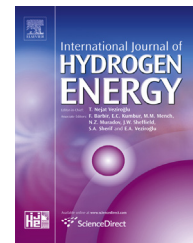




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# Catalytic hydrogen generation from hydrolysis of ammonia borane using octahedral Au@Pt nanoparticles

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## ABSTRACT

Hydrogen generation from hydrolysis of ammonia borane was investigated using octahedral Au@Pt nanoparticles (NPs) as catalysts. The octahedral Au@Pt NPs were synthesized via a polyol method. Pt NPs were fabricated on the octahedral Au NPs with different atomic ratios of Pt to Au and at different temperatures. The presence of poly(diallyldimethylammonium chloride) as a capping agent is crucial for the successful formation of Pt NPs on the Au nanooctahedra. The synthesized octahedral Au@Pt NPs showed a moderate performance of hydrogen generation from hydrolysis of  $\text{NH}_3\text{BH}_3$ . The highest catalytic activity of the Au@Pt NPs for the hydrogen generation was observed with activation energy of 44.28 kJ/mol when the Pt coverage on the Au NPs was optimized at the Pt/Au ratio of 1 and the Pt synthetic temperature of 160 °C.

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## Introduction

Hydrogen is one of the strongest candidates for the next-generation energy carriers replacing current fossil fuels due to its high energy content and environmental friendliness [1,2]. However, safe and efficient methods of hydrogen storage and transport are still the key problem to realize the potable hydrogen-powered systems. To solve this problem, various approaches have been studied [3–11]. Chemical hydrogen storage using metal hydrides [8,9] or chemical hydrides with light elements [10,11] has also been regarded as a promising method for the hydrogen carrier because they contain high volumetric and gravimetric amount of hydrogen. Among the

several candidates of the chemical hydrogen storage materials, ammonia borane ( $\text{NH}_3\text{BH}_3$ ) draws significant attention for several reasons: high hydrogen content (19.6 wt%), high solubility & stability in water at room temperature without any stabilizer, and environmentally nontoxicity [12–14]. Moreover,  $\text{NH}_3\text{BH}_3$  is easily hydrolyzed to generate hydrogen by catalysts even at room temperature and the stoichiometric amounts of hydrogen ( $\text{H}_2/\text{NH}_3\text{BH}_3$ ) can reach up to 3. However, development of suitable catalysts to hydrolyze  $\text{NH}_3\text{BH}_3$  is a remaining issue for practical application for  $\text{NH}_3\text{BH}_3$ .

So far, a variety of heterogeneous catalysts for efficient hydrolysis of  $\text{NH}_3\text{BH}_3$  have been reported [15–23]. Among various catalysts, noble metal nanoparticles (NPs) such as Pt, Rh, and Ru supported on various nanomaterials exhibited

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comparatively high catalytic hydrogen generation rate through hydrolysis of  $\text{NH}_3\text{BH}_3$  [15–18]. Recently, bimetallic metal NPs have been investigated to improve the catalytic efficiencies and stabilities, which includes Pt-M (M = Fe, Co, Ni) [19], Au@Co [20], AuNi alloy [21], Fe@Pt [22], and Pd-Rh@PVP [23] NPs. In addition, it has been revealed that the shape of NP significantly influences the overall activity of the catalyst because the surface energy of the NP depends on the shape of crystalline sides. For example, rhombic dodecahedral Au NPs show higher catalytic activities for reduction of 4-nitroaniline than cubic and octahedral Au NPs [24]. Moreover, AuPt NPs with different shapes show different electrocatalytic behaviors of oxygen reduction [25], and PdPt NPs also exhibited shape-dependent catalytic activities toward  $\text{NH}_3\text{BH}_3$  hydrolysis [26].

Here, we report the catalytic behavior of octahedral Au@Pt NPs for hydrogen generation from  $\text{NH}_3\text{BH}_3$  hydrolysis. The octahedral Au@Pt NPs were synthesized by a repeated polyol process in ethylene glycol solution with poly(diallyldimethylammonium chloride) (PDDA) as a capping agent. The catalytic activities of the Au@Pt NPs were systematically analyzed at different synthetic conditions.

## Experimental

### Chemicals and materials

Ammonia borane ( $\text{NH}_3\text{BH}_3$ , 97%), gold(III) chloride trihydrate ( $\text{HAuCl}_4$ ,  $\geq 99.9\%$ ), chloroplatinic acid hydrate ( $\text{H}_2\text{PtCl}_6$ ,  $\geq 99.9\%$ ), poly(diallyldimethylammonium chloride) (PDDA,  $M_w = 400,000$ – $500,000$ , 20 wt% in  $\text{H}_2\text{O}$ ), were purchased from Sigma–Aldrich. Ethylene glycol (guaranteed reagent grade) was purchased from Junsei Chemical Co, Ltd. All the chemicals and materials were used as received form without a further purification step. Deionized water (DI water,  $\geq 18.3 \text{ M}\Omega \text{ cm}$ ) obtained from a water purification system (Human Power+, Human Corporation, Korea) was used in the experiments.

### Octahedral Au NPs synthesis

Octahedral Au NPs were synthesized by a modified polyol method using PDDA as a capping agent. The detailed synthetic procedure was described in our previous reports [27]. In a typical procedure, 1.0 mL of PDDA solution was added to 50 mL of ethylene glycol in a 100 mL glass bottle. The mixture was sonicated for 2 min. A 50  $\mu\text{L}$  of 0.5 M aqueous  $\text{HAuCl}_4$  solution was introduced while sonicating. Then the bottle was sealed tightly and subsequently heated at 198.5 °C for 40 min in a pre-heated oil bath. For the  $\text{NH}_3\text{BH}_3$  hydrolysis, synthesized octahedral Au NPs were collected by centrifugation at 8000 rpm, washed one time with acetone and 7 times with water to remove excess reagent left in the solution, and then re-dispersed in water (20 mL).

### Octahedral Au@Pt NPs synthesis

Octahedral Au@Pt NPs were synthesized by seed-mediated polyol process using octahedral Au NPs as seed. In typical

synthesis, 50  $\mu\text{L}$  of 0.5 M aqueous  $\text{H}_2\text{PtCl}_6$  solution was introduced into as-synthesized octahedral Au NPs solution, and then sonicated for 2 min. Subsequently, the bottle was sealed tightly and heated at different temperatures ranging from 160 to 198.5 °C for 30 min in a pre-heated oil bath. Synthesized octahedral Au@Pt NPs were collected by centrifugation at 8000 rpm, washed one time with acetone and 7 times with water and re-dispersed in water (20 mL) for further use. To investigate the effect of PDDA capping layer on the formation of octahedral Au@Pt NPs, octahedral Au NPs after intense washing process was used as seed for Au@Pt NPs. All other experimental procedure was same as described above.

### Characterization

The structural morphologies of the synthesized products were characterized by a field-emission scanning electron microscope (FESEM, Hitachi S-4800) and a field-emission transmission electron microscope (FETEM, JEOL JEM-2100F). High-angle annular dark-field - scanning transmission electron microscope (HAADF-STEM) images, cross-sectional compositional line profile, and HAADF-STEM-energy-dispersive X-ray spectroscopy (HAADF-STEM-EDS) mapping were obtained with the use of Titan Double Cs corrected TEM (FEI Titan cubed G2 60-300) to assess the morphology of the layers. Thin-film X-ray diffractometer (Thin-film XRD, RIGAKU Ultima IV) was used for identifying the crystalline structure of the synthesized NPs. Zeta potential of the NPs were measured with zeta potential & particle size analyzer (Otsuka Electronics ELS-Z2).

### Hydrogen generation experiment

A closed-loop hydrogen generation device was designed and used for measuring the hydrogen evolution from the aqueous  $\text{NH}_3\text{BH}_3$  solution. The reaction chamber was made of Pyrex glass and the total volume of the chamber was 250 mL. The reaction chamber was cooled by external water cooling system to control the temperature of reaction. To remove the dissolved gas remaining in water, the reaction chamber was evacuated for 3 min before hydrogen evolution experiment. Hydrogen evolution rate was monitored by measuring a pressure change in the reaction chamber with a pressure gauge (Thyracont VSC43MV). The monitored pressure was converted to hydrogen generation rate based on ideal gas law [28].

## Results and discussions

### Synthesis and characterization of the octahedral Au@Pt NPs

Fig. 1 shows the FESEM images of octahedral Au and Au@Pt NPs synthesized at 180 °C following the polyol method with PDDA as the capping agent. As shown in Fig. 1a, the Au NPs have well-controlled octahedral morphologies with the size of 90–100 nm and the octahedral Au NPs were separated with each other. The as-synthesized octahedral Au NPs were covered with a PDDA layer. When the Pt precursor was added

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