

Direct Formation of Platinum Nanoparticles by Internally Isopropanol-Modified Dendritic Poly(amido amine)

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We report a reducing agent-free method for preparing platinum (Pt) nanoparticles by internally isopropanol (IPA)-modified dendritic poly(amido amine) (PAMAM). The internally modified dendritic PAMAM were synthesized via divergent strategy using 1,3-diaminopropanol as a linking spacer, and NMR analyses confirm the embedded IPA moieties within the dendrimers by the appearance of characteristic proton and carbon resonances at 3.81 and 67.9 ppm, respectively. The *in situ* formation of stable Pt colloids was carried out by thermal treatment in the presence of internally modified dendritic PAMAM bearing either ester or alcohol peripherals, suggesting that the internal IPA functionalities dominate the reduction of Pt⁴⁺ ions. Moreover, the overall reducing rate was accelerated with increasing pH values. This result agreed with a reaction feature for preparing metal nanocomposites through polyol process in which basic environment facilitates the thermal-promoted reduction of metal ions accompanied with the oxidation of internal hydroxyl groups. The morphology of the dendrimer/Pt composite monitored by a transmission electron microscope (TEM) exhibited narrowly dispersed and roughly spherical shaped nanoparticles with a mean diameter of 5.4 nm.

Keywords: PAMAM Dendrimers, Platinum Nanoparticles, Isopropanol, Polyol, Fuel Cells.

1. INTRODUCTION

Dendrimer-stabilized metallic nanostructures (DSMNs) were intensively explored in recent years because of their useful applications on homogeneous catalysis and on electrocatalytic redox reaction, especially alcohol oxidation and oxygen reduction in direct methanol fuel cells.¹ Since the first synthesis of poly(amido amine) (PAMAM) dendrimer-stabilized Cu clusters was reported by Crooks and co-workers,² many different types of monometallic and bimetallic metal-dendrimer nanocomposites have been successfully prepared.³ DSMNs are usually prepared by a two-step process. First, metal ions are uptook by dendrimer, which coordinates them stoichiometrically with either interior or exterior functional groups. On the basis of several recent reports, it is believed that a complex formation between metal ions and dendrimer is the rate-limiting step.⁴ The mechanism of this critical step is definitively

unestablished. The exact location of these metal ions subsequently uptaken by dendrimer is still unclear because of the multiple functionalities in dendritic structure. However, on the basis of successful identification by UV-vis, NMR, and extended X-ray absorption fine structure (EXAFS) measurements, platinum precursor ions (PtCl₆²⁻ and PtCl₄²⁻) are able to perform a slow ligand exchange reaction with tertiary amines as well as amide groups in PAMAM dendrimer, forming a stable metal/ligand complex in aqueous solution.⁵⁻⁷

The second step involves the reduction of metal ions to yield zero valence metallic nanostructures under the trigger of chemical reagents, UV, laser, X-ray irradiation, or heat-treatment.⁸⁻¹⁰ Among all the chemical reduction methods, chemical-reducing-agent free methods are noticed to provide an alternative route for preparing versatile metal-based nanostructures.¹¹ In general, by using liquid polyol suchlike ethylene glycol as a solvent, noble metal ions are reduced to form a stable metal colloid upon heating. It is

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proposed that electron flux generated from the oxidation of ethylene glycol to glycolic acid induces the reduction of those metal ions.¹² The size and shape control of metallic nanostructures prepared in this manner is governed by the reaction temperature and concentration of organic stabilizer such as polymers and surfactants.¹³ However, it becomes an unpleasant problem to use a large excess amount of polyol because of its high boiling point and toxicity.

In our previous study, internally isopropanol (IPA)-modified PAMAM dendrimer was successfully synthesized via divergent strategy using 1,3-diaminopropanol as linking spacer.¹⁴ The interior modified PAMAM dendrimer also demonstrates a noticeable post-functionalized capability, allowing the oxidation of internal secondary alcohols to ketone groups through chemical method.¹⁵ Moreover, the cyclic voltammogram of the internally modified dendrimer in an acidic medium exhibits a remarkable anodic current on electrodeposited Pt electrode. This finding is attributed to the Pt-catalyzed oxidation of IPA groups embedded inside the dendrimers.¹⁶ In the present work, an inverse strategy following polyol process was investigated (Scheme 1); oxidation of those internal hydroxyl groups might result in the reduction of Pt metal ions, which would be encapsulated within the dendrimer by ligand exchange. Accordingly, the formation of Pt nanostructures was successfully carried out by simply mixing the internally IPA-modified dendritic PAMAM and metal salts without additional reducing agents and further purification.

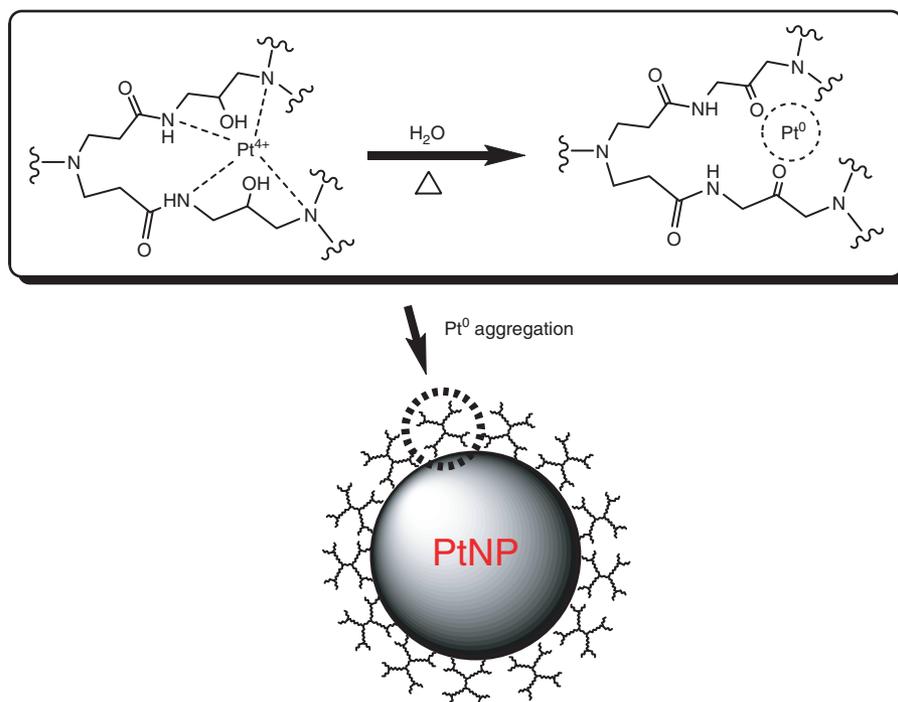
2. EXPERIMENTAL DETAILS

2.1. Materials and Instruments

1,3-diamino-2-propanol, methyl acrylate, sodium borohydride (NaBH_4), and chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were all obtained as high-purity reagent-grade chemicals from Acros; NH_2 and OH terminated G4 PAMAM dendrimers (10 wt% in methanol) and poly(diallyldimethylammonium chloride) (PDDA) solution (20 wt% in H_2O) were purchased from Aldrich. All chemicals were used without further purification. Ultrapure water (Millipore Milli-Q) was used throughout all experiments for the preparation of aqueous solution. Nuclear magnetic resonance (NMR) spectra were recorded by a Varian Mercury Plus 400 MHz spectrometer at room temperature using CDCl_3 or D_2O as a solvent, and the signal of additive tetramethylsilane was adopted as an internal standard. Fourier-transform infrared absorption (FT-IR) spectra were recorded by a Jasco FT/IR 4100 spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out by a VG ESCA/AES MT-500 with a monochromator Al- $\text{K}\alpha$ source (10 kV, 10 mA). Transmission electron microscopy (TEM) images were taken by a Jeol JEM-1230 with Gatan dual vision CCD camera operated at an accelerating voltage of 120 kV.

2.2. Preparation of Internally Functionalized Dendritic PAMAM

A methanol solution (6 cm^3) of 1,3-diamino-2-propanol (187 mg, 2.08 mmol) was added dropwise into a



Scheme 1. Proposed mechanism for the reduction of platinum ion by the oxidation of internal isopropanol groups.

round-bottomed flask that contained methyl acrylate (1.08 g, 12.5 mmol) and methanol (4 cm³) at 0 °C using an ice/water bath. The reaction mixture was allowed to warm at room temperature and stirred for 2 days under N₂ atmosphere. Then the volatiles were removed under reduced pressure using a rotary evaporator, resulting in **D0** in a quantitative yield.

A methanol solution (3 cm³) of **D0** (476 mg, 1.09 mmol) was added dropwise into a round-bottomed flask that contained 1,3-diamino-2-propanol (2.01 g, 22.3 mmol) and methanol (7 cm³) at 0 °C using an ice/water bath. The reaction mixture was allowed to be warm at room temperature and stirred for 7 days until the complete disappearance of terminal methyl ester groups monitored by NMR. The mixture was then diluted with methanol (60 cm³) and directly transferred dropwise to another round-bottomed flask that contained methyl acrylate (12.0 g, 139 mmol) and methanol (40 cm³) at 0 °C using an ice/water bath. The reaction mixture was allowed to be warm at room temperature and stirred for 2 days under N₂ atmosphere. The volatiles were removed under reduced pressure using a rotary evaporator. The crude product was purified by flash column chromatography on SiO₂ and eluted with dichloromethane (CH₂Cl₂)/methanol, gradually increasing from 98:2 to 90:10, to yield **D1** with the terminal groups of methyl esters as a pale yellowish gum (1.04 g, 70%).

Ethanol (5 cm³) was added into a round-bottomed flask that contained NaBH₄ (417 mg, 11.0 mmol) and **D1** (190 mg, 0.14 mmol), and then the reaction mixture was stirred at 70 °C for overnight. After being cooled to room temperature, the gel-like mixture was extracted with 10 cm³ of a mixture of ethanol and water (1:1, v/v). The organic layer was then washed with brine twice to remove excess boric acid and dried completely by a rotator evaporator, resulting in **D2** with the terminal groups of primary alcohols as a white gum in a quantitative yield. The ¹H NMR characterization of **D1** and **D2** are illustrated in Figure 1.

2.3. Synthesis and Characterization of Dendrimer-Stabilized Platinum Nanoparticles

A general procedure was described as follows. An aqueous mixture of internally modified dendritic PAMAM **D1** and platinum ions (PtCl₆²⁻) with an initial molar ratio of 1:1 was vigorously stirred for 24 h at room temperature and then heated at reflux temperature until the yellowish color of solution gradually turned either dark brown or black, indicating the formation of Pt nanoparticles. The pH of the reaction mixtures were adjusted to a specific value by carefully adding 1 mol/L HCl or NaOH aqueous solution.

A clean indium-doped tin oxide (ITO) substrate (1 cm²) was immersed in 4% PDDA solution for 30 min, allowing the substrate to absorb polyelectrolytes with multiple positive charges onto the surface. After being rinsed

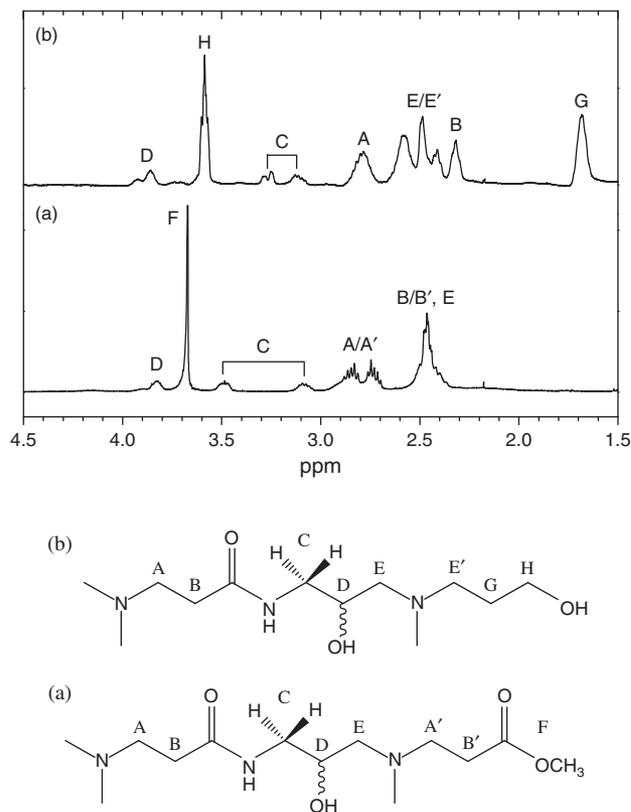
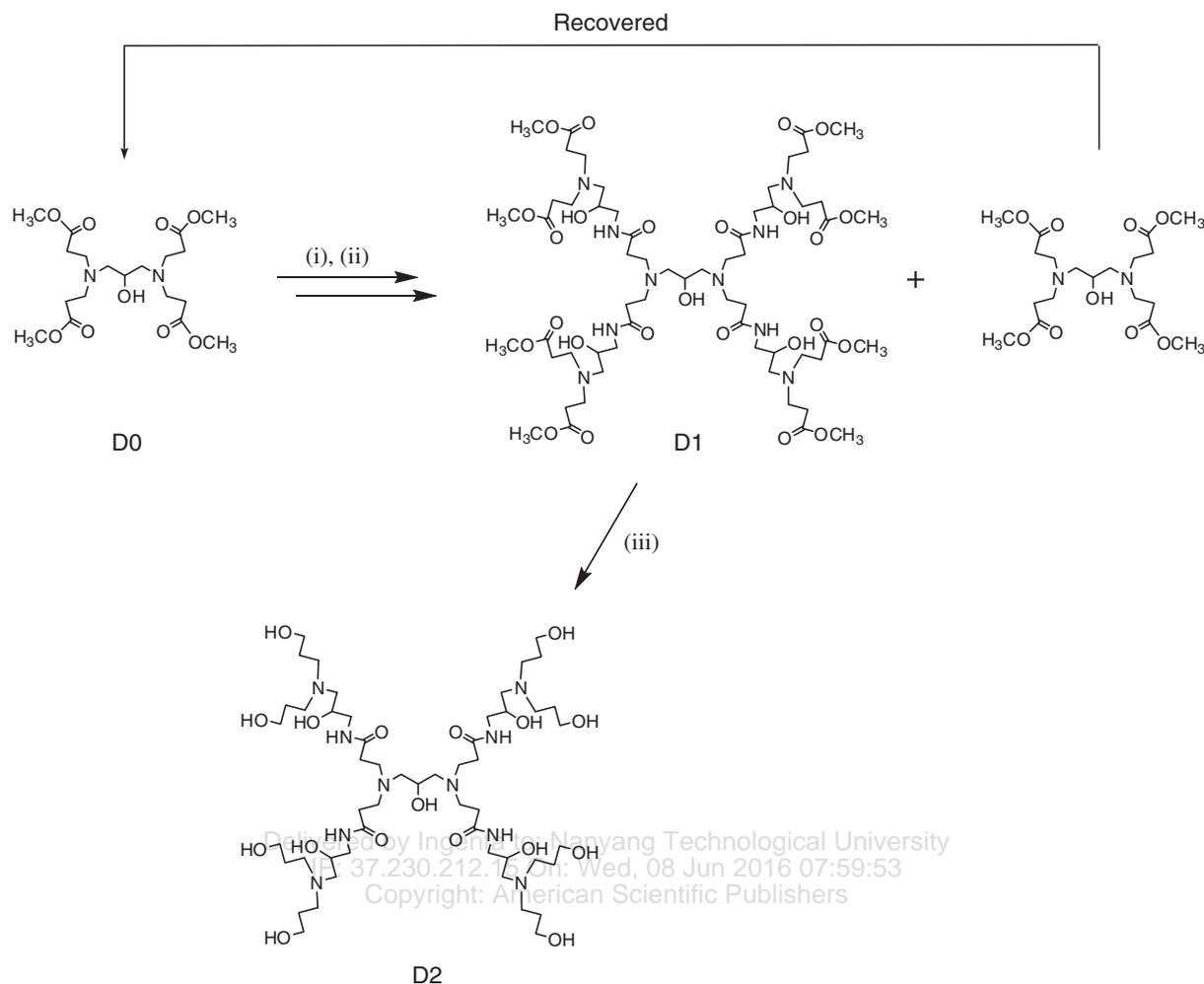


Fig. 1. (Top) ¹H NMR spectra of (a) **D1** and (b) **D2** in CDCl₃ and D₂O, respectively. (Bottom) Schematic representation indicates the assignment of the protons referring to the methyl (CH₃), methylene (CH₂), and methine (CH) groups as the building blocks of dendrimer.

with water and dried by nitrogen flow, the substrate was dipped in the solution of **D1**-stabilized Pt nanoparticles for overnight. After being rinsed with water and dried in vacuum, the thin film of dendrimer/Pt composite deposited on the ITO/PDDA surface was then characterized by XPS analyses.

3. RESULTS AND DISCUSSION

The synthetic route for internally IPA-modified dendritic PAMAM was depicted in Scheme 2. Based on divergent strategy, sequential Michael addition and amidation using methyl acrylate and 1,3-diaminopropanol as building blocks were introduced to synthesize dendritic PAMAM with internal multiple IPA functionalities. Notably, the surface methyl esters of dendrimer **D1** (i.e., half generation) were concerned to decrease overall hydrophilicity upon the purification process. Therefore, the excess amount of **D0** was recovered by flash column chromatography using silica gel as a stationary phase, and recycled **D0** was used repeatedly, resulting in 70% yield of **D1**. The successive construction of the internally modified dendritic PAMAM was confirmed by NMR analyses. The appearances of a proton resonance at 3.81 ppm and a carbon resonance at



Scheme 2. Synthesis of internally isopropanol-modified dendritic poly(amido amine) (PAMAM). (i) 1,3-diamino-2-propanol, MeOH, rt, 7 days; (ii) methyl acrylate, MeOH, rt, 3 days; (iii) NaBH₄, EtOH, reflux, overnight.

67.9 ppm clearly suggested the grafting of IPA groups as pendant functionality on the spacer. Furthermore, we carefully assign the proton signals A to F through the combination of 1D (Fig. 1) and 2D ¹H-¹H gCOSY NMR experiments (Fig. 2). Noteworthy, the diastereotopic protons H_C split each other with a remarkable germinal coupling because the embedded IPA moiety creates one stereocenter adjacent to the methylene groups C and E.

On the basis of the assumption that the oxidation of one internal hydroxyl group into ketone might generate a pair of electron, an initial molar ratio of **D1** containing five internal secondary hydroxyl groups and platinum ions (PtCl₆²⁻) was adjusted to 1:1 allowing the complete reduction of one Pt⁴⁺ to Pt⁰ by single **D1**.¹⁷ Formation of a complex composed of platinum ions and **D1**, being the first step of nanoparticle synthesis, was monitored by ¹H NMR using D₂O as a solvent. Within 24 h after the addition of PtCl₆²⁻ to aqueous **D1** solution, the methylene protons adjacent to the branched tertiary amines show noticeable down-field shifts, indicating the successful complexation

of Pt⁴⁺ ions and amines in **D1**.⁷ Moreover, the less resolved proton resonance was attributed to more restricted conformation that affects the relaxation time of the nuclei.

Though the standard reduction potential of PtCl₆²⁻ (0.55 V) is lower than AuCl₄⁻ (1.00 V) and Ag⁺ (0.79 V), meaning a slow reduction rate of Pt⁴⁺ to zerovalent Pt, the strong binding of platinum ion and tertiary amine within the dendrimer gives even lower Pt⁴⁺ reduction potential.¹⁹ Therefore, large excess chemical reagent such as NaBH₄ is essential for reducing the metal-dendrimer complex within minutes, forming a stable metal colloid. In the case of the mixture of PtCl₆²⁻ and **D1**, thermal treatment without additional reducing agent surprisingly brings about a change in color, being a quick indicator for the formation of zerovalent Pt-based aggregation. The result implied an *in situ* reduction of platinum ions within **D1** upon heating. By analyzing the thin film of the **D1**/Pt composite on surface-modified ITO, XPS measurements thus confirmed an *in situ* reduction. Figure 3(a) shows the binding energy of Pt(4f) region for the unreduced complex. According

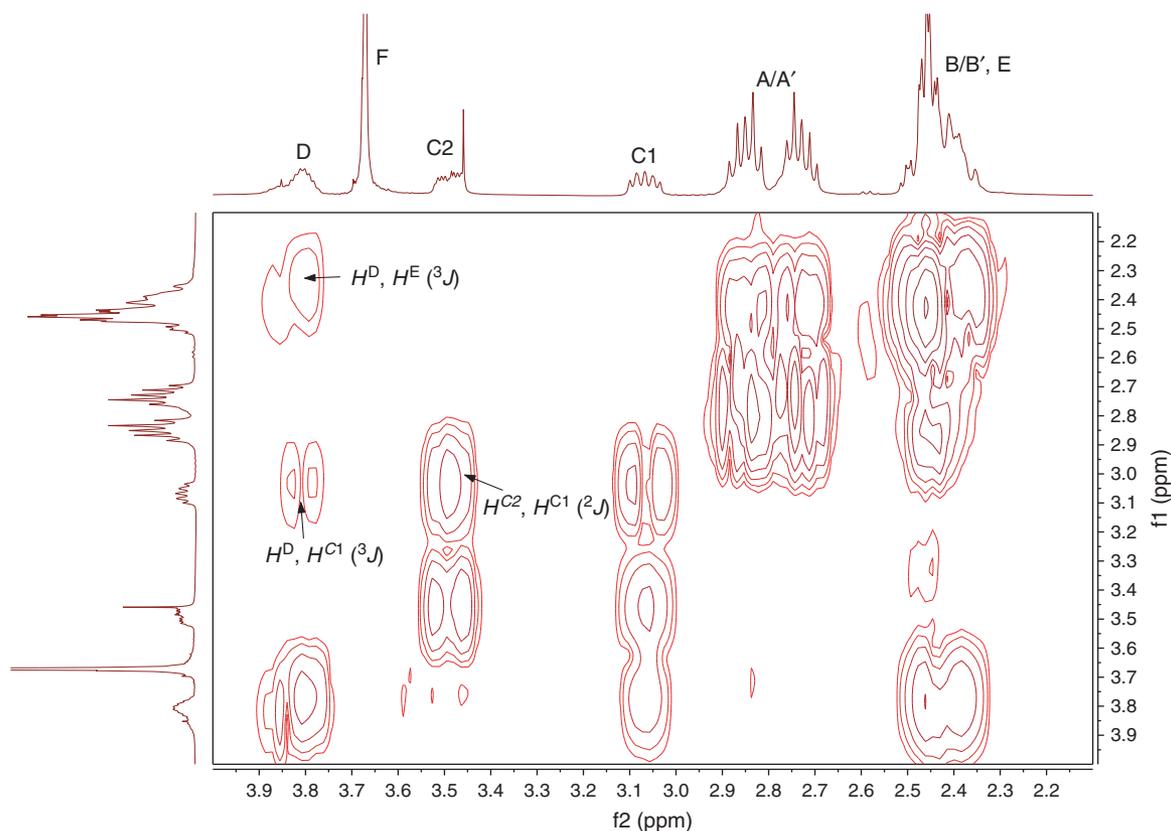


Fig. 2. Homocorrelation $^1\text{H}-^1\text{H}$ gCOSY NMR spectrum of D1.

to the NIST database value, the two peaks lying at 75.1 and 78.5 eV are assigned to be $\text{Pt}(4f_{7/2})$ and $\text{Pt}(4f_{5/2})$ of PtCl_6^{2-} , respectively. On the other hand, the binding energy for the complex after thermal treatment shifts to lower values lying at 71.5 and 74.8 eV (Fig. 3b), being consistent with $\text{Pt}(4f_{7/2})$ and $\text{Pt}(4f_{5/2})$ of bulk Pt, respectively. The

result clearly suggests the thermal-induced reduction of platinumic ions in the presence of D1.

Sun et al. reported a heat-treated-based strategy for the preparation of Au nanoparticles using poly(propyleneimine) (PPI) dendrimers.¹⁰ They suggested that the spontaneous formation of Au nanoparticles is

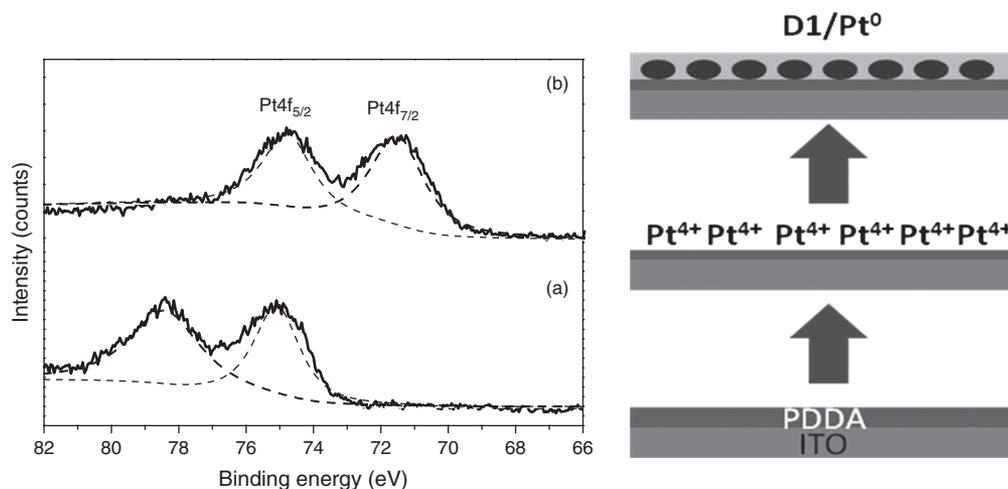


Fig. 3. X-ray photoelectron spectroscopy (XPS) of (a) Pt^{4+} and (b) D1- Pt^0 complex on poly(diallyldimethylammonium chloride) (PDPA)-modified indium-doped tin oxide (ITO) substrate. The modified ITO was dipped in the solution for 24 h to absorb Pt^{4+} ions and D1- Pt^0 complex for XPS analysis.

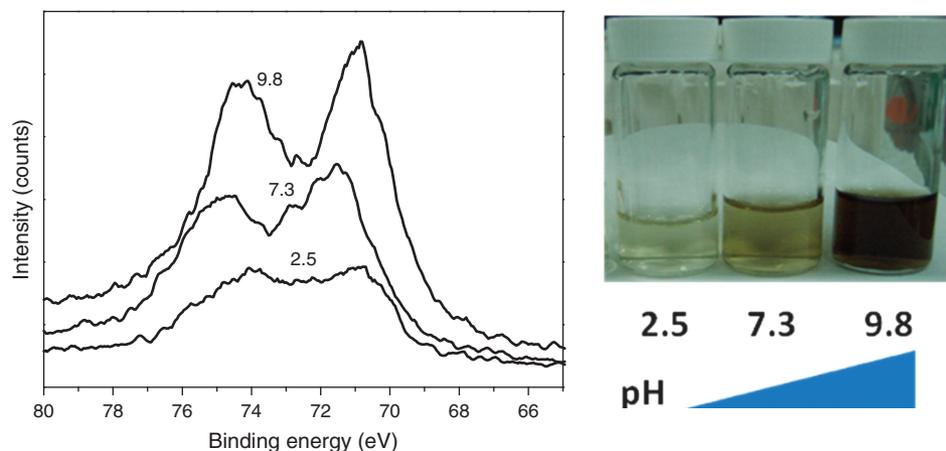


Fig. 4. X-ray photoelectron spectroscopy (XPS) of stable D1-Pt⁰ complexes prepared at pH 2.5, 7.3, and 9.8.

attributed to the direct redox reaction between AuCl₄⁻ and the tertiary amines within PPI dendrimer. Wang et al. also described a procedure for the synthesis of Au microplates using NH₂-terminated PAMAM dendrimer as a reducer and a stabilizer.¹⁸ However, our controlled experiment showed that thermal treatment was incapable of reducing the complex of NH₂-terminated G4 PAMAM dendrimer (2 × 10⁻⁴ M) and PtCl₆²⁻ (1 × 10⁻² M), presumably due to much higher reduction barrier of Pt⁴⁺ than that of Au³⁺. In other words, neither primary nor tertiary amines were necessarily the electron donors for reducing Pt⁴⁺ ions.

On the basis of our previous study, the internal secondary hydroxyl groups within **D1** can be oxidized into ketones by chemical and electrochemical methods. Accordingly, the reduction of **D1**/Pt⁴⁺ complex might be attributed to a galvanic reaction of the internal alcohols toward the platinum ions pre-coordinated with the tertiary amines (Scheme 1). Bock et al. proposed a reaction mechanism for the reduction of metal salts accompanied by the oxidation of ethylene glycol.¹⁹ It is noted that the

reduction rate can be accelerated by the thermal energy provided by heating and by an increase in pH of the solution. Figure 4 shows a pH-dependency of the thermal-induced reduction of the **D1**/Pt⁴⁺ complex. Compared with the complex at pH 2.5, the complex at pH 9.8 showed a darker solution upon heating, indicating a faster reduction in a specific time. In addition, by analyzing the thin films of reduced complexes, XPS measurements revealed more intense Pt(4f) peaks corresponding to more concentrated Pt aggregates in the basic complex solution. Therefore, the overall reduction rate for the **D1**/Pt⁴⁺ complex was accelerated as a function of pH in a sequence of basic > neutral > acidic environment. Accordingly, this finding agreed with our statement that the internal IPA groups within **D1** result in the metal reduction following the characteristic of polyol process.

It is fail to determine the ketone groups of **D1**/Pt composite by FT-IR analyses because of the spectroscopic

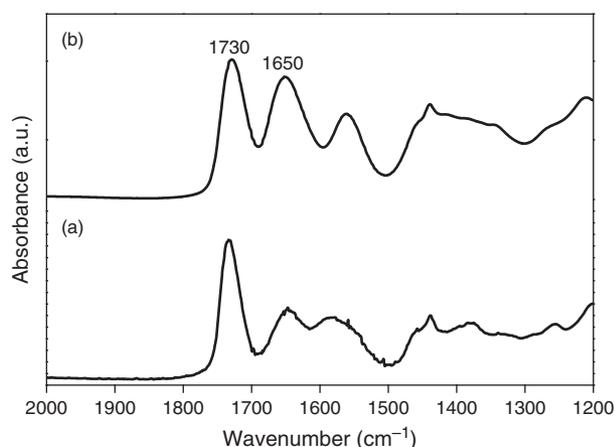


Fig. 5. FT-IR spectra of D1 before (a) and after (b) PtCl₆²⁻ complexation. 1730 and 1650 cm⁻¹ are assigned to the ester and amide (C=O stretching), respectively.

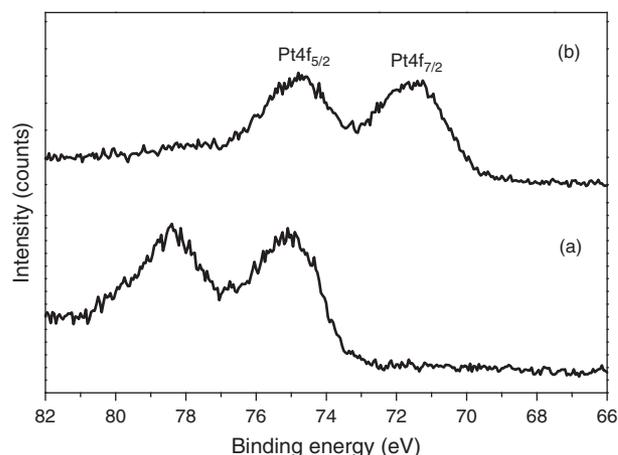


Fig. 6. X-ray photoelectron spectroscopy (XPS) of (a) Pt⁴⁺ and (b) D2-Pt⁰ complex on poly(diallyldimethylammonium chloride) (PDDA)-modified indium-doped tin oxide (ITO) substrate. The modified ITO was dipped in the solution for 24 h to absorb Pt⁴⁺ ions and D2-Pt⁰ complex for XPS analysis.

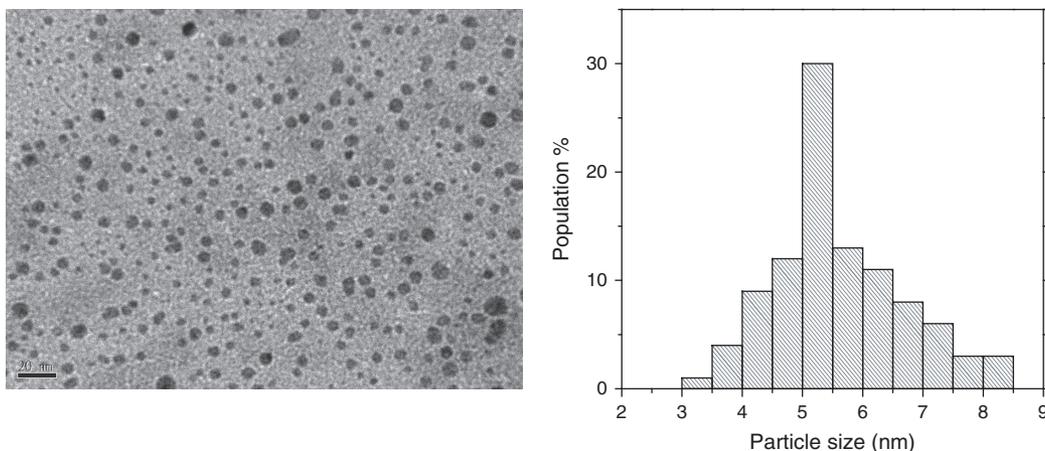


Fig. 7. TEM micrograph of D1-stabilized Pt nanoparticles and the particle distribution.

overlap of carbonyl and carboxyl stretching bands;¹⁴ whereas FT-IR analyses (Fig. 5) for **D1** before and after PtCl_6^{2-} complexation found a slight decrease in the relative intensity of carbonyl stretching of ester to amide (i.e., 1730 to 1650 cm^{-1}), implying that the intrinsic basic nature of **D1** due to internal tertiary amines might promote the partial hydrolysis of the terminal methyl esters. Therefore, to avoid the uncontrollable structural degradation in water, **D1** with terminal esters was treated with NaBH_4 to yield **D2** with terminal alcohols in a quantitative yield (Scheme 2). Moreover, the base-promoted hydrolysis of ester was able to generate terminal carboxylates as a chelating site and a moderate reducer toward metal ions. Therefore, it is preferable to use non-ionic peripherals suchlike hydroxyl groups to simplify the factors in reducing Pt^{4+} ions.²⁰ The ^1H NMR analyses thus confirmed the complexation of PtCl_6^{2-} and **D2** within 24 h, and the fact that pale-yellow mixture turned to a dark brown solution upon thermal treatment in 30 min indicated the formation of zerovalent Pt aggregates. As shown in Figure 6, XPS measurement for the thin film of **D2**/Pt complex confirmed the reduction of Pt^{4+} ions. Nevertheless, our controlled experiment revealed that only heating in the same time was unable to result in the reduction of Pt^{4+} (1×10^{-2} M) ions using hydroxyl-terminated G4 PAMAM dendrimer (2×10^{-4} M) as a reductant and stabilizer.²¹ As a result, the *in situ* reduction of metal ions in the presence of **D2** obviously supported that the internal hydroxyl groups facilitated the reduction of Pt^{4+} ions at elevated temperature.

TEM was performed on **D1**-stabilized metal aggregate drop cast from an aqueous solution ($\text{pH} = 2.5$) on Cu grid and revealed narrowly dispersed Pt nanoparticles (Fig. 7). The roughly spherical shaped nanoparticles had a mean diameter of 5.4 nm as measured from 100 metal particles. This was a good agreement with the size expected based on a polyol process,¹¹ securely supporting that the internal hydroxyl groups played a key role in the formation of Pt nanoparticles.

4. CONCLUSIONS

We report a divergent synthesis of internally IPA-modified dendritic PAMAM bearing the peripherals of methyl esters and primary alcohols in moderate yields. The *in situ* formation of Pt nanoparticles in aqueous solution was carried out by thermal treatment in the presence of either ester- or alcohol-terminated dendritic PAMAM without additional reducing agent. The reducing rate of Pt^{4+} to zerovalent Pt showed a noticeable pH-dependency, suggesting that

- (1) the *in situ* reduction followed the reaction feature of polyol process and
- (2) the internal IPA groups facilitated the reduction of metal ions at elevated temperature.

This procedure provided a facile route for the direct preparation of dendrimer/Pt nanocomposites on electroactive substrates such as ITO, and further investigation is now underway.

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Supporting Information Available

Additional figures showing the NMR and FT-IR spectra.

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