Supplementary Information

Reductant-Directed Formation of PS-PAMAM-Supported Gold Nanoparticles for Use as Highly Active and Recyclable Catalysts for the Aerobic Oxidation of Alcohols and the

Homocoupling of Phenylboronic Acids

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1. Reagents and Materials

All chemicals were purchased from Alfa Aesar Chemical Company and used without further purification. Deionized water was used in all experiments. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) using UV light as visualizing agent. Tsingdao silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. The five micrometer polystrene-divinylbenzene microspheres (5% w/w DVB) were purchased from Suzhou Nano-Micro Biotech Co., Ltd.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Nuclear Magnetic Resonance (NMR) spectra were recorded on Brüker Advance 300 (1 H: 300 MHz, 13 C: 75.5 MHz), Brüker Advance 500 (1H: 500 MHz, 13 C: 125 MHz). X-ray Diffraction (XRD) was carried out on a D/max 2500PC X-ray diffractometer at room temperature. UV-vis SCINCO-S4100 Ultraviolet-visible spectroscopy was carried out on spectrophotometer. Scanning Electron Microscopy (SEM) was performed using a FEI Quant 400 scanning electron microscope. The instrument was fitted with an Energy Dispersive X-Ray (EDX) detector for elemental analysis. Transmission electron microscopy (TEM) was performed using a JEOL 2010. Element analysis was performed on a Profile Spec. inductively coupled plasma-atomic emission spectrometer.

2. General Procedures for Preparing the Polymer-Supported AuNPs.

Chloromethylation of the microspheres.

The 5 μ m PS-DVB microspheres (5%, w/w DVB) (10.0 g) were suspended in 100 mL of dry chloroform. After sonication for 30 min and cooled to 0 °C, a solution of chloromethyl methyl ether (8.0 mL) was added under mechanical stirring. Then the anhydrous tin tetrachloride (1.7 mL) was added dropwise to the mixture. Next, keep the system at room temperature for 3 hours. The microspheres were separated by filtration, washed with deionized water, 5% HCl, THF, ethanol, and acetone, each for three times , then dried under vacuum for 12 hours.

Amination of the Microspheres.

The chloromethyl functionalized microspheres (5.0 g) were suspended in 70 mL dry DMF. After sonication for 30 min, a solution of 12.5 mL of ethylenediamine was added under mechanical stirring. The solution was heated at 80 $^{\circ}$ C for 16 hours. Then the microspheres were separated by filtration, washed three times with ethanol and three times with acetone, then dried under vacuum for 12 hours.

Preparation of Polyamidoamine (PAMAM) Dendrimer on the PS-DVB Microspheres.

The amino functionalized microspheres (5.0 g) were suspended in 60 mL dry methanol, and after sonication for 30 min, 2.1 mL of methyl acrylate were added and the mixture was heated at 50 $^{\circ}$ C for 16 hours. After cooling to room temperature, the particles were separated by filtration, washed three times with ethanol and three times with acetone, then dried under a vacuum for 12 hours. The dried material was then suspended again in 60 mL of dry methanol and sonicated for 30 min. After the addition of 5 mL of ethylenediamine dropwise at room temperature, the solution was heated at 50 $^{\circ}$ C for 16 hours. The particles were separated by filtration, washed three times with ethanol and three times with acetone, then dried under a vacuum for 12 hours to give generation one PAMAM (G1). The second and third generations were prepared following the same manner, using a 2-fold excess of methyl acrylate and methylenediamine for 4-fold excess of methyl G2 and acrylate and *N*,*N*-dimethylethylenediamine for G3.

Complexation of Sodium Borohydride

G3 PAMAM-dendronized microspheres (5.0 g) were suspended in 50 mL deionized water, and after sonication for 30 min, 27 mL concentrated hydrochloric acid was added to the solution. The mixture was stirred for 3 hours at room temperature, and the particles were separated by filtration, washed three times with deionized water, three times with acetone, and then dried under vacuum for 12 hours. The dried material was then suspended in 50 mL of dry DMF and sonicated for 30 min. Sodium borohydride (5.0 g) was then added slowly to the suspension. The mixture was stirred for 16 hours at room temperature. Then the particles were separated by filtration, washed three times with DMF, three times with deionized water and three times with

acetone. The resulting materials were dried under vacuum for 12 hours.

Immobilization of Gold Nanoparticles

The reductant-grafted microspheres (1.0 g) were suspended in 100 mL deionized water and sonication for 30 min. Then potassium tetrachloroaurate (0.5 g) dispersed in 50 mL deionized water was added dropwise to the microsphere suspension. The mixture was stirred for 24 hours. Then the resulting catalyst was separated by filtration and washed three times with deionized water and three times with acetone. The catalyst was dried under vacuum for 12 hours.

Preparation of the Polymer-Supported AuNPs Through Scheme 1(a)

The PS-G3 PAMAM microspheres (5.0 g) were suspended in 50 mL deionized water, and after sonication for 30 min, 27 mL concentrated hydrochloric acid was added to the solution. The mixture was stirred for 3 hours at room temperature, and the particles were separated by filtration, washed three times with deionized water, three times with acetone, and then dried under vacuum for 12 hours. The dried material was then suspended in 100 mL deionized water and sonicated for 30 min. Then potassium tetrachloroaurate (0.5 g) dispersed in 50 mL deionized water was added dropwise. The mixture was stirred for 24 hours at room temperature. The particles were separated by filtration, washed three times with deionized water and three times with acetone. The resulting materials were dried under vacuum for 12 hours. Then the materials were suspended in 50 mL deionized water, and sodium borohydride (5.0 g) was added slowly to the suspension with vigorous stirring for 16 hours at room temperature. Then the particles were separated by filtration, washed three times with deionized water and sodium borohydride (5.0 g) was added slowly to the suspension with vigorous stirring for 16 hours at room temperature. Then the particles were separated by filtration, washed three times with deionized water and three times with deionized water and three times with acetone. The resulting materials were dried under vacuum for 12 hours.

3. General Procedure for the Polymer-Supported Gold Nanoparticles Catalyzing Oxidation of Benzyl Alcohols.

The benzyl alcohol (0.5 mmol), K_2CO_3 (1.5 mmol, 208 mg), catalyst (7.5 mg, 0.007 mmol), water (1.0 mL) and dichloromethane (1.0 mL) were combined in a centrifuge tube. The mixture was stirred under oxygen atmosphere (balloon pressure) at room temperature. After the reaction, the catalyst was centrifuged and washed with diethyl ether and water, then reused directly in the next run. The aqueous layer was extracted with diethyl ether. The yield was determined by GC-MS analysis. The products were confirmed by NMR.

4. General Procedure for the Polymer-Supported Gold Nanoparticles Catalyzing Homocoupling of Phenylboronic Acids.

The substituted phenylboronic acid (0.5 mmol), K_2CO_3 (1.5 mmol, 208 mg), catalyst (7.5 mg, 0.007 mmol), water (2.0 mL) were combined in a centrifuge tube. The mixture was stirred under air at room temperature for 24 hours. After the reaction, the catalyst was centrifuged and washed with diethyl ether and water. The aqueous layer was extracted with diethyl ether. The filtrate was concentrated *in vacuo*, and the

residue was purified by a flash chromatography (hexane/ethyl acetate =10/1) on silica gel to give the homocoupling product. All the products were confirmed by NMR.



5. Images for Characterizations of PS-PAMAM-AuNPs

Fig S1 SEM images of polymer-supported AuNPs prepared through procedures drawn in (a) Scheme 1c; (b) Scheme 1a.









Fig S2 (a) EDS analysis of a cross-section of a hemispherical polymer bead; (b) BSE image of the distribution of gold along the surface of the polymer bead; (c) XRD pattern (left) and (d) UV–Vis absorption spectrum of polymer-supported AuNPs.

6. NMR Data and Spectra of the Products

4-Methoxybenzaldehyde

¹H NMR (300 MHz, CDCl₃): δ = 9.89 (s, 1 H), 7.85 (d, *J* = 8.7 Hz, 2 H), 7.01 (d, *J* = 8.7 Hz, 2 H), 3.90 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 190.76, 164.54, 131.93, 129.98, 114.24, 55.52.

4-Ethoxybenzaldehyde



¹H NMR (300MHz, CDCl₃): δ = 9.87 (s, 1 H), 7.82 (d, *J* = 8.7 Hz, 2 H), 6.98 (d, *J* = 8.7 Hz, 2 H), 4.12 (q, *J* = 6.9 Hz, 2 H), 1.45 (t, *J* = 6.9 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 190.78, 163.99, 131.93, 129.69, 114.64, 63.85, 14.56.

4-Methylbenzaldehyde



¹H NMR (500 MHz, CDCl₃): δ = 9.97 (s, 1 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.44 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ = 191.92, 145.50, 134.23, 129.82, 129.68, 21.84.

4-Isopropylbenzaldehyde

¹H NMR (300 MHz, CDCl₃): δ = 9.98 (s, 1 H), 7.82 (d, *J* = 8.1 Hz, 2 H), 7.40 (d, *J* = 8.1 Hz, 2 H), 3.00 (h, *J* = 6.9 Hz, 1 H), 1.29 (d, *J* = 6.9 Hz, 6 H). ¹³C NMR (75 MHz, CDCl₃): δ = 191.99, 156.18, 134.48, 129.94, 127.08, 34.41, 29.63, 23.56.

Benzaldehyde

¹H NMR (300 MHz, CDCl₃): δ = 10.01 (s, 1 H), 7.90-7.86 (m, 2 H), 7.66-7.60 (m, 1 H). 7.55-7.50 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ = 192.36, 136.31, 134.40, 129.67, 128.92.

4-Chlorobenzaldehyde

¹H NMR (500 MHz, CDCl₃): δ = 9.89 (s, 1 H), 7.83 (d, *J* = 8.5 Hz, 2 H), 7.52 (d, *J* = 8.5 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ = 190.78, 140.94, 134.73, 130.87, 129.43.

4-Bromobenzaldehyde

¹H NMR (500 MHz, CDCl₃): δ = 9.99 (s, 2 H), 7.76 (d, *J* = 8.5 Hz, 2 H), 7.70 (d, *J* = 8.5 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ = 190.97, 135.10, 132.43, 130.94, 129.76.

4-Methoxyactophenone



¹H NMR (300 MHz, CDCl₃): δ = 7.94 (d, *J* = 8.7 Hz, 2 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 3.87 (s, 3 H), 2.56 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 196.81, 163.42, 130.53,

130.23, 113.61, 55.40, 26.28.

4-Methylactophenone

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¹H NMR (300 MHz, CDCl₃): δ = 7.87 (d, *J* = 8.1 Hz, 2 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 2.59 (s, 3 H), 2.42 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 197.88, 143.84, 134.63, 129.18, 128.38, 26.47, 21.57.

Acetophenone

¹H NMR (300 MHz, CDCl₃): δ = 7.99-7.95 (m, 2 H), 7.61-7.55 (m, 1 H), 7.50-7.44 (m, 2 H), 2.62 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 198.16, 137.05, 133.05, 128.51, 128.24, 26.56.

4-Chloroactophenone

¹H NMR (300 MHz, CDCl₃): δ = 7.88 (d, *J* = 8.7 Hz, 2 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 2.58 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 196.75, 139.48, 135.34, 129.65, 128.80, 26.47.

4-Bromoactophenone

¹H NMR (300 MHz, CDCl₃): δ = 7.81 (d, *J* = 8.7 Hz, 2 H), 7.59 (d, *J* = 8.7 Hz, 2 H), 2.58 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 196.97, 135.72, 131.82, 129.77, 128.24, 26.47.

3,3'-dimethoxylbiphenyl



¹H NMR (500 MHz, CDCl₃): δ = 7.350 (t, *J* = 8.0 Hz, 2 H), 7.18 (d, *J* = 7.5 Hz, 2 H), 7.13 (d, *J* = 7.5 Hz, 2 H), 6.91-6.89 (m, 2 H), 3.86 (s, 6 H). ¹³C NMR (125 MHz, CDCl₃): δ = 159.92, 142.65, 129.70, 119.71, 112.97, 112.83, 55.30.

Biphenyl



¹H NMR (300 MHz, CDCl₃): δ = 7.68-7.64 (m, 4 H), 7.53-7.47 (m, 4 H), 7.43-7.38 (m, 2 H), ¹³C NMR (75 MHz, CDCl₃): δ = 141.20, 128.72, 127.22, 127. 14.

3,3'-dimethylbiphenyl



¹H NMR (500 MHz, CDCl₃): δ = 7.39-7.37 (m, 4 H), 7.31 (t, *J* = 7.5 Hz, 2 H), 7.15 (d, *J* = 7.5 Hz, 2 H), 2.41 (s, 6 H). ¹³C NMR (125 MHz, CDCl₃): δ = 141.35, 138.21, 128.56, 127.95, 127.87, 124.25, 21.49.

4,4'-dimethylbiphenyl



¹H NMR (300 MHz, CDCl₃): δ = 7.47 (d, *J* = 8.1 Hz, 4 H), 7.23(d, *J* = 8.1 Hz, 4 H), 2.38 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃): δ = 138.22, 136.62, 129.36, 126.73, 20.99.

4,4'-dimethoxylbiphenyl



¹H NMR (300 MHz, CDCl₃): δ = 7.49-7.44 (m, 4 H), 6.97-6.92 (m, 4 H), 3.85 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃): δ = 158.65, 133.45, 127.72, 114.13, 55.33.









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MeO -				AuNPs cat.(1.4 mol%)				о н			
				K ₂ CO ₃ , DCM/H ₂ O(1:1) 5 h, r.t.			MeO				
Run ^a	1	2	3	4	5	6	7	8	9	10	
$\text{Yield}^{b}(\%)$	55	54	54	55	54	53	53	53	53	52	

7. Results for recycling experiments with the reaction time set at 5 hours.

^a Reaction condition: catalyst (0.007 mmol), substrate (0.5 mmol), K_2CO_3 (1.5 mmol), CH_2Cl_2 (1 mL), water (1 mL). ^b determined by GC-MS