Thermally Induced Self-assembly of Gold Nanoparticles Sputter-deposited in Ionic Liquids on Highly Ordered Pyrolytic Graphite Surfaces

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Gold nanoparticles sputter-deposited in ionic liquids were densely immobilized on the surface of highly ordered pyrolytic graphite (HOPG) by spreading the ionic liquid containing Au nanoparticles on HOPG and then heating. The density of immobilized Au particles was greatly dependent on the kind of ionic liquid used, and their size was controlled by the heating temperature. The resulting nanoparticle films were stable and electrochemically active for oxygen reduction.

The development of new techniques for assembling metal nanoparticles on solid substrates has been an important subject of research in various fields, such as catalysis, electrocatalysis, and biosensor technology.[1–3] Several techniques, including physical vapor deposition,[4] electrodeposition,[5] and immobilization of colloidal particles,[6] have so far been reported. For the preparation and stabilization of metals and semiconductors nanoparticles, room-temperature ionic liquids (RTILs) have attracted much attention.[7–9] Recently, we have reported an extremely clean method to fabricated metal nanoparticles, such as Au, Ag, and AuAg, in RTILs using a sputter deposition technique without additional chemical species, such as reducing agents and/or stabilizing agents.[10,11] The extremely low vapor pressure enabled sputter deposition of Au in RTILs under high vacuum, resulting in the dispersion of Au nanoparticles with diameters of several nanometers. Furthermore, the thus-obtained Au nanoparticles could be attached to thiol-modified silicon substrates through the chemical bond between Au and –SH groups.[12] However, the density of immobilized particles was relatively low. Here we report the facile immobilization of Au nanoparticles sputter-deposited in RTILs onto HOPG via a thermally induced self-assembling process. The density and size of immobilized Au particles can be controlled by the reaction conditions, such as the kind of RTIL used and the heating temperature.

RTILs of *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA-TFSA), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (BMI-TFSA), and 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6) were purchased from Kanto Chemical Co., Inc. and dried for 3 h at 378 K under vacuum before use. A 0.60-cm^3 aliquot of RTIL was spread on a glass plate (10 cm^2) that was horizontally set in a sputter coater (JEOL, JFC-1300). It was located at a distance of 35 mm from a Au foil target (99.99% in purity) (diameter: 5 cm). Sputter deposition of Au in RTILs was carried out for 300 s with a current of 40 mA under an argon pressure of ca. 20 Pa at room temperature. A 20-mm^3 aliquot of thus-obtained Au nanoparticle RTIL solutions was spread on the HOPG surface ($1.2 \times 1.2\,cm^2$), followed by heat treatment at various temperatures under vacuum. After washing with acetonitrile several times, the resulting Au-immobilized HOPG was used for measurements.

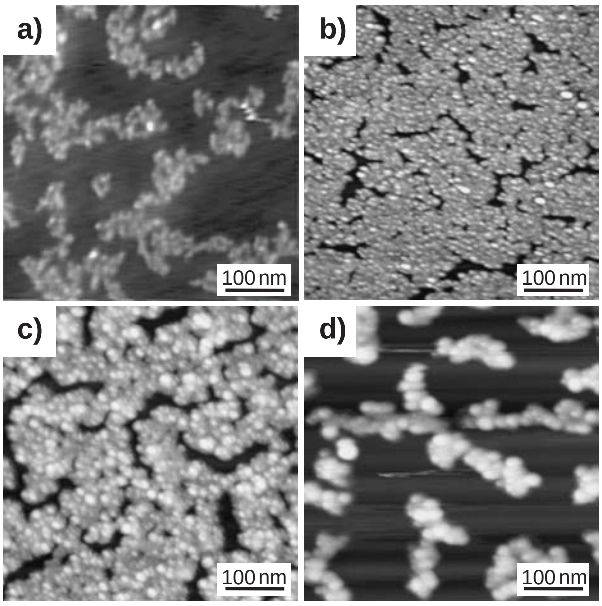

Figure 1. AFM images of Au-immobilized HOPG surface. HOPG was treated with Au-sputter-deposited TMPA-TFSA without (a) and with heating at 373 (b) and 423 K (c). A sample for image (d) was obtained by treating HOPG with Au-deposited BMI-PF_6 at 423 K.

The sputter deposition of Au in TMPA-TFSA turned the solution from colorless to brown. The concentration of Au in RTILs was determined by ICP-AES analyses to be ca. 7 mmol dm^{-3} as Au atoms. TEM measurement revealed that spherical Au nanoparticles were formed in TMPA-TFSA with an average diameter (d_{av}) of 2.3 nm and standard deviation (σ) of 0.3 nm. Au nanoparticles were immobilized by treating the HOPG surface with Au-sputter-deposited TMPA-TFSA at various temperatures, as shown in Figure 1. In the case of no heat treatment, immobilized Au nanoparticles formed island-like aggregations, the average height of which was determined to be ca. 2.3 nm. Considering d_{av} of 2.3 nm for Au nanoparticles uniformly dispersed in TMPA-TFSA, the fact indicated that a small amount of nanoparticles could be attached to the HOPG surface without any coalescence of particles, just by the contact between HOPG and TMPA-TFSA solution containing Au particles. On the other hand, heating at 373 and 423 K resulted in almost complete

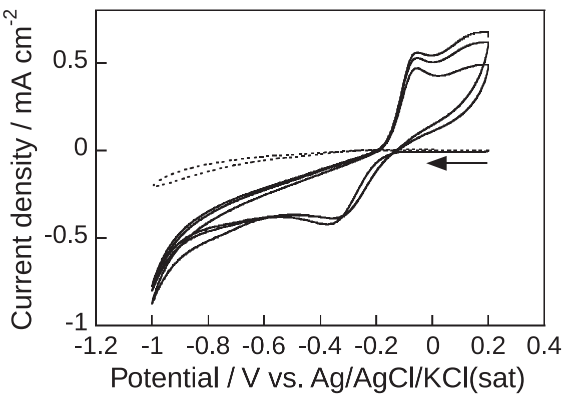

Figure 2. Cyclic voltammograms for ORR in O_2-saturated aqueous KOH solution at a bare HOPG electrode (dotted line) and an Au nanoparticle-immobilized HOPG electrode (solid line). Potential scan rate: $0.10\,V\,s^{-1}$.

coverage of the surface with Au nanoparticles, though the increase in temperature increased the surface roughness of the nanoparticle films. By measuring the height of particle images, it was found that during the immobilization with heating, Au nanoparticles coalesced with each other to form larger particles and the d_{av} of immobilized particles increased from 5.4 to 10 nm when the heat treatment temperature was raised from 373 to 423 K.

Treatment of HOPG substrates with Au-sputter-deposited BMI-PF_6 at 423 K resulted in the formation of island-like aggregations of large Au nanoparticles but not a uniform film on the surface as shown in Figure 1d. In contrast, heat treatment with Au-sputter-deposited BMI-TFSA at 423 K resulted in dense immobilization of Au nanoparticles on the HOPG surface (not shown) as was the case when TMPA-TFSA was used. These facts indicated that the presence of hydrophobic TFSA anions was essential for the dense immobilization of particles. It is well known that TFSA anions make a coordination bond with metal ions.[13] Furthermore, in our previous study, it was found that the presence of TFSA anions suppressed the growth and/or coalescence of metal particles in RTILs, probably due to their strong adsorption on particle surfaces.[10] Therefore, it was reasonable to assume that TFSA anions were adsorbed to form the hydrophobic surface of Au particles, and then the hydrophobic interaction between TFSA-adsorbed Au nanoparticles and the HOPG surface caused dense immobilization of particles. This assumption was supported by the fact that few Au nanoparticles dispersed in TMPA-TFSA were immobilized regardless of the heating temperature if hydrophilic substrates such as quartz glasses, instead of HOPG, were used.

Figure 2 shows typical cyclic voltammograms of various electrodes in O_2-saturated $0.5\,mol\,dm^{-3}$ aqueous KOH solution. Though a bare HOPG electrode showed no peak in this potential region, a quasi-reversible behavior was observed in the case of a Au nanoparticle-immobilized HOPG electrode: a cathodic peak appeared at ca. $-0.30\sim-0.35\,V$ due to the two electron reduction of O_2 to form HO_2^- and an anodic peak appeared at $-0.05\,V$ owing to the oxidation of HO_2^-.[14] It is well known that gold electrodes exhibit different activities for oxygen reduction reaction (ORR), being dependent on the crystallographic orientation of the Au surface:[15] ORR is quasi-reversible at Au(111) and Au(110) single-crystalline electrodes, while irreversible ORR is observed at Au(100) single crystalline electrodes. Therefore, the results shown in Figure 2 suggested that the particles on HOPG had surfaces enriched with Au(111) and/or Au(110) facets. Furthermore, it was confirmed from AFM images after electrochemical measurements that the density and the size of immobilized Au nanoparticles on HOPG were almost unchanged.

In conclusion, Au nanoparticles sputter-deposited in TMPA-TFSA were successfully immobilized on an HOPG surface, and their size could be controlled by the temperature used in the immobilization process. The obtained nanoparticle films were stable during electrochemical measurements. Various kinds of metal nanoparticles can be easily prepared by sputter deposition in RTILs without additional stabilizing agents such as thiol compounds, which sometimes cause deterioration of catalytic activities. The present technique will enable facile construction of electrodes functionalized with various kinds of metal nanoparticles having a desired size for developing effective electrocatalysts in applications such as fuel cells. Study along this line is in progress.

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