Electronic Supplementary Information (ESI)

Enhanced stability of charged dendrimer-encapsulated Pd nanoparticles in ionic liquids

Guangnan Ou\textsuperscript{a, b}, Li Xu\textsuperscript{a}, Biyan He\textsuperscript{b}, and Youzhu Yuan\textsuperscript{a*}

\textsuperscript{a} State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Department of Chemistry, Xiamen University, Xiamen 361005, China; \textsuperscript{b} School of Bioengineering, Jimei University, Xiamen 361021, China

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I. General

Carboxylated-terminated polyamidoamine dendrimers (PAMAM dendrimers) G5.5-COONa (5% methanol solution) and G4-OH (10% methanol solution) were obtained from Aldrich. Prior to use, the methanol was removed under vacuum at room temperature. Styrene was passed through a neutral alumina column before use. [BMIM][BF_4], [BMIM][PF_6] and [C_2OHMIM][BF_4] were synthesized according to published procedures and checked for the absence of chloride and acid.\textsuperscript{1,2} K_2PdCl_4 was synthesized according to literature.\textsuperscript{3}

The \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were obtained on a Bruker AV-400 Fourier transform NMR spectrometer. \textsuperscript{1}H NMR spectra were referenced to tetramethylsilane in CDCl\textsubscript{3}. Mass spectra were acquired using a Bruker ESQUIRE-3000 plus ion trap spectrometer equipped with a gas nebulizer probe, capable of analyzing ions up to m/z 6000.

Transmission electron microscopy (TEM) images were obtained on a Philips TECNAI F-30 FEG instrument at an accelerating voltage of 300 kV. The sample was dispersed in aqueous solution.

II. Synthesis of PAMAM dendrimers

The first three generations (generations -0.5–1.5) of EDA core PAMAM dendrimers were synthesized in the stepwise process described in literature.\textsuperscript{4} In order to obtain less complicated MS spectra (minimize both the intramolecular defects, missing repeating units, intramolecular loops) and intermolecular aggregates (dimers) as well as lower generation dendrimers, different chromatographic purification procedures of the multiester compounds G-0.5-COOCH\textsubscript{3}–G1.5-COOCH\textsubscript{3} were used. The generations -0.5, 0.5, and 1.5 were purified by column chromatography on a silica gel. In all cases, mixture of methanol with dichloromethane was used as the eluent.

Carboxylic-terminated G1.5-COOH was prepared by saponification of G1.5-COOCH\textsubscript{3} and its negative ion ESI spectra at different pH were shown in Figure 6S. ESI-MS (m/z) calcd for G1.5-(COO)\textsuperscript{−} 859.96 obsd 859.6; ESI-MS (m/z ) calcd for G1.5-(COO)\textsuperscript{−} 644.72 obsd 644.6; ESI-MS (m/z ) calcd for G1.5-(COO)\textsuperscript{−} 515.57 obsd 515.4; ESI-MS (m/z ) calcd for G1.5-(COO)\textsuperscript{−} 429.48 obsd 429.3.

Positive ion ESI spectra of G-0.5-COOCH\textsubscript{3}–G1.5-COOCH\textsubscript{3} were shown in Figure 7S. ESI-MS (m/z) calcd for G-0.5-COOCH\textsubscript{3} 404.46 obsd 404.9 (+ H\textsuperscript{+}), 426.8 (+ Na\textsuperscript{+}); ESI-MS (m/z ) calcd for G0.5-COOCH\textsubscript{3} 1205.42 obsd 1206.0 (+ H\textsuperscript{+}), 1228.1 (+ Na\textsuperscript{+}); ESI-MS (m/z ) calcd for G1.5-COOCH\textsubscript{3} 2807.33 obsd 2806.2 (+ H\textsuperscript{+}), 1405.0 (+ 2H\textsuperscript{+}).
III. Capillary Electrophoresis (CE)

Experiments were carried out on a Beckman P/ACE MDQ system (Beckman, Fullerton, CA) with UV detection at 214 nm. Thirty-two karat workstation was used for data processing (Fullerton, CA). The capillaries were thermostated at 298 K by using liquid coolant and the samples were injected by pressure (0.5 psi) for 5 s. Untreated fused silica capillaries (Yongnian Ruifeng Instrumental Co., Hebei, China) with 50 μm inner diameter were of 31 cm total length and 21 cm effective length (distance from the injection end to the detector). To ensure complete ionization of the dendrimer carboxyl groups, samples were prepared with boric acid buffer (20 mmol L⁻¹ borate buffer, pH 9.18) in a calculated amount to give a concentration of 1 mg/mL. The separation voltage was kept at 20 kV for all the measurements, and the capillary temperature was maintained at 298 K.

Mobilities were measured by reference to the neutral marker methoxylbenzyl alcohol MBA (0.05 mg/mL in borate buffer). Samples were introduced by hydrodynamic injection at a pressure of 50 mbar for 3 s. Prior to each experiment, the capillary was rinsed for 30 min with 0.1 mol L⁻¹ NaOH, for 30 min with Milli-Q water, and for 30 min with the run buffer. Between runs, the capillary was rinsed with 0.1 mol L⁻¹ NaOH.

The electrophoretic mobility $\mu_E$ was calculated from

$$\mu_E = \frac{v_o - v_s}{E} = \frac{V}{l} \left( \frac{1}{t_m} - \frac{1}{t_s} \right)$$

where $v_o$ and $v_s$ are the electroosmotic velocity and the solute velocity respectively, $E$ is the applied field strength, $l$ and $L$ are the effective and total length of the capillary, respectively, $V$ is the applied voltage, and $t_m$ and $t_s$ are the retention times of the neutral marker and the sample, respectively. Duplicate runs of each sample showed that the electrophoretic mobility, $\mu_E$, was reproducible to within 2%.
IV. Hydrogenation of styrene by G4-OH-Pd in [C$_2$OHMIM][BF$_4$] biphasic system

![Bar chart showing conversion percentages for different molar ratios of G4-OH to Pd atom.]

Figure 1S  Hydrogenation of styrene by G4-OH-Pd$_n$ in [C$_2$OHMIM][BF$_4$] biphasic system under molar ratio of styrene/Pd=500 at 323 K and 0.5 MPa of H$_2$ for 180 min.
V. Effect of pH on hydrogenation of styrene by G1.5-Pd in [C2OHMIM][BF4]

![Graph showing the effect of pH on hydrogenation of styrene by G1.5-Pd in [C2OHMIM][BF4].]

Figure 2S  Effect of pH on hydrogenation of styrene by G1.5-Pd in [C2OHMIM][BF4] under molar ratio of styrene/Pd at 500 at 323 K and 0.5 MPa of H2 for 180 min.

VI. Model for Pd particles stabilized by low generation PAMAM dendrimer with negatively charged functional groups on their periphery

![Model diagram showing Pd particles stabilized by low generation PAMAM dendrimer with negatively charged functional groups.]

Figure 3S  Model for Pd particles stabilized by low generation PAMAM dendrimer with negatively charged functional groups on their periphery.
VII. TEM micrograph and Particle-size histogram of G5.5-COO$^{−}$-Pd$_{150}$ DENs after 12 recycling

Figure 4S  TEM micrograph and Particle-size histogram of G5.5-COO$^{−}$-Pd$_{150}$ DENs after 12 recycling.
VIII. Capillary electropherograms for G5.5-COO\(^-\) dendrimers and G5.5-COO\(^-\)-Pd\(_n\)

Figure 5S  Capillary electropherograms for G5.5-COO\(^-\) dendrimers and G5.5-COO\(^-\)-Pd\(_n\) in borate buffer (pH 9.18), at 20 kV voltage. X-axis is converted from time to mobility; the neutral marker is the peak at zero.
Figure 6S Negative ion ESI spectra of G1.5-COOH at different pH.
Figure 7S  Positive ion ESI spectra of G-0.5-COOCH₃-G1.5-COOCH₃.
X. References


