Modulation of Graphene/Au(111) Interaction by Electrocatalytic Hydrogen Evolution Reaction

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Abstract. Electronic structure of monolayer graphene with metal contacts can be modified by control of interfacial interaction. Here, we show that the strength of local interfacial interaction between graphene and Au(111) surface can be electrochemically controlled by the hydrogen evolution reaction process. Graphene/Au(111) electrodes were prepared by the chemical vapour deposition. Raman spectroscopy indicated existence of monolayer of graphene over Au surface. Local interaction of graphene/Au(111) interaction can be differentiated by intercalation of H₂ molecules at interface. This study shed lights on the possibility of proton penetration through the graphene to modify the strength of interaction between graphene and Au(111) surface.

1. Introduction
Two-dimensional materials have attracted attentions due to their multi-functionality and designability through the interfacial interaction [1]. One of the representative two-dimensional materials is graphene. Graphene shows excellent electronic properties [2], and their electronic structure can be modified by metal contacts [3]. On the other hand, one of the feasible properties of graphene is permeability of proton through basal plane of graphene [4,5], which is even not observed for He gases [6]. Recently it has been shown that electrocatalytic hydrogen evolution reaction process induces the formation of “nanobubble” between graphene sheets [7]. We envisioned that graphene/metal interaction can be modulated by intercalation of hydrogen through the nanobubble formation process, which can be also regarded as a novel method for controlling the interaction between metal and graphene contacts.

Here, we show that interaction between graphene and Au (111) can be modified by electrochemical hydrogen evolution reaction (HER). Graphene / Au (111) electrode was fabricated by chemical vapor deposition (CVD). Electrocatalytic HER process differentiates the graphene/Au(111) interaction evidenced by observation of Raman G band and Raman 2D band.

2. Experimental Section

2.1. Materials
Ag/AgCl electrodes were prepared by anodization of Ag wire in saturated KCl aqueous solution. Au beads were prepared by frame-annealing method. Ar gas (99.999%) and CH₄ gas (99.999%) was employed for CVD. Graphene/Au (111) electrodes were prepared with the according to literature methods.
procedure [8]. Monolayer graphene was synthesized through the CVD [9]. Quartz furnace was cleaned by oxidation of contaminates at 900 °C in air, and subsequent H₂/Ar treatment at 900 °C. Monolayer graphene was grown on the Au (111) surface by annealing at 1035 °C for 15 min under 250 sccm (standard cubic centimeter per minute) of Ar, and thereafter 1 sccm of CH₄ and 250 sccm of Ar flow for 3 min. This graphene-covered Au electrode was denoted as G/Au. The quality of crystallinity was confirmed from Raman spectroscopy.

2.2. Methods
Three-electrode cell was employed for electrochemical measurements. Ag/AgCl (saturated KCl aqueous solution) and Pt electrodes were used as reference electrode and counter electrode, respectively. All the electrochemical potentials were referenced to Ag/AgCl (saturated KCl aqueous solution). All solutions were bubble with Ar gas to deoxygenate for 20 min, and then electrochemical experiments were conducted. Microscopic Raman spectroscopy measurements were conducted by using Nanofinder under 514 nm laser excitation (3.0 mW, 60 sec).

3. Results and Discussion
Figure 1 shows cyclic voltammograms for Au and G/Au electrodes in 0.1 M H₂SO₄ aqueous solution. Decrease in electrochemical potential leads to the increase in cathodic current, which can be attributed to the electrocatalytic HER current. Furthermore, the current from G/Au electrodes is lower than one from Au electrodes. These observations suggest that graphene coating results in decrease of electrocatalytic activity for HER.

![Cyclic voltammograms for Au (black line) and G/Au (red line) electrodes in 0.1 M H₂SO₄ aqueous solution. Scan rate 50 mV/sec. Immersed electrode surface area was 0.05 cm² approximately.](image)

The structure of graphene was characterized from Raman spectroscopy. The G band (1560 cm⁻¹) is ascribed to the in-plane bond stretching motion between neighbouring carbon-carbon bonding, which confirms graphene formation over the Au(111) electrode. The 2D band (2700 cm⁻¹) is a double resonance phonon process of graphene and serves as a fingerprint for the number of graphene layers [8,10]. We confirmed the formation of monolayer graphene over Au(111) [8], and subsequently exposed G/Au electrodes under electrocatalytic HER condition.

Figure 2 shows the Raman spectra of G/Au after electrolysis at −0.4 V in 0.1 M H₂SO₄ aqueous solution for 1 min. G band and 2D band wavenumbers are variable for different spot sites, and G band wavenumbers are increased as 2D band wavenumbers increased. This is due to the thermal fluctuation of graphene lattice [11,12]. Since Au surface can interact with graphene via charge-doping as well as...
dielectric screening [12,13], intercalation between graphene and Au is expected to decrease 2D band wavenumber. Figure 3 shows the Raman spectra of G/Au after electrolysis at −0.5 V in 0.1 M H₂SO₄ aqueous solution for 1 min. Positive correlation between G band wavenumber and 2D band wavenumber was not observed. In addition, decrease in 2D band wavenumbers were generally observed. We are assuming that this breakdown of positive correlation between G band and 2D band wavenumbers was induced by a decrease in the interfacial interaction via graphene nanobubble formation. Proton penetration through tunneling might trigger the switching of graphene/Au(111) interaction.

**Figure 2.** Raman spectra of G/Au after electrolysis at −0.4 V in 0.1 M H₂SO₄ aqueous solution for 1 min. Different spots (i)-(v) are measured for (a) G band region and (b) 2D band region. Dotted lines are shown for eye guide.

**Figure 3.** Raman spectra of G/Au after electrolysis at −0.5 V in 0.1 M H₂SO₄ aqueous solution for 1 min. Different spots (i)-(v) are measured for (a) G band region and (b) 2D band region. Dotted lines are shown for eye guide.
4. Conclusions
We demonstrated that graphene/Au(111) interfacial interaction can be modified by electrocatalytic hydrogen evolution reaction. Difference in interaction was observed for high overpotential in 0.1 M H₂SO₄. Intercalation of H₂ molecules into graphene/Au(111) interface during HER process might trigger the switching of graphene/Au(111) interaction. Detailed proton penetration mechanism and the effect of chemical modification of graphene surfaces are under investigation.

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