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Short Communication

Ammonium oxidization at room temperature and plasmonic photocatalytic enhancement

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ABSTRACT

In an alkaline condition, ammonium can be efficiently reduced with hydroxide ion using a spinning disk reactor at room temperature. To some extent, illumination can boost the processing efficiency by warming water. A homogeneous 8 nm crystallized platinum thin film deposited on a B270-glass substrate by plasma-enhanced atomic layer deposition absorbs light from 350 nm to 2500 nm. The absorbed light transforms plasmonic resonance energy on the platinum thin film and forms a high temperature hot layer. The plasmonic heating effect, or plasmonic photocatalytic reaction, enhances the activity of the Pt thin film for the oxidation of NH_4^+.

1. Introduction

Ammonia generated from organic pollutants is becoming a severe problem [1–4]. In natural environments, the ammonium (NH_4^+) produced by organic materials can be reduced in the nitrogen cycle [5]. Biological nitrification and denitrification processes are typically used in aquariums. Nitrosomonas bacteria, nitrospira bacteria, algae, and water plants help complete the nitrogen cycle. However, the nitrogen cycle may cease when NH_4^+ concentration, temperature, or the pH of water suddenly changes. Previous studies have presented methods for artificial nitrogen cycle processes using Pt as a catalyst at high temperatures [6–9]. In such artificial processes, the ammonia removal efficiency was largely affected by the initial pH and the ammonia concentration [9].

A spinning disk reactor (SDR) is a well-known and very efficient tool. It has a high mass transfer rate [10–16] that accelerates chemical reactions. SDRs have a high processing efficiency, low power consumption, and do not require recycling of the photocatalyst. The room temperature oxidization process of NH_4^+ in water using a SDR is presented with or without illumination in this study. Furthermore, Pt is typically used as the catalyst to boost the oxidization of NH_4^+ in a high temperature and high pressure environment. Pt also has great plasmonic optical response under external illumination. Plasmons are the collective motion of highly concentrated free electrons on a metal surface that elicit a very high electromagnetic field and a hot layer with high temperature [17]. Many studies have examined the plasmonic photocatalytic (PC) reaction [16,18–25]. This study reports that the high temperature generated by plasmons can further increase the catalytic activity of Pt [25]. Plasmonic heating to enhance the catalytic process of Pt in a SDR is also reported. The Pt thin film was deposited by plasma-enhanced atomic layer deposition (PE-ALD), which provides homogeneous thickness, a crystal structure, and stability under illumination [26–28].

2. Experimental details

2.1. Spinning disk reactor

The schematic for the SDR is shown Fig. 1. A halogen lamp with an aluminum bow reflector supplies light for boosting the chemical reaction. No light filter was used in all of the experiments. The illuminated area is approximately 2×5 cm^2. The lowest part of the reflector was 1 cm above the reaction disk. The halogen lamp irradiated light ranging from 350 nm to more than 2500 nm, which was determined by a Field Spectro Pro (Analytical Spectral Devices, USA) (Fig. 2, black solid line). The servo motor rotated the supporting spindle and reaction disk constantly at 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. The sample solution was dispensed on the reaction disk, quickly splashed away, collected in a glass container (Schott Duran, Germany), and recirculated. For the chemical reaction, each experiment used 100 mL of the sample solution processed for 30 min. The pH adjustments were achieved by adding sodium hydroxide (NaOH) to the test solution. In experiments with illumination, the halogen lamp was turned on

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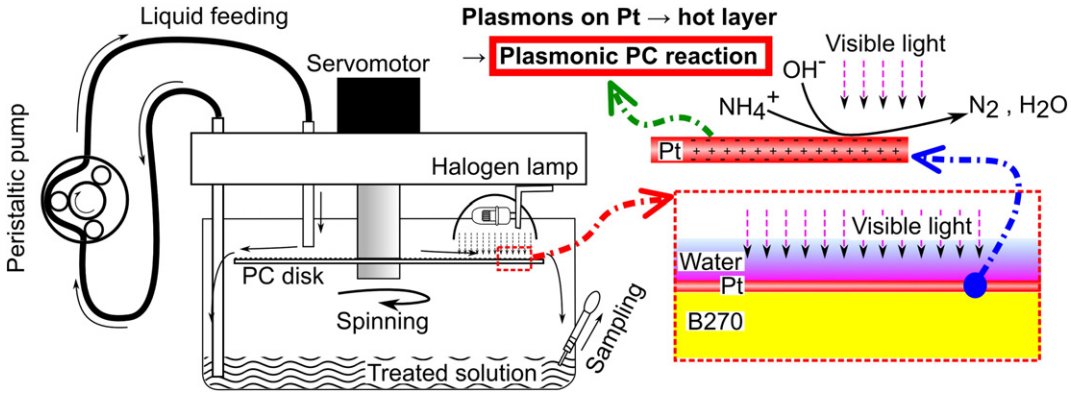

Fig. 1. SDR schematics.

3 min prior to application of the sample solution and the start of the process.

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 homogeneous 8 nm platinum (Pt) thin film, was used as the reaction disk. The Pt thin film was deposited by PE-ALD with 200 reaction cycles at 200 °C. The resistivity of the deposited Pt thin film was determined to be 16.2 μΩ-cm by the Hall effect. X-ray diffraction (XRD) showed that the deposited Pt thin film had 2θ reflection peaks at 40°, 46.54°, and 67.74°. X-ray photoelectron spectroscopy (XPS) showed that the deposited Pt thin film had peaks at $4f_{5/2}$ (74.3 eV) and $4f_{7/2}$ (71.0 eV). The Pt peaks were calibrated with respect to carbon C 1*s* (285.5 eV). The transmission electron microscope (TEM), Fig. 2, measurement showed that the deposited Pt thin film was smooth, crystallized and condensed metal layer. The transmission of the Pt thin film for light from 430 nm to 2500 nm is 56 ± 2% (Fig. 2, red solid line). The absorbed light of external illumination could transform to plasmons and form a high temperature surface on the Pt thin film. This plasmonic heating effect resulted in the Pt thin film becoming an active catalyst for the chemical oxidation of ammonium.

2.3. Test solution and material analysis

A solution of dissolved ammonium chloride (2.3 mM, NH_4Cl, Mallinckrodt Baker Inc., USA) was prepared. The purchased chemicals were used without further purification. Deionized water containing no detectable nitrogen contaminates was used to prepare the sample solution for all experiments. Sample solutions of 2 mL, 25 mL, and 25 mL were taken after performing the experiments to measure the concentrations of NH_4^+, nitrite (NO_2^-), and nitrate (NO_3^-), respectively. The dissolved chemicals were measured before and after the process. When measuring the concentration of NH_4^+, a 1 mL sample solution was carefully diluted 25 times to 25 mL in order to match the detection limit. The concentration of the target-dissolved chemicals was measured using a digital water analyzer (Lambda-9000, Kyoritsu Chemical-Check Lab., Corp., Japan). Specific reagent sets of LR-NH_4-A, LR-NO_2, and LR-NO3 that only reacted with NH_4^+, NO_2^-, and NO_3^- in solution, respectively, were added to three different bottles containing the collected solutions. After the standard processes, a blue or pink color in the sample solution revealed the concentration of the target chemicals. The absorption of 637 nm light was measured by a digital water analyzer to determine the concentration of NH_4^+ and the absorption of 539 nm light was measured by the digital water analyzer to determine the concentrations of NO_2^- and NO_3^-. The pH value was also acquired at each process time mark using a bench-top pH meter (CyberScan pH2100, Eutech Instruments).

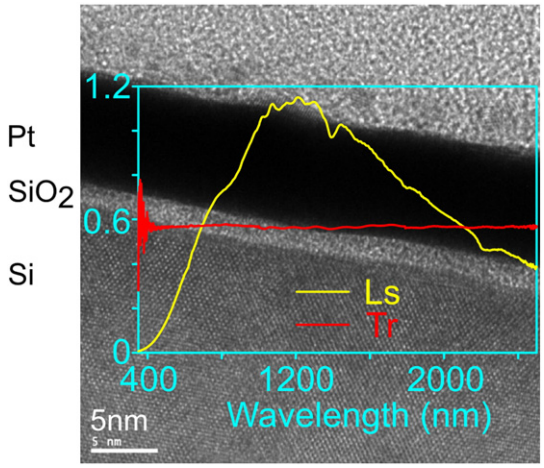

Fig. 2. TEM data of the 8 nm Pt thin film on silicon substrate with native oxide (Si/SiO_2). Embedded data is irradiance intensity spectrum of the light from the halogen lamp and transmission spectrum of the 8 nm Pt thin film.

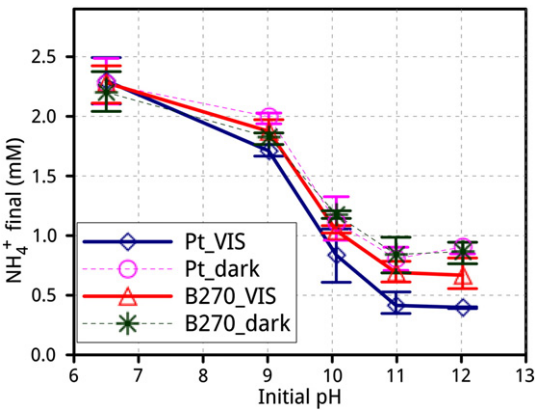

Fig. 3. Effects of various initial pH levels on the oxidation of NH_4^+ presented with final NH_4^+ concentration. Pt_VIS and B270_VIS denote the process on the reaction disk with and without the Pt thin film under illumination, respectively. Pt_dark and B270_dark denote no illumination.