Catalysis Communications 59 (2015) 40–44

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

A novel catalyst for ammonia synthesis at ambient temperature and pressure: Visible light responsive photocatalyst using localized surface plasmon resonance

Haisheng Zeng *, Shinji Terazono, Toshihiro Tanuma

Asahi Glass Co., Ltd., Research Center, Japan

ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form 19 September 2014
Accepted 21 September 2014
Available online 28 September 2014

Keywords:
Localized surface plasmon resonance
Photocatalyst
Ammonia synthesis

ABSTRACT

A novel catalyst for ammonia synthesis using localized surface plasmon resonance (LSPR) was investigated. Os–Au composite nanoparticles showed a high catalytic activity in ammonia synthesis reaction under visible light irradiation at room temperature and atmospheric pressure. Photo energy was likely to be transferred to Os via Au particles, and contributed to the enhancement of the catalytic activity, because the ammonia production rate and the LSPR absorbance of Au particles showed similar dependence on the irradiation wavelength.

1. Introduction

1.1. Ammonia synthesis

The artificial fixation of nitrogen to ammonia ($N_2 + 3H_2 \rightarrow 2NH_3$) is so important to human beings that the invention of the Haber–Bosch process is considered to be much more important in the 20th century than those of the aeroplane, television, and computer [1]. Thus, the research and development on catalytic ammonia synthesis is still being conducted as a "never-ending story" [2,3]. The following are some examples of new approaches: Ru/C catalysts which can be used at a lower reaction temperature and pressure, compared to iron-based catalysts [4], Ru/($C_{12}A_7$:e^-) catalysts in which the $12CaO \cdot 7Al_2O_3$ support has a high electron-donating ability [5], metal complexes which induce dinitrogen cleavage and hydrogenation at an ambient temperature and pressure [6], a proton-conducting cell reactor which has no thermodynamic restrictions imposed on conventional catalytic reactors [7,8], and first-principles calculation that is capable of describing the activity of ruthenium catalysts [9].

Currently, ammonia is manufactured on a large scale by the Haber–Bosch process, which uses a thermal catalytic reaction, requiring high temperature (400–600 °C) and high pressure (20–40 MPa) [5]. It consumes a great deal of energy and accounts for around 1–2% of the worldwide energy supply [3]. Any findings that can improve either the synthesis process or the catalyst performance have a great significance in this field.

1.2. Photocatalyst and localized surface plasmon resonance (LSPR)

Titanium oxides, one of the common semiconductor photocatalysts, absorb only ultraviolet light, which accounts for merely 5% of the energy contained in sunlight, and they cannot use visible light that makes up approximately 43% of solar energy [10]. Over the past few decades, a considerable number of studies have been made to develop photocatalysts with a wide excitation wavelength range that can make the best use of sunlight [10]. As a result of research on energy band modulation, the optical absorption range of photocatalysts has been greatly extended, but the photocatalytic efficiency remains low due to inherent drawbacks [10].

Recently, great attention has been paid to localized surface plasmon resonance (LSPR) of metal particles. A plasmon is a collective oscillation of the conduction electrons stimulated by incident light, and if the plasmon resonance occurs on a nano-scale fine structure, it is called LSPR [11]. Gold nanoparticles, for example, exhibit strong absorption bands in the visible light region around 550 nm [11,12]. The absorption range is controllable by modifying the size and shape of the particle [12]. The use of LSPR excitation to drive photocatalysis instead of semiconductors, therefore, is of great significance, opening up new possibilities of making the most of solar energy.

Direct and indirect photocatalyses using LSPR have been studied for a long time, and Kale et al. [13,14] have recently published a review showing that plasmonic nanostructures can be used to drive direct photocatalysis with visible photons, where nanostructures act as both

* Corresponding author at: Hazawa-cho 1150, Kanagawa Ward, Yokohama City, Kanagawa Prefecture 221-8755, Japan. Tel.: +81 45 374 7591; fax: +81 45 374 8871.
E-mail address: haisheng-zeng@agc.com (H. Zeng).

http://dx.doi.org/10.1016/j.catcom.2014.09.034
1566-7367/

the light absorber and the catalytic active site. Although plasmonic catalysts are reported to be promising, the reaction rates are low and an intense irradiation is indispensable [15,16], indicating that its performance is still far from satisfactory. Regardless of the mechanisms for the catalysis relating to LSPR [13], photo-energy transfer from LSPR particles to catalytic particles appears to be inefficient.

1.3. Ammonia synthesis catalyst using LSPR

Based on the above considerations, we conceived a novel idea of composite nanoparticles for ammonia synthesis of low energy-consuming, by applying catalytically active metal (Os) [4] directly to LSPR particles (Au) so that plasmonic energy could be transferred directly and easily to the catalytically active metal particles (Scheme 1). We propose a hypothesis that excitation of LSPR is used to transfer photon energy to the adjacent catalyst particles, enhancing its catalytic activity. In this study, we prepared Os–Au composite nanoparticles for the ammonia synthesis reaction in order to verify the above hypothesis. The reaction was carried out under visible-light irradiation at room temperature and ambient pressure.

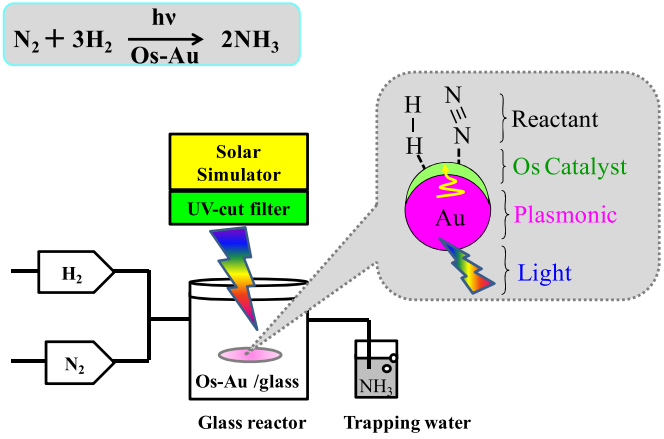
2. Experimental

Os–Au composite nanoparticles were prepared on a glass substrate by using a sputtering and heat treating process. First, Au was sputtered on the substrate (Φ50 mm) to form a 3 nm Au layer (Auto Fine Coater JFC-1600 by JEOL) and then heated at 250 °C for 0.5 h under a H_2 atmosphere, forming Au particles on the substrate. Os was then sputtered onto the Au particles to form a 3 nm Os layer (Osmium Plasma Coater OPC60 by SPI Supplies) and then the same heat treatment was applied so that Os particles were formed on the Au particles. The particle size was measured by a scanning electron microscope (SEM S-4300, Hitachi), and UV–VIS spectra (including LSPR) were measured by a spectrophotometer (U-4100, Hitachi).

An electron-donating catalyst promoter (Cs_2O) was added to Os–Au composite particles by dipping the Os–Au sputtered substrate into a CsOH aqueous solution (27 mM) for three times so that the Cs/Os ratio would be 5–10 [4]. The Cs_2O-promoted Os–Au composite nanoparticles were evaluated as a catalyst after heat treatment at 250 °C for 30 min.

Catalyst performance was evaluated in the ammonia synthesis reaction (Scheme 1). The glass substrate with Os–Au composite nanoparticles (with Cs_2O) was placed in a glass reactor, where N_2 (15 ml/min) and H_2 (45 ml/min) were supplied while irradiating with a solar simulator system (200 mW/cm^2, SAN-EI XES-301S equipped with a 450 nm cut-off filter), or a monochromatic light irradiation apparatus (3.54 mW/cm^2, Asahi Spectra MAX-303) for 2 h. The produced ammonia was identified by ion chromatography (Dionex DX-500) and quantified by using an ammonia selective electrode (TiN-9001, Toko Chemical).

For comparison, both Au and Os nanoparticles were also prepared and evaluated in the same manner, respectively.



Scheme 1. Schematic diagram of an Os–Au composite nanoparticle for ammonia synthesis.

3. Results and discussion

In order to prepare Au nanoparticles that have the best LSPR, sputtering and heat treatment conditions were optimized as shown in Fig. 1. First, three Au layers of different thicknesses (1, 3, 6 nm) were sputtered (sputtering current: 10 mA) by changing the sputtering time (10, 30, 60 s). The Au layers having a thickness of 1 nm and 3 nm exhibited visible light absorption at 670 nm and 740 nm, respectively, but the 6 nm-Au layer showed no clear absorption (Fig. 1-a, b, c). SEM observation shows that the first two layers are composed of densely aggregated nanoparticles, but no nanoparticles were observed on the 6 nm layer (Fig. 1-d, e, f).

When heating the Au layers with a thickness of 1 nm and 3 nm at 150 °C and 250 °C, the LSPR peaks shifted to a shorter wavelength and they became more pronounced (Fig. 1-a, b). The SEM photos show that the two Au nano layers became nano-sized particles through the heat treatment (Fig. 1-g, h). It seems that the higher the temperature, the more isolated and spherical the particles became. However, in the case of the 6 nm-Au layer, no peak shift or nanoparticles were observed following the heat treatment at 250 °C (Fig. 1-c, i). These obtained spectra and SEM images show that LSPR wavelength is affected by the size and shape of particles, which is consistent with the report by Hutter and Fendler [12].

It should be mentioned that Au nanoparticles showing LSPR can be obtained using different combinations of sputtering (e.g. sputtering current and time) and heat treatment (e.g. heating temperature, time, and atmosphere) conditions. As a result, the Au particles prepared by heat treating the 3 nm-Au layer at 250 °C for 30 min (Fig. 1-h) was selected for further investigation. The SEM observation indicates that Au particles on the glass substrate are around 25 nm in size, well dispersed, and showing strong LSPR absorbance at 585 nm.

The pure 3 nm-Os layer sputtered on the glass substrate was similar in appearance to the 3 nm-Au layer (Fig. 1-e). Os was sputtered onto Au particles (Fig. 1-h) and then heated at 250 °C for 30 min, forming Os–Au composite particles, which were slightly larger in size but less uniform as shown in Fig. 2-a. After loading a catalyst promoter, Cs_2O, more densely aggregated particles were observed as shown in Fig. 2-b.

The surface plasmon resonance was observed at around 550 nm for Au nanoparticles and Os–Au composite nanoparticles (Fig. 3). Compared to the clear pink of the former, the latter was light gray. Os nanoparticles themselves did not show LSPR activity, and their bonding onto the Au particle surface did not affect the LSPR of Au in this study (Fig. 3).

We examined the ammonia production rate dependence on the irradiation wavelength, using a monochromatic light source (Asahi Spectra MAX-303) with a band-pass filter in the wavelength region of 450–700 nm at every 50 nm. It was confirmed that N_2 and H_2 reacted to form ammonia under the irradiation of visible light at room temperature in the presence of Os–Au composite nanoparticles with a catalyst promoter (Cs_2O). As indicated in Fig. 4, ammonia was hardly observed in the reaction carried out under the irradiation of visible light below 450 nm and over 700 nm, whereas a relatively large amount of ammonia was detected in the experiments conducted under the irradiation of light between 550 and 650 nm.

In contrast, neither pure Au nor Os nanoparticles, which were prepared on the glass substrate in the same manner, showed a catalytic activity in the ammonia synthesis reaction. This is because pure Au