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ARTICLE TYPE

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

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The inherent property of palladium to form hydride is effectively exploited for the removal of adsorbed stabilizer and capping agents. Formation of hydride on exposure of Pd nanoparticles to sodium-borohydride weakens the metal's
10 **interaction with the adsorbed-impurities and thus enables their easy removal without compromising the shape, size and dispersion.**

Syntheses of shape-controlled nanoparticles to tailor the physical, chemical and catalytic properties for myriad of applications are
15 well-established and reported in the literature.[1, 2, 3] Several capping agents have been used to obtain the required shape-selectivity, *e.g.*, Br⁻ ions for cubic shape with dominant (100) facets; Cl⁻ ions for cubo-octahedra shape with (100) and (111) facets; and citrate ions for truncated-octahedral shape with
20 dominant (111) facets. Polyvinylpyrrolidone (PVP) has been used as the most common stabilizer for the synthesis of shape-controlled Pd nanoparticles.[4–6] The final shape and size of the nanoparticles are obtained by minimizing their surface free energy through the adsorption of stabilizers/capping agents. Since
25 the adsorption capability of each plane (hkl) is different, various capping agents are used to control the shape of the nanoparticles.[2] Thus, precious metal nanoparticles with controlled size and shape can be obtained with the help of stabilizers and capping agents, but, the reagents used in the synthesis adsorb strongly on the
30 surface of the shape-controlled nanoparticles and these impurities inhibit their direct use. For instance, adsorbed-impurities hinder the diffusion of the reactant species towards the active catalyst surface leading to poor electrocatalytic response of the shape-controlled Pd nanoparticles.[7] It is really a challenging task to
35 remove all the stabilizer/capping agents from various shape-controlled nanoparticles for realistic applications.

The strong interaction of stabilizers and capping agents with the catalyst surface necessitates the use of harsh reagents or processes for their removal which might often result in change of
40 shape, size, and dispersion. Thus, in the literature, depending on the chemical nature of the adsorbed impurities (acidic, alkaline, organic and polymeric), various methods are reported for cleaning different shape-controlled Pd nanoparticles, *viz.*, UV-ozone treatment (Pd nanocubes), acetic acid washing (spherical)
45 and NaOH washing (Pd nanocubes).[8–10] In our previous study,

tert-butylamine (TBA) was used for the simultaneous removal of capping agent (Br⁻) and stabilizer (PVP) from the Pd nanocube surface without affecting the shape, size and dispersion of the nanoparticles; the removal of Br⁻ occurs because of its ability to
50 form quaternary ammonium salt with TBA.[7] Use of the same reagent for the removal of stabilizer (PVP) and capping agent (citric acid) from the Pd truncated-octahedral shape proved ineffective as evidenced by the absence of sharp electrochemical features thus confirming the presence of impurities on the catalyst
55 surface. This suggests that the stabilizers and capping agents have different adsorption capabilities on various catalyst surfaces and a single reagent or process cannot be used for their removal.

In the present study, a well-known reducing agent, NaBH₄ is used for the first time as a simple and effective cleaning agent for the
60 removal of impurities from various shape-controlled Pd nanoparticles. Different shape-controlled Pd nanoparticles such as cubic, cubic/cubo-octahedra (mixed shapes) and truncated-octahedral have been synthesized with capping agents such as potassium bromide (KBr), potassium chloride (KCl), and citric
65 acid, respectively, in the presence of PVP as a common stabilizer. After initial wash, the as-synthesized Pd nanoparticles were treated with NaBH₄ solution at 85°C for 8 h followed by washing with DI water. The unique ability of Pd surface to form hydride weakens the interaction between catalyst and any of the
70 adsorbed-impurities and hence facilitates their easy removal from the surface of Pd irrespective of the chemical nature. The extent of cleanliness of borohydride-treated Pd nanoparticles is confirmed with the physical (XPS, TGA, FTIR, and CHN elemental analysis) as well as electrochemical characterizations
75 (cyclic voltammograms (CVs) and oxygen reduction reaction (ORR) in 0.1 M HClO₄ solution). The clean electrochemical features confirm that NaBH₄ can be effectively used for the removal of inorganic capping agents (Cl⁻, Br⁻, citrate ions) and organic stabilizer (PVP) from various shape-controlled Pd
80 nanoparticles.

Synthesis of various shape-controlled Pd nanoparticles is carried out in the presence of different capping agents with PVP as a common stabilizer. Citric acid is used for the synthesis of truncated-octahedral Pd nanoparticles with dominant (111) facets
85 by the selective adsorption of citrate ions. KBr has been used for

the synthesis of cubic nanoparticles with dominant (100) facets by the selective-adsorption of Br⁻ ions. Similarly, KCl has been used for the synthesis of cubo-octahedra with both (100) and (111) facets. But, in this study, for the sake of comparison and to evaluate the effectiveness of our cleaning procedure, we have used the same amount (300 mg) of KBr and KCl. However, 300 mg of KCl produces mixed shapes, *i.e*, cubic and cubo-ocatahedra, and a lower amount (180 mg) would produce only cubo-octahedra.[5] The complete details of the synthesis of different shape-controlled Pd nanoparticles and the cleaning procedure are mentioned in the experimental section of the supplementary information (**SI**). The shape, size and dispersion of the as-prepared and cleaned catalysts are investigated from the TEM analysis. The TEM images of the as-prepared and cleaned Pd nanocubes (NCs) and Pd truncated-octahedral (TOs) are shown in **Fig. 1.** The images suggest that there is no change in shape, size, and dispersion even after cleaning the catalyst with borohydride. The size of Pd-NC and Pd-TO is ~8 and ~7 nm, respectively. From the high resolution images shown in insets to the Fig. 1, the calculated lattice spacing of the as-prepared and borohydride-treated Pd-NC is 0.195 and 0.198 nm, and that of Pd-TO is 0.226 and 0.230 nm, respectively. The lattice spacing of the as-prepared Pd nanoparticles is almost comparable with that of standard Pd (JCPDS file no. 03-065-6174). Whereas, the lattice spacing of borohydride-treated Pd nanoparticles is almost comparable with that of the H-loaded Pd (JCPDS file no. 01-087-0641).
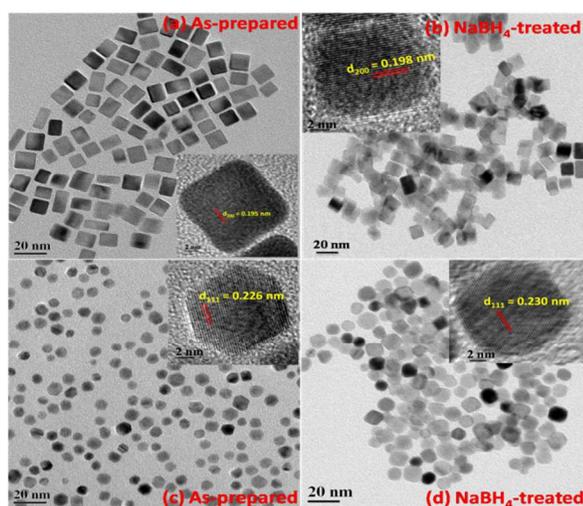

Fig. 1. TEM images of the Pd nanoparticles: (a) as-prepared Pd-NCs; (b) NaBH₄-treated Pd-NCs; (c) as-prepared Pd-TOs, and (d) NaBH₄-treated Pd-TOs.

The increase in lattice spacing observed after borohydride treatment suggests the hydride formation of Pd during the treatment. The TEM images shown in **Fig. S1(a)** and **(b)** of the as-prepared and borohydride-treated Pd nanoparticles of mixed shapes (cubo-octahedra and cubic) suggest that there is no change in the shape and size (~8 nm) of any of these Pd nanoparticles after the cleaning; insets to Fig. S1 (a) and (b) show the high resolution images of the as-prepared and borohydride-treated Pd-

CO nanoparticles. The structural information of the as-prepared and borohydride-treated catalysts is shown in **Fig. 2(a)**. The XRD patterns in Fig. 2(a) show a peak shift to the left with borohydride-treated catalysts (dotted line) compared to that of the as-prepared Pd nanoparticles (solid line) suggesting a lattice expansion due to the hydride formation of palladium.[11, 12] The particle size is calculated using Debye-Scherrer formula from (220) peak of the XRD patterns and it is ~8 nm with both as-prepared and borohydride-treated catalysts; it matches with that obtained from the TEM images. To quantify the PVP content in the as-prepared and borohydride-treated catalysts, the samples were subjected to thermogravimetric analysis (TGA). The TGA data shown in **Fig. 2(b)** reveals significant weight loss with the as-prepared shape-controlled Pd nanoparticles when compared to that of the borohydyride-treated catalysts suggesting the presence of large amount of residual organic impurities on the catalyst surface.
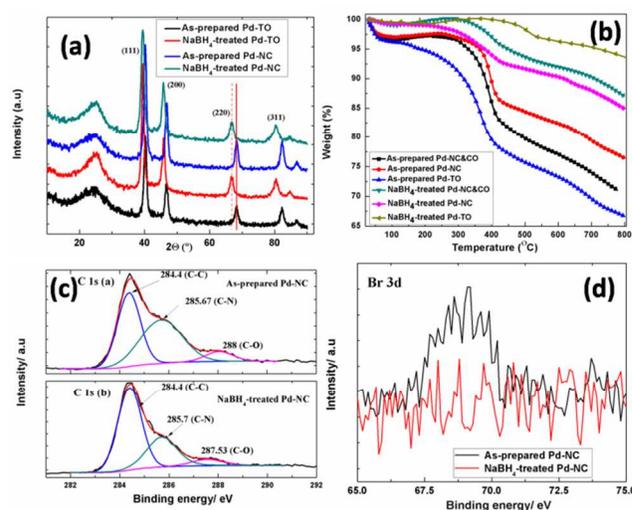

Fig. 2. Physical characterizations of the as-prepared and NaBH₄-treated Pd nanoparticles: (a) XRD patterns, (b) TGA (c), and (d) XPS of C1s and Br⁻ 3d, respectively.
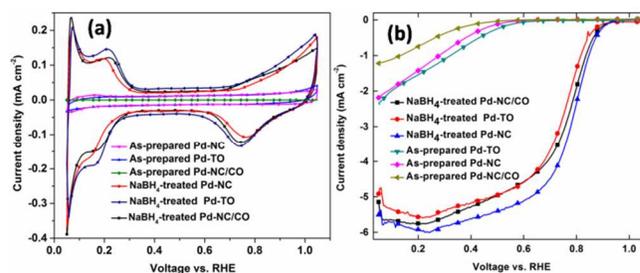

Fig. 3. (a) Cyclic voltammograms (CVs), (b) oxygen reduction reaction (ORR) voltammograms of the as-prepared and NaBH₄ treated shape-controlled Pd nanoparticles.

In the temperature range of 30–200°C, the weight loss could be assigned to the evaporation of moisture and low molecular weight organic impurities from the sample. Thereafter, in the region of 200–500°C, there is a steep and gradual increase in weight loss corresponding to the decomposition of PVP and it is more prevalent in the case of as-prepared catalysts.[13] A minute change

in the weight with the borohydride-treated samples in this temperature region suggests that the amount of PVP is negligible on the catalyst surface. In both cases there is a weight loss after 500°C due to the carbon decomposition [13]; here we have used carbon as the support for Pd nanoparticles for recording the electrochemical response. The surface purity of the borohydride-treated Pd nanoparticles is confirmed further with the XPS analysis and for comparison we have also included the XPS spectra (**Fig. 2(c)**) of the as-prepared Pd nanoparticles. The C 1S spectrum of the as-prepared Pd-NCs is deconvoluted to three peaks corresponding to binding energy of 284.4 eV from graphitic carbon, 285.7 and 288 eV from pyrolidine ring of PVP.[14] The peaks corresponding to pyrolidine group are dominant in the as-prepared catalyst when compared to those of the borohydride-treated catalyst. It suggests that more PVP remains on the surface of the as-prepared catalyst and this is the reason for the poor electrochemical properties (see the discussion below). The Br 3d spectra of the as-prepared and borohydride-treated catalysts are shown in **Fig. 2(d)**. In the as-prepared Pd-NC sample, an intense peak of Br^- confirms the presence of adsorbed Br^- ions on the surface of Pd-NC after initial wash. The Br 3d state can be assigned to a binding energy of 69.25 eV which is comparable with that reported in the literature and there is no such peak at this binding energy after borohydride treatment.[15] The fourier transform infrared spectra (FTIR) of borohydride-treated catalysts and those of the as-prepared catalysts are compared for the presence of any organic group in the samples. The FTIR spectra (**Fig. S2**) show the typical characteristic vibrational modes at ~1260, ~1420 and ~1660 cm^{-1} corresponding to C–N, C–H$_2$, and C=O stretching, respectively, of the pyrolidine ring of PVP.[16] The relative intensities of these groups on all borohydride-treated catalysts are much lower than those of the as-prepared counterparts. This confirms that, irrespective of the shape, significant amount of PVP has been removed from the catalyst surface. To quantify the extent of cleaning achieved, the samples were analysed for their elemental composition using a CHN analyzer. The percentage of carbon and nitrogen in the as-prepared and cleaned samples show that ~90% cleaning is achieved with all the shape-controlled Pd nanoparticles (**Table S1**). The electrochemical characteristics are recorded for the confirmation of surface cleanliness of the borohydride-treated Pd nanoparticles and are compared with those of the as-prepared Pd nanoparticles. The CVs of the as-prepared and borohydride-treated shape-controlled Pd nanoparticles are shown in **Fig. 3(a)**. The CVs of all the as-prepared catalysts do not show the typical precious metal features such as H$_{upd}$ (0.0–0.35 V), double-layer region (0.35–0.65 V), and oxide formation/reduction at potential above 0.65 V. Even after repeated cycling of the electrode, the catalysts do not show any features indicating that the catalyst surface is covered with the strongly adsorbing PVP and capping agents (Cl$^-$, Br$^-$ and citrate ions). On the other hand, the CVs of the borohydride-treated Pd nanoparticles with sharp features of precious Pd metal from the initial cycle itself confirm that the catalyst has a clean surface. **Fig. 3(b)** shows the ORR voltammograms of all the catalysts. The inactiveness of the as-prepared catalysts towards the ORR even after repeated potential cycling can be clearly

observed, whereas, the borohydride-treated catalysts show significant activity. The half-wave potentials of the borohydride-treated catalysts are 743, 763, and 778 mV with Pd-TO, Pd-NC/CO, and Pd-NC, respectively. Interestingly, this order supports the fact that (100) facet-dominated Pd-NC is more active than (111) facet-dominated Pd-TO. This is in line with the studies on single-crystal surfaces where (100) plane was reported to be more active than (111) plane towards ORR in 0.1 M HClO$_4$ solution.[17] To further confirm the impurity removal due to the hydride formation on Pd, as-prepared Pd-NCs were subjected to the same cleaning procedure as-reported in this manuscript but instead of NaBH$_4$, hydrogen was bubbled. Interestingly, only ~38% impurity removal is observed from CHN analysis (**Table S2**). This can be explained based on the difference in nature of hydrogen in both the cases. The nascent hydrogen evolved during the NaBH$_4$ treatment is reported to be highly reactive and easily forms hydride with Pd.[18] Hence, lattice expansion is seen only in the NaBH$_4$-treated samples and not with those subjected to H$_2$ bubbling (**Fig. S3**).

In the present investigation, NaBH$_4$ is introduced as a common reagent for the simultaneous and effective removal of stabilizer and capping agents from different shape-controlled Pd nanoparticles, *viz*., Pd-NC, Pd-TO, and Pd-NC/CO. The inherent ability of Pd to form hydride weakens the interaction between the adsorbed-impurities and Pd surface which facilitates the removal of the former. Irrespective of their chemical nature, capping agents such as Cl$^-$, Br$^-$ (inorganic) and citric acid (acidic) – and most importantly – high molecular weight stabilizer such as PVP (organic and polymeric) can be removed with the NaBH$_4$ treatment without compromising the shape, size, and dispersion of the Pd nanoparticles. This sodium borohydride treatment can be the simplest cleaning procedure for obtaining Pd nanoparticles with significantly reduced impurities (~90% cleaning) for various applications. The remaining ~10% impurities do not have a notable effect on the electrochemical properties as seen from the CVs; in fact, the traces of PVP may actually help in preventing the agglomeration of the highly active Pd nanoparticles.

Notes and References

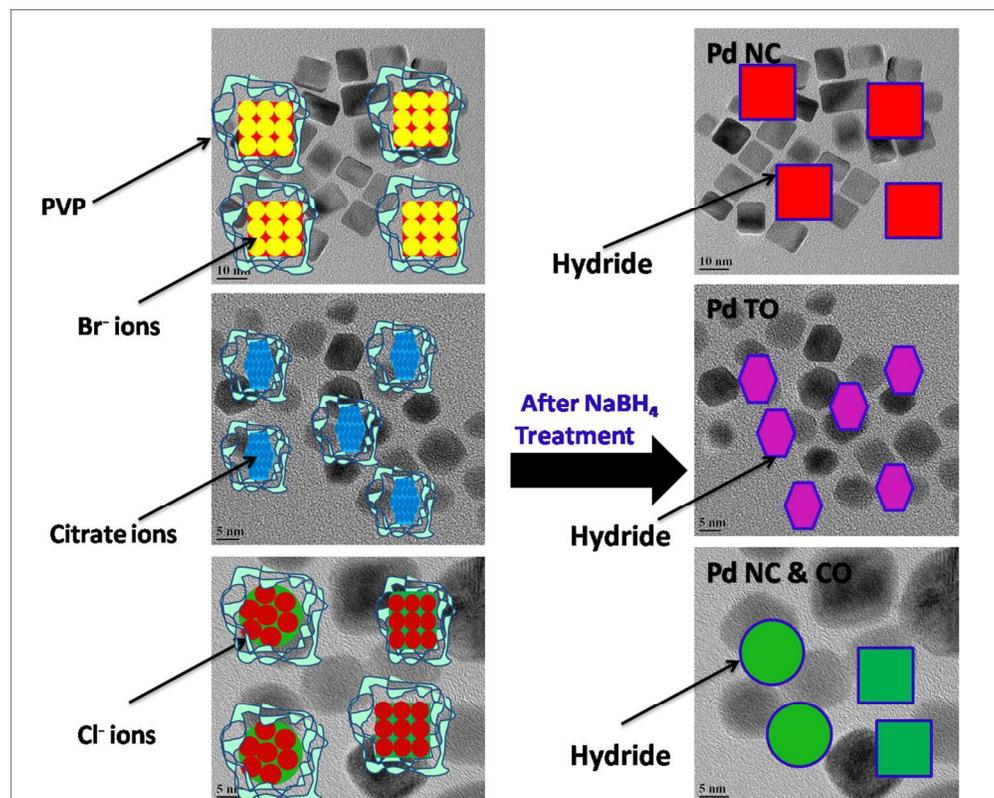[a]IITB-Monash Research Academy, Powai, Mumbai, India–400076
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Using the hydride formation property of Pd for the removal of strongly-adsorbed impurities from the nanoparticle surface
230x184mm (150 x 150 DPI)