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学位論文内容の要旨

博士 (環境科学)

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学位論文題名

Electrocatalytic nitrate and nitrous oxide reduction reactions at trimetallic interfaces
of Pt, Pd and Sn

(白金, パラジウム, スズの三元金属界面における硝酸イオンおよび亜酸化窒素の
電極触媒還元反応)

Contamination of nitrate anions (NO_3^-) in groundwater, which is mainly caused by anthropogenic activities: agriculture and industrial effluents, has a negative effect on the environment and human health, such as methemoglobinemia (blue baby syndrome) and human cancer. The electrocatalytic NO_3^- removal is the most promising technique as it can be powered by renewable energy at room temperature and pressure, in which NO_3^- can be reduced to harmless dinitrogen (N_2) with many by-products: nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), ammonium ion (NH_4^+), and hydroxylammonium ion (NH_3OH^+). N_2O is a potential by-product, which is accountable for global warming and the depletion of the ozone layer. Therefore, efficient electrocatalysts are needed to develop for both NO_3^- reduction reaction (NO_3RR) and N_2O reduction reaction (N_2ORR) to keep the world sustainable. In the previous studies, Sn-modified Pt and Pd electrodes were widely studied for NO_3RR but the same electrodes were not studied for the reduction of its potential by-products: NO_2^- , NO, and N_2O . In a reverse system, only Pt nanoparticle (NP)-modified fluorine-doped tin oxide (FTO) substrate electrodes (Pt/FTO) were studied for NO_3RR , in which the Pt/Sn interface acts as catalytic active site. Therefore, the objective of this thesis is to expand the investigation on (i) the reverse system: (Pt+Pd) mixture NP-modified FTO electrodes and (ii) chemically synthesized Pt-Pd-Sn NP electrodes for the reduction of NO_3^- and its potential by-products: NO_2^- , NO, and N_2O . This thesis includes five chapters. Chapter 1 describes those backgrounds and the objective of this study, and the conclusions were summarized in Chapter 5.

In Chapter 2, Pt and/or Pd NPs on FTO substrate electrodes, Pt/FTO, Pd/FTO, and Pt/Pd/FTO, were prepared by a dry method: arc-plasma deposition (APD) under high vacuum conditions. The APD method enables the direct deposition of metal NPs on the substrates by changing the number of pulses for controlling the amount of metal NPs. The electrodes were characterized by transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive spectroscopy (EDS) mapping, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV) (**Figure 1**).

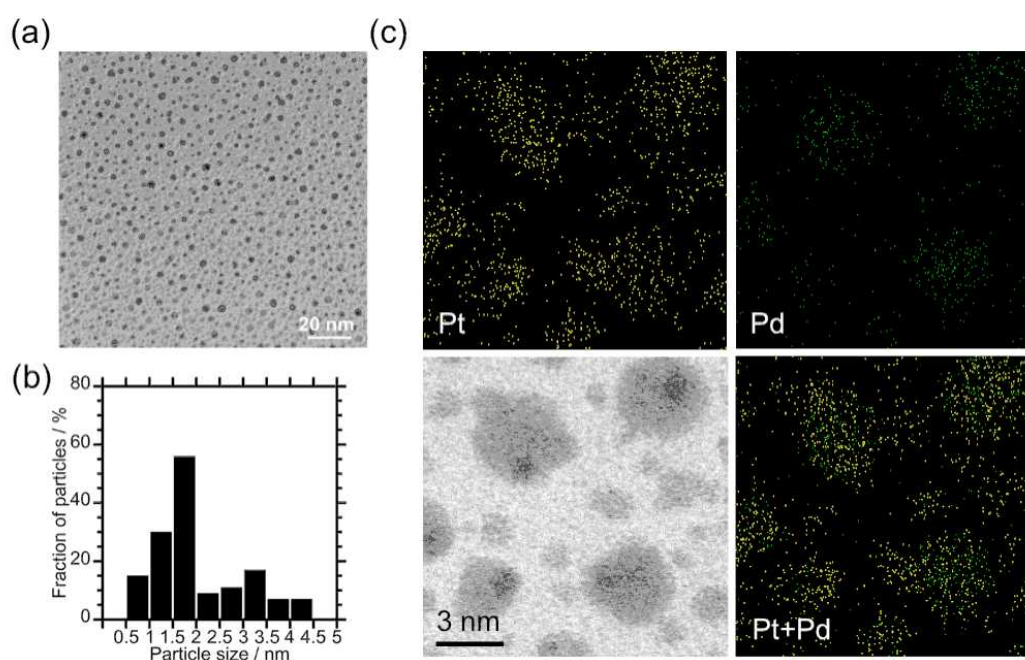


Figure 1 (a) TEM image, (b) size distribution, and (c) STEM image and EDS mapping of Pt/Pd NPs on a silicon oxide grid. The yellow and green color images indicate the Pt and Pd elements, respectively.

The Pt/FTO and Pd/FTO electrodes were optimized for electrocatalytic NO₃RR in acidic media by CV with respect to the pulse number of Pt and Pd. Keeping the same optimized pulse number, Pt/Pd/FTO electrodes were prepared by changing Pt-to-Pd pulse ratios and optimized for electrocatalytic NO₃RR. The optimized trimetallic electrode shows higher NO₃RR activity than the bimetallic electrodes: the order of NO₃RR activity was found as follows: Pt/Pd/FTO > Pt/FTO > Pd/FTO. The presence of the trimetallic PtPd/Sn interface and the Pt:Pd = 3:2 atomic ratio in the optimized Pt/Pd/FTO electrode was confirmed by STEM and EDS mapping images (**Figure 1**). The effective role of the PtPd/Sn interface for NO₃RR was confirmed from the comparison with

experimental results using Pt/Pd/glassy carbon (GC) electrodes: Pt/Pd/GC electrodes showed almost no NO₃RR activity (**Figure 2a**). Then, the optimized Pt/Pd/FTO and Pt/Pd/GC electrodes were investigated for the reduction of each potential intermediates of NO₃RR: NO₂⁻, NO, and N₂O in acidic media to understand the role of the Pt/Pd/Sn interface (**Figure 2b, c, and d**).

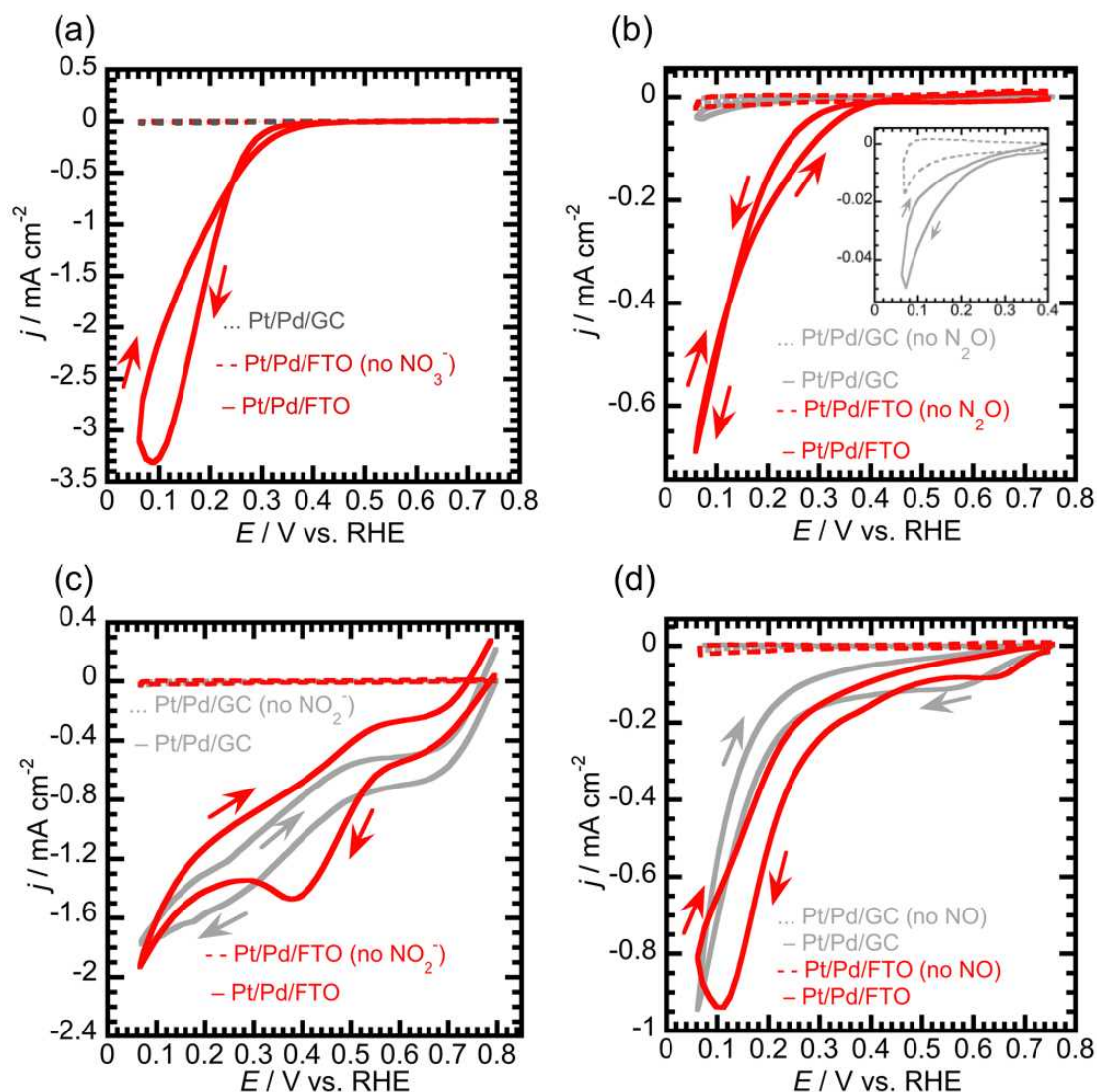
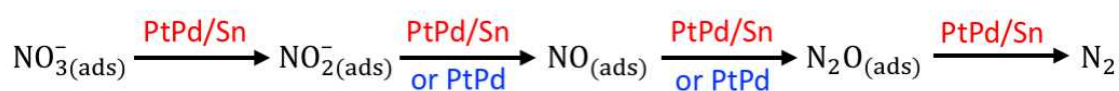


Figure 2 CVs of Pt/Pd/GC and Pt/Pd/FTO electrodes recorded at a sweep rate of 10 mV s⁻¹ in an aqueous solution of 0.1 M HClO₄ (a) containing 0.01 M NaNO₃ under Ar, (b) under N₂O (the inset shows the magnified CVs of Pt/Pd/GC electrode), (c) containing 0.01 M NaNO₂ under Ar, and (d) under NO.

The PtPd/Sn interface of the Pt/Pd/FTO electrode efficiently catalyzed the NO₃RR and N₂OORR, whereas it showed no drastic contribution to the electrocatalytic NO₂⁻ reduction reaction (NO₂RR) and NO reduction

reaction (NORR) (**Figure 2** and **Scheme 1**). Because the NO₃RR and N₂ORR occur in the potential region of H-adsorption on Pt and Pd electrodes, the PtPd/Sn interface could enhance NO₃⁻ and N₂O adsorption and/or suppress the H-adsorption. The modulation of the adsorption ability of NO₃⁻, N₂O, and H at the PtPd/Sn interface was supported by the charge transfer from Sn to Pt and Pd for the Pt/Pd/FTO electrode in XPS: lower binding energy shifts than Pt/Pd/GC in the Pt 4f and Pd 3d regions. Thus, the trimetallic PtPd/Sn interface enables us to finely tune the adsorption ability of NO₃⁻, N₂O, and H at the PtPd/Sn interface, resulting in the high NO₃RR and N₂ORR activity.



Scheme 1 Highly active catalytic sites for the electrocatalytic NO₃RR, NO₂RR, NORR, and N₂ORR.

As the synthesis of NPs by APD method is a model study, Pt–Sn and Pt–Pd–Sn NPs were synthesized by a wet chemical method for the electrocatalytic N₂ORR in acidic media by CV in Chapter 3. The carbon-supported NPs (Pt–Sn/C and Pt–Pd–Sn/C) were characterized by TEM, STEM, EDS mapping, XPS, X-ray powder diffraction (XRD), and CV. The Pt–Pd–Sn/C showed higher N₂ORR activity than the Pt–Sn/C. N₂ was the only product of N₂ORR, which was detected by gas chromatography.

In Chapter 4, Pd nanocubes (NCs) were synthesized and immobilized on carbon support, modified with Sn, and then studied for the electrocatalytic N₂ORR in acidic media by CV. TEM images revealed the formation of the NC with six {100} facets. The Sn modification of the Pd NCs increases the N₂ORR activity.

In conclusion, it was demonstrated that the enhancement of NO₃⁻ and N₂O adsorption and/or suppression of H-adsorption is necessary at the electrode surface for the improvement of the NO₃RR and N₂ORR in acidic media. The trimetallic PtPd/Sn interface can highly modulate such competitive adsorption processes, resulting in the high NO₃RR and N₂ORR activity. Furthermore, Sn-modified Pd NCs show higher N₂ORR activity than unmodified Pd NCs. These findings will encourage us to develop highly efficient electrocatalysts for the NO₃RR and N₂ORR.