Cathodic Arc-plasma Deposition of Platinum Nanoparticles on Fluorine-doped Tin Oxide for Electrocatalytic Nitrate Reduction Reaction

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ABSTRACT

For conventional electrocatalysts for the nitrate reduction reaction, Pt substrates have been used and modified with Sn adatoms to form Sn/Pt interfaces, which work as highly efficient catalytic active sites. In this work, Pt nanoparticles were deposited on fluorine-doped tin oxide (FTO) substrates by cathodic arc plasma deposition (APD) to produce Pt/Sn interfaces. As expected, APD–Pt/FTO showed the electrocatalytic nitrate reduction activity in acidic media and the Pt/Sn interfaces worked as the catalytic active site. Our interfacial design concept and synthetic approach will offer new catalyst development strategies at nanoscale.

Keywords : Platinum Nanoparticle, Nitrate Reduction, Arc Plasma Deposition, Electrocatalyst

1. Introduction

Denitrification is an important process in the global nitrogen cycle and converts nitrate (NO3–) to nitrite (NO2–), nitric oxide (NO), nitrous oxide (N2O), and finally to harmless dinitrogen (N2). This sequential reduction is carried out by certain bacteria under low-oxygen conditions for their cell growth.1 This natural biological process removes excess nitrogen, which is the main inorganic nitrogen contaminant, from groundwater. However, the overuse of fertilizers and excess emission of NOx from industrial plants and automobiles cause an imbalance in the nitrogen cycle, leading to human health problems.2,3

Electrochemical nitrate reduction is a promising approach to remove nitrate from contaminated groundwater and wastewater, and there is a need to develop highly efficient electrocatalysts for the nitrate reduction reaction. Fundamental studies on nitrate reduction electrocatalysts have focused on noble metal electrodes such as Pt and Pd.1,3,4 Their catalytic activity has been drastically enhanced by the surface modification with p-block metal adatoms including Sn,5–13 in which the interfaces between the noble metal substrate and the p-block metal adatoms may work as the catalytic active sites. To produce such interfaces, noble metal substrates have been widely used and modified with p-block elements even though the deposition of noble metal nanoparticles on conductive materials containing p-block elements can, in principle, give similar interfaces. Furthermore, the use of noble metal nanoparticles would minimize the amount of metals used and maximize the electrochemically active surface area. However, there is a lack of detailed studies on the electrochemical nitrate reduction at interfaces between metal nanoparticles and p-block-metal-based substrates.14

Herein, we report the preparation and electrocatalytic activity of platinum nanoparticles deposited on fluorine-doped tin oxide (FTO) for the nitrate reduction reaction in acidic media. Pt nanoparticles were produced by cathodic arc plasma deposition (APD) under high vacuum conditions. The APD is a physical vapor deposition technique and provides pure metal and metal alloy nanoparticles without neither surfactants nor surface modifiers, which are usually used for solution-based methods and suppress the (electro)catalytic activity. The APD also provides strong adhesion of the deposited metal nanoparticles to substrates because of the generation of metal ion species with high kinetic energies,21 which can give ideal Pt/Sn interfaces for electrocatalytic reactions.

2. Experimental Section

FTO substrates (SPD Laboratory) were cleaned in 2-propanol, acetone and then Milli-Q water under ultrasonication for 20 min each, kept in the mixture of 30% H2O2–28% NH4–Milli-Q water (1:1.5, v/v/v) at 343 K for 1 h, rinsed with Milli-Q, and then dried under N2. Glassy carbon (GC) substrates were polished with alumina, cleaned in 2-propanol, acetone and then Milli-Q water under ultrasonication for 10 min each, and then dried under N2. For electrochemical measurements, Pt metal nanoparticles were deposited on cleaned FTO or GC substrates at room temperature at 10–12 Pa by using a coaxial pulsed APD system (ADVANCE RIKO, ARL-300).21 The APD was performed at an arc voltage of 100 V and a condenser capacity of 1080 µF in the APD pulse number range from 50 to 1000 pulses to control the amount of Pt nanoparticles deposited on substrates, which were placed ca. 20 cm away from the Pt cathode. For TEM observations, plasma-polymerized naphthalene films (Super Support Film, Nisshin EM) were used and the Pt-deposited film was transferred onto a copper grid with 400 mesh. TEM images were taken on JEM-2000FX (JEOL) at an acceleration voltage of 200 kV.

Cyclic voltammograms (CVs) were recorded using a conventional three-electrode setup on a potentiostat HZ5000 (Hokuto Denko). The platinized Pt foil counter electrode and the Ag/AgCl (sat. KCl) reference electrode were used. A geometrical surface area of the working electrode was 0.283 cm2. All potentials shown are converted to the reversible hydrogen electrode (RHE). CVs were recorded in 0.1 M HClO4 under Ar and charges for hydrogen adsorption in the potential range from 0.06 to 0.26 V vs. RHE were used to determine electrochemically active surface areas of Pt nanoparticles. Electrochemical nitrate reduction experiments were carried out in an electrolyte solution containing 0.1 M HClO4 and 0.01 M NaN3 under Ar. A bias potential of −0.09 V vs. RHE was applied before electrochemical nitrate reduction measurements.5,15

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3. Results and Discussion

TEM observations revealed that the amount of the deposited Pt nanoparticles increased as the number of APD plasma pulses were increased (Fig. 1). In the APD method, an arc discharge between the target metal cathode and the anode generates metal nanoparticles and the number of metal nanoparticles deposited can be controlled by the number of plasma pulses.15 Pt nanoparticle densities were determined to be $7.8 \times 10^{12} \text{cm}^{-2}$ for 100 pulses and $1.4 \times 10^{13} \text{cm}^{-2}$ for 200 pulses. The average diameters of Pt nanoparticles with 100 and 200 pulses were determined to be 1.9 nm and 2.6 nm, respectively (Figs. 1a, 1b, 1d and 1e). These sizes are quite close to those previously reported for APD Pt nanoparticles.15,17 The APD with more than 400 pulses gave no individual nanoparticle, indicating the agglomeration of Pt nanoparticles (Fig. 1c).

To obtain information on the surface coverage of APD Pt nanoparticles on substrates, GC substrates were modified with Pt nanoparticles (APD–Pt/GC) and then their CVs were recorded in 0.1 M HClO₄ under Ar. APD–Pt/GC electrodes showed characteristic CVs of Pt (Fig. 2a) for greater than or equal to 200 pulses, indicating that Pt nanoparticles were electrochemically active on the GC. For 100 pulses, the electrochemical behavior is slightly different from that of the others, which could be caused by the strong adhesion of Pt nanoparticles with substrates.21,22 Hydrogen adsorption/desorption peaks on the Pt surface were observed in the potential range from 0.06 to 0.26 V vs. RHE. Charges involving the hydrogen adsorption were plotted as a function of the number of APD pulses (Fig. 2b). The charge increased as the number of APD pulses were increased and the plateau was observed at around 400 pulses, the number of which is in agreement with that for the agglomeration of Pt nanoparticles, as mentioned above (Fig. 1). In the plateau region, the APD–Pt/GC electrodes gave more than 210 µC cm⁻², which corresponds to the charge required for the monolayer hydrogen adsorption/desorption on platinum. Note that GC substrates were used to estimate the surface coverages because strong metal/support interactions between metal nanoparticles and metal oxide supports would give the lower electrochemically active surface areas.22

To understand the electrocatalytic nitrate reduction activity of FTO modified with APD–Pt nanoparticles (APD–Pt/FTO), CVs of APD–Pt/FTO were recorded in an electrolyte solution containing 0.01 M NaNO₃ and 0.1 M HClO₄ under Ar. APD–Pt/FTO electrodes showed reduction currents in the potential range from 0 to 0.35 V vs. RHE in the presence of NO₃⁻ in the electrolyte solution (Fig. 2c). These reduction currents are associated with the electrochemical nitrate reduction.12–14 No catalytic currents were observed for APD–Pt/FTO in the absence of NO₃⁻. Furthermore, APD–Pt/GC and bare FTO showed no catalytic currents even in the presence of NO₃⁻ (Fig. 2c). Thus, the Pt/Sn surface produced by the deposition of Pt nanoparticles on FTO plays an important role in the electrocatalytic nitrate reduction.

Catalytic current densities of APD–Pt/FTO electrocatalysts for the nitrate reduction reaction depended on the number of APD pulses. The APD–Pt/FTO with 200 pulses exhibited the highest catalytic activity. The APD with 200 pulses gave Pt nanoparticles on the surface (Fig. 1b) and approximately 80% coverage of the electrode surface (Fig. 2b). This surface coverage with Pt nanoparticles might produce highly active Pt/Sn interfaces for the electrocatalytic nitrate reduction. The APD–Pt/FTO with 200 pulses gave a current density of 1.2 mA cm⁻² at 0.16 V vs. RHE, corresponding to $-0.1 \text{V vs. Ag/AgCl (sat. KCl)}$. This current density is nearly equal to that previously reported for Sn-modified polycrystalline Pt electrodes (1.0 mA cm⁻²).10 These results imply that the APD of Pt nanoparticles on FTO produced catalytically active Pt/Sn interfaces that showed almost the same electrocatalytic nitrate reduction activity as the Sn-modified Pt electrodes.

4. Conclusions

Surfactant-free Pt nanoparticles were immobilized on FTO substrates by the APD and the resulting APD–Pt/FTO electrodes showed the electrocatalytic nitrate reduction activity in acidic media. Our work demonstrated that Pt/Sn interfaces play an important role in the electrocatalytic activity for the nitrate reduction reaction and there is no need to use Pt substrates. Our findings will open up new possibilities for developing nitrate reduction electrocatalysts prepared by the deposition of noble metal nanoparticles on p-block-metal-based conductive materials such as not only FTO but also indium-doped tin oxide and antimony-doped tin oxide,22 possibly leading to maximizing the catalytic activity and minimizing the amount of noble metals used.
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References