Supplementary Information

Post-synthesis Dispersion of Metal Nanoparticles by Poly(amidoamine) Dendrimers: Size-Selective Inclusion, Water Solubilization, and Improved Catalytic Performance

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Experimental

Materials:

A methanol solution containing G2OH dendrimer (20 wt.%), G5OH dendrimer (5 wt.%) and G6OH dendrimer (5 wt.%) was purchased from Aldrich. The organometallic Pt precursor, Pt(1,5-cyclooctadiene)Cl₂, (99%) and Ti precursor, Ti(tetrahydrofuran)₂Cl₄ (97%), were purchased from STREM Chemicals and Aldrich, respectively. Sodium metal and naphthalene were purchased from Aldrich and Kishida Chemicals, respectively. The solvents, tetrahydrofuran (99.5%), hexane (96%), methanol (99.8%), and isopropanol (99.5%), were received from Kishida Chemicals. Nafion dissolved in aliphatic alcohols (5%) were purchased from Aldrich. Tetrahydrofuran and hexane were distilled prior to use under vacuum to remove oxygen and moisture. Methanol was de-aired by bubbling with dry Ar for 30 minutes. The chemical reagents and solvents were always treated under a dry Ar atmosphere.

*Synthesis of Pt*₃*Ti*@*G*5*OH*

Intermetallic Pt₃Ti NPs (particle size = 1.0 to 4.0 nm) were first synthesized and used as a starting material for the synthesis of Pt₃Ti@G5OH.⁸ A precursor solution was prepared by dissolving of Pt(1,5-cyclooctadiene)Cl₂ (15.6 mg, 0.04 mmol) and TiCl₄(tetrahydrofuran)₂ (55.7 mg, 0.16 mmol) in dry tetrahydrofuran (10 ml) under a dry Ar atmosphere. A sodium-naphthalide solution was prepared by dissolving of sodium metal (34.5 mg, 1.5 mmol) and naphthalene (192.3 mg, 1.5 mmol) in tetrahydrofuran (50 ml). The precursor solution was transferred to the sodium-naphthalide solution without being exposed to air. The dark green color of sodium naphthalide turned dark brown

immediately upon transfer of the precursor solutions. After overnight stirring, the solvent was removed by distillation under reduced pressure to leave a dark brown precipitate. The precipitate was washed with hexane and methanol in sequence and was dried under vacuum. The obtained products were stable in air and were black in color. Similarly, Pt NPs were prepared by using Pt(1,5-cyclooctadiene)Cl₂ (15.6 mg, 0.04 mmol). An aliquot of Pt or Pt₃Ti NPs (5 mg) was mixed with G2OH, G5OH or G6OH aqueous solutions (5 ml, 0.2 mM) and stirred for 8 days at room temperature. After stirring, these solutions were centrifuged at 6000 rpm for 30 min. The resulting supernatant was a transparent, brown solution (Fig. S1).



Fig. S1 Optical images of an aqueous solution of 0.2 mM pristine G5OH and Pt₃Ti@G5OH. *Characterization*

The stoichiometry and the face-centered cubic structure of the intermetallic Pt₃Ti NPs ($Fm\bar{3}m$, a = 0.3904 nm) were confirmed prior to the synthesis of Pt₃Ti@G5OH by single-particle electron probe microanalysis (EPMA) employing an ultra-high vacuum scanning transmission microscope (UHV-STEM, Tecnai G², acceleration voltage: 300 kV) and powder X-ray diffractometry (*p*XRD, RIGAKU RINT2000). The *p*XRD measurements were performed using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) for 12 h at a count time of 10 s in 0.02 deg increments.



Fig. S2 EPMA profile for an as-prepared Pt₃Ti NP.

Electron-probe microanalysis (EPMA) was performed to determine the composition of Pt₃Ti NPs (Fig. S2). The EPMA profile showed a peak at 8 keV which is assigned to Cu, the TEM grid material. In addition, four more peaks are recognized at 2.1, 4.5, 9.4 and 11.1 keV. The peaks at 2.1, 9.4, and 11.1 keV correspond to Pt. The weak peak at 4.6 keV corresponds to Ti. The mole ratio of Pt and Ti was calculated as 74±4 and 23±4, respectively. A large-area scan over ($\approx 100 \ \mu m^2$) also resulted in the same mole ratio within experimental errors (Pt:Ti = 73±4 and 27±6). The EPMA profile of Pt₃Ti NPs showed no chlorine peak at 2.7 keV, indicating that as-prepared Pt₃Ti NPs are free from capping agents.



Fig. S3. *p*XRD profile for as-prepared Pt_3Ti NPs. Simulated *p*XRD peaks for atomically disordered Pt_3Ti are shown by solid lines.

Fig. S3 shows a *p*XRD profile for as-prepared Pt₃Ti NPs. The *p*XRD profile shows three broad peaks at $2\theta = 40^{\circ}$, 68°, and 82°. In addition, a shoulder peak at $2\theta = 46^{\circ}$ was observed. These peaks were consistent with an atomically disordered FCC-type structure of Pt₃Ti phase as shown by solid lines (*Fm*3*m*, *a* =0.3904 nm).

High-angle annular dark-field transmission electron microscopy (HAADF-TEM) micrographs of Pt₃Ti@G5OH were obtained using a JEOL JEM-2010F, operated at an accelerating voltage of 200 kV. Samples for HAADF-TEM observation were prepared by placing a few drops of the aqueous solution of Pt₃Ti@G5OH onto collodion-coated copper TEM grids (200 mesh, Nisshin EM Co., Ltd.). The chemical composition of the metal core of Pt₃Ti@G5OH was determined using an energydispersive X-ray spectroscopy (EDS) instrument with a silicon drift detector (Bruker XFlash 5030) attached to the HAADF-TEM. Samples for ¹H NMR measurements (a Bruker spectrometer operating at 600.13 MHz for ¹H, 14.1 T) were prepared by substituting the solutions with D₂O. A sodium salt of 2,2,3,3-tetradeutero-3-trimethylsilylpropionic acid was used as an internal standard. Fourier transform IR (FTIR) spectra were obtained with a Perkin-Elmer FTIR (Spectrum GX-R) system equipped with a MIRTGS detector in single-beam absorbance mode with a resolution of 4 cm⁻¹. FTIR samples were prepared by placing the sample solutions (200 μ l) onto the surface of CaF₂ crystals (Daico Mfg. Co., Ltd.) and drying them under vacuum. Hard X-ray photoemission spectroscopy (HX-PES) measurements were performed using X-rays with a photon energy of 5.95 keV, at the undulator beamline BL15XU of SPring-8.^{8b} Samples for HX-PES measurements were prepared by mixing the sample solutions with carbon black (Vulcan XC-72, Cabot Co. Ltd.) to avoid charging effects. An aliquot of the sample solutions (100 μ l) was placed onto carbon substrates (Nilaco Co., Ltd.) and dried under vacuum. The core-level states of the samples were examined at room temperature in UHV using a hemisperical electron energy analyzer (VG SCIENTA R4000). The total energy resolution was set to 220 meV. The binding energy was referenced to the Fermi edge of a Au thin film.



Fig. S4. FTIR spectra for Pt₃Ti@G5OH and G5OH in the wavenumber region for hydroxyl- and hydrogen-bonded N-H groups.



Fig. S5. HX-PES spectra for Pt₃Ti@G5OH and G5OH in the N 1s region.



EPMA was performed to determine the composition of Pt_3Ti NPs after post-synthesis dispersion of Pt_3Ti NPs (Fig. S6). In addition to the Cu peak for TEM grid material at 8 keV, four more peaks are recognized at 2.1, 4.5, 9.4 and 11.1 keV. The peaks at 2.1, 9.4, and 11.1 keV correspond to Pt. The weak peak at 4.6 keV corresponds to Ti. The sediment after post-synthesis dispersion retained their stoichiometry within the experimental error (Pt:Ti = 72±5and 25±6).



Fig. S7. HX-PES spectra for Pt₃Ti bulk, as-prepared Pt₃Ti NPs and the sediment that were obtained from Pt₃Ti@G5OH in the Pt $3d_{5/2}$ region.

Fig. S7 shows the HX-PES spectra for Pt_3Ti bulk, as-prepared Pt_3Ti NPs and the sediment of $Pt_3Ti@G5OH$ in the Pt $3d_{5/2}$ region. Pt $3d_{5/2}$ emission from the sediment of $Pt_3Ti@G5OH$ had a binding energy of 2122.5±0.2 eV, consistently with as-prepared Pt_3Ti NPs and Pt_3Ti bulk, indicating that Pt_3Ti NPs were neither degraded nor dissolved through the long stirring in water.

To verify the size-selective inclusion of Pt₃Ti NPs by G5OH, vacuum-annealed Pt₃Ti NPs, with particle sizes ranging from 2.0 to 6.0 nm, were dispersed in an aqueous solution of G5OH. The Pt₃Ti NPs were first annealed at 400 °C for 15 h to achieve a larger particle size. The annealed NPs were dispersed in an aqueous solution of G5OH in the same mater as Pt₃Ti@G5OH, to yield a colorless solution of Pt₃Ti(400 °C)/G5OH. Fig. S8 shows the HX-PES spectra for Pt₃Ti(400 °C)/G5OH and Pt₃Ti@G5OH in the Pt 3*d*_{5/2} region (Fig. S8 (*a-b*)). The Pt₃Ti NPs were annealed at 400 °C for 15 h to achieve a larger particle size (> 2 nm). The Pt 3*d*_{5/2} core level peak was not observed in the case of Pt₃Ti(400 °C)/G5OH. However, Pt₃Ti@G5OH showed the photoemission peak of Pt 3*d*_{5/2} at 2124.5±0.2 eV. The core level peaks in the N 1*s* region are shown as an inner standard that was observed from both Pt₃Ti(400 °C)/G5OH and Pt₃Ti@G5OH (Fig. S8 (*c- d*)). The *p*XRD profile of the Pt₃Ti NPs showed that the precipitate consisted of pure-phase Pt₃Ti (Fig. S8*e*). HAADF-TEM image of the Pt₃Ti NPs that were obtained from the precipitate is shown in Fig. S8*f*. The Pt₃Ti NPs were observed as bright spots, and their particle size showed an asymmetrical distribution ranging from 2 to 6 nm (Fig. S8g). Pt₃Ti NPs larger than the pore size of G5OH, most likely 1.7 nm, were not enveloped by G5OH to form Pt₃Ti@G5OH. These results indicate that a Pt₃Ti particle size smaller than pore size can be implanted solely into the PAMAM dendrimer.



Fig. S8. HX-PES spectra for Pt₃Ti(400 °C)/G5OH (*a*) and Pt₃Ti@G5OH (*b*) in the Pt $3d_{5/2}$ region. HX-PES spectra for Pt₃Ti(400 °C)/G5OH (*c*) and Pt₃Ti@G5OH (*d*) in the N 1*s* region. The *p*XRD profile for Pt₃Ti NPs that were obtained from the precipitate of Pt₃Ti(400 °C)/G5OH (*e*). The simulated *p*XRD

peaks for atomically disordered Pt_3Ti are shown by solid lines. HAADF-TEM image of the Pt_3Ti NPs that were obtained from the precipitate (*f*). Histogram of the size of the metal core (*g*).



Fig. S9. HX-PES spectra in the Pt $3d_{5/2}$ region for Pt₃Ti bulk, Pt₃Ti NPs, Pt₃Ti/G2OH, Pt₃Ti@G5OH and Pt₃Ti/G6OH.

As-prepared Pt₃Ti NPs were dispersed in an aqueous solution of G6OH in the same manner as Pt₃Ti@G5OH. Fig. S9 shows the HX-PES spectra in the Pt $3d_{5/2}$ region for Pt₃Ti/G6OH, together with those for Pt₃Ti bulk, as-prepared Pt₃Ti NPs, Pt₃Ti/G2OH, Pt₃Ti@G5OH. A Pt $3d_{5/2}$ emission peak was observed at 2122.5±0.2 eV for Pt₃Ti@G6OH. This value was consistent with the Pt $3d_{5/2}$ binding energy for the reference surface of bulk Pt₃Ti, 2122.5±0.2 eV, whereas the Pt $3d_{5/2}$ binding energy for Pt₃Ti@G5OH shifted by +2.2 eV toward larger energies due to a strong final-state effect. Pt₃Ti NPs were most unlikely included in G6OH, because no final state was recognized. The very dense terminal groups of G6OH inhibited the inclusion of Pt₃Ti NPs from the outside. The N 1*s* photoemission peak was observed on Pt₃Ti/G6OH at 400.6±0.2 eV, showing no charging effect (Fig. S10).



Fig. S10. HX-PES spectra for Pt₃Ti/G6OH in the N 1s region.

Pure Pt NPs were synthesized using $Pt(COD)Cl_2$ as a precursor and were dispersed in an aqueous solution of G5OH to yield Pt/G5OH, in the same manner as $Pt_3Ti@G5OH$. Fig. S11*a* shows a HAADF-TEM image of Pt/G5OH. The metal particles in Pt/G5OH are observed as bright spots. The size of the Pt NPs, evaluated from this HAADF-TEM image, showed a symmetrical distribution around a maximum of 1.2 nm, ranging from 0.5 to 1.7 nm (Fig. S11*b*).







Fig. S12. HX-PES spectra for Pt/G5OH in the Pt $3d_{5/2}$ region.

Fig. S12 shows the HX-PES spectra for Pt bulk and Pt@G5OH in the Pt $3d_{5/2}$ region. The Pt $3d_{5/2}$ emission from Pt bulk had a binding energy of 2122.2±0.2 eV. The Pt $3d_{5/2}$ emission peak for Pt/G5OH was +2.5 eV shifted relative to that for Pt bulk. The large Pt $3d_{5/2}$ binding energy for Pt@G5OH is interpreted as a final-state effect on the Pt NPs, which were surrounded by the insulating pore of G5OH.

Electrochemical analyses

A conventional electrochemical setup was used to evaluate the electro-catalytic activity of the materials. The oxygen reduction reaction (ORR) activity of Pt₃Ti@G5OH and as-prepared Pt₃Ti NPs was examined at room temperature in an O₂-saturated, aqueous 0.5 M H₂SO₄ solution. Pt₃Ti@G5OH was immobilized on a glassy carbon (GC) electrode by cycling the electrode potential between 0 and +1.0 V relative to a reference Ag/AgCl (3 M NaCl) electrode in a 0.1 M LiClO₄ solution dissolving 20 μ M of Pt₃Ti@G5OH.¹⁵ As-prepared Pt₃Ti NPs (15 μ g μ l⁻¹) were dispersed in a solution of distilled water (76 μ l), isopropanol (20 μ l) and Nafion solution (4 μ l) by sonication for 1 h. An aliquot of Pt₃Ti ink (4 μ l) was dropped and dried on a GC electrode. The loading weight of Pt in the as-prepared Pt₃Ti NPs was calculated as 55 μ g.

The loading weight of Pt in Pt₃Ti@G5OH was calculated by X-ray fluorescence measurements (JSX-3202EV). All the measurements were performed in air using an Rh target (tube voltage = 50 kV, tube current = 300 μ A) at a counting time of 300 s. The samples were irradiated by a circular X-ray beam that was 7 mm in diameter.

Pt_L lines were observed at 9.4 and 11.1 keV for as-prepared Pt₃Ti NPs, which contained 55 μ g of Pt (Fig. S13*a*). The detection limit for Pt was calculated as 3.4 μ g, using the standard deviation of this Pt_{La} line. No Pt_L lines were observed for Pt₃Ti@G5OH, indicating that the Pt loading weight was lower than 3.4 μ g (Fig. S13*b*). It was confirmed by HX-PES that the Pt₃Ti@G5OH on a GC electrode

contained Pt (Fig. S14). The ORR currents for as-prepared Pt₃Ti NPs and Pt₃Ti@G5OH were normalized using the calculated Pt loading weights, 55 μ g and 3.4 μ g, respectively.



Fig. S13. X-ray fluorescence spectral profiles for as-prepared Pt₃Ti NPs (*a*) and Pt₃Ti@G5OH (*b*) on GC electrodes.



Fig. S14. HX-PES spectrum in the Pt $3d_{5/2}$ region for Pt₃Ti@G5OH immobilized on a glassy-carbon electrode.