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PAPER

Synthesis, characterization, and electrocatalysis using Pt and Pd dendrimer-encapsulated nanoparticles prepared by galvanic exchange†‡

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In this report we present the synthesis and characterization of Pt and Pd dendrimer-encapsulated nanoparticles (DENs) using the method of galvanic exchange. Sixth-generation hydroxyl-terminated poly(amidoamine) dendrimers were used to prepare Cu DENs composed of 55 atoms. In the presence of either PtCl_4^{2-} or PdCl_4^{2-} , the less noble Cu DENs oxidize to Cu^{2+} leaving behind an equal-sized DEN of Pt or Pd, respectively. DENs prepared by direct reduction with BH_4^- , which is the common synthetic route, and those prepared by galvanic exchange have the same composition, structure, and properties as judged by UV-vis spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and electrochemical methods. However, the galvanic exchange synthesis is much faster (3 h vs. 96 h), and the yield of reduced DENs is significantly higher (nearly 100% in the case of galvanic exchange).

Introduction

Here we report the synthesis, characterization, and electrocatalytic properties of Pt and Pd dendrimer-encapsulated nanoparticles (DENs) prepared by intradendrimer galvanic exchange. Galvanic exchange involves replacement of one zerovalent metal nanoparticle by another, more noble, metal. The results reported here are significant for three reasons. First, the time required to prepare Pt DENs by galvanic exchange is just 3 h, compared to 96 h *via* the normal borohydride synthesis.¹ Second, galvanic exchange leads to fully reduced DENs, whereas borohydride reduction can lead to only partial reduction of the precursor.¹ Third, DENs prepared by galvanic exchange are stable, highly monodisperse, and compositionally pure.

Our group^{1–4} and others^{5–8} have used poly(amidoamine) (PAMAM) dendrimers for the synthesis of mono- and bimetallic DENs in the ~1–2 nm size range.^{9–16} The usual

DENs synthesis consists of two steps. First, solutions containing appropriate metal ions and dendrimers are mixed. This leads to encapsulation of metal ions within the dendrimer interior. We refer to this species as the precursor complex. Second, the encapsulated metal ions are chemically reduced using BH_4^- or another suitable reducing agent. This step yields stable, water-soluble, size-monodisperse, and catalytically active mono- and bimetallic (alloy and core@shell) metal nanoparticles composed of Cu,^{10,17} Pd,⁴ Pt,^{1,18} Au,⁹ PdCu,¹³ Au@Ag,¹⁶ Pd@Au,^{11,12} and PtPd^{14,15} DENs. We have also reported the synthesis of easily oxidizable monometallic DENs (Ni,¹⁹ Sn,²⁰ and Fe²¹) and bimetallic alloy (NiSn)²⁰ DENs using hydrophobic dendrimers dissolved in organic solvents.

Pt DENs are usually synthesized by adding PtCl_4^{2-} to an aqueous dendrimer solution. A number of studies have shown that one or two of the Cl^- ligands are replaced with water before the complex reacts with interior tertiary amines of the dendrimer.^{1,18,22,23} Once formed, the $\text{G6-OH}(\text{Pt}^{2+})_n$ precursor complex is reduced with BH_4^- . Here, G6-OH refers to a sixth-generation, hydroxyl-terminated PAMAM dendrimer, and Pt^{2+} refers to all forms of Pt^{2+} regardless of its ligand field. We recently reported that this synthesis results in a bimodal distribution of fully reduced DENs ($\text{G6-OH}(\text{Pt}_n)$, $n = 55, 147$, and 240) and unreduced $\text{G6-OH}(\text{Pt}^{2+})_n$ precursor.¹ For example, if the synthesis is performed using a 55:1 ratio of $\text{Pt}^{2+}:\text{G6-OH}$, only ~14% of the precursor complex is reduced to $\text{G6-OH}(\text{Pt}_{55})$. If the $\text{Pt}^{2+}:\text{G6-OH}$ ratio is 147, the extent of reduction rises to ~44%.¹ However, $\text{G6-OH}(\text{Pt}^{2+})_n$ can be fully reduced using electrochemical methods.²⁴ It has also been found that different synthetic methods can lead to different products.^{6,22,23,25} Specifically,

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† Dedicated to Prof. Didier Astruc on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: High-resolution XPS spectrum of $\text{G6-OH}(\text{Pd}_{55})$ DENs, cyclic voltammograms demonstrating immobilization of $\text{G6-OH}(\text{Pt}_{55})$ onto GCEs, cyclic voltammograms for the ORR using $\text{G6-OH}(\text{Pt}_{55})$ DENs before and after immobilization onto GCEs, electrochemical cleaning scans, and electrochemical data used to calculate the surface areas of Pt DEN-modified GCEs. See DOI: 10.1039/c1nj20083f

the time allotted for formation of the precursor complex, the solution pH, the temperature, and the identity of the functional group on the periphery of the dendrimer influence the Pt DENs synthesis.^{6,23}

Galvanic exchange is used to synthesize metal nanomaterials in a process governed by the difference in the electrochemical potentials of the two metals involved.²⁶ This process has previously been used to prepare a number of different types of nanoparticles,^{27–31} including those templated by dendrimers.^{5,26,32} With regard to DENs, we published a preliminary report describing the synthesis of monometallic Au, Ag, Pd, and Pt DENs by galvanic exchange,²⁶ and more recently we showed that Au@Pt DENs can be synthesized by this method.³² In the latter case, Au@Cu DENs were synthesized, and then the Cu shell was exchanged for Pt using an approach first described by Adzic and coworkers.³³ Chandler and coworkers prepared supported bimetallic Pt₁₆Au₁₆ dendrimer-stabilized nanoparticles (DSNs) using this same Cu-exchange method.⁵

Here, we report a detailed examination of the synthesis of G6-OH(Pt₅₅) and G6-OH(Pd₅₅) DENs by galvanic exchange using G6-OH(Cu₅₅) precursors. Transmission electron microscopy (TEM), UV-vis spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and electrochemical methods confirm the formation of fully reduced, stable Pt and Pd DENs. Finally, the electrocatalytic properties of Pt DENs, synthesized by galvanic exchange, toward O₂ reduction are described.

Experimental section

Chemicals

The G6-OH PAMAM dendrimers in methanol were purchased from Dendritech, Inc. (Midland, MI). Prior to use, methanol was removed under vacuum and then the dendrimer was reconstituted in sufficient deionized water to yield a 100.0 μM solution. All other chemicals were used as received: Cu(NO₃)₂, NaBH₄, K₂PtCl₄, K₂PdCl₄, and LiClO₄ were purchased from Sigma-Aldrich (Milwaukee, WI); high-purity HClO₄ and H₂SO₄ were purchased from J. T. Baker (Phillipsburg, NJ); and NaOH was from Fischer Scientific (Pittsburgh, PA). Aqueous solutions were prepared using 18 MΩ cm Milli-Q water (Millipore, Billerica, MA). Dialysis sacks having a nominal molecular weight limit (NMWL) of 12 kDa were purchased from Sigma Diagnostics.

Synthesis of Cu, Pt, and Pd DENs

Cu DENs, which are the precursors for Pt and Pd DENs synthesized by galvanic exchange, were prepared using a previously described procedure.¹⁰ Briefly, 1.0 mL of the 100.0 μM G6-OH stock solution was diluted with 8.68 mL of water. For G6-OH(Cu₅₅) DENs, 55 equiv. of a freshly prepared 20.0 mM Cu(NO₃)₂ solution (0.275 mL) were added to the G6-OH solution. Prior to reduction, the pH of this solution was adjusted to 7.5 using 0.3 M aqueous NaOH. This solution was sealed in a serum vial and purged continuously with N₂ gas. The solution was allowed to stir for a minimum of 15 min to ensure complete complexation between the tertiary

amines of the dendrimer and Cu²⁺. Finally, under N₂, a 5-fold molar excess of an aqueous 1.0 M NaBH₄ solution was added to the G6-OH(Cu²⁺)₅₅ precursor complex. Reduction was allowed to proceed for 40–45 min. The final concentration of G6-OH(Cu₅₅) was 10.0 μM.

Pt DENs were synthesized by galvanic exchange using the following procedure. First, 1.0 M HClO₄ was added to the G6-OH(Cu₅₅) solution to lower its pH from 7.5 to 3.0. The presence of the acid ensures complete decomposition of excess BH₄[−]. Second, galvanic exchange was initiated by adding a stoichiometric amount of aqueous 10.0 mM PtCl₄^{2−} to the DENs solution under a N₂ purge to prevent oxidation of the Cu DENs. This solution was stirred for 50–60 min. To ensure that galvanic exchange, rather than direct BH₄[−] reduction, was responsible for Pt DEN formation, the synthetic procedure described above was repeated except that Cu²⁺ was not added during the first step of the procedure. This experiment resulted in formation of G6-OH(Pt²⁺)_n rather than reduced G6-OH(Pt_n), indicating that BH₄[−] was successfully removed from the solution by lowering its pH.

Pd DENs were synthesized using the same procedure described for the Pt DENs, except PdCl₄^{2−} was substituted for PtCl₄^{2−}.

Characterization

UV-vis absorption spectra were obtained using a Hewlett-Packard HP8453 spectrometer. The optical path length of the quartz cuvette was 1.0 mm. A 10.0 μM aqueous solution of the metal-free G6-OH dendrimer was used for background subtraction.

TEM micrographs were obtained using a JEOL-2010F TEM operating at 200 kV. Samples were prepared by placing 2–3 drops of the appropriate DEN solution on a 400-mesh, carbon-coated Cu grid (EM Sciences) and allowing the liquid to evaporate in air. The particle-size distribution was based on 100 randomly selected particles using Gatan Digital Micrograph software.

XPS compositional analysis was carried out using a Kratos Axis Ultra spectrometer equipped with a monochromatic Al Kα radiation source. Spectra were collected at a pass energy of 20 eV with a step size of 0.1 eV and a dwell time of 1 s per step for all elements except Cu, which employed an extended dwell time of 5 s to ensure maximum sensitivity to its presence. Prior to obtaining XPS spectra, the Pt DENs sample was dialyzed in water adjusted to pH = ~3 (unless otherwise noted) using 1.0 M HClO₄. XPS samples were prepared by dropping 10.0 μL of the dialyzed DEN solutions onto small pieces of Si wafers and drying in air. For Pd DENs, 10 μL of an undialyzed DENs solution was placed on pieces of Si wafer, and then it was dried under H₂ to ensure that the nanoparticles remained in the zerovalent state.³⁴ A control consisting of a DEN-free Si wafer revealed no characteristic peaks for Pt, Pd, or Cu. For Pt and Pd DENs, C1s peaks were observed at 285.2 and 284.5 eV. To compensate for sample charging, the XPS peak positions were referenced to the C1s feature at 284.5 eV.^{6,35}

X-Ray absorption spectroscopy (XAS) measurements were carried out at beamline X18B of the National Synchrotron

Light Source at the Brookhaven National Laboratory. Prior to transporting the DENs to the beamline, they were dialyzed using pH = ~3 water and then freeze-dried in a Labconco FreeZone 12 L lyophilizer. At the beamline, the dried DENs were partially reconstituted using a 1:1 methanol:water mixture, spread onto transparent tape, and then allowed to dry. Prior to XAS, this tape was folded multiple times to ensure homogeneity of the sample. All XAS data were obtained in transmission mode. A reference Pt foil was measured simultaneously and used for energy alignment. Data analysis was completed using the IFEFFIT software package.³⁶

Electrochemical studies were performed using a CH Instruments 760B bipotentiostat. A glassy carbon electrode (GCE) was used as the working electrode, Hg/Hg₂SO₄ as the reference electrode, and a Pt wire as the counter electrode (all electrodes from CH Instruments). The 3 mm diameter GCE was successively polished with 1.0, 0.3, and 0.05 μm alumina (Buehler), sonicated in water for 10 min to remove polishing compound, and then dried under flowing N₂ gas. Prior to electrochemical studies, the DENs were dialyzed at pH 7.0 using Milli-Q water. Dialyzed DENs were immobilized by scanning (10 mV s⁻¹) the electrode potential 3 times between -0.60 and 0.60 V (all potentials are reported vs. Hg/Hg₂SO₄) in a solution containing 10.0 μM G6-OH(Pt₅₅) and 0.1 M LiClO₄ (pH 2.5). For the oxygen reduction reaction (ORR) study, the scan rate was 50 mV/s, 0.1 M HClO₄ was used as electrolyte, and the solutions were saturated with O₂ or N₂, as appropriate, for at least 30 min before measurements. Prior to obtaining electrocatalytic data, electrochemical cleaning scans were carried out by scanning the potential of the DEN-modified GCE between -0.80 and 0.90 V at 100 mV s⁻¹ using N₂-purged 0.1 M HClO₄.

Results and discussion

Synthesis and UV-vis analysis of G6-OH(Cu₅₅) DENs

The synthesis of Cu DENs has been described previously^{10,17} and is reviewed in the Experimental Section. Briefly, however, 55 equiv. of Cu²⁺ are mixed with an aqueous solution of G6-OH, and this results in a precursor complex (G6-OH(Cu²⁺)₅₅) in which Cu²⁺ ions are coordinated to the interior tertiary amine groups of the dendrimers. The pH of this solution is adjusted to 7.5, and then the BH₄⁻ reducing agent is added. This results in formation of Cu DENs containing an average of 55 atoms (G6-OH(Cu₅₅)). Cu DENs oxidize easily in air, and therefore they are maintained in a N₂ atmosphere.

Fig. 1 provides absorbance spectra for each step of the G6-OH(Cu₅₅) synthesis. The spectrum of G6-OH is featureless over the spectral region examined. However, the spectrum of aqueous Cu(NO₃)₂ exhibits a broad, weak feature centered at ~810 nm, which is attributable to the d-d transition of [Cu(H₂O)₆]²⁺.^{2,10} In the presence of G6-OH, this band shifts to 605 nm due to complexation of Cu²⁺ with the tertiary amines of the dendrimer.^{2,10} In addition to this band, the Cu²⁺-dendrimer precursor complex also reveals a strong absorbance at 300 nm. This is due to a ligand-to-metal charge transfer (LMCT) between Cu²⁺ and the tertiary amines of dendrimer. After addition of the reducing agent, the 300 and

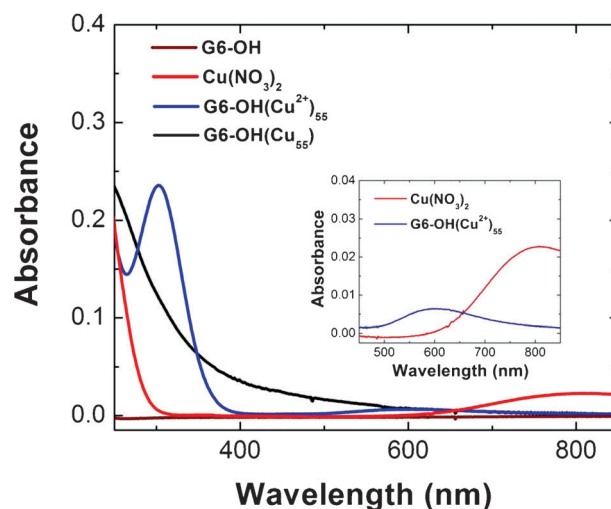
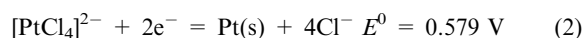
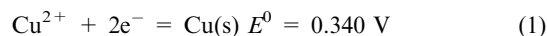


Fig. 1 Absorption spectra of empty G6-OH, aqueous solution of Cu(NO₃)₂, G6-OH(Cu²⁺)₅₅, and G6-OH(Cu₅₅). Conditions: [G6-OH] = 10.0 μM, [Cu(NO₃)₂] = 1.0 mM. 1.0 mm cuvette was used. 10.0 μM G6-OH or water was used for reference. All the solutions were freshly prepared. The pHs of G6-OH(Cu²⁺)₅₅ and G6-OH(Cu₅₅) solutions are 7.5 and 8.0 respectively. Inset shows an expanded view UV-vis spectra for Cu(NO₃)₂ and G6-OH(Cu²⁺)₅₅.

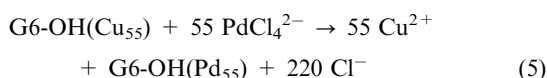
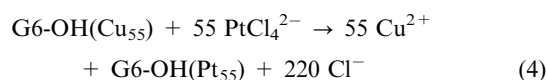
605 nm bands are replaced with a spectrum exhibiting monotonically increasing absorbance toward higher energy, which is characteristic of G6-OH(Cu₅₅).^{37,38} The absence of a plasmon band at ~570 nm in this spectrum suggests that the diameter of the Cu nanoparticles is < 4 nm.^{39,40}

Galvanic replacement of G6-OH(Cu₅₅) by Pt²⁺ and Pd²⁺

Galvanic replacement is driven by differences in the electrochemical potentials of the two metals involved. The half-reactions and standard potentials used in this study are given in eqn (1)–(3).



Note, however, that it is likely the standard potentials⁴¹ for these reactions differ somewhat for nanoscale metal particles.²⁶ The galvanic exchange process is initiated by adding a stoichiometric amount of either PtCl₄²⁻ or PdCl₄²⁻ to a solution of Cu DENs. This results in spontaneous oxidation of Cu and reduction of PtCl₄²⁻ or PdCl₄²⁻ according to eqn (4) and (5).



Based on the standard potentials of eqn (1)–(3), the approximate driving forces for eqn (4) and (5) are 0.239 V and 0.280 V, respectively.

Fig. 2a shows the UV-vis spectra of a solution containing G6-OH(Pt₅₅) DENs and Cu²⁺ at pH 3.0 and 7.5 following galvanic exchange (eqn (4)). At pH 3.0, the Pt DEN solution

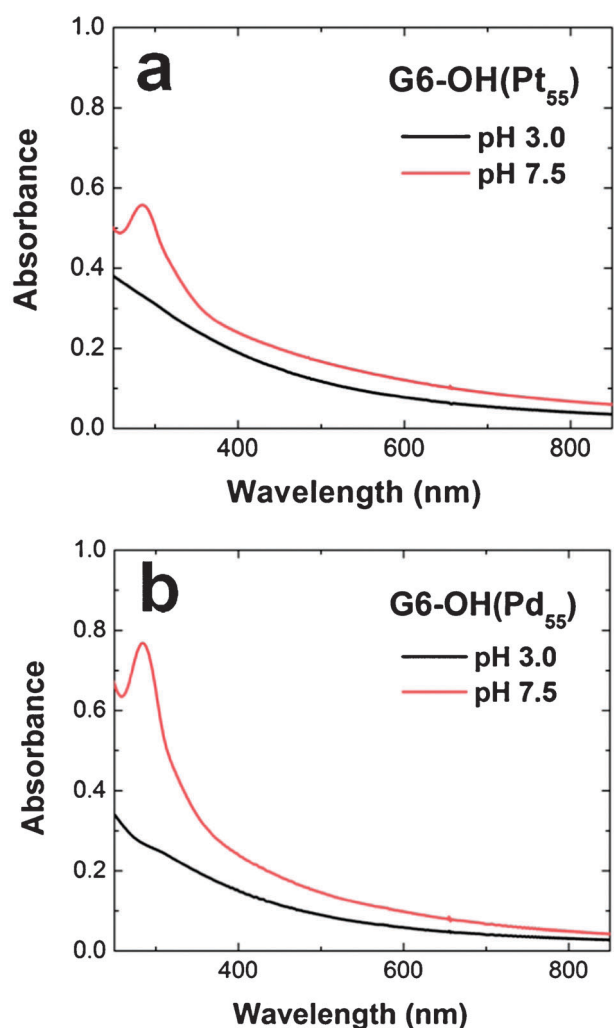


Fig. 2 Absorption spectra of (a) G6-OH(Pt₅₅) DENs at pH 3.0 and 7.5, and (b) G6-OH(Pd₅₅) DENs at pH 3.0 and 7.5. All the spectra were taken using a 1.0 mm cuvette. 10.0 μ M G6-OH or water was used as reference depending on the sample. 1.0 M HClO₄ and 0.3 M NaOH were used to change the pH of the DENs solution.

exhibits only a monotonically increasing absorbance toward higher energies. This behavior is consistent with previously reported spectra of Pt DENs.^{18,26} The spectrum of the same solution at pH 7.5 is similar, but it exhibits a prominent peak at $\lambda_{\text{max}} = 290$ nm. This is the same LMCT band shown in Fig. 1, and it arises from complexation between Cu²⁺ and the tertiary amines following galvanic exchange.²⁶ This peak is absent at pH 3.0, because under those conditions H⁺ present in solution successfully competes with Cu²⁺ for dendrimer binding sites. The important point is that the presence of the Cu²⁺ LMCT band and the monotonically increasing background confirm the galvanic exchange occurred. Note that the position of the LMCT band in Fig. 2a ($\lambda_{\text{max}} = 290$ nm) is a little lower than it is for G6-OH(Cu²⁺)₅₅ in Fig. 1, because of the presence of another metal (Pt) inside the dendrimer.²⁶ Fig. 2b displays the analogous UV-vis spectra for G6-OH(Pd₅₅) DENs at pH 3.0 and 7.5, and they exhibit similar characteristics to those for the Pt DENs shown in Fig. 2a.

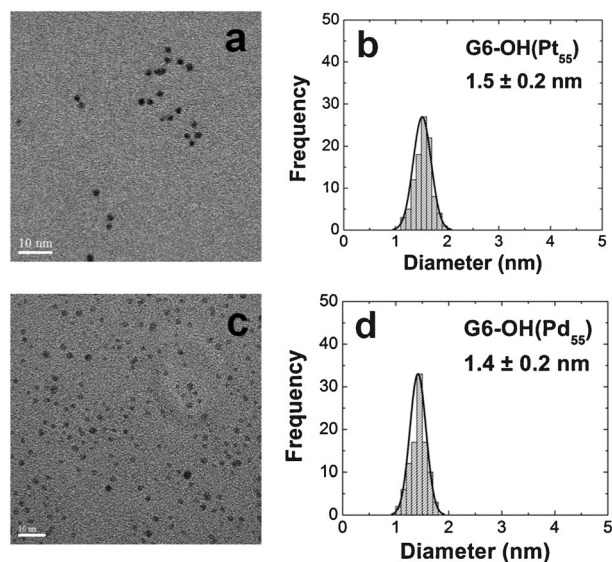


Fig. 3 TEM images and particle-size distribution histograms for the G6-OH(Pt₅₅) (a and b) and G6-OH(Pd₅₅) (c and d) DENs respectively. The particle-size distribution is based on 100 randomly selected particles.

TEM analysis of Pt and Pd DENs

Fig. 3a and b are a representative TEM micrograph and the corresponding size-distribution histogram for G6-OH(Pt₅₅) DENs synthesized by galvanic exchange. The diameter of these Pt DENs is 1.5 ± 0.2 nm, comparable with the size of Pt DENs synthesized by direct reduction with BH₄⁻ (1.3 ± 0.3 nm).¹ Fig. 3c and d present the analogous results for G6-OH(Pd₅₅) DENs. The size of Pd DENs is 1.4 ± 0.2 nm, while the value for the same materials prepared by BH₄⁻ reduction is 1.3 ± 0.3 nm.⁴² Assuming a cubo-octahedral shape, the calculated size for 55-atom Pt and Pd DENs is 1.2 nm.^{42,43} The key point is that Pt and Pd DENs prepared by galvanic exchange have the same size characteristics as those synthesized by BH₄⁻ reduction of the corresponding precursor complexes.

XPS analysis of Pt DENs

Fig. 4a and b are high-resolution XPS spectra showing the Pt and Cu regions, respectively, for G6-OH(Pt₅₅) DENs prepared by galvanic exchange. Prior to analysis, the DENs solution was adjusted to pH 3.0 and then dialyzed to remove free Cu²⁺. The two Pt peaks are present at 71.1 eV (4f_{7/2}) and 74.4 eV (4f_{5/2}). These values correlate to those reported for bulk Pt: 71.3 eV (4f_{7/2}) and 74.6 eV (4f_{5/2}),⁴⁴ which suggests complete reduction of PtCl₄²⁻ by G6-OH(Cu₅₅). The Cu spectrum (Fig. 4b) is featureless, indicating the absence of intra-dendrimer Cu or Cu²⁺. This finding is consistent with the UV-vis results shown in Fig. 2a. Finally, a survey XPS spectrum of a dialyzed G6-OH(Pt₅₅) solution (not shown) reveals peaks for C, N, and O, which confirms the presence of dendrimers in the analysis solution.

Previously, we reported XPS spectra for G6-OH(Pt₅₅) DENs prepared by BH₄⁻ reduction.¹ Four distinct peaks were observed: a pair corresponding to zerovalent Pt at 71.3 and

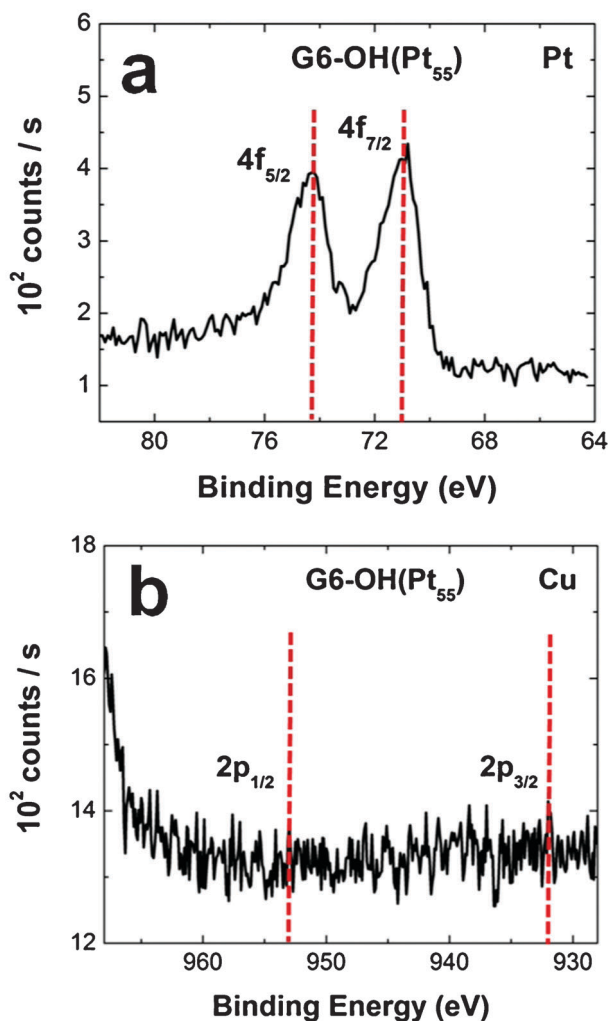


Fig. 4 (a) A high-resolution XPS spectrum of the Pt(4f) region, and (b) a high-resolution XPS spectrum of the Cu(2p) region for G6-OH(Pt₅₅) DENs. All XPS spectra were taken using a Si-wafer as the substrate and the binding energies were corrected with respect to C1s (284.5 eV) peak. The dotted line in the XPS spectrum represents the reported position for bulk Pt and Cu respectively. Prior to analysis, the DENs solution was adjusted to pH 3.0 and then dialyzed to remove free Cu²⁺.

74.5 eV, and a pair at higher binding energy corresponding to a more highly oxidized form of Pt at 72.9 and 76.2 eV.^{1,35} In contrast to the complete reduction resulting from galvanic exchange, these findings were interpreted in terms of just partial reduction in the presence of BH₄⁻. Chen and coworkers reported the binding energy of the Pt(4f_{7/2}) peak for a G4-OH(Pt₄₀) DEN thin film and a monolayer of G4-OH(Pt₄₀) DENs.⁶ The Pt peak for the thin film initially appeared at 74.6 eV, but after heating to 500 °C it shifted to 72.3 eV. The Pt peak appeared at 73.3 eV for the DEN monolayer.⁶

High-resolution Pd and Cu XPS spectra for G6-OH(Pd₅₅) DENs are provided in the ESI† (Fig. S1). The Pd peaks are centered at 335.4 eV (3d_{5/2}) and 340.6 eV (3d_{3/2}), which are consistent with those for bulk Pd (335.4 eV⁴⁵ and 341.0 eV,³⁴ respectively), indicating that galvanic exchange leads to

formation of Pd DENs. The Cu XPS spectrum (Fig. S1b, ESI†) exhibits multiple low-intensity peaks at 932.1, 932.6, 935.0, 952.10, 952.70, and 955.1 eV. These peaks indicate a mixture of both zerovalent and oxidized Cu.³⁵ Because the XPS analysis was carried out using undialyzed solutions corresponding to the products of eqn (5), we expect to observe small amounts of oxidized Cu. The very small amount of remaining zerovalent Cu is somewhat surprising and must correspond to a small amount that did not undergo galvanic exchange for Pd.

XAS analysis of Pt DENs

XAS analysis provides information about the coordination number (CN) of the metals in DENs, and comparison of these experimentally determined CNs with calculated values for model structures can lead to insights into nanoparticle structure. For example, we previously used XAS data of this type to show that BH₄⁻ reduction of G6-OH(Pt²⁺)_n leads to a bimodal distribution of fully reduced DENs and unreduced precursor.¹ Specifically, BH₄⁻ reduction of G6-OH(Pt²⁺)₅₅ results in a material having a measured Pt-Pt CN of 1.07 ± 0.55.¹ However, the calculated CN for a perfect 55-atom cuboctahedron is 7.86.⁴⁶ Comparison of the measured and calculated CNs suggest, as mentioned earlier, that only 14% of G6-OH(Pt²⁺)₅₅ is reduced by BH₄⁻ and the remainder resides in the unreduced form.

Fig. 5a shows the k-space data for G6-OH(Pt₅₅) DENs prepared by galvanic exchange, and Fig. 5b provides both the r-space data and the corresponding fitting analysis. The Pt-Pt CN for G6-OH(Pt₅₅) DENs synthesized by the galvanic exchange method was found to be 7.4 ± 0.8. This value is much higher than previously measured for G6-OH(Pt₅₅) DENs synthesized by chemical reduction (1.07 ± 0.55), and close to the value predicted for a fully reduced, 55-atom cubo-octahedral (7.86).⁴⁶ These results indicate that the galvanic exchange synthesis results in nearly complete reduction of Pt²⁺. In addition, the presence of a small Pt-E (where, E is O and N) contribution (0.59 ± 0.28) explains the slightly lower than expected Pt-Pt CN. This Pt-E contribution may result from any of several sources, for example association of dendrimeric amines or water with Pt.

Electrocatalytic properties of Pt DENs prepared by galvanic exchange

The analysis methods discussed so far provide information about the bulk structure and composition of DENs prepared by galvanic exchange, but they do not reveal much about the surface. For that we turn to an examination of the electrocatalytic oxygen reduction reaction (ORR), which at the level discussed here can yield some qualitative information about the surface properties.

A previously reported method⁴⁷ was used to immobilize Pt DENs onto a glassy carbon electrode (GCE), and Fig. S2 (ESI†) provides cyclic voltammograms (CVs) confirming robust attachment of the DENs to the electrode surface.

We have previously reported that G6-OH(Pt₅₅) DENs prepared by BH₄⁻ reduction are catalytically active for the ORR.⁴³ Fig. 6 shows CVs for G6-OH(Pt₅₅) DENs prepared by both galvanic exchange and a typical BH₄⁻ reduction method.

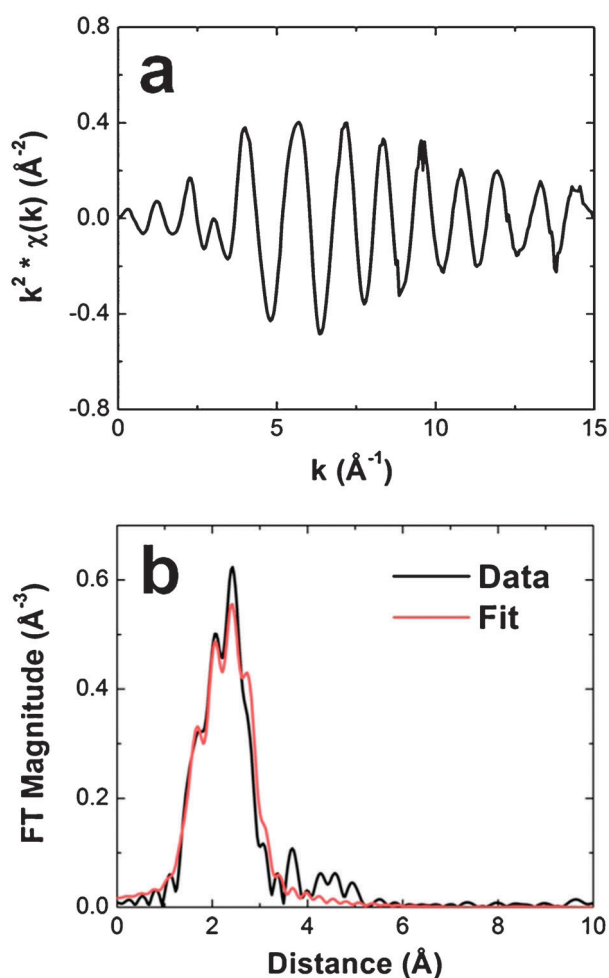


Fig. 5 (a) k -space data for G6-OH(Pt₅₅) DENs, demonstrating the data quality in the fitting region and (b) both the r -space data and the associated fit. A dry powder sample was used for the XAS study. Details of sample preparation are in the Experimental Section.

Both cyclic voltammograms were obtained after scanning the electrode potential 20 times between -0.80 V and 0.90 V in a N_2 -purged, 0.1 M HClO_4 electrolyte solution. The latter step, which is described in more detail in the ESI†, removes impurities from the Pt surface and leads to improved electrocatalytic performance. Such cleaning scans are commonly used on bulk Pt electrodes prior to kinetic measurements.⁴⁸ The peak potential for both voltammograms is nearly the same: -0.32 V and -0.31 V, for DENs prepared by galvanic exchange and BH_4^- reduction, respectively. Note, however, that the peak current is significantly higher in the case of G6-OH(Pt₅₅) DENs prepared by galvanic exchange. One might think that this could be a consequence of different numbers of immobilized DENs on the two electrodes.⁴⁹ However, we measured the total surface area of Pt on both types of DEN-modified GCEs *via* hydrogen desorption^{50,51} in the range -0.43 V and -0.74 V (Fig. S4, ESI†), and found they were almost the same (0.0048 cm² and 0.0046 cm², respectively) and in accord with previous reports.⁴³ Therefore, a complete understanding of the differences in peak currents shown in Fig. 6 must await a comprehensive kinetic analysis.

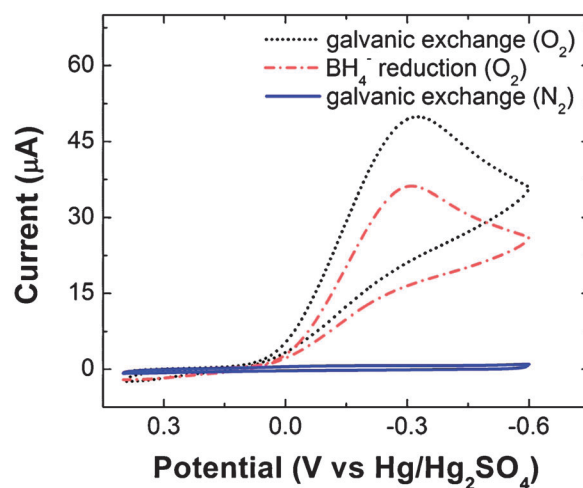


Fig. 6 (a) Cyclic voltammograms obtained in O_2 -saturated, 0.1 M HClO_4 using a glassy carbon electrode modified with G6-OH(Pt₅₅) DENs synthesized by galvanic exchange and a typical BH_4^- reduction method. The solid line was obtained under the same conditions used for the galvanic exchange (O_2), except the solution was saturated with N_2 . All voltammograms were measured after applying cleaning scans, as described in the text. The scan rate was 50 mV s⁻¹.

One final point: in the absence of O_2 (solid line, Fig. 6) no significant current attributable to the ORR is observed using a GCE modified with Pt DENs prepared by galvanic exchange.

Summary and conclusions

In summary, we have reported the synthesis and characterization of G6-OH(Pt₅₅) and G6-OH(Pd₅₅) DENs prepared by galvanic exchange. The results indicate that this synthetic method leads to nearly complete reduction of Pt and Pd within the dendrimer. This observation is in contrast to our earlier report that direct BH_4^- reduction of a G6-OH(Pt²⁺)₅₅ results in a very low percentage of similar sized Pt DENs. The likely reason for this much-improved yield is that the Cu precursor used for galvanic exchange acts as a catalyst for reduction of PtCl_4^{2-} and PdCl_4^{2-} . This mechanism would be consistent with our earlier suggestion that catalytic Pt seeds facilitate formation of Pt DENs synthesized by direct BH_4^- reduction.¹ The important point, however, is that the Pt and Pd DENs syntheses presented here are significantly more efficient and have much better yields than other methods presently in use. Equally important, the detailed characterization presented here demonstrates that the structure and composition of Pt and Pd DENs synthesized by direct BH_4^- reduction and galvanic exchange are indistinguishable.

At present, we are examining the feasibility of using galvanic exchange for preparing core@shell DENs of various sorts,³² and characterizing the catalytic properties of the resulting materials. The results of these studies will be reported in due course.

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