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Short Communication

Plasmonic energy transformation in the photocatalytic oxidation of ammonium

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ABSTRACT

The plasmonic transformation of light into energy for a chemical reaction is demonstrated in the endothermic oxidation of ammonium ions. The plasmonic heating effect physically triggers a platinum thin film, which becomes an active catalyst for the plasmonic catalytic reaction. The amount of chemical energy consumed in the plasmonic photocatalytic reaction was less than that in the normal chemical process. A homogeneous, condensed, pinhole-less 8 nm platinum thin film fabricated via plasma-enhanced atomic layer deposition served as a medium that transformed the energy in two steps.

1. Introduction

Plasmons are collective electron oscillations generated by the interaction of light with metallic structures such as thin films or nanoparticles [1,2]. Various novel applications in nano-optics and the localized near-field enhancement have been demonstrated in many applications. The enhancement of light by metallic nanostructures leads to useful applications of the energy transformation of plasmons. Examples have been previously demonstrated and published, such as the surface-enhanced Raman scattering [3], cancer diagnosis and therapy [4], sensors [5], plasmonic lasers [6], fuel cells [7], and plasmonic photocatalytic reactions (PPC) [8–19]. In these applications of plasmons, external light illumination supplies the energy to physically enhance a chemical reaction. The external illuminated light is absorbed and induces localized giant electromagnetic field and high density free electrons in collective oscillation. The high power electromagnetic field and high density free electrons can enhance the photocatalytic reaction in a variety of chemical processes [8–19]. Platinum (Pt) has a high plasmonic optical response and is commonly used as a catalyst in a variety of applications. In the catalytic wet air oxidation (WAO) of ammonium (NH_4^+) ions, the removal efficiencies of ammonia were strongly affected by processing temperature, initial pH value, and NH_4^+ concentration [20,21]. The typical WAO method consumes a large amount of power because of the high-temperature and high-pressure processes involved. In our previous study, we demonstrated the room temperature oxidation of NH_4^+ with hydroxyl ions (OH^-) under alkaline conditions [16] processed by a high-efficiency spinning disk reactor (SDR) [15,16,22] without a Pt photocatalyst. We have also demonstrated the plasmonic photocatalytic oxidation of NH_4^+ using a Pt thin film catalyst. However, the physical energy transformation is not clearly resolved in the later process.

In this study, plasmonic heating to enhance the catalytic process on Pt in a SDR is characterized through advanced experiments on temperature variation. The energy of plasmons is demonstrated to transform into a chemical reaction that reduces the energy consumed during the oxidation of NH_4^+.

2. Experimental details

2.1. Spinning disk reactor

The experiments were performed using a home-built SDR (Fig. 1). The experiments were similar to those described in our previous study [16]. A halogen lamp with an aluminum bow reflector was used as a wide-spectrum visible light source. The light-illuminated area was about $2 \times 5\ cm^2$. A servo motor rotated the reaction disk in the reactor at a constant speed of 150 rpm for all experiments. The sample solution was circulated using a peristaltic pump (BT 102S, Yeong Shin Co., Ltd., Taiwan) with an average flow rate of 89 ± 1 mL/min during the 30 min experimental process. The sample solution was dispensed onto the reaction disk, quickly splashed away, collected by a glass container (Schott Duran, Germany), and circulated again.

2.2. Reaction disk

The B270 glass substrate (120 mm diameter, 0.5 mm thickness; modified soda-lime glass, Schott Duran, Germany), with or without a

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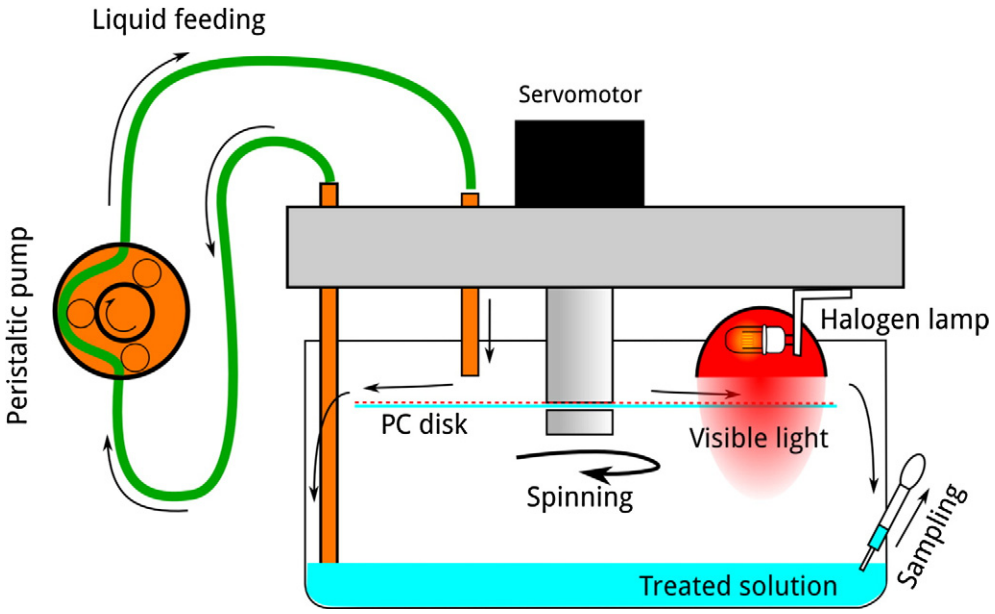

Fig. 1. Schematics of the spinning disk reactor and the plasmonic photocatalytic (PC) oxidation of NH_4^+.

homogeneous 8 nm Pt thin film, was used as the reaction disk (Fig. 2). The Pt thin film with a resistivity of 16.2 μΩ/cm was deposited by plasma-enhanced atomic layer deposition (PEALD) with 200 reaction cycles at 200 °C. The reaction disks used in this paper are the same as that used in the previous works. The deposited Pt thin film is a condensed single layer. The grain boundary structures were not observed in the TEM measurement in our previous work [16]. The deposited Pt thin film was smooth, crystallized, and condensed [23].

The sample disk has processed many experiments and very long processing time in the experimental works. Only a small area of the deposited Pt thin film stripped from the substrate after the more than 100 runs. Therefore, the stability of the deposited Pt thin film appears suitable for future applications.

2.3. Test solution and material analysis

A 100 mL sample solution of dissolved ammonium chloride (2.3 mM, NH_4Cl, Mallinckrodt Baker Inc., USA) was prepared with deionized water containing no detectable nitrogen contaminates. The pH adjustments were performed by the addition of sodium hydroxide (NaOH) to a test solution, and the pH levels were measured with a bench-top pH meter (CyberScan pH2100, Eutech Instruments). In experiments with light

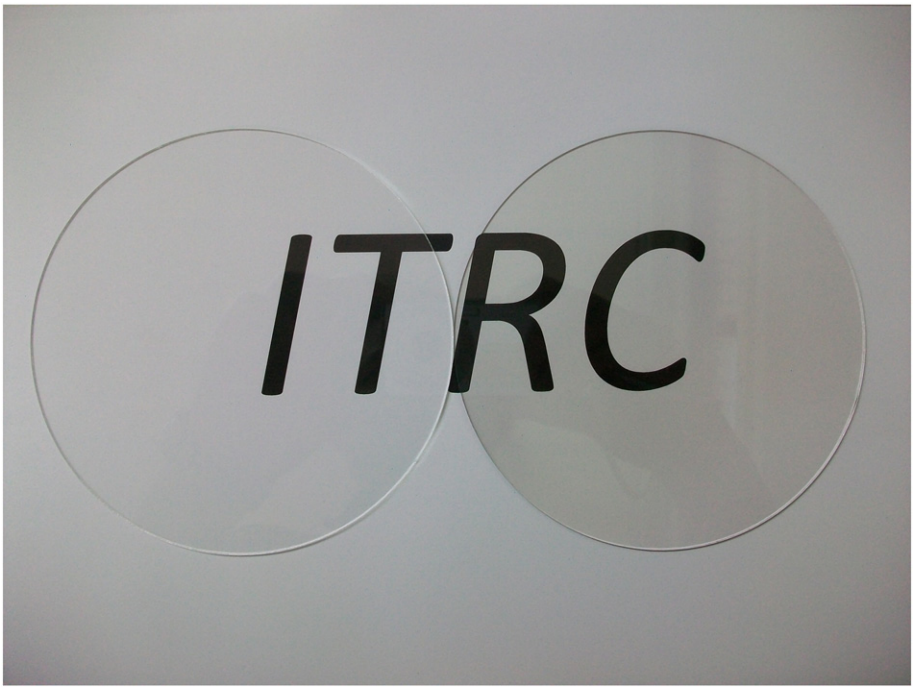

Fig. 2. Photographs of the B270 glass substrate (left) and the B270 substrate coated with 8 nm Pt thin film (right).