

## Enhancement of the Electrocatalytic Activity of Gold Nanoparticles *via* Anodic Treatment and the Decrease of the Enhanced Activity with Aging

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*Received November 9, 2010, Accepted December 13, 2010*

**Key Words:** Gold nanoparticle, Anodic treatment, Aging, Hydrogen peroxide, Formic acid

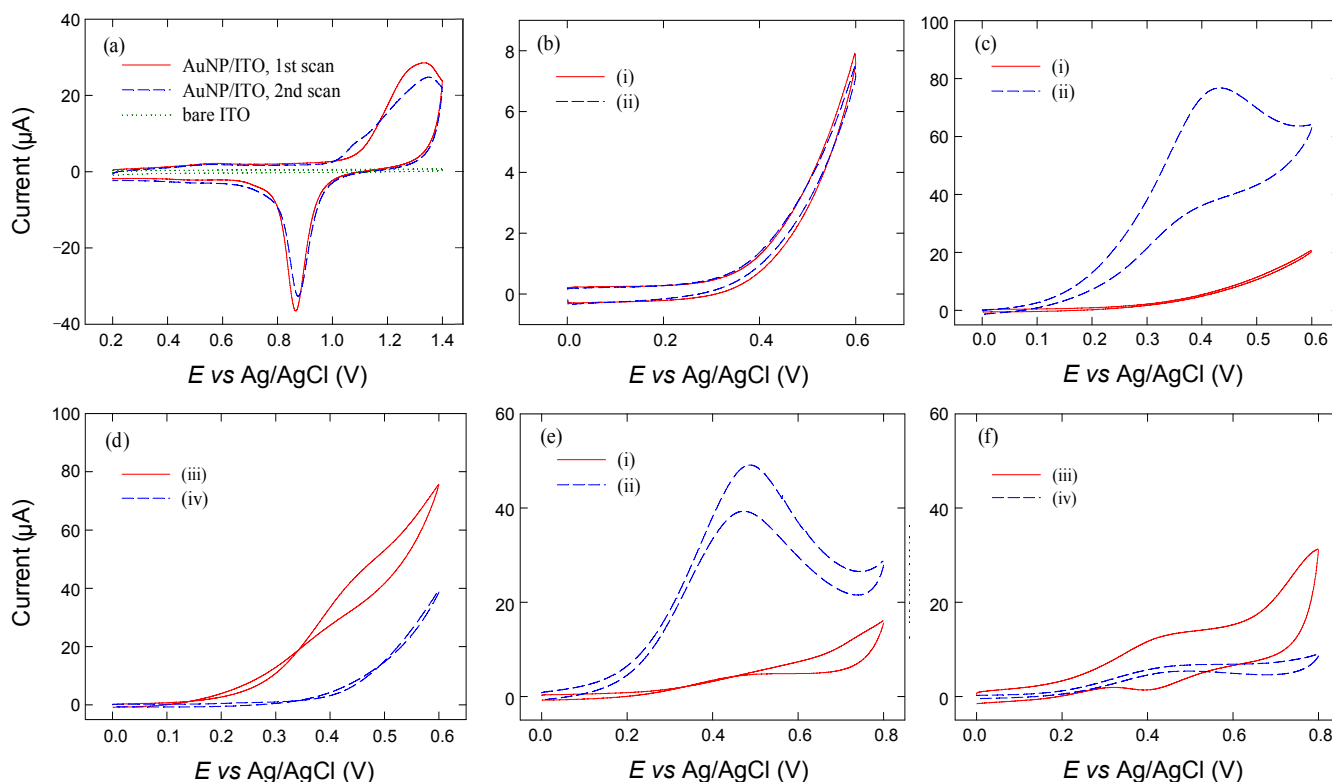
The electrocatalytic activity of metal electrodes depends on electrode-treatment history<sup>1,2</sup> and surface contamination,<sup>3</sup> which makes it difficult to obtain reproducible electrochemical data. Generally, to address such problem, the electrocatalytic activity of metal electrodes is enhanced prior to their use; the enhancement is based on thermal,<sup>4</sup> chemical,<sup>5</sup> cathodic<sup>6</sup> (application of a potential at which hydrogen is generated), and anodic treatment<sup>1,2,7,8</sup> (formation of metal oxide and its subsequent reduction). In particular, multiple anodic treatments of metal electrodes offer highly enhanced electrocatalytic activity, which even enables one to observe substantial currents of hydrogen sorption and desorption at Au electrodes.<sup>1,2</sup>

We have recently shown that the electrocatalytic activity of Au nanoparticles (AuNPs) can be enhanced *via* NaBH<sub>4</sub> treat-

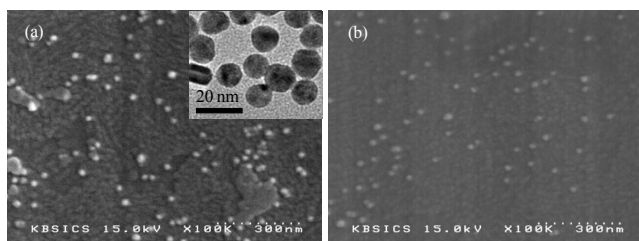
ment and cathodic treatment and that the enhanced activity slowly decreases with aging.<sup>3,5</sup> We have also demonstrated that the electrocatalytic activity of the AuNPs freshly prepared by electrochemical or chemical reduction slowly decreases with aging in both air and solution.<sup>9</sup> Likewise, the electrocatalytic activity of anodically treated Au electrodes or AuNPs might change with aging.

Herein, we report that the electrocatalytic activity of long-aged AuNPs can be enhanced *via* anodic treatment and that the enhanced electrocatalytic activity decreases with aging in air. The change in the electrocatalytic activity of AuNPs was evaluated by comparing cyclic voltammograms for the electrooxidation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and formic acid.

To assess electrocatalytic activity, AuNPs were adsorbed



**Figure 1.** (a) Cyclic voltammograms obtained in 0.1 M H<sub>2</sub>SO<sub>4</sub> at a bare ITO electrode and an AuNP-modified ITO electrode. (b-d) Cyclic voltammograms obtained in 0.1 M carbonate buffer (pH 10.0) containing 1.0 mM H<sub>2</sub>O<sub>2</sub> at (b) bare ITO electrodes and (c, d) AuNP-modified ITO electrodes. (e, f) Cyclic voltammograms obtained in a solution containing 0.25 M formic acid and 0.5 M NaHCO<sub>3</sub> at AuNP-modified ITO electrodes. The scan rate of all voltammograms was 50 mV/s. In Figures b-f, the voltammograms were recorded (i) before, (ii) just after, (iii) one week after, and (iv) three months after the anodic treatment (the experiment of Figure a).

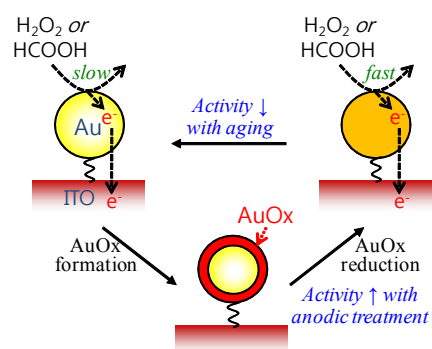


**Figure 2.** SEM images of the AuNP-modified ITO electrodes obtained (a) before and (b) after the anodic treatment. The inset in Figure a shows a TEM image of the synthesized AuNPs.

onto the ITO electrodes modified with an amine-terminated dendrimer, which allows the formation of AuNP-modified electrodes without a significant change in the intrinsic electrocatalytic activity of AuNPs.<sup>3,5,9</sup> The combination of the high electrocatalytic activity of freshly prepared AuNPs and the low activity of both ITO electrodes and long-aged AuNPs enables facile observation of the change in the electrocatalytic activity of AuNPs.

Three-month-aged AuNPs, prepared using citrate as a reducing agent,<sup>10</sup> were taken for the immobilization of AuNPs, because they have much lower electrocatalytic activity than freshly prepared AuNPs.<sup>9</sup> Figure 1a shows cyclic voltammograms obtained in 0.1 M H<sub>2</sub>SO<sub>4</sub> at an AuNP-modified ITO electrode and a bare ITO electrode. The characteristic anodic and cathodic peaks associated with the formation of Au oxide or Au hydroxide (AuOx) and the reduction of AuOx,<sup>11,12</sup> respectively, were observed at an AuNP-modified ITO electrode, whereas no such peaks were observed at a bare ITO electrode. Interestingly, the total charges of anodic and cathodic peaks in the second scan were not much different from those in the first scan (Figure 1a), meaning that a similar amount of Au participates in the formation of AuOx (and the reduction of AuOx). Figure 2 shows SEM images of the AuNP-modified ITO electrodes obtained before and after the anodic treatment. There was no significant difference in the surface density of AuNPs between two images. These results indicate that the most of AuNPs remains stably adsorbed on the dendrimer-modified ITO electrode during the anodic treatment.

To investigate the change of the electrocatalytic activity of AuNPs with anodic treatment and aging in air, the electrooxidation of H<sub>2</sub>O<sub>2</sub> and formic acid was tested. Figure 1b and c show cyclic voltammograms obtained in 1.0 mM H<sub>2</sub>O<sub>2</sub> before and after the anodic treatment. Two cyclic voltammograms for bare ITO electrodes (curves i and ii of Figure 1b) were similar, and H<sub>2</sub>O<sub>2</sub> electrooxidation did not occur well in this range of potentials. It shows that the anodic treatment has no effect on the electrocatalytic activity of ITO electrodes. As for AuNP-modified electrodes, anodic currents significantly increased after the anodic treatment (Figure 1c), although the currents (curve i of Figure 1c) were not much higher than those for bare ITO electrodes (curve i of Figure 1b) before the anodic treatment. This result clearly shows that the electrocatalytic activity of AuNPs was substantially enhanced by the anodic treatment. Importantly, the enhanced activity was obtained with only two cyclic scans; the activity obtained with one cyclic scan was also similar (data



**Figure 3.** Schematic for the change of the electrocatalytic activity with anodic treatment and aging.

not shown). The activity enhancement was also observed by cathodic treatment or NaBH<sub>4</sub> treatment in our previous study.<sup>5</sup> Moreover, we have observed that the enhanced electrocatalytic activity decreased with aging.<sup>5</sup> To check the effect of aging on the electrocatalytic activity of anodically treated AuNPs, cyclic voltammograms were obtained one week after and three months after the anodic treatment (Figure 1d). The voltammograms show that the enhanced electrocatalytic activity decreased with aging.

We also examined the effect of the anodic treatment on the electrocatalytic oxidation of formic acid. The electrocatalytic activity for the oxidation of formic acid was significantly enhanced after the anodic treatment (Figure 1e), and the enhanced activity decreased with aging (Figure 1f). The enhanced activity after the anodic treatment and its decrease with aging were also true for the electrocatalytic oxidation of formic acid.

Figure 3 schematically summarizes our experiment results. The electrocatalytic activity of long-aged AuNPs is enhanced *via* the anodic treatment, and the enhanced activity decreases with aging. It is believed that the high electrocatalytic activity of freshly prepared, cathodically treated, and NaBH<sub>4</sub>-treated AuNPs might be due to the formation of structurally metastable and highly active states and that the activity decrease with aging might be due to the formation of less active surface states *via* slow structural reorganization.<sup>5,9</sup> It is known that substantial structural changes occur on the surface of Au electrodes during their anodic treatment.<sup>13</sup> This structural changes might allow the enhanced electrocatalytic activity of AuNPs. Further studies of the detailed mechanism for the enhancement of electrocatalytic activity and the decrease of the enhanced activity with aging are required.

## Experimental Section

Amine-terminated G4 poly(amidoamine) dendrimer and all other chemicals were obtained from Sigma-Aldrich. The preparation of AuNPs with citrate as a reducing agent was performed by a reported method.<sup>10</sup> The diameter of AuNPs was *ca.* 13 nm. ITO-coated glass substrates were purchased from Samsung Corning (Daegu, Korea). Dendrimer-modified ITO electrodes were prepared as described previously.<sup>3,5,9</sup> To obtain AuNP-modified ITO electrodes, dendrimer-modified electrodes

were immersed in a solution of 3-month-aged AuNPs for 2 h, and the electrodes were then washed with distilled water. The AuNP-modified ITO electrodes were aged at room temperature. The electrochemical cell consisted of a modified or bare ITO working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode. The area of the working electrode was 0.28 cm<sup>2</sup>. All electrochemical data were obtained with different electrodes.

**Acknowledgments.** This work was supported for two years by Pusan National University Research Grant.

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