Preparing water-dispersed palladium nanoparticles *via* polyelectrolyte nanoreactors

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1. General Considerations

Commercial reagents were purchased from Sigma Aldrich, Strem, VWR or Alfa Aesar and used without further purification. All salts were purchased from Aldrich or Caledon and used without purification. Deionized water was used for nanoparticle synthesis (resistivity >12 MΩ•cm) and Suzuki coupling reactions (resistivity 18 MΩ•cm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer. NMR spectra were internally referenced to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz).

2. Characterization of poly(acrylic acid) Stabilized Palladium Nanoparticles (NP-Pd-PAA)

(i) UV-visible absorption spectroscopy

UV-vis spectra were obtained on a Tecan Safire^2 plate reader using 96-welled Corning plates with UV transparent bottoms (Corning 3679). UV visible spectra were taken of: 1) the aqueous Pd^{II} precursor solution prior to its addition to poly(acrylic acid) (see Experimental Section of manuscript), 2) Pd^{II} complexed to collapsed poly(acrylic acid) (PAA) prior to reduction with NaBH$_4$, and 3) NP-Pd-PAA.

(ii) Transmission electron microscopy (TEM)

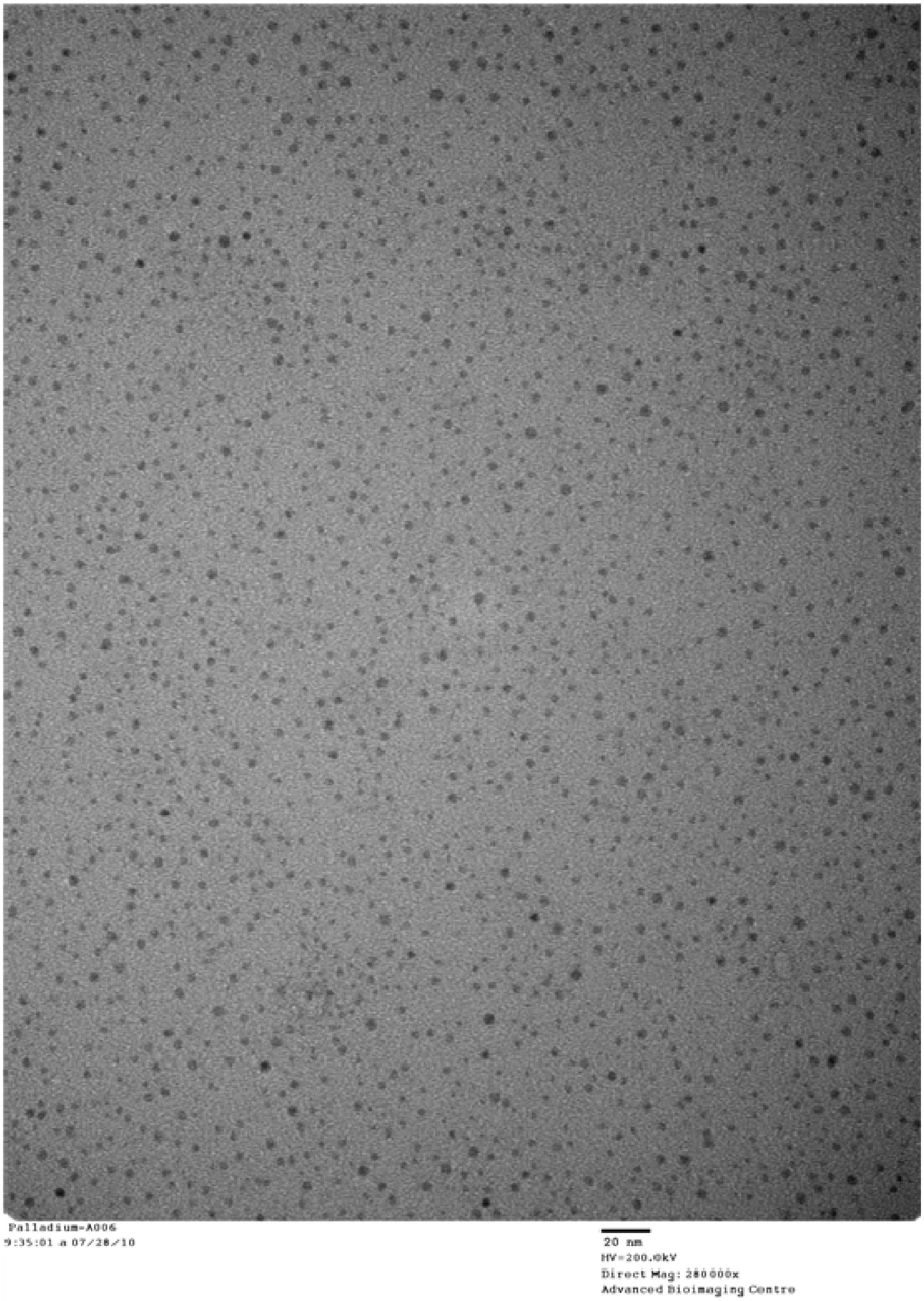
Generally, if TEM samples are prepared from an aqueous solution of Vive Nano nanoparticles, the quality of the image is poor. This is mainly because the slow evaporation of an aqueous solution leads to agglomeration of the sample as well as non-uniform deposition of the sample on the TEM grid. To obtain a better dispersion of the nanoparticles on the TEM grid, which is hydrophobic in nature, a dispersion of the nanoparticles in toluene is preferred. The nanoparticles in aqueous solution thus need to be phase transferred into toluene.

Procedure for phase transfer of nanoparticles into toluene and TEM grid preparation

50 mg of Tetrakis(Decyl)Ammonium Bromide (DTAB) was dissolved in 15 mL toluene with shaking. 50 μL of the aqueous nanoparticle solution at 1.5 mg mL^{-1} were added to 1 mL of the DATAB solution. The mixture was shaken gently and allowed to sit for approximately 10 minutes until the two layers separated. A drop of the toluene layer was casted onto the TEM grid and allowed to dry. TEM was performed using a FEI Tecnai-20 Transmission Electron Microscope operating at 100 kV and 30 mA beam current.

Particle size was measured using ImageJ (ver. 1.42q) image processing and analysis software (Wayne Rashband, National Institutes of Health, USA).

Full TEM Image:



(iii) *Composition analysis*

Pd content was determined by ICP analysis after digestion of the solid catalyst with aqua regia. ICP analysis was performed on a 1.5 mg mL^{-1} sample of NP-Pd-PAA.

Elements	mg/L	% metals basis	% metals basis (excluding Na)	% of residue	% of residue (excluding Na)
Al	0.40	0.08%	0.21%	0.05%	0.1%
B	39.2	7.82%	20.72%	4.86%	7.9%
Ba	0.42	0.08%	0.22%	0.05%	0.1%
Ca	1.5	0.30%	0.80%	0.19%	0.3%
K	3.0	0.59%	1.56%	0.37%	0.6%
Mg	0.36	0.07%	0.19%	0.04%	0.1%
Na	312	62.26%		38.72%	
Pd	142	28.36%	75.16%	17.64%	28.8%
Si	1.7	0.33%	0.89%	0.21%	0.3%
Zn	0.47	0.09%	0.25%	0.06%	0.1%
Total inorganic	501.55				
Total organic carbon	305.00				

Carbon content was determined using a TOC-VCPH Shimadzu analyzer equipped with a ASI-V auto sampler and solid sampler module.

Chloride analysis was performed using the Mhor method. Concentration of chloride: 265 mg/ml.

(iv) *Dynamic light scattering (DLS)*

DLS measurements were performed with a Malvern Zetasizer Nano-ZS. This instrument detects scattered light from a 4mW He-Ne (632.8 nm) at 12.8^{o} and 175^{o} (backscatter detection) and has a built-in correleator (min sample time 25ns, max delay time 8000 s, max 4000 channels). The volume size distribution is obtained using the Malvern Zetasizer software provided by the manufacturer. The software generates the volume size distribution from the sample refractive index and the correlation function by using an algorithm that employs either Cumulants analysis or a multiple exponential fit. Details of the calculation are available from the manufacturer's website: www.malvern.com. Volume size distribution reported in the paper is an average of at least 10 runs and is presented as is, without further data analysis. Samples for DLS were prepared by taking 2 mL of a 1.5 mg mL^{-1} solution of NP-Pd-PAA and diluting this with 2 mL

0.2 M NaCl. The resulting solution was then filtered though a 0.2 micron filter to remove dust and then equilibrated at 25 °C prior to the DLS measurement.

(v) ***Powder X-ray diffraction (XRD)***

Powder X-ray diffraction measurements (p-XRD) were performed by a Rigaku Ultima III pXRD with Cu K_{α} source (1.5418 A).

(vi) ***X-ray photoelectron spectroscopy (XPS)***

A Physics Electronics PHI 5000 series XPS with a non-monochromated and uncollimated Mg Ka X-Ray source was used for XPS analysis. The photo-electron take-off angle was generally measured at 45 degrees. The position of the energy scale was adjusted to place the main C 1s feature (C-C) at 285.0 eV.

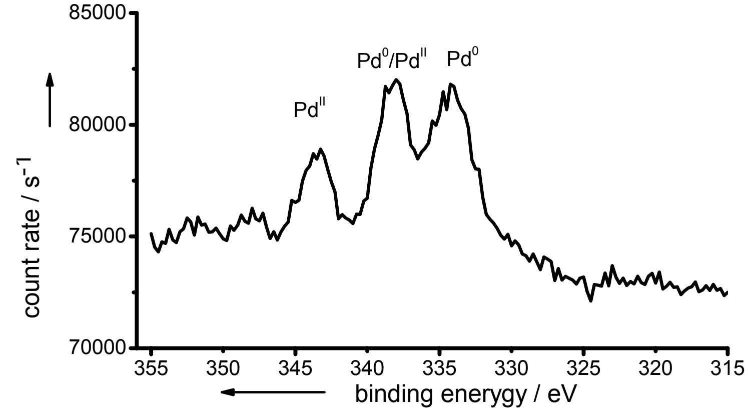


Figure 1. XPS spectrum of the Palladium region of NP-Pd-PAA.

Figure 1 shows a low resolution XPS spectrum of NP-Pd-PAA, which suggests the presence of two palladium species [1]. The measured binding energy (BE) value of ~334 eV was assigned to Pd^{0} 3d$_{5/2}$ [2], while that of ~343 eV likely corresponds to the 3d$_{3/2}$ binding energy of a Pd^{II} species [3]. The peak at ~338-9 eV contains signals from both Pd^{0} 3d$_{3/2}$ and Pd^{II} 3d$_{5/2}$. This overlap causes the Pd^{0} 3d$_{5/2}$ signal to appear smaller than that of Pd^{0} 3d$_{3/2}$.

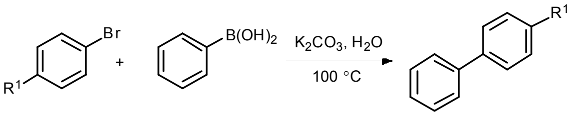
3. NP-Pd-PAA Catalyzed Suzuki Coupling Reactions

Products were identified by ^{1}H NMR and GC/MS (Agilent Technologies 5975C InertXL EI MSD spectrometer). Reactions were carried out as described in the Experimental section of the manuscript.

General procedure for NP-Pd-PAA catalyzed Suzuki couplings carried out with argon protection:

0.2 mmol (1.0 equiv) aryl halide, 0.24 mmol (1.2 equiv) arylboronic acid, and 0.3 mmol (1.5 equiv) potassium carbonate were added to a vial equipped with a magnetic stirbar. 920 µL of deionized H_2O and 81 µL of a suspension of NP-Pd-PAA (0.1 mol % palladium loading) were added via pipette. The vial was sealed with screw-cap fitted with a re-sealable septum and purged with argon for 15 minutes. The reaction was heated at 100 °C for the indicated period of time. The reaction mixture was then diluted with water and extracted three times with ethyl acetate. The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness in vacuo. The desired product was isolated by preparative thin layer chromatography.

Control Reactions with no Added Catalyst[a]

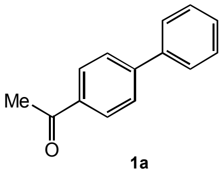


R^1	**Time**	**Conversion**[b]
Ac	80 min	Trace (< 5 %)
OMe	80 min	None

[a] These reactions were carried out using the representative procedure outlined in the Experimental section of the manuscript. Reaction conditions: aryl halide (1.0 equiv), phenylboronic acid (1.2 equiv), K_2CO_3 (1.5 equiv), 100 °C, H_2O, air atmosphere. [b] Conversion based on ^{1}H NMR analysis of crude reaction mixture

4-Acetylbiphenyl (1a) [4,5]

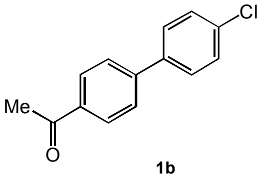
Purified via preparative thin layer chromatography in hexanes/acetone. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2. 64 (s, 3H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 8.6 Hz, 2H).



1a

4-Acetyl-4'-chlorobiphenyl (1b) [6]

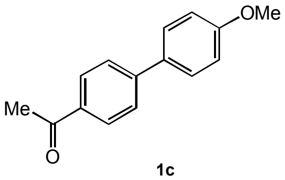
Purified via preparative thin layer chromatography in hexanes/acetone. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.64 (s, 3H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H).



1b

4-Acetyl-4'-methoxybiphenyl (1c) [4]

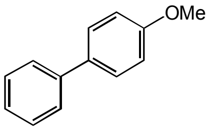
Purified via preparative thin layer chromatography in hexanes/dichloromethane. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.63 (s, 3H), 3.86 (s, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H).



1c

4-Methoxybiphenyl (1d) [4,7]

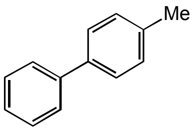
Purified via preparative thin layer chromatography in hexanes/ethyl acetate. ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.87 (s, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.53-7.59 (m, 4H).



1d

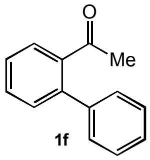
4-Methylbiphenyl (1e) [7,8]

Purified via preparative thin layer chromatography in hexanes. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.41 (s, 3H), 7.26-7.36 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.59-7.61 (m, 2H).



1e

2-Acetylbiphenyl (1f) [4,9]



1f

Purified via preparative thin layer chromatography in hexanes/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 7.34-7.46 (m, 7H), 7.49-7.57 (m, 2H).

4. References for Electronic Supplementary Information

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