

## Preparation of Au-Pd core-shell nanoparticles supported TiO<sub>2</sub> and influence of photocatalytic activity on the shell thickness

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### Abstract

TiO<sub>2</sub> Photocatalysts fixed with Au core Pd shell (Au@Pd) nanoparticle were prepared by ultrasonic irradiation. We prepared Au@Pd Nanoparticles with constant core size and controlled shell thickness, and investigated the correlation between shell thickness and photocatalytic activity. The Photocatalytic activities were evaluated from H<sub>2</sub> formation on ethanol decomposition. It was found that the activities has maximum with specific Pd shell thickness, reaching the activity comparable to bulk one as increasing the shell thickness.

*Keywords:* Photocatalyst, Core-shell nanoparticle, Ultrasonic reduction, H<sub>2</sub> Formation

### Introduction

TiO<sub>2</sub> Photocatalyst is applied to the various fields because it has high activity for decomposition of the organic compounds. To improve the activity, it is necessary to inhibit recombination of electron-hole pair which is formed by photo excitation. The immobilization of noble metal nanoparticles on TiO<sub>2</sub> surface is one of the promising ways to suppress recombination of electron-hole pair due to modification of its electronic state. The electronic state of bimetallic nanoparticles with core-shell structure was strongly depended on its structure, such as core diameter and shell thickness. In this paper, we report the preparation and investigation of TiO<sub>2</sub> photocatalyst fixed core-shell nanoparticles with constant core diameter by sequential procedure.

### Experimental

Au@Pd Nanoparticles were prepared by ultrasound irradiation (200 kHz, 6 W/cm<sup>2</sup>) of aqueous solution containing HAuCl<sub>4</sub>·4H<sub>2</sub>O, PdCl<sub>2</sub>·2NaCl·3H<sub>2</sub>O and PEG-MS. In the case of reduction of Au and Pd simultaneously, it is difficult to control a Pd shell thickness and Au core diameter because Pd reduced by ultrasound irradiation act as reductant for Au ion. Therefore we used sequential reduction procedure as follows. First, the solution included HAuCl<sub>4</sub>·4H<sub>2</sub>O and surfactant were irradiated under Ar gas, to produce Au nanoparticles as core metal. Secondly, the solution of PdCl<sub>2</sub>·2NaCl·3H<sub>2</sub>O with the different Pd atomic ratio was added, and irradiated with ultrasound to make core-shell nanoparticles with different shell thickness. The Au@Pd nanoparticles

were immobilized on the TiO<sub>2</sub> surface by adding to TiO<sub>2</sub> powder in the colloidal solution followed with ultrasound irradiation. In order to elucidate the correlation between geometric structure in the nanoparticle and catalytic activity, mixture of Au and Pd nanoparticles were also immobilized on TiO<sub>2</sub> photocatalyst (Pd atomic ratio = 0.25, 0.5 and 0.75, denoted as Au+Pd). Formation of core-shell structure was confirmed with UV-vis spectra and XPS. The shape and diameter of noble metal nanoparticles were measured by HR-TEM. Photocatalytic activity of Au@Pd/TiO<sub>2</sub> and Au+Pd/TiO<sub>2</sub> was evaluated by H<sub>2</sub> formation from ethanol decomposition.

### Result and Discussions

UV-vis Spectra indicated that absorption peaks corresponded to surface plasmon resonance were observed in Au+Pd solutions, whereas the peaks disappeared in the Au@Pd solutions because Au nanoparticles were covered with Pd atoms completely. Furthermore the peaks around 353 eV due to Au 4d<sub>3/2</sub> were also observed in XPS spectra of Au+Pd and Au/TiO<sub>2</sub>. The peak was never observed in Au@Pd solution. These results were suggested that Au@Pd core-shell nanoparticles formed. Fig.1 shows TEM image of Au@Pd nanoparticles with 0.73 of Pd atomic ratio. It was obvious that Pd shell thickness increased and became not constant with increasing Pd atomic ratio. In order to elucidate photocatalytic activity, the thickness and specific surface area of core-shell nanoparticles were calculated because hydrogen generation reaction proceeds on supported noble metal nanoparticles. Fig.2 showed photo catalytic activities of Au@Pd and Au+Pd nanoparticles on TiO<sub>2</sub> normalized specific surface area of noble metal nanoparticles. The result indicated that the activities of Au@Pd had the maximum at 0.53 of Pd atomic ratio while all of the Au+Pd supported TiO<sub>2</sub> photocatalysts were independent. In addition, both catalytic activities of Pd+Au and Au@Pd were about the same at 0.73 of Pd atomic ratio. These results indicated that the activities became bulk Pd one with increasing Pd shell thickness.

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### Conclusions

TiO<sub>2</sub> Photocatalysts fixed with Au@Pd nanoparticles were successfully prepared with sonochemical procedure. Au@Pd/TiO<sub>2</sub> had higher catalytic activity than Au+Pd/TiO<sub>2</sub> with same Pd ratio and showed maximum activity as function of Pd thickness. We concluded that the thickness of Pd shell strongly affected the catalytic activities.

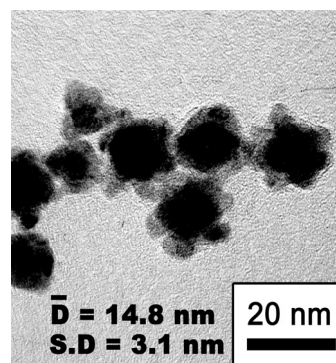


Fig.1 TEM image and average diameter of Au@Pd nanoparticles with 0.73 of Pd atomic ratio.

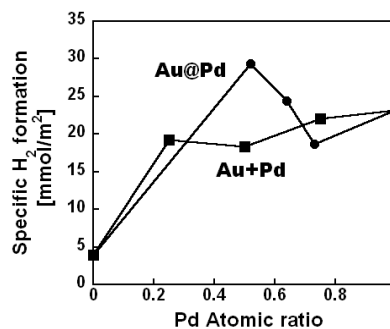


Fig.2 The dependence of specific H<sub>2</sub> formation on Pd atomic ratio in Au/Pd bimetallic nanoparticles.