## Supporting information

# Sodium borohydride treatment: A simple and effective process for the removal of stabilizer and capping agents from shape-controlled palladium nanoparticles

Naresh Nalajala<sup>a, b, c</sup>, Wasim Feroze Gooty Saleha<sup>a, b, c</sup>, Bradley. P. Ladewig<sup>b</sup> and Manoj

#### Neergat<sup>c,\*</sup>

<sup>a</sup>IITB-Monash Research Academy, Powai, Mumbai, India-400076

<sup>b</sup>Department of Chemical Engineering, Monash University, VIC 3800, Australia

<sup>c</sup>Department of Energy Science and Engineering, Indian Institute of Technology Bombay (IITB), Mumbai, India–400076

## **Experimental details**

#### Materials

Potasium tetracholoropalladate (K<sub>2</sub>PdCl<sub>4</sub>) from Alfa Aesar; polyvinylpyrrolidone (PVP) and ascorbic acid (AA) from Sigma-Aldrich; citric acid (CA), potassium bromide (KBr), potassium chloride (KCl), sodium borohydride (NaBH<sub>4</sub>) and all other solvents (acetone, hexane, ethanol) from Merck, India were used without further purification for the synthesis of the catalysts.

#### Synthesis of Pd nanocubes (NCs)

Synthesis of Pd-NCs has been carried out by following the procedure reported in the literature [4]. Briefly, 105 mg of PVP, 60 mg of AA, and 300 mg of KBr were dissolved in 8 mL of DI water in a 25 mL round-bottom flask (RBF) and the temperature was raised to  $85^{\circ}$ C. After 10 min., 57 mg of K<sub>2</sub>PdCl<sub>4</sub> dissolved in 3 mL of DI water, was added to the above-mentioned preheated solution and the reaction was allowed to continue for 3 h. The solution was cooled to room temperature and the product was washed one time with 50 ml of acetone at 10,000 rpm for 10 min. Thereafter, the product was washed again three times with 40 ml of ethanol/hexane (1:3 by volume) solution at 10,000 rpm for 10 min to remove the excess impurities from the catalyst surface. Finally, Pd nanoparticles were dispersed in 10 ml of water/ethanol for further characterization.

\* Corresponding author. Tel.: +91 22 2576 7893; Fax: +91 22 2576 4890 E-mail address: <u>mmanoj@iitb.ac.in</u>

#### Synthesis of Pd mixed shapes (nanocube (NC) and cubo-octahedra (CO))

The procedure for synthesis of Pd mixed shapes is same as that of Pd NCs except for the use of 300 mg of KCl instead of KBr; all other experimental parameters remain unchanged.

#### Synthesis of Pd truncated-octahedral (TO)

The synthesis of Pd-TO was carried out by following the procedure reported by B. Lim, *et al* [6]. Briefly, 105 mg of PVP, 60 mg of AA, and 60 mg of CA were dissolved in 8 mL of DI water in a 25 mL RBF and the solution was heated to 90°C. After 10 min., a solution of 57 mg of  $K_2PdCl_4$  in 3 mL of DI water was added to the above pre-heated solution at 90°C and the reaction was allowed to continue for 3 h. The reaction mixture was cooled to room- temperature and the product was washed with acetone one time and three times with ethanol/hexane solution as mentioned above (centrifuging at 10,000 rpm for 10 min.) to remove the excess surfactants from the catalyst surface. Finally, the as-prepared shape-controlled Pd nanoparticles were dispersed in water/ethanol for further characterization.

## Stabilizer and capping agent removal from as-synthesized Pd nanoparticles

Removal of impurities from the as-prepared catalysts using NaBH<sub>4</sub> solution: To the washed asprepared Pd nanoparticles (one time with acetone/ three times with ethanol/hexane mixture) dispersed in 10 mL of DI water taken in a 50 ml bottle, NaBH<sub>4</sub> solution (60 mg NaBH<sub>4</sub> in 10 ml of DI water) was added. The bottle was closed with an airtight cap and Teflon tape to avoid the leakage of hydrogen. Thereafter, the solution was sonicated for 30 min. followed by heating at 85°C (hot-plate temperature) under stirring for 8 h. Later on, the solution was centrifuged at 14,000 rpm for 10 min. with excess DI water (50 ml) and the supernatant was discarded; this was repeated 3 times to ensure the complete removal of suspended-impurities from the solution. Finally, the catalyst was collected in a beaker and kept for drying at 70°C for 8 h. The dried catalyst was ground with a mortar/pestle to get a fine powder for further characterization. The same cleaning procedure was followed for all the catalysts.

## Carbon-supported Pd nanoparticles (as-prepared and cleaned)

To study the electrocatalytic properties of the as-prepared and cleaned catalysts, Pd nanoparticles were supported on Vulcan carbon XC-72. The procedure is as follows: for 20 wt% of metal loading on the carbon-support, required amount of carbon was dispersed in 10 mL of ethanol and the mixture was sonicated for 30 min. to form a homogeneous carbon-slurry. Pd nanoparticles dispersed in DI water were added to the carbon-slurry and again sonicated for 30 min. to get a proper homogenous dispersion of Pd nanoparticles on the carbon. The solution was kept for drying at 65°C to evaporate the ethanol and other organic impurities from the catalyst. The resultant catalyst was ground with a mortar and pestle to get a fine catalyst powder for further characterization. All the carbon-supported catalysts were prepared by the same procedure.

#### **Physical Characterizations**

For the structural information of the as-prepared and cleaned catalysts, XRD patterns were recorded using a PANalytical X'Pert Pro machine (30 mA, 40 kV) with Cu Ka radiation of wavelength ( $\lambda$ ) 1.5406 Å. The morphological details such as size, shape and dispersion of asprepared and cleaned catalysts were recorded using JEOL JEM 2100 F field emission electron microscope operated at 200 kV. The sample preparation for TEM analysis is as follows: a small amount of the catalyst was dispersed in ethanol and it was sonicated for 15 min. The suspension was drop-cast on a copper grid and it was dried for 10 min. under an IR lamp. The FTIR spectra were recorded using a vertex 80 model, Bruker instruments and OPUS software was used for baseline correction, smoothening and peak assignment. The sample preparation to record the FTIR spectrum is as follows: a known amount of catalyst and the reference material KBr were ground with a mortar/pestle for homogeneous mixing and the resultant mixture was made into pellet form. The FTIR spectrum was recorded from 400 to 4000 cm<sup>-1</sup> with 32 counts. The thermogravimetric analysis of the as-prepared and cleaned catalysts was conducted with Diamond TG/DTA, PerkinElmer Instruments. The sample was heated from room temperature to 800°C under nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>. The surface composition of asprepared and cleaned catalysts was investigated with an XPS (MultiLab Thermo VG Scientific spectrometer) using Al K $\alpha$  radiation of energy 1486.6 eV at a chamber pressure of  $ca.1.5 \times 10^{-7}$ Pa. For peak fitting, we used XPS Peak 4.1 software. The peaks were calibrated with the standard C1s peak fixed at 284.4 eV. The extent of PVP removal was determined from the elemental composition of the samples obtained from CHNS Analyzer, Thermo finnigan, Italy. A known amount (2 mg) of sample was subjected to flash combustion and the evolved gases were analyzed through a thermal conductivity detector. Based on the difference in carbon content between the as-prepared and cleaned samples, the percentage cleaning was calculated.

#### **Electrochemical characterization**

The electrochemical characterization of the as-prepared and cleaned catalysts were recorded using a WaveDriver 20 Bi-potentiostat from Pine Research Instruments, U.S with Aftermath software installed on a Windows 7 operating system. All the catalysts were tested in a three electrode cell assembly with Ag/AgCl (sat. KCl solution) reference electrode; Pt wire counter electrode; and catalyst-coated glassy-carbon rotating disk electrode (RDE) of area 0.196 cm<sup>2</sup> as the working electrode. All the potentials are reported against RHE in the manuscript.

The procedure for the deposition of catalyst thin-film layer on the electrode is as follows: 5 mg of catalyst dispersed in 5 mL of DI water with 10  $\mu$ L of Nafion<sup>@</sup> (5 wt%) was sonicated for 15 min. Thereafter, 10 mL of IPA was added to the above solution and again sonicated for 15 min. for the homogenous dispersion of the catalyst. The required amount of ink was drop-cast on the glassy-carbon disk to get a precious metal loading of 15  $\mu$ g cm<sup>-2</sup>. The CVs of the as-prepared

and cleaned catalysts were recorded in argon-saturated 0.1 M HClO<sub>4</sub> solution at a scan rate of 20 mV s<sup>-1</sup> from 0.05 to 1.05 V. The ORR voltammograms of the as-prepared and cleaned catalysts were recorded in oxygen-saturated 0.1 M HClO<sub>4</sub> solution at 1600 rpm with a scan rate of 20 mV s<sup>-1</sup> from 0.05 to 1.05 V.



Fig. S1. TEM images of (a) as-prepared Pd-NC/CO; and (b) NaBH<sub>4</sub>-treated Pd-NC/CO.



**Fig. S2.** FTIR spectra of the as-prepared and NaBH<sub>4</sub>-treated nanoparticles (a) Pd-NC, (b) Pd-TO, and (c) Pd-(NC/CO).



Fig. S3 XRD patterns of as-prepared, H<sub>2</sub> bubbled and NaBH<sub>4</sub> treated Pd-NC.

Catalyst		Carbon (%)	Nitrogen (%)	Hydrogen (%)	Total CHN (%)
Pd-NC	As-prepared	41.829	8.125	6.329	56.283
	NaBH <sub>4</sub> treated	4.174	0.981	0.457	5.611
Pd-TO	As-prepared	46.864	9.093	6.924	62.881
	NaBH <sub>4</sub> treated	4.365	0.894	0.676	5.936
Pd-NC/CO	As-prepared	44.936	8.760	6.757	60.453
	NaBH <sub>4</sub> treated	3.793	0.788	0.418	4.999

Table S1: CHN analysis of the as-prepared and cleaned shape-controlled Pd nanoparticles

Hence, from the change in elemental composition (before and after cleaning), we conclude that the % cleaning achieved is ~90, ~92 % for Pd-NC, Pd-TO and Pd-NC/CO, respectively.

Table S2: CHN analysis of the as-prepared and cleaned shape-controlled Pd nanoparticles

	Catalyst	Carbon (%)	Nitrogen (%)	Hydrogen (%)
Pd-NC	As-prepared	41.829	8.125	6.329
	NaBH <sub>4</sub> -treated	4.174	0.981	0.457
	H <sub>2</sub> bubbled	26.05	4.881	3.761