

SERS Study of BNNS on Au as a Catalyst for Oxygen Reduction Reaction

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Abstract:

Non-precious-metal catalysts for the oxygen reduction reaction (ORR) in fuel cells are in high demand to decrease fuel cell cost and increase cathode stability. One candidate for an ORR catalyst in fuel cells that use an acidic electrolyte is boron nitride nanosheets (BNNS). In order to better understand the potential of BNNS as a catalyst, identification of the intermediates during the ORR of BNNS on a gold (Au) substrate was performed by *in situ* measurements using surface enhanced Raman scattering (SERS) spectroscopy.

Introduction:

Boron nitride nanosheets (BNNS) are a promising material for use in catalysts for the oxygen reduction reaction (ORR) in fuel cells that use an acidic electrolyte. Uosaki, et al., reported that BNNS on gold showed high electrocatalytic activity for ORR. Ordinarily an insulator, BNNS has semiconducting properties when deposited on a conducting substrate. In order to better understand the reaction catalyzed by this material, this project focused on the use of Raman spectroscopy to view surface intermediates formed during the reaction of BNNS on Au. However, since intensity during the reaction was low and peaks were initially difficult to identify, a technique known as surface enhanced Raman scattering (SERS), was implemented to increase intensity and allow for better characterization of the reaction.

Experimental Procedure:

BNNS was prepared from the suspension of hexagonal BN in 2-propanol by ultrasonic irradiation for 96 h [1]. A sputter deposited layer of 150 nm thick Au on a n-Si<111> wafer was used as a substrate. A 0.1 mg/mL solution of BNNS was drop casted onto substrates, then heated for two hours at 200°C. To increase Raman intensity by plasmon resonance effect [2], BNNS was modified with gold nanoparticles, which were prepared by chemical reduction of HAuCl₄ with NaBH₄. The substrate was chemically roughened in 0.1 M KCl by repeated oxidation-reduction cycles (ORCs) for 3-7 minutes. The ORCs was performed from -0.28 V to +1.22 V (vs. NaCl saturated Ag/AgCl) with the sweep rate of 500 mV/s. Samples were also analyzed using SEM imaging and EDS.

In order to measure *in situ* Raman spectra during the reaction, a three-electrode electrochemical cell with a

fused quartz window was used. The electrolyte for the reaction was a 0.5 M H₂SO₄ aqueous solution, the reference electrode was Ag/AgCl, and the counter electrode was Pt wire. The electrochemical cell was mounted on the stage of a confocal Raman microscope (RAMANtouch, Nanophoton Co.) with a CCD detector and a CW laser (785 nm, 9 mW at focal point). The scattered signal was exposed to the CCD for seven seconds, with four accumulations per spectra. A scan rate of 2 mV/s was used during SERS measurements.

Results and Discussion:

SEM images of samples showed differences in surface morphology between the original (Figure 1A) and roughened samples (Figure 1B, C). The BNNS with gold nanoparticles on the gold substrate roughened for 7 min (Au/BNNS on Au) is shown in Figure 1D as 200~300 nm sheets (BNNS) and < 30 nm particles (Au) in diameter, respectively. Figure 2 shows the linear sweep voltammograms of bare Au and Au/BNNS on Au. In the case of Au/BNNS on Au, a reduction current less than 4 $\mu\text{A}/\text{cm}^2$ was observed at the potential from +0.6 V to +0.2 V, in addition to a larger reduction current (< 80 $\mu\text{A}/\text{cm}^2$) at the negative potential than +0.2 V. The reduction current at +0.2 V was also measured on the bare Au electrode. This result suggests that a part of ORR on Au/BNNS contained the four electron reduction process of O₂ catalyzed by BNNS.

The SERS spectra measured during potential sweeping are shown in Figure 3. On the bare gold, broad peaks at 1150 cm⁻¹ and 1500 cm⁻¹ were observed at +0.13 V (Figure 3A). They correspond with O-O stretching bonds of HO₂ radical and molecular O₂, respectively. The SERS spectra

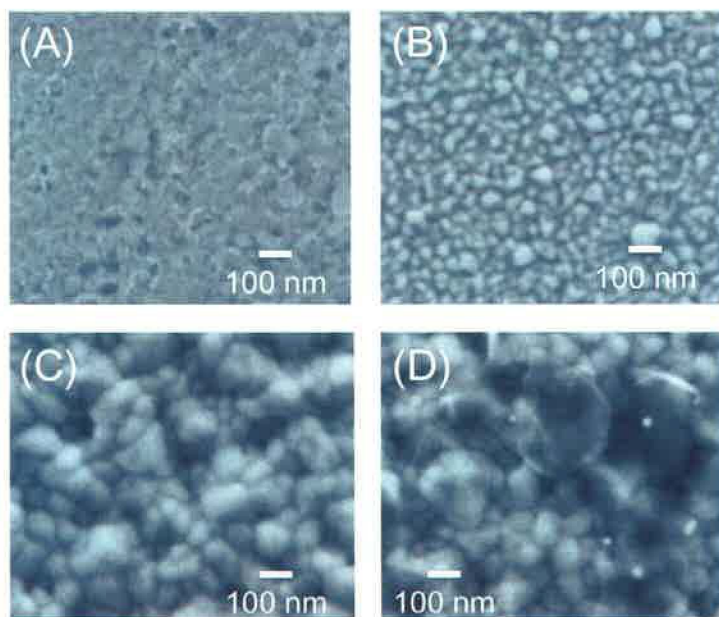
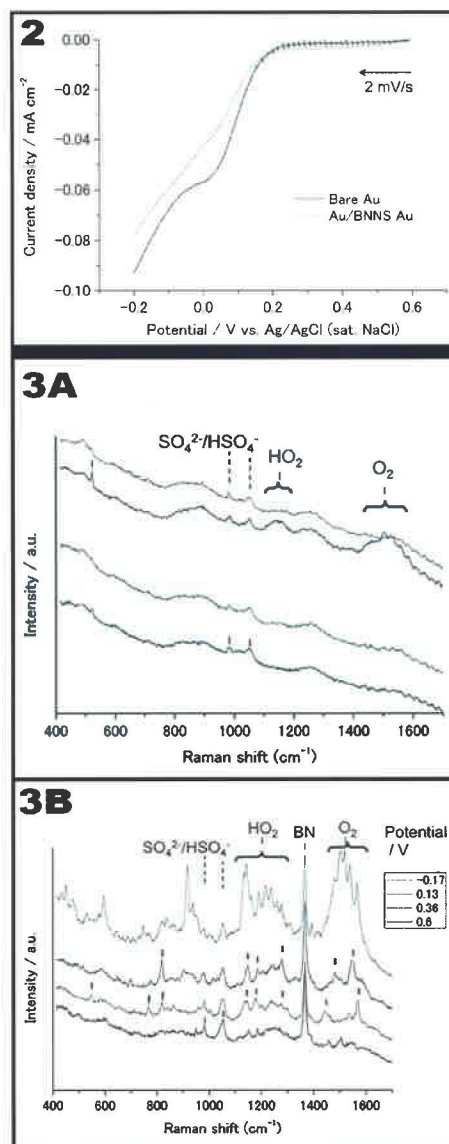


Figure 1: SEM images of (A) sputtered Au, (B) three and (C) seven minutes roughened Au, and (D) Au/BNNS on seven minutes roughened Au. Figure 2, top right: Linear sweep voltammograms of bare Au (black curve) and AuNPs/BNNS on Au (grey curve) measured in O₂ saturated 0.5 M H₂SO₄ solution. Figure 3, bottom right: SERS spectra of (A) bare Au and (B) AuNPs/BNNS on Au during potential sweep. The corresponding voltammograms are shown in Figure 2.



of Au/BNNS contained a sharp peak at 1366 cm^{-1} , which corresponds with the E_{2g} phonon mode of bulk hexagonal BN. Similarly, the frequency of BNNS suggested the formation of aggregations of BNNS [3]. In Figure 3B, the spectra measured at 0.38V and +0.13 V contained additional peaks at 545 cm^{-1} , 775 cm^{-1} and 818 cm^{-1} , $1100\sim 1300\text{ cm}^{-1}$, and $1400\sim 1600\text{ cm}^{-1}$. By comparison with Raman spectrum of boric acid [4], these frequencies correspond to O-B-O bending, B-O stretching (ν_1), B-O-H bending, and B-O stretching (ν_6), respectively.

Future Work:

Although repetition of the measurements is required in order to confirm peak position of these intermediates, the formation of B-O bonding seemed to be the key process of the catalytic activity of BN. Further study of the intermediates formed during the reaction will help to construct BNNS based catalyst for use in the cathode of fuel cells.

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