Design of Plasmonic Catalysts for Efficient H_2 Production from Hydrogen Carrier Molecules

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Abstract: The efficient catalytic performances for H_2 production from NH_3BH_3 and HCOOH as hydrogen storage and carrier molecules were achieved by the localized surface plasmon resonance (LSPR) inductive promotion effect of bimetallic Pd/Ag/SBA-15 mesoporous silica, Pd/MoO_{3-x} nanosheet and Au@Pd / UiO-66 metal-organic-frameworks (MOFs) catalysts. The moderate control of electron density of Pd metal and surface acid-basic properties of support are key factors to realize efficient H_2 production.

Keywords: H_2 production, Plasmonic catalysts, Hydrogen carrier molecules

1. Introduction

Hydrogen is regarded as a promising fuel due to its high energy content per mass and non-pollution. Ammonia borane (NH_3BH_3) and formic acid (HCOOH) containing high hydrogen content are attractive candidates as chemical hydrogen storage and carrier molecules. 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[1-10]. Plasmonic nanostructures are capable of utilization of abundant solar energy by localized surface plasmon resonance (LSPR). LSPR can be described as the collective oscillation of valence electrons for establishing a resonance between the photons and surface electrons of nanoparticles (NPs), driven by the electromagnetic field of incident light. Such LSPR has promising applications in the energy conversion and storage.

In this study, we demonstrated that the plasmonic nanostructures, bimetallic Pd/Ag NPs on SBA-15 mesoporous silica, Pd/MoO_{3-x} nanosheet hybrid, core-shell Au@Pd NPs supported on titanium doped zirconium based amine-functionalized MOFs (UiO-66($Zr_{100-x}Ti_x$)), can be used as highly efficient catalysts under visible light for H_2 production from NH_3BH_3 and HCOOH.

2. Experimental

The Ag/SBA-15 was synthesized employing microwave-assisted alcohol reduction method. The decoration of Ag/SBA-15 with Pd NPs was achieved via LSPR-assisted deposition under visible light irradiation. Pd/MoO_{3-x} hybrid was prepared by a two-step route; thermal decomposition of ammonium heptamolybdate to form MoO_3, followed by standard impregnation-reduction method to form the hybrid nanostructure. UiO-66($Zr_{85}Ti_{15}$) was suspended in a mixture of H_2O, ethanol and aqueous $HAuCl_4$ solution. After the Au reduction by $NaBH_4$, the products were extracted and washed with water and ethanol, affording Au/UiO-66. Au@Pd/UiO-66 was synthesized by photodeposition of Pd on Au/UiO-66.

3. Results and discussion

Pd NPs associated with plasmonic Ag NPs or Ag nanorods create an efficient light harvesting system to achieve unique photocatalytic activity. The prepared plasmonic catalysts were explored for visible light enhanced activity for the H_2 production from NH_3BH_3. Pd/Ag/SBA-15 catalysts showed higher catalytic activities than the inherent Ag/SBA-15 catalyst under both dark and visible-light irradiation conditions. It can be expected that such Ag-based plasmonic catalyst can form the basis for designing hybrid composites for carrying out visible-light driven chemical reactions.

Plasmonic semiconductor such as MoO_{3-x} is another novel category with low resistive loss and earth abundance. Under visible light irradiation, such plasmonic MoO_{3-x} displayed dramatically enhanced H_2 production from NH_3BH_3. Pd-deposited MoO_{3-x} exhibited the higher activity than MoO_{3-x} under both dark and visible-light irradiation for dehydrogenation of NH_3BH_3 and Suzuki-Miyaura coupling reaction.

Plasmonic core-shell Au@Pd/MOFs (UiO-66($Zr_{100-x}Ti_x$)) can demonstrate efficiently for H_2 production from HCOOH under visible light irradiation. The electronically promoted Pd sites by the LSPR effect of Au as well as the doping of amine-functionality in the MOFs with titanium ions play crucial roles in achieving exceptional catalytic performance.

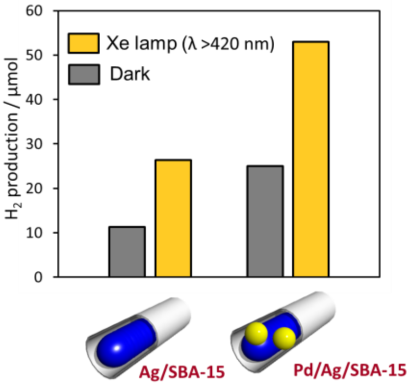

Figure 1. H_2 production from NH_3BH_3 on plasmonic Ag/SBA-15 and Pd/Ag/SBA-15 catalysts.

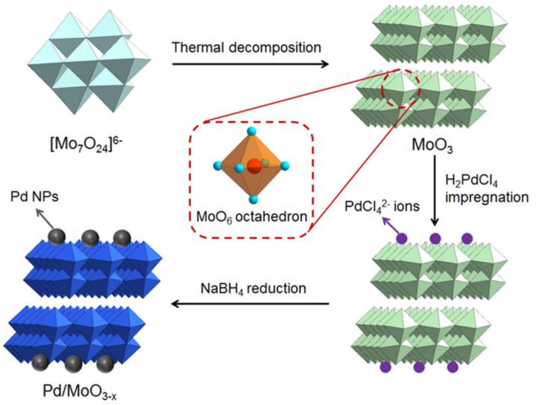

Figure 2. Preparation of plasmonic Pd/MoO_{3-x} hybrid catalyst.

4. Conclusions

The efficient catalytic performances for H_2 production from NH_3BH_3 and HCOOH as hydrogen storage and carrier molecules were achieved by the localized surface plasmon resonance (LSPR) inductive promotion effect of bimetallic Pd/Ag/SBA-15, Pd/MoO_{3-x} and Au@Pd / UiO-66 catalysts.

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