



## Short communication

# Gold nanoparticle decoration of insulating boron nitride nanosheet on inert gold electrode toward an efficient electrocatalyst for the reduction of oxygen to water



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## ABSTRACT

Overpotential for oxygen reduction reaction (ORR) at Au electrode is reported to be reduced by 0.27 V by the modification with boron nitride nanosheet (BNNS) but oxygen is reduced only to H<sub>2</sub>O<sub>2</sub> by 2-electron process at Au electrode. Here we demonstrate that the decoration of BNNS with gold nanoparticles (AuNP) not only reduces the overpotential for ORR further by ca. 50 mV, but also opens a 4-electron reduction route to water. Both rotating disk electrode experiments with Koutecky–Levich analysis and rotating ring disk electrode measurements show that more than 50% of oxygen is reduced to water via 4-electron process at Au–BNNS/Au electrode while less than 20 and 10% of oxygen are reduced to water at the BNNS/Au and bare Au electrodes, respectively. Theoretical analysis of free energy profiles for ORR at the BN monolayer with and without Au<sub>8</sub> cluster placed on Au(111) shows significant stabilization of adsorbed oxygen atom by the Au<sub>8</sub> cluster, opening a 4-electron reduction pathway.

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## 1. Introduction

Large overpotential for oxygen reduction reaction (ORR) is one of the most crucial problems to be solved in the development of fuel cells [1–4] and there are worldwide efforts to develop novel electrocatalysts for ORR with high efficiency and long term stability based on low cost and abundant materials including non-precious metals and their alloys [1,2,5–11], metal oxides [12], metal nitrides [13,14], metal oxynitrides [15,16], metal carbides [14,17], and N- and B-doped carbon materials with and without metal doping [18–22]. N- and B-doped carbon materials have been well studied as possible candidates of precious metal free efficient ORR catalysts. Recently, we theoretically predicted that hexagonal boron nitride (h-BN) placed on various metal substrates would act as an effective electrocatalyst for ORR [23–25] and experimentally proved [25,26] that Au electrodes modified with various types of h-BN indeed act as effective ORR electrocatalysts. Overpotential for ORR at gold electrode is reduced by 0.27 V by the modification with BN nanosheet (BNNS), although it is still high compared with Pt electrode and oxygen is mainly reduced to

H<sub>2</sub>O<sub>2</sub> via 2-electron process [25,26]. Substrate dependencies suggest that the interaction between BN and Au plays essential role for ORR activity [26]. Thus, one would expect higher ORR activity by increasing BN–Au interactions. There are several methods to increase the interaction and one of them is to deposit gold nanoparticles (AuNPs) on BNNS (Au–BNNS), which is then placed on a Au electrode (Au–BNNS/Au). In this communication, we have investigated the electrocatalytic properties of Au–BNNS/Au for ORR and found that not only the overpotential is reduced further by ca. 50 mV but also the 4-electron reduction pathway to water is opened by the decoration of BNNS with gold nanoparticles. Theoretical analysis suggests that increased stabilization of adsorbed oxygen atom by Au nanocluster leads to the 4-electron reduction.

## 2. Experimental

## 2.1. Materials

Ultrapure reagent grade H<sub>2</sub>SO<sub>4</sub>, isopropyl alcohol (IPA), HAuCl<sub>4</sub> (99.9%), NaBH<sub>4</sub>, ethanol and acetone were purchased from Wako Pure Chemicals. Water was purified using Milli-Q system (Yamato, WQ-500, Japan). BN powder (99%) was purchased from High Purity Chemicals (BBIO3PB4).

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## 2.2. Preparation of Au electrode modified with AuNP decorated BNNS (Au–BNNS/Au)

BNNS were prepared by a modified Hummer's method [27]. BN powder was thermally treated at 1050 °C in Ar atmosphere in a tubular furnace for 1 h to exfoliate the BN powder into BNNS. Then, 20 mg of BNNS was dispersed in 60 ml IPA solution and sonicated about 3 h. 4 ml of 10 mM HAuCl<sub>4</sub> aqueous solution was added slowly to the N<sub>2</sub> saturated BNNS dispersed IPA solution under N<sub>2</sub> atmosphere and stirred well about 30 min. To decorate BNNS with AuNPs, 2 ml of 50 mM NaBH<sub>4</sub> aqueous solution was added drop wise to the above reaction mixture and stirred well for 4 h [28,29]. The products were collected by filtering (Whatman, pore size: 0.1 μm) and washed with ultra-pure water and ethanol. The obtained pink color product was dried at 100 °C in vacuo for overnight. 15 μl of the dispersion of 1 mg/3 ml of BNNS or Au–BNNS in IPA solvent was spin coated on the Au electrode at 500 rpm and then the modified electrodes were dried at 100 °C for 30 min in vacuo.

## 2.3. XRD, TEM and electrochemical measurements

X-ray diffraction (XRD) and transmission electron microscope (TEM) measurements were carried out using Altimat-2200 (Rigaku, Japan) with monochromatic Cu–Kα radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and JEM-2100F (JEOL, Japan), respectively. Electrochemical measurements were carried out in three electrode configuration. Pt wire and Ag/AgCl (sat'd NaCl) electrodes were used as a counter and a reference electrode, respectively. A dual potentiostat/function generator (Hokuto Denko, HR101B/HB111) and a rotation control unit (Pine Research, AFMSRCE02) were used to control the potential and the rotation rate of rotating (ring) disk electrode, respectively. All the electrochemical measurements were carried out in Ar or O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at room temperature. All electrodes were pre-treated by cycling the potential between –0.1 and +1.5 V at a sweep rate of 100 mV/s for 100 cycles.

## 3. Results and discussion

Fig. 1(A) shows XRD patterns of the (i) BNNS and (ii) Au–BNNS. While only the diffraction peaks corresponding to pure h-BN were observed for BNNS, peaks corresponding to Au were observed for Au–BNNS [30,31]. The average crystallite size of Au particles was estimated to be ca. 30 nm using Debye–Scherrer equation [32]. Fig. 1(B) shows low ((a), (c)) and high ((b), (d)) resolution TEM images of BNNS ((a), (b)) and Au–BNNS ((c), (d)). HRTEM image of BNNS with FFT (Fig. 1(B)(b)) shows that BNNS are composed of a single to few layers

of h-BN as already reported [25]. AuNPs are randomly distributed on BNNS surface as shown in Fig. 1(B)(c). Fig. 1(B)(d) shows the lattice images of AuNPs with and the size of AuNPs on BNNS ranges between 5 and 30 nm, which is in good agreement with XRD results.

Fig. 2(A) shows linear sweep voltammograms (LSVs) of (a) bare Au, (b) BNNS/Au, (c) Au–BNNS/Au, and (d) bare Pt disk electrodes in RDE configuration with various rotation rates with a potential scan of negative direction of 10 mV/s measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The potentials at which ORR current becomes  $-0.02 \text{ mA/cm}^2$  are 210, 480, 530 and 770 mV at the bare Au, BNNS/Au, Au–BNNS/Au, and bare Pt electrodes [33], respectively. Overpotential for ORR at BNNS/Au electrode was reduced by 50 mV by the AuNP decoration. Although it does not look significant, one must note that not only the current–voltage relation is shifted toward positive potential direction but also the limiting current at a given rotation rate became higher, suggesting that number of electrons involved in the ORR is larger at the Au–BNNS/Au electrode than at the BNNS/Au electrode.

This can be quantitatively analyzed by utilizing Koutecky–Levich (K–L) equations (Eq. (1)).

$$1/i = 1/i_k + 1/B\omega^{1/2} \quad (1)$$

Here  $B$  is given by:

$$B = 0.620nFC_{O_2}^*D^{2/3}\nu^{-1/6} \quad (2)$$

where  $n$  is the number of electrons transferred in the overall reaction process,  $F$  is the Faraday constant ( $96,490 \text{ C mol}^{-1}$ ),  $\nu$  is the kinematic viscosity ( $0.01 \text{ cm}^2\text{s}^{-1}$ ) [34],  $D$  and  $C_{O_2}^*$  are the diffusion coefficient and the bulk concentration ( $1.1 \times 10^{-6} \text{ mol cm}^{-3}$ ) of the oxygen [35, 36],  $\omega$  is the rotation rate, and  $i_k$  is the kinetic current without any mass transfer limitation, which is given by:

$$i_k = nFAkC_{O_2}^* \quad (3)$$

Thus, one expects a linear relation between  $1/i$  and  $1/\omega^{1/2}$  (K–L plot). The extrapolation of this relation to  $1/\omega^{1/2} = 0$  yields  $1/i_k$  and, then, the rate constant  $k$  can be obtained from Eq. (3).

K–L plots of each electrode at various potentials are shown as the inset of each figure. Linear relations are observed in all cases and the number of electrons transferred at each electrode potential is calculated to be ca. 2 for (a) the bare Au and (b) BNNS/Au electrodes, ca. 4 for (d) the bare Pt electrode, and ca. 3 for (c) the Au–BNNS/Au electrode, suggesting the partial generation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O at the Au–BNNS/Au electrode.

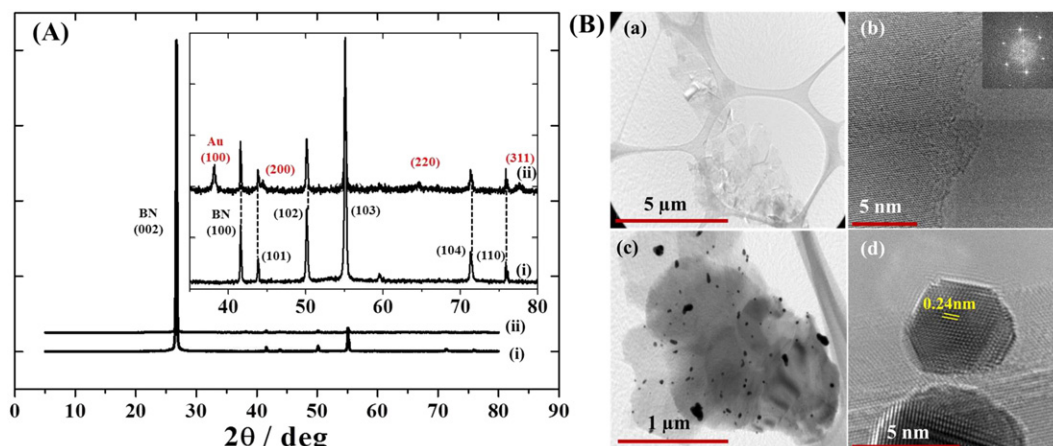


Fig. 1. (A) XRD patterns of (i) BNNS and (ii) Au–BNNS. Inset: enlarged patterns. Diffraction peaks are marked by black and red for BN and Au peaks, respectively. (B) TEM images of BNNS ((a), (b)) and Au–BNNS ((c), (d)). Inset of (b) is the FFT of the central part of the image.

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