Preparation of Au-Pd core-shell nanoparticles supported TiO_2 photocatalyst with sonochemical technique

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Abstract

TiO_2 Photocatalysts fixed with Au core Pd shell (Au@Pd) nanoparticle were prepared and evaluated these catalytic activities. Au@Pd Nanoparticles were prepared by ultrasound irradiation toward aqueous solutions containing $HAuCl_4 \cdot 4H_2O$, $PdCl_2 \cdot 2NaCl \cdot 3H_2O$ and surfactant (PEG-MS: polyethylene glycol-monostearate). The photo catalytic activities were evaluated from H_2 formation on ethanol decomposition. It was found from the results that Pd shell thickness on the Au@Pd nanoparticles strongly affected the activity of H_2 formation.

Introduction

TiO_2 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_2 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 was strongly depended on its structure. Especially, we have already reported the bimetallic nanoparticle with core-shell structure, which has one metal core covered with another metal as a shell, show high activity. In this paper, we report the preparation of bimetallic nanoparticles with core-shell structure supported on TiO_2 by ultrasound reduction and photo catalytic activity for H_2 formation from ethanol decomposition.

Experimental

Au@Pd Nanoparticles were prepared by ultrasound irradiation (200 kHz, 6 W/cm^2) of aqueous solution containing $HAuCl_4 \cdot 4H_2O$, $PdCl_2 \cdot 2NaCl \cdot 3H_2O$ and PEG-MS. To control the thickness of the shell, the solutions included the different Pd/Au atomic ratio were used as starting materials. The Au@Pd nanoparticles were immobilized on the TiO_2 surface by adding to TiO_2 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_2 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. The shape and diameter of noble metal nanoparticles were measured by HR-TEM. Photocatalytic activity of Au@Pd/TiO_2 and Au+Pd/TiO_2 was evaluated by H_2 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 nanoparticles completely. It was suggested that Au@Pd core-shell nanoparticles formed. TEM Images and average diameter of noble metal nanoparticles indicated that the diameter decreased with increasing initial Pd concentration. Fig.1 shows the comparison of photo catalytic activities between Au@Pd and Au+Pd nanoparticles on TiO_2 powder. The result indicated that the activities of all of the Au@Pd supported TiO_2 photocatalysts were higher activity than those of Au+Pd/TiO_2 catalysts and the H_2 evolution from Au@Pd had the maximum at 0.52 of Pd atomic ratio. In addition, the shell thickness and core diameter of Au@Pd nanoparticles strongly depend on Pd atomic ratio as shown in Table 1. These results led us to the conclusion that noble metal nanoparticles with core-shell structure probably inhibited a recombination of electron-hole pair, and that Pd shell thickness strongly influenced the catalytic activities.

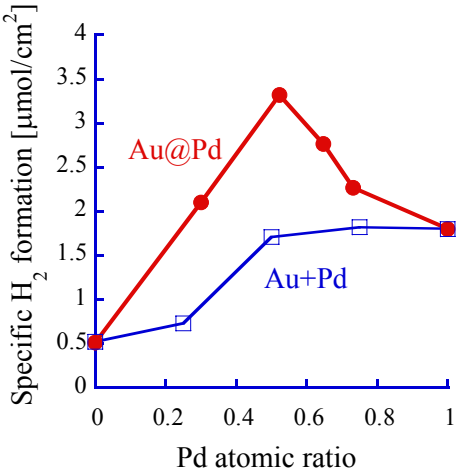

Fig.1 The dependence of specific amount of H_2 formed on Pd atomic ratio in Au/Pd bimetallic nanoparticles.

Conclusions

TiO_2 Photocatalysts fixed with Au@Pd nanoparticles were successfully prepared with sonochemical procedure. The catalytic activities of ethanol decomposition on Au@Pd/TiO_2 were higher than those of Au+Pd/TiO_2 catalysts. The thickness of Pd shell strongly affected the catalytic activities due to the specific H_2 formation decreased with increasing Pd shell thickness.

Table 1 Core size and shell thickness of Au@Pd calculated from TEM observation

Pd Atomic ratio	Core nm	Shell nm	Surface area cm^2
0	-	-	58
0.52	5.2	0.65	84
0.64	4.6	0.80	96
0.73	3.9	0.95	108
1	-	-	155