

Electrochemical Synthesis and Electrocatalytic Properties of Au@Pt Dendrimer-Encapsulated Nanoparticles

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Abstract: Dendrimer-encapsulated Au nanoparticles comprised of an average of 147 atoms were synthesized and immobilized on a glassy carbon electrode. A one-atom-thick shell of Cu was added to the Au core by electrochemical underpotential deposition, and then this shell was replaced with Pt by galvanic exchange. The results indicate that this synthetic approach leads to well-defined core/shell nanoparticles <2 nm in diameter. The rates of oxygen reduction at the Au@Pt electrocatalysts were compared to Pt-only and Au-only, 147-atom dendrimer-encapsulated nanoparticles.

Here we report the electrochemical synthesis of Au@Pt (core@shell) nanoparticles encapsulated within sixth-generation, poly(amidoamine) (PAMAM) dendrimers (G6-OH) and their electrocatalytic activity for the oxygen reduction reaction (ORR). These results are significant because the synthesis and catalytic activity of core/shell nanoparticles in this size range (~1.4 nm), and having this degree of monodispersity, have not previously been reported. Importantly, well-defined catalytic nanoparticles in this size range provide good experimental models for comparison to first-principles calculations.^{1,2}

We have previously demonstrated that Pt^{3,4} and PtPd bimetallic alloy⁵ dendrimer-encapsulated nanoparticles (DENs) immobilized on a glassy carbon electrode (GCE) are active electrocatalysts for the ORR, and that the activity of DENs toward the ORR is a function of the nanoparticle size⁴ and composition.⁵ We have also reported a homogeneous chemical synthesis of Au@Pd, Au@Ag, and Ag@Au core/shell DENs by sequential complexation and chemical reduction of, first, the core metal and, second, the shell.^{6–8} However, neither we nor others have measured electrocatalytic activity using core/shell nanoparticles having diameters of <3.7 nm.⁹

Au@Pt DENs are good candidates for an initial investigation of the electrocatalytic activity of core/shell DENs due to the high ORR activity of nanoparticles having a Pt shell,^{9–13} and because Au@Pt nanoparticles are stable over a wide potential window. Core/shell nanoparticles are also interesting because their electronic and catalytic properties can be tuned by manipulating their structure. For example, Adzic and co-workers have reported the electrocatalytic properties of core/shell nanoparticles as a function of their size (~4–9 nm), the thickness of the shell (1–3 atomic layers), and the identity of their core (Au, Ag, Pd, Rh, Ir, Ru, and Pd₃Co).^{9,12–14} These materials were prepared by underpotential deposition (UPD) of a sacrificial metal onto the core, followed by galvanic exchange for the final shell metal.^{10–15}

Here we used the UPD/galvanic exchange approach for preparing Au@Pt DENs (Scheme 1). Experimental details regarding the synthesis, characterization, and immobilization of Au DENs containing an average of 147 atoms (G6-OH(Au₁₄₇)) onto a GCE are provided in the Supporting Information. To show that the Au

Scheme 1

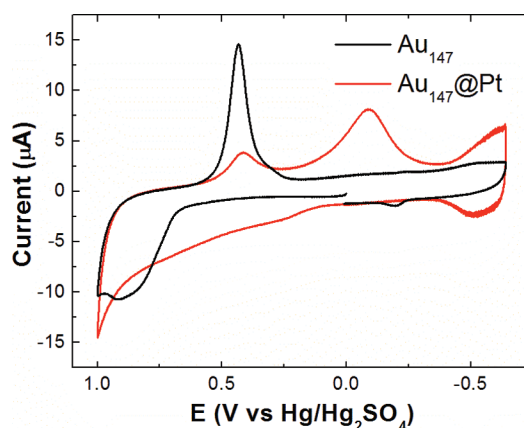


Figure 1. Cyclic voltammograms of Au₁₄₇ (black line) and Au₁₄₇@Pt (red line) DENs immobilized on a GCE (geometric area = 0.071 cm²). Scan rate = 100 mV/s; electrolyte, Ar-saturated 0.50 M H₂SO₄.

DENs are attached to the GCE, the electrode potential was scanned from 0 V (vs Hg/Hg₂SO₄) to 1.00 to -0.64 V and back to 0 V in 0.50 M H₂SO₄ (Figure 1, black trace). The characteristic Au surface oxidation at potentials > 0.65 V and the corresponding oxide reduction between 0.55 and 0.30 V confirm that the surfaces of the Au DENs are electrochemically active. The oxide reduction peak was integrated and converted to total Au surface area using the widely accepted conversion factor of 390 µC/cm².¹⁶ This value is only valid for bulk, polycrystalline Au, but with this caveat the total area of the Au DENs is 0.034 cm². Using simple assumptions outlined previously,⁴ the expected surface area for DENs of this size is estimated to be ~0.040 cm². On the basis of this result, we conclude that most of the Au DENs are in electronic contact with the GCE.

A Pt shell was added to the (average) 147-atom Au core by first depositing a monolayer of Cu by UPD and then exchanging the Cu layer for Pt. Figure S2 (Supporting Information) is a cyclic voltammogram (CV) showing the UPD and subsequent stripping of Cu from the Au DENs. To form the Pt shell, the Au DENs-coated GCE was scanned at 50 mV/s from 0.40 to -0.42 V in a Ar-purged solution containing 0.10 M HClO₄ and 1.0 mM Cu²⁺ and then immediately immersed in a freshly prepared Ar-purged solution of 0.10 M HClO₄ containing 5.0 mM K₂PtCl₄ for 5 min.

The galvanic exchange of the Cu shell for Pt was confirmed by scanning the electrode in 0.50 M H₂SO₄ over the same potential

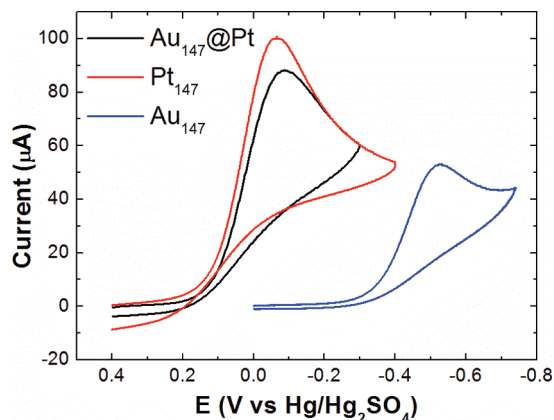


Figure 2. Cyclic voltammograms for the ORR obtained using a GCE (geometric area = 0.071 cm²) modified with Au₁₄₇@Pt DENs (black), Pt₁₄₇ DENs (red), and Au₁₄₇ DENs (blue). Scan rate = 100 mV/s; electrolyte, O₂-saturated 0.10 M HClO₄.

range used for the Au core. The results are shown as the red line in Figure 1. The formation of Pt oxide is apparent at potentials positive of 0 V, and this oxide is subsequently reduced between 0.21 and -0.35 V. Hydrogen adsorption and desorption waves, which were absent on the Au cores prior to addition of the Pt shells, are also apparent negative of -0.35 V. These results are in accord with our previous findings for monometallic Pt DENs, and they establish the presence of Pt.⁴ In addition to these characteristic Pt features, a small peak centered at ~0.4 V corresponds to oxidation of exposed Au. On the basis of the Au oxide reduction peak areas before and after addition of the Pt shell, we estimate that ~20% of the originally present Au is electrochemically active after addition of the Pt shell. The Pt surface area was determined independently by integrating the Pt oxide reduction wave between 0.21 and -0.35 V. Assuming a conversion factor of 420 $\mu\text{C}/\text{cm}^2$,¹⁶ the Pt coverage is 0.029 cm². By this measure, ~85% of the original Au surface is covered with a Pt shell. The good agreement of these two independent measures of surface coverage is not too surprising, because Pt is present only as a monolayer shell and therefore there is no risk of forming multilayers of Pt oxide. Additional information about the surface area determination is provided in the Supporting Information. XPS results (Supporting Information) are also in qualitative accord with the electrochemical results.

The ORR activities of Au₁₄₇, Pt₁₄₇, and Au₁₄₇@Pt DENs were qualitatively evaluated by cyclic voltammetry in an O₂-saturated 0.10 M HClO₄ solution (Figure 2). The peak potential for the ORR at the Au₁₄₇ DEN-modified electrode is -0.51 V. Upon addition of the Pt shell, however, this value shifts positive by 0.43 to -0.08 V. For comparison, the ORR peak potential for Pt₁₄₇ DENs is just 20 mV more positive than that for the Au₁₄₇@Pt electrocatalyst. The slight difference in peak currents may be due to differences in the number of particles immobilized on the electrode surface. These results are consistent with findings reported for Au@Pt nanoparticles having sizes of 5 ± 1 nm.¹¹

To verify that the Au₁₄₇@Pt nanoparticles remain encapsulated within the dendrimer templates, and are thus stable following immobilization and electrocatalytic measurements, we carried out the following control experiment. The Au₁₄₇@Pt DEN-modified GCE was immersed in CH₂Cl₂ containing 3 mM 1-dodecanethiol (C12SH) for 10 min. Second, the electrode was removed from the C12SH solution, rinsed, and then cycled in an O₂-saturated, aqueous, 0.10 M HClO₄

solution to test its activity for the ORR. We know from previous studies that the dendrimer collapses onto the encapsulated nanoparticles in poor solvents, like CH₂Cl₂, and this protects them from being poisoned by the thiol.^{3,17} However, this effect will only be observed if the nanoparticles are fully encapsulated within the dendrimer. The results of this experiment for the Au₁₄₇@Pt DENs are provided in the Supporting Information (Figure S3), and they clearly demonstrate that the DENs remain encapsulated throughout the electrocatalytic experiments described herein.

In conclusion, we have demonstrated a means for preparing core/shell DENs consisting of Au cores containing an average of 147 atoms and a single atomic layer shell of Pt. This methodology is applicable to the synthesis of other core/shell configurations that would otherwise be difficult or impossible to synthesize using traditional complexation and chemical reduction steps.¹⁸ In the present report, we have relied primarily on electrochemical methods to confirm the structure of these materials, but the results of UPD, hydrogen desorption, Au and Pt oxide reduction, the ORR, and an experiment designed to show that the nanoparticles are stable and remain within their dendrimer hosts are compelling. The results of studies focused on other core/shell configurations, the use of more sophisticated characterization methods, and comparison of experimental kinetic measurements to theoretical calculations are currently underway.

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Supporting Information Available: Experimental procedures, TEM, CVs for Cu UPD, an experiment demonstrating encapsulation of DENs, XPS results, and a discussion of surface area measurements are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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