Photocatalytic water splitting using Au doped Ti^{3+}/TiO_2 hierarchical microspheres for hydrogen production under visible light

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Abstract: A novel and simple approach for the synthesis of Au doped Ti^{3+}/TiO_2 hierarchical microspheres by hydrothermal method were proposed. Synthesis of TiO_2 with a defect structure and doping Au nanoparticles can significantly enhance the photocatalytic activity by a new energy level from Ti^{3+} ions and surface plasmon resonances. The materials were characterized by SEM, TEM, XRD, EPR, BET, UV-Vis DRS and Raman and the photocatalytic activity was tested for hydrogen production. The highest H_2 production rate was 1806 mL/h for sample which contains 0.5 wt% of Au concentration, which demonstrated five times better than pristine TiO_2. Furthermore, photocatalytic activity is still maintained with no noticeable decrease observed even after illumination 20 h, demonstrating the excellent stability of the materials.

Keywords: Au nanoparticles, Ti^{3+} self-doped, Hydrogen production.

1. Introduction

Photocatalytic water splitting to generate hydrogen and oxygen has attracted attention as a renewable energy source. And, titanium dioxide (TiO_2) is the most widely used photocatalyst for hydrogen production. In particular, Au nanoparticles doped onto titania can extend the light absorption into visible region and enhance the surface electron excitation due to strong surface plasmon resonances (SPR).[1] Recently, reduce TiO_2 containing Ti^{3+} ions have been reported to improve visible light photocatalytic activity.[2] However, synthesizing defects and doping noble metal on the titania in the same time is still need more investigation.

Herein, we report a novel and simple approach for the synthesis of Au doped Ti^{3+}/TiO_2 hierarchical microspheres by hydrothermal method. Owing to the injection of hot electrons from Au nanoparticles and a new energy level generated by the presence of Ti^{3+} ions below the conduction band, resulting in photocatalytic hydrogen production rate was remarkably enhanced.

2. Experimental

In this work, Au doped Ti^{3+}/TiO_2 hierarchical microspheres were prepared by two steps hydrothermal. First step was used to synthesize microspheres with Au and Ti precursor. In the second step, titanium contained in the precursor was reduced by $NaBH_4$ and formed hierarchical structure in the same time. The synthesis process shown in Figure 1. Afterward, the sample were characterized by various physical techniques such as SEM, TEM, XRD, EPR, BET, UV-Vis DRS and Raman. The photocatalytic activity of the prepared materials was evaluated in terms of hydrogen production from water splitting. In the photoreactor of closed-gas circulation system, 50 mg of photocatalyst was suspended into 80 ml of 50% ethanol aqueous solution. And, the photoreactor was illuminated with a Xe lamp and a filter with a cut-off at 400 nm.

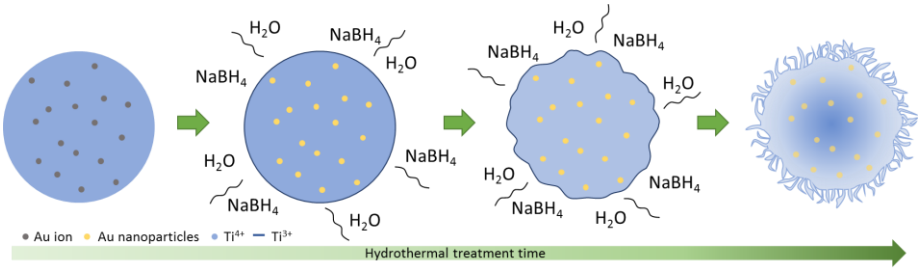

Figure 1. Image of synthesis process of Au Ti^{3+}/TiO_2 hierarchical microspheres.

3. Results and discussion

The morphology and structure of Au doped Ti^{3+}/TiO_2 hierarchical microspheres were showed by TEM. Figure 2 shows the TEM image of the hierarchical structure with discernible nanofibers on the spherical shell from all the sample, which is in agreement with the SEM image. The hierarchical structure was formed possibly due to the high pressure in the hydrothermal process. However, photocatalytic H_2 production of materials were performed and results are shown in Figure 3. The rate of H2 production shows that all the sample generate hydrogen from water splitting under visible light irradiation. The highest H_2 production rate was 1806 mL/h for sample which contains 0.5 wt% of Au concentration, which demonstrated five times better than pristine TiO_2. Even after 20 h illumination, there is no deactivation occurred during the photocatalytic H_2 production reaction, exhibiting the excellent stability of the materials.

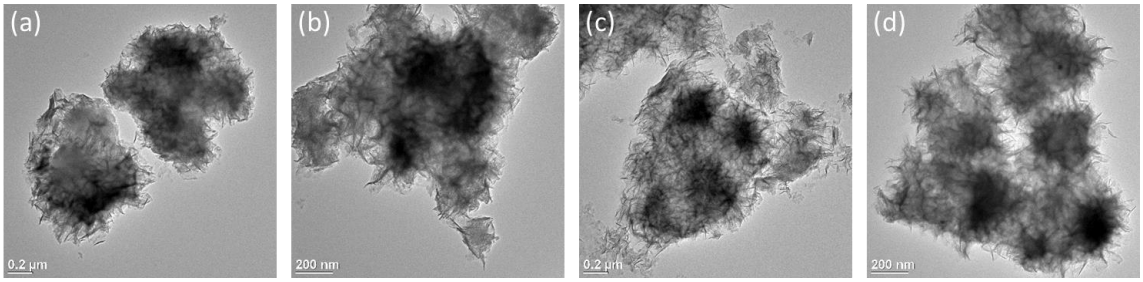

Figure 2. TEM image of Au doped Ti^{3+}/TiO_2 (a)0.1wt%, (b)0.25wt%, (c)0.5wt%, (d)1.0wt%.

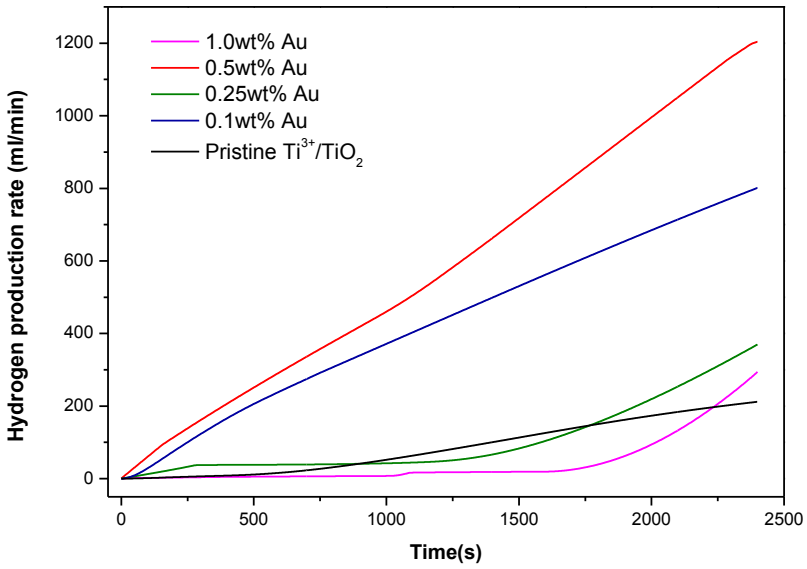

Figure 3. Photocatalytic H_2 production rate of Au doped Ti^{3+}/TiO_2 under visible light irradiation.

4. Conclusions

In this study, we report a novel and simple approach for the synthesis of Au doped Ti^{3+}/TiO_2 hierarchical microspheres by hydrothermal method. Through a serial measurements and analysis, the sample shows high absorption of visible light because of a new energy level from Ti^{3+} ions and surface plasmon resonances from Au nanoparticles. The highest H_2 production rate was 1806 mL/h for sample which contains 0.5 wt% of Au concentration, which demonstrated five times better than pristine TiO_2.

References

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