Design of Plasmonic Nanocatalysts for Highly Efficient H_2 Production from Ammonia Borane under Visible Light Irradiation

Hefeng Cheng[1], Kojirou Fuku[1], Yasutaka Kuwahara[1], Takashi Kamegawa[1,2], Kohsuke Mori[1,2], Hiromi Yamashita[1,2*]

[1]*Graduate School of Engineering, Osaka Unviersity,2-1 Yamada-oka, Suita,Osaka 565-0871, Japan*

[2]*Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Kytoto 615-8520, Japan*

**corresponding author: yamashita@mat.eng.osaka-u.ac.jp*

Introduction

As the modern society develops so rapidly, the request of our human beings for next-generation sources of energy has been becoming more and more urgent. In contrast with the traditional fossil energy (e.g., coal, petroleum and natural gas), hydrogen is regarded as a promising fuel in future due to its high energy content per mass and non-pollution. Therefore, the search for efficient and safe hydrogen storage materials is of crucial significance, which may provide a long-term solution to people's concern. Various hydrogen storage materials including metal hydrides, metal-organic frameworks and organic materials have been studied extensively. Ammonia borane (NH_3BH_3) contains as high as 19.6 wt% of hydrogen and exceeds that of gasoline, making it an attractive chemical hydrogen storage candidate.

In the exploitation of highly efficient nanocatalysts, special attention has been drawn to the plasmonic nanostructures, including conventional noble metals and non-conventional semiconductor nanocrystals. Such localized surface plasmon resonance (LSPR) phenomenon could strongly concentrate the incident light and is capable of harvesting light at the nanoscale, which has promising applications in the energy conversion and storage. In this context, we demonstrated that the plasmonic nanostructures, including color-controlled Ag nanoparticles and novel MoO_{3-x} nanosheets, can be used as highly efficient catalysts under visible light[1-4].

Materials and Methods

The supported Ag NPs were prepared on SBA-15 by microwave-assisted alcohol reduction with varying irradiation times in the presence or absence of sodium laurate. MoO_{3-x} nanosheets were prepared by oxidizing metal molybdenum powders with hydrogen peroxide followed by the solvothermal treatments in ethanol solution. The catalytic performances were carried out by dehydrogenation of NH_3BH_3 in aqueous suspensions with plasmonic catalysts under argon gas atmosphere. The reaction was carried out with magnetically stirred both in the dark condition and under visible light irradiation Xe lamp. The yield of H_2 in gas phase was determined by GC using TCD detector.

Results and Discussion

Using the microwave heating method, the spherical or rod-like Ag nanoparticles having different sizes were obtained in the interior of SBA-15 channels and their colors turned into yellow (Lau-3), red (Without-3) and blue (Without-5). All samples exhibited H_2 production activity, and higher activity was observed on smaller Ag nanoparticles. In addition, the activity was greatly enhanced by the visible light irradiation with the order of Lau-3 < Without-3 < Without-5, which was in close agreement with their photo-absorption induced by LSPR.

Different from the conventional plasmonic noble metals, plasmonic semiconductors is one novel category with low resistive loss and earth abundance. By a facile nonaqueous access, MoO_{3-x} nanosheets with tunable LSPR from visible light to near infrared without the addition of any surfactants. It was found that under visible light irradiation, such plasmonic MoO_{3-x} nanosheets displayed dramatically enhanced H_2 production rate from NH_3BH_3 by a factor of 4 than did in dark condition.

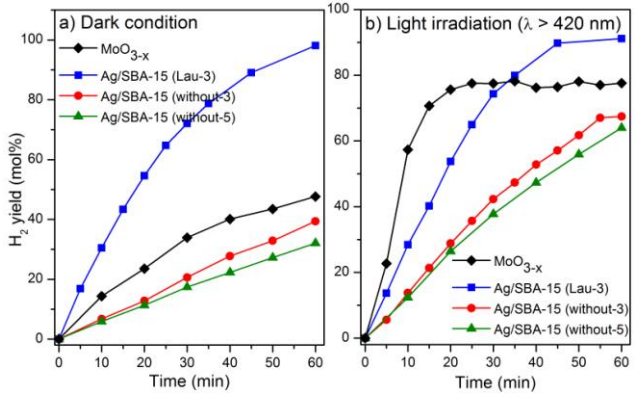

Figure 1 The comparison of the as-prepared plasmonic MoO_{3-x} nanosheets and Ag/SBA-15 for H_2 yield time course from NH_3BH_3 solution a) in the dark condition and b) under visible light irradiation.

Significance

To exploit highly efficient catalysts is always the hotspot of researches. We demonstrate here that the plasmonic nanostructures could dramatically enhance the H_2 production from NH_3BH_3 by LSPR. Such work illustrates the realization of plasmonic nanostructures with high efficiency, which may offer the guidelines to develop highly active nanocatalysts by rational design and controlled synthesis.

References

1. Cheng, H. F.; Kamegawa, T.; Mori, K.; Yamashita, H. *Angew. Chem. Int. Ed.* **2014**, *53*, DOI: 10.1002/anie.201309759.
2. Fuku, K.; Kamegawa, T.; Mori, K.; Yamashita, H. *Angew. Chem. Int. Ed.* **2013**, *52*, 7446.
3. Kamegawa, T.; Matsuura, S.; Yamashita, H. *Angew. Chem. Int. Ed.* **2013**, *52*, 916.
4. Mori, K.; Kawashima, M.; Yamashita, H. *Angew. Chem. Int. Ed.* **2010**, 49, 8598.