

Supporting Information

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Decoration of Glassy Carbon Surfaces with Dendrimer-Encapsulated Nanoparticles with a View to Constructing Bifunctional Nanostructures

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Experimental Section

Chemicals and materials Amine-terminated sixth-generation polyamidoamine dendrimers (G6-NH₂ PAMAM dendrimers), K₂PtCl₄, NaBH₄, cellulose dialysis sacks (MW cutoff of 12,000), LiClO₄, H₂O₂, and glucose were purchased from Sigma-Aldrich, Inc. (USA). Streptavidin-conjugated glucose oxidase (Streptavidin-GOx) was used as received from Fitzgerald Industries International (USA). *N*-hydroxysuccinimide (NHS) esters of biotin (EZ-Link® Sulfo-NHS-LC-LC-Biotin) were obtained from Pierce Biotechnology (USA). Both a glassy carbon (GC) disk (CH Instruments, USA) and a GC plate (Tokai Carbon Co., Japan) were used as electrodes. 18 MΩ•cm deionized water was used to prepare aqueous solution (Ultra370, Younglin Co., Korea)

Preparation of Pt dendrimer-encapsulated nanoparticles (Pt DENs) Pt DENs were prepared using a slight variation of a previously reported procedure.^[1] At first, 210 mol equivalent of an aqueous 10 mM K₂PtCl₄ was added to an aqueous 10 μM G6-NH₂ PAMAM dendrimer solution. The mixture was stirred for 72 h to complex Pt ions with the interior amines of the dendrimers. Then, a 20 fold excess of an aqueous NaBH₄ solution was added slowly to the mixture with vigorous stirring. The mixture solution was kept in a closed vial for overnight to ensure complete reduction of Pt. Finally, the Pt DENs solution was dialyzed using a cellulose dialysis sack for overnight to remove impurities.

Electrochemical experiments Electrochemical measurements were carried out in a small-volume electrochemical cell using a standard three-electrode configuration with a Model 440 electrochemical analyzer (CH Instruments, USA). The glassy carbon working electrodes

were polished with 0.3 μm alumina powder on a polishing pad (Buehler, USA), and then rinsed with deionized water. Residual alumina particles were thoroughly removed by sonicating the glassy carbon electrodes successively in ethanol and deionized water. The electrodes were then rinsed with deionized water and blown dry with a N_2 stream. A Pt wire and a Ag/AgCl electrode were used as a counter and a reference electrode, respectively. The electrochemical immobilization of Pt DENs on glassy carbon electrodes (GCEs) was carried out as we reported previously.^[2] Briefly, the potential of the electrode was cycled three times between 0.2 and 1.0 V (vs. Ag/AgCl) in an aqueous 10 μM Pt DEN solution containing 0.1 M LiClO_4 . After immobilization, the modified GCE was rinsed thoroughly and blown dry. The modified GCE electrodes were additionally characterized. For estimation of the surface density of immobilized Pt DENs, the electrodes were placed in a CO-saturated 0.5 M H_2SO_4 solution and the electrode potential was held at 0.1 V (vs. Ag/AgCl) for 3 min. This results in adsorption of CO on the Pt surface.^[3] Then, the electrolyte solution was purged with N_2 gas for 10 min to remove dissolved CO gas in the solution. Finally, the potential of the electrode was scanned to strip the adsorbed CO on the Pt surface. After stripping the adsorbed CO, the potential scan was repeated to make sure absence of the CO oxidation peak, which confirms that the oxidation of CO arises from adsorbed CO and not from dissolved CO.

Attachment of GOx on Pt DEN-immobilized glassy carbon electrode Streptavidin-conjugated GOx enzymes were attached onto Pt DEN-immobilized GCEs through biotin-streptavidin chemistry. Briefly, the Pt DEN-immobilized GCE was exposed to a 10 mM NHS esters of biotin solution for biotinylation of the terminal amine groups of immobilized dendrimers. Then, a 1 mg/mL streptavidin-GOx conjugate solution was introduced onto the biotinylation GCE

surface, which results in binding of the GOx enzymes onto the GCE surface. After rinsing with PBS buffer (pH 7.4), the electrode was blown dry by N₂ stream.

Characterization Transmission electron microscope (TEM) images were collected using a Tecnai G2 F30 TEM (FEI Co., USA). TEM samples were prepared by evaporating a drop of aqueous Pt DEN solution on a 200 mesh carbon-coated copper grid (Ted Pella Inc., USA). XPS spectra were obtained using a PHI 5800 spectrometer (Physical Electronics Inc., USA). The GC plates (1cm x 1 cm x 0.3 cm) were used to prepare XPS samples.

References

- 1 M. Zhao and R. M. Crooks, *Angew. Chem. Int. Ed.* **1999**, *38*, 364-366.
- 2 T. H. Kim, H. S. Choi, B. R. Go and J. Kim, *Electrochem. Commun.* **2010**, *12*, 788-791.
- 3 Gilman, S. *J. Phys. Chem.* **1962**, *66*, 2657-2664.

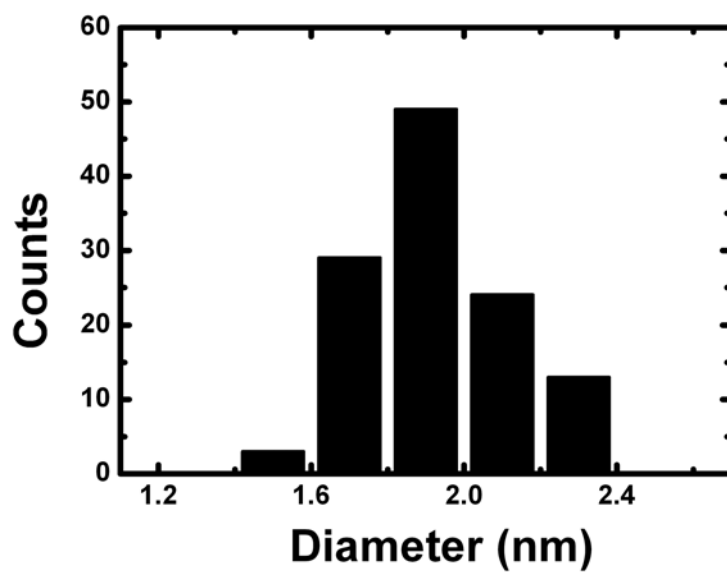


Fig. S1 Particle size distribution of as-prepared G6-NH₂(Pt₂₁₀) DENs.

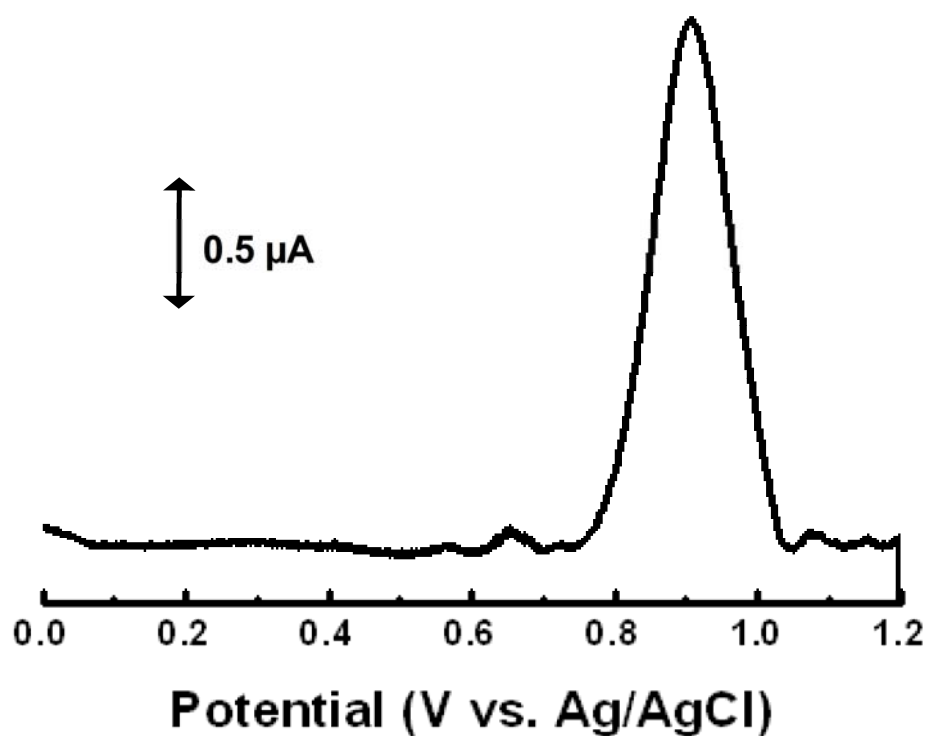


Fig. S2 CO stripping voltammogram obtained from a Pt DEN-decorated GCE after baseline correction, which shows an oxidation peak of adsorbed CO on Pt nanoparticles. Integration of the CO oxidation peak makes it possible to calculate the total surface area of immobilized Pt nanoparticles. Based on the measured surface area and average size of Pt nanoparticles, we estimated the surface density of Pt DENs, i.e. 5.50×10^{11} particles/cm². Scan rate: 0.1 Vs⁻¹. Electrolyte solution: N₂-saturated 0.5 M H₂SO₄.