Electronic Supplementary Information

Enhancement of the Electrocatalytic Activity of Gold Nanoparticles via NaBH₄ Treatment

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Chemicals and reagents. Amine-terminated G4 poly(amidoamine) dendrimer, H₂O₂, 3-phosphonopropionic acid, (3-aminopropyl)triethoxysilane, p-benzoquinone, NaBH₄ and were purchased from Aldrich. Citrate-stabilized Au nanoparticle (10 nm, 0.01% HAuCl₄) was purchased from Sigma. The actual size of Au nanoparticle was 8.1 ± 0.8 nm. All buffer reagents and other inorganic chemicals were supplied by Sigma, Aldrich, or Fluka, unless otherwise stated. All chemicals were used as received. All aqueous solutions were prepared in doubly distilled water.

The phosphate buffered saline (PBS) solution (pH 7.4) consisted of 0.01 M phosphate, 0.138 M NaCl, and 0.0027 M KCl. The carbonate buffer solution (pH 10.0, 0.1 M) was composed of Na₂CO₃ and NaHCO₃.

Formation of Dendrimer-Modified ITO Electrodes. Dendrimer-modified ITO electrodes were prepared as described previously. Briefly, cleaned ITO electrodes were modified with 3-phosphonopropionic acid to form carboxylic acid-terminated phosphonate monolayers. After the carboxylic acid group was activated, dendrimer was immobilized on the activated electrode, which was followed by washing with PBS and water.

Immobilization of Au Nanoparticles and Their Treatment. Au nanoparticles were dropped onto and spread over the dendrimer-modified ITO electrodes for 2 h, and then the electrodes were washed with distilled water. NaBH₄ treatment of the electrodes was performed by dipping the electrodes for 15 min in a carbonate buffer solution containing 10 mM NaBH₄, and then the electrodes was washed with distilled water. The cathodic treatment was carried out by applying a potential of −0.6 V for 10 min in 0.1 M H₂SO₄. The p-benzoquinone treatment was performed by immersing the NaBH₄-treated electrode for 20 min in a PBS solution containing 5 mM p-benzoquinone.

Electrochemical Measurement. All electrochemical experiments were performed using a CHI708C instrument (CH Instruments Inc). The electrochemical cell consisted of a modified ITO working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The area of working electrodes was 0.28 cm². The H₂O₂ solution was prepared fresh every day.
Scheme S1. Schematic representation of an Au-nanoparticle- and dendrimer-modified ITO electrode.

Fig. S1 Cyclic voltammograms obtained at Au electrodes in a carbonate buffer solution containing 1 mM H₂O₂ (at a scan rate of 50 mV/s) (i) before and (ii) after NaBH₄ treatment. The Au electrodes were formed by sputtering of Cr (300 Å) and Au (2000 Å) on a 6" Si wafer. The electrodes were successively cleaned with ethanol, trichloroethylene, and water for 15 min with sonication before their electrochemical measurement.
Fig. S2 SEM images of Au-nanoparticle-modified ITO electrodes that were obtained (a) before NaBH₄ treatment, (b) after NaBH₄ treatment, and (c) after NaBH₄ treatment followed by the electrooxidation of H₂O₂. To clearly see the image of nanoparticles, 20-nm Au nanoparticles were used in place of 10-nm Au nanoparticles. When 20-nm Au nanoparticles were used, the enhancement of the electrocatalytic properties was also observed after NaBH₄ treatment.

Fig. S3 Cyclic voltammograms obtained at Au-nanoparticle- and (3-aminopropyl)triethoxysilane-modified ITO electrodes (a) in a carbonate buffer solution containing 10 mM glucose or (b) in a 0.5 M NaHCO₃ solution containing 0.25 M formic acid (at a scan rate of 50 mV/s) (i) after and (ii) before NaBH₄ treatment. (3-aminopropyl)triethoxysilane-modified ITO electrode was formed by dipping the pretreated ITO into a methanolic solution containing 2% (3-aminopropyl)triethoxysilane for 12 h, which was followed by washing with methanol and water.
Fig. S4 Cyclic voltammograms obtained at Au-nanoparticle-modified ITO electrodes in a carbonate buffer solution containing 1 mM H$_2$O$_2$ (at a scan rate of 50 mV/s): (a) by increasing the treatment time in an NaBH$_4$-containing solution ((i) before NaBH$_4$ treatment and after (ii) 1, (iii) 15, and (iv) 30-min NaBH$_4$ treatment), and (b) by increasing the incubation time in air after the activation of the Au nanoparticles ((i) just after the NaBH$_4$ treatment, (ii) one hour after the NaBH$_4$ treatment, (iii) one month after the NaBH$_4$ treatment, and (iv) after NaBH$_4$ retreatment in one month).

Fig. S5 Cyclic voltammograms obtained at Au-nanoparticle-modified ITO electrodes in a carbonate buffer solution containing 1 mM H$_2$O$_2$ (at a scan rate of 50 mV/s): by increasing the incubation time in 10 mM phosphate buffer (pH 7.4) (i) one month after the NaBH$_4$ treatment and (ii) after NaBH$_4$ retreatment in one month). The enhanced electrocatalytic activity decreased with increasing incubation time, and the enhanced activity was recovered after retreatment with NaBH$_4$. 
**Fig. S6** Cyclic voltammograms obtained at Au-nanoparticle-modified ITO electrodes in a PBS solution (at a scan rate of 10 mV/s) (i) just after the NaBH₄ treatment, (ii) 1 h after the NaBH₄ treatment, and (iii) 12 h after the NaBH₄ treatment.

**Fig. S7** Concentration dependence of linear-sweep voltammograms in a carbonate buffer solution containing different concentrations of H₂O₂ ((i) 100 mM, (ii) 10 mM, (iii) 1 mM, and (iv) 100 μM) at a scan rate of 50 mV/s.
Fig. S8 Dependence of the anodic current at 0.25 V on the concentration of H$_2$O$_2$ (full range). The error bars represent the standard deviation of three measurements.