Sonochemical preparation of Au-Pd bimetallic nanoparticle-supported TiO$_2$
photocatalysts

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Designing nano-morphologies is expected to be one of the most promising approaches to develop the novel high performance catalysts. Using chemical effects of ultrasound, bimetallic nanoparticles consisting of Au-core/Pd-shell can be obtained [1], and noble metal nanoparticles can be immobilized on the surface of metal oxide supports [2]. In this study, we report sonochemical preparation of Au/Pd bimetallic nanoparticle-supported TiO$_2$ photocatalysts utilizing the above techniques. To evaluate their activities, photocatalytic H$_2$ generation from alcoholic aqueous solution is employed as a model reaction.

Au-core/Pd-shell bimetallic nanoparticle-dispersions are prepared by the sonochemical method previously reported [1]. TiO$_2$ (P-25) was added to the dispersion, and followed by the sonication (200 kHz, 6 W/cm$^2$) under Ar atmosphere in order to immobilize noble metal nanoparticles on the surface of TiO$_2$. The weight ratio of noble metal to TiO$_2$ was 1/100 in all cases. The obtained photocatalysts were collected by filtration, rinsed and dried at 50℃. In addition to the bimetallic nanoparticle-supported TiO$_2$ (sample 1), the mixtures of Au and Pd monometallic nanoparticles individually prepared were also immobilized (sample 2). Molar ratios of Au to Pd are 100:0, 75:25, 75:25, and 0:100. The obtained photocatalysts (15 mg) were added to 5 M ethanol aqueous solution in a quartz vessel. The argon-purged closed vessel containing the sample solution was irradiated with a Xe lamp in a dark room. During the irradiation, the solution was stirred with a magnetic stirrer. Head gas phase of the vessel was periodically sampled and the generated H$_2$ was measured by GC-TCD.

Fig.1 shows the H$_2$ generation over the prepared photocatalysts. Even in the same content of noble metal, bimetallic sample 1 shows superior activity to the sample 2. Using the average diameters of supported nanoparticles and their elemental contents, it can be calculated that Pd shell thickness is 0.6 nm. It was reported that core-shell structure of sonochemically prepared bimetallic nanoparticles was broken by annealing and changed into ordered state [3]. The catalytic activity of annealed sample 1 (400℃×1 h, under H$_2$) is also displayed in Fig.1. By annealing, the activity falls into the same level of sample 2 or lower. These results suggest that the high activities of the photocatalysts are coming from the nanostructure, i.e. a few layers of Pd atom shell covering the Au core.

![Graph](image)

Fig.1 Time courses of H$_2$ evolution over sonochemically prepared photocatalysts (Au/Pd = 25:75 mol/mol).

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