light is close to the frequency of plasma on the surface of nanogold particles, it will cause the collective oscillation of free electrons on the surface and form dipole oscillation along the electric field direction of light, so it is called surface plasmon resonance.

2. Experimental
80 ml of anhydrous ethanol, 40 ml of ether, 40 ml of glycerol, were added to the serum bottle, stirred at 400 rpm at room temperature to clarify state and add 2 ml of TiOSO$_4$ stirred for 10 minutes, and seal it to autoclave at 110 degrees for 4 hours, then cool it to room temperature and rinse with 250 ml of ethanol to remove excess organic matter and dry it at 100 °C to form a smooth surface solid Ti-Org as a precursor of hollow titanium dioxide microspheres. Respectively, hydrolysis with 4% and 10% of deionized water. Deionized water and ethanol in accordance with proper content are put to a Teflon cup, and then seal it to a stainless steel autoclave at 70 °C for 6 hours of hydrothermal reaction, and then weigh 0.1g of titanium dioxide microspheres, 100ml of deionized water, an appropriate proportion of gold tetrachloride, after mixing, aeration with nitrogen for 30 minutes, then 420 nm wavelength light lamp are used for the light deposition method for 3 hours. Then films were characterized by SEM, TEM, BET and XRD for its microstructures and morphologies. All the photochemical measurements were performed on HPLC with 200 ppm paracetamol solution at room temperature.

3. Results and discussion
After a series of hydrothermally synthesized process, the Au particles were attached on the surface of the TiO$_2$ by the photo-deposition method to obtain titanium dioxide microspheres with the nanogold particles on the outer surface of the spherical shell (Figure 1). In order to get the best degradation efficiency, we tried 0 weight percentages of Au, 0.1 weight percentages of Au, 0.25 weight percentages of Au, 0.5 weight percentages of Au, 1.0 weight percentages of Au, respectively, and using acetaminophen as the pollution source to analyze which percentage of Au is the best. Eventually, it was found that when the Au content was increased to 0.25% by weight and 0.5% by weight. The best and almost similar trend of degradation, degradation efficiency decreased again at 1.0% by weight. The highest degradation rate for sample which contains 0.5 wt% of Au concentration, which demonstrated 2 times better than pristine TiO$_2$. Even after 20 h illumination, there is no deactivation occurred during the photocatalytic reaction, exhibiting the excellent stability of the materials.

4. Conclusions

In summary, we used a two-step hydrothermal synthesis to form titanium dioxide microparticles. In order to make titanium dioxide work in the visible light condition and understand what’s the percentages of Au is the best for degradation, that means the efficiency will reach the highest, we respectively use 0.1wt%, 0.25wt%, 0.5wt%, 1.0wt% gold ratio to mix with the titanium dioxide and make sure the gold will be attached on its surface. Then we use paracetamol as a pollution source and analyze its efficiency to select the best one. And the result of the analysis showed that the 0.25wt% and 0.5wt% 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