Palladium nanoparticles on hierarchical carbon surfaces: A new architecture for robust nano-catalysts

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** Abstract **

Surface activity of heterogeneous catalysts can be enhanced if their sizes are reduced to nanometers. However, loose nanomaterials pose potential health and environmental risks. This issue has been addressed by attachment of palladium nanoparticles on multi-scale hierarchical carbon supports that have exceptionally high surface area per volume. The supports consist of porous carbon foam whose surface has been either chemically functionalized, or morphologically altered by grafting of carbon-nanotubes. It is seen that whereas chemical functionalization does provide some increase in nano-catalyst loading, morphological modification is significantly more powerful. It has the potential to create orders of magnitude increase in catalytic activity within the same overall volume. The synthesis techniques have been investigated in sufficient detail to provide significant control over the density and size of nanoparticles. Abundant distribution of nanoparticles is observed even within the deeper pores of the microporous foam. The nanoparticles are seen to be metallic Pd having face centered cubic structure. Additionally, the nano-particles and nanotubes are durable, and remain attached to the base support after long periods of rapid rotation in water. These robust hybrid structures show promise in future applications such as sensors, water purification systems, fuel cell electrodes and hydrogen storage sponges.

1. Introduction

Metal nanoparticles offer several unique properties related to size, shape and surface chemical activity [1,2]. These properties can enhance their performance as sensors and catalysts for cutting edge technologies applicable in bio-medicine [3,4], electronics [5], environment [6], catalysis [7], optics and optical sensing [8]. Among various transition and rare earth metals, palladium (Pd) is widely recognized as an important heterogeneous catalyst useful in many reactions [9,10]. In addition to its catalytic activity, Pd has the unique ability of absorbing hydrogen while being impervious to other gases [11]. At room temperature and moderate pressure, hydrogen can readily diffuse into the metal lattice, thereby introducing strain in the lattice and it coexists in both metallic and metal-hydride phases simultaneously [12,13]. These properties make Pd a very useful element in a wide range of applications such as fuel cell catalysts [14], sensors [15], dechlorination catalysts [16], and hydrogen storage media [17,18].

For surface dependent heterogeneous reactions, nano-size particles of precious metals can provide high surface-to-volume ratio resulting in higher catalytic activity per unit volume. Moreover, the catalytic properties may change dramatically at nanoscale dimensions compared to their bulk counterparts resulting in unprecedented uses [19]. Nanocatalysts can be used as stand-alone particles, or often attached to larger supports. Nanoparticles (NPs), when used in isolated form tend to agglomerate, compromising their reactivity. They are sometimes suspended in colloidal solutions by using surfactants, capping agents, or polymeric binders [1,20–23]. While these additives can stabilize the particles, they may also coat the surface leading to reduced catalytic activity [1].

Supported metal NPs, on the other hand, may provide advantages in stabilizing the size without coating the surface. The common materials that are adopted to support NPs include oxides such as silica and alumina; and carbon structures such as activated carbon and nanostructures of carbon [24–26]. The electronic properties of the support are significant in that they can influence the catalytic activity of the metal through specific metal-support interactions [27–30]. Strong metal–support interactions, often seen in oxide supports, may result in altered (often suppressed) catalytic activity. Carbon based structures offer chemical inertness and weak metal–support interaction, therefore may not suppress the chemical activity of the metal–surface [31]. Moreover, carbon supports, provide the benefits of high mechanical strength as well as electrical and thermal conductivity. In addition, they are considered economically and ecologically friendly, as the simple process of combustion can be used to recover and recycle maximal amount of precious metals while producing minimal solid waste in the form
of remnant ashes [32,33]. The geometry of support becomes an important consideration. Supports having high surface area per unit overall bulk are desirable for effective catalysis. This has resulted in the use of high surface-area carbon structures such as activated carbon or graphene, free-standing–carbon nanotubes, and carbon nano-fibers [30–34]. However, these structures are mostly in the form of loose powder which, similar to isolated NPs, get dispersed into the surrounding medium during use, and may result in material loss as well as health and environmental hazards.

This paper addresses the above concern by introducing high surface area carbon nano-structures that are strongly attached to larger robust supports which do not disperse into the environment. These supports are then used for attaching NPs of the selected catalyst – Palladium. These types of hierarchical structures [35] can surpass all currently available architectures by combining the robustness, structural integrity, and ease of handling of larger materials along with the high surface area of nano-materials.

The base substrate is microcellular carbon foam, an open cell structure with three dimensional arrays of interconnected pores having a high surface area. Their porosities can range from 68% to 94% depending on the grade of foam. The results reported here have been performed on a standardized commercial grade having porosity of about 80%. Three different surface modification techniques have been compared in this study, two involving to chemical functionalization (or coating) and one involving morphology alteration. Surface functionalization approaches presented are: chemical etching with nitric-acid, and silica coating using plasma deposition methods prior to attaching Pd-NPs: (1) nitric acid etching, and (2) plasma assisted silica coating. Nitric acid etching was performed by immersing the carbon foam in 16 M HNO₃ for few minutes followed by sonication with distilled water to release traces of the support. This technique is also known to add oxygen containing functional groups on the surface, and has been reported in a previous publication [36]. The morphology alteration approach involves complete alteration of the surface morphology by attachment of carbon nanotubes (CNT) on the walls. This creates a fuzzy-hierarchical surface profile at the nano-scale designed to increase the surface area of the porous structure by orders of magnitude. CNT attachment was accomplished for interconnected micro-cellular carbon foam using a two-step process: initial pre-deposition of silica layer in microwave plasma followed by chemical vapor deposition (CVD) in a floating catalyst environment. Details of this process have been previously published [35]. Earlier results had confirmed successful growth of multi-walled CNT on the outer surface as well as deep inside the pores of the foam. The length and distribution of CNT can be controlled by process parameters such as temperature, gas mixture ratios, and CVD deposition time. CNT attached to pore walls create a 3-dimensional hierarchical template for supporting well-dispersed palladium nanoparticles (Pd-NPs).

Pd deposition was performed by a liquid-phase synthesis process combined with thermal reduction process. This involves soaking the solid substrates in tetra-amine palladium nitrate (TAPN) solution, followed by drying, calcination, and controlled thermal reduction [37,38]. Process parameters that can help control the size and distribution of Pd-NPs have been identified. Micro-structural investigation was performed using scanning electron microscopy (SEM) in scanning mode, and in scanning transmission mode (STEM). Spectroscopic analysis was performed using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDAX) techniques. Crystal structure investigation of Pd-NPs was performed using X-ray diffraction (XRD). The mechanical durability of the supported Pd-NPs was also investigated by monitoring the microstructure and elemental composition after subjecting these structures to prolonged rotation in water. In order to obtain information on surface composition and chemical states, identical surface processing and Pd deposition was performed on flat surfaces of highly oriented pyrolytic graphite (HOPG). The HOPG surface is well understood, and discussed in the literature [39–41]. In this study, such a substrate offers identical surface chemistry as that of carbon foam without the uneven and irregular geometry [39], hence better suited for surface analysis. Materials characterization results have been used to understand the potential effectiveness of these structures as future catalytic components.

2. Experimental procedures

2.1. Materials used

Microcellular graphitic carbon foam was provided by Koppers Inc. The foam used in this study was L1a grade foam. Highly oriented pyrolytic graphite (HOPG) was obtained from commercial sources. All the reagents were purchased analytical grade and used without further purification. These included: Hexamethyl-di-siloxane (HMDSO, Sigma–Aldrich chemicals), Xylene (PTI Process Chemicals), Ferrocene (99%, Alfa-Aesar Ltd.), Tetra-amine Palladium (II) Nitrate solution (TAPN, 99.9%, 5% Pd, Alfa-Aesar Ltd.), methanol and concentrated nitric acid (HNO₃, 70%). Ultra high purity hydrogen gas (H₂, 99.999%), and laboratory purity argon gas (Ar) were used. The water used in this study was distilled water.

2.2. Substrate preparation methods

Blocks of carbon foam were carved into desired dimensions by machining and subsequent sanding to accomplish a uniform thickness of 2 mm ± 0.1 mm. Sheets of HOPG of thickness 3 mm were cut into blocks and used as flat supports.

2.2.1. Surface functionalization of carbon foam support

The as-received carbon foam was pretreated by two different methods prior to attaching Pd-NPs: (1) nitric acid etching, and (2) plasma assisted silica coating. Nitric acid etching was performed by immersing the carbon foam in 16 M HNO₃ for few minutes followed by sonication with distilled water to ensure complete removal of acid. This technique is also known to add oxygen containing functional groups on the surface, and has been reported in a previous publication [36]. Silica nano-coating was deposited in a microwave plasma reactor using HMDSO precursor. Detailed investigation of this process has been reported in earlier publications [36,42,43]. Untreated carbon foam was used as a control support for comparisons.

2.2.2. Morphology alteration of carbon foam support by attachment of carbon nanotubes (CNT)

These were fabricated using a two-step process as discussed in earlier publications [35,44,45]. The first step involves coating the CNT with a silica nanolayer, and the second step involves a CVD process. A solution of xylene–ferrocene was used as catalyst as well as carbon source. The reactions were allowed to take place in an Ar/H₂ environment to facilitate the growth of CNT. In this study, 15 min of silica coating time and 20 min of CVD run time were used as the optimal conditions for the CNT growth. The CNT-grafted foam samples were used as 3-dimensional hierarchical templates for attaching Pd-NPs. Unlike strong and potentially damaging functionalization of CNT often reported in the literature [46,47], these samples did not need any additional chemical treatment prior to metal loading.

2.2.3. Flat support for surface quantification

HOPG substrate was used as model flat support suitable for XPS analysis. Pd-NPs were fabricated on two types of supports, untreated HOPG and CNT-grafted HOPG. CNT were grafted on HOPG by the identical process of CVD used for carbon foam.
2.3. Synthesis of palladium nanoparticles

All the supports were rinsed with methanol and water prior to palladium deposition. In this study, supported Pd-NPs were fabricated by the liquid-phase synthesis technique combined with thermal reduction process. TAPN of optimized concentration was used as the metal precursor solution. The supports were immersed (soaked) in aqueous precursor solution, and then dried in a furnace followed by calcination at elevated temperatures. Heating rates needed to be carefully controlled in order to avoid sintering. Calcination step was done in oxygen rich atmosphere (air) for foam samples, and oxygen deficient inert atmosphere (Ar) for CNT-attached hierarchical samples. The samples were subsequently reduced at higher temperature with hydrogen gas in an inert atmosphere (reduction step). The furnace was finally allowed to cool to room temperature in the flowing mixture of Ar and H₂. For additional metal loading, the soaking, drying and calcining steps can be repeated multiple times (multiple coating cycles) prior to reduction until desired amount of Pd is obtained.

2.4. Micro-structural characterization

Surface morphology of metallic nanoparticles and hierarchical architectures were observed using JEOL 7401F field emission scanning electron microscope (FE-SEM). Statistical analysis was carried out on SEM micrographs using Scandium® SEM imaging software coupled with JEOL 7401F for FE-SEM.

2.5. Surface chemical characterization

X-ray photoelectron spectroscopy (XPS) was performed using Kratos (Axis Ultra) system with mono-chromatized Al Kα (1486.6 eV) source in ultra-high vacuum environment (UHV ~ 10⁻⁹ Torr). The survey scans (BE: 1000–0 eV) were taken in the retarding sweep modes and similarly high resolution fine scans of respective elements were also collected. The static charge (if any) in the samples was corrected by assigning a value of 284.4 eV to C 1s spectrum, a well-known binding energy value of carbon in graphite [48]. Energy Dispersive Spectroscopy (EDAX) using Ametek Inc. EDAX system was also performed on these samples for elemental data analysis.

2.6. Crystal structure analysis

X-ray diffraction (XRD) patterns were obtained by X-ray mini-diffraactometer, MD-10, using a monochromatized Cu Kα radiation (λ = 1.5418 Å) at 25 kV and 0.4 mA. XRD data was collected in the range of 20° < 2θ < 90°. The interplanar distance, d_L was calculated from first order Bragg’s reflection.

2.7. Durability testing

The durability of Pd-NPs fabricated on carbon foam and CNT-grafted carbon foam was tested by subjecting it to prolonged rotations in water. The samples were taped to the walls of sealed serum bottle filled with water (~60%). These bottles were rotated at 32 revolutions per minute (rpm) continuously for 24–48 h per cycle for 3–5 cycles. The samples were analyzed before and after these tests for microstructural and spectroscopic elemental data using SEM and EDAX respectively.

3. Results and discussions

SEM micrographs of the carbon support are shown in Fig. 1. Fig. 1(a) is the original foam and Fig. 1(b) shows the higher magnification surface morphology of the walls if CNT are attached on the foam.

3.1. Structural characterization of nanoparticles

The density (numbers per unit area) of metal NPs obtained on the support depends on the interaction of the support with the metal-precursor solution as well as on the surface morphology of the support. The size, density, and dispersion of NPs can also be fine-tuned by optimizing various process parameters. The major variables identified in this case were the concentration of TAPN solution, the composition and temperature of the reducing environment, as well as the number of coating cycles (each cycle includes soaking, drying and calcination) prior to reduction. It was observed that higher concentrations of TAPN solution led to micron sized particles and the particle size decreased with reduction in concentrations of the TAPN solution. The goal of this study was to identify the influence of surface pretreatment on Pd nanoparticle distribution, therefore concentration and soaking times was optimized initially, and then maintained constant for all subsequent studies. The influence of number of coating cycles was observed to depend upon the substrate morphology, as seen by the comparison of one-coating cycle and two-coating cycle results shown below.

3.1.1. Influence of functional coatings

Fig. 2 shows the SEM micrographs of Pd-NPs deposited on the untreated (a), nitric-acid treated (b), and silica coated (c) carbon foam supports by a one-coating cycle process. The SEM micrographs reveal that both the pretreatment methods show noticeable...
improvement in the amount of Pd-NPs loading in comparison with the untreated support.

Nitric-acid etching is a pretreatment method for oxidizing the carbon supports [36]. This approach etches the surface and results in the attachment of oxygen functional groups desirable for the nucleation of the metal NPs. After treating with the HNO₃, the foam support was rinsed thoroughly with distilled water in order to stop additional oxidation [36], and also to avoid the effects of varying pH of the metal-precursor solution while soaking the support [49]. The SEM micrograph of Pd-NPs fabricated on HNO₃ treated foam shows some improvement in the density of NPs as shown in Fig. 2b.

Pd-NPs on silica-coated porous foam were obtained as shown in Fig. 2(c). Among all the surface functionalized foam supports, silica-coated foam appeared to be the most effective for depositing Pd-NPs. The silica-coated sample consists of a nano-layer of oxide on the surface which enables the porous hydrophobic foam to become permanently hydrophilic. It improves the wetting ability of the support as well as its interaction with the metal-precursor solution and therefore has better particle deposition.

Since Pd-NPs were successfully deposited throughout the pores of the foam samples, it can be inferred that the precursor solution has effectively infiltrated into the porous support. However, some variation in the density of Pd-NPs was observed at different levels of foam, from the top-ligament to the inner pores. There were also some “abnormal” regions showing different particle sizes and/or densities compared to the rest of the surface. Such variations were significantly reduced by the two coating-cycle process as shown below.

### 3.1.2. Influence of number of coating cycles

In an effort to increase the amount of Pd loading and uniformity in nanoparticle distribution, an additional method of two-coating cycles was investigated. This implied repeating the cycles of soaking, drying, and calcination steps twice, prior to a reduction step.

The SEM micrographs, as shown in Fig. 3, reveals that the two-coating cycles of Pd significantly enhances the amount of NPs per area. More importantly, uniform and well-dispersed, smaller Pd-NPs were obtained with the two-coated cycle of Pd in comparison to their single coated (one-coating cycle) counterparts. It was also noticed that the areas with disparity in nanoparticle distribution, an additional method of two-coating cycles was investigated. This implied repeating the cycles of soaking, drying, and calcination steps twice, prior to a reduction step.

It was again noticed that after the two-coating cycle deposition, Pd loading was maximum on silica treated foam, followed by HNO₃ treated, and least on untreated foam samples. It can be concluded from this part of the study that the surface pretreatment of foam increases density of Pd-NPs on the foam surface. This is probably related to increased surface activity of the substrate that results in enhanced wettability with the precursor solution and also facilitates active sites for Pd nucleation.

### 3.1.3. Influence of nanotube-grafting

The SEM micrographs as shown in Figs. 1(b) and 4(a) shows that CNT-grafted on carbon foam by the CVD process results in forest-like nanotubes. Pd-NPs were fabricated on such supports by a similar process discussed earlier but with one difference, the calcination step was performed in inert environment of Ar. This was done because, the CNT thermally decompose when calcined in air or oxygen-rich environment at elevated temperatures (above 400 °C) as shown in Fig. 4(b). However, when the samples were calcined in an inert atmosphere of Ar no decomposition of CNT was observed as shown in Fig. 4(c). Fig. 5 shows the SEM micrographs of Pd-NPs on CNT-grafted foam samples synthesized by the one-coating cycle (a), and two-coating cycles (b) of Pd deposition process. The remarkable increase in the number of NPs per area of the CNT-grafted sample is clearly evident. It was also observed that, unlike what was seen in bare foams, the particles size became larger and more uneven with two-coating cycles of Pd in this case. This may be attributed to the overlapping and intertwining of CNT that increases the chances of more precursor clogging and particle coalescence during the second coat.

Irrespective of the number of coating cycles, Pd-NPs on CNT-grafted supports were larger in size compared to that on the carbon foam supports. Such a difference can be attributed to the (i) higher retention of precursor solution in the CNT forests and/or (ii) the calcining environment. It is reported in the literature that at a given temperature, the oxygen-deficit environment enhances the mobility of particles [49–51]. The CNT-samples are calcined in inert atmosphere where the absence of oxygen may provide more scope for particle mobility and coalescence in the given time.

It is worth noting that earlier studies in the literature related to CNT supported metal NPs involved loose CNT suspended in air or solution. Moreover, earlier studies often reported the need for either electric field-dependant techniques, or “surface functionalization” treatments in order to attach NPs on nanotubes. Many surface functionalization approaches are harsh enough to alter the CNT chemistry and/or damage its structural integrity [46,47]. In this study, metal NPs have been attached to nanotubes anchored on large porous solids. Moreover, this has been achieved without any additional functionalization of the CNT. It is possible that the dense CNT forest grown by the CVD technique in this study provides sufficient surface-active defects as well as significant precursor retention during formation, which enables improved nucleation of NPs without the need of damaging surface etch.
3.2. Statistical analysis

The size distribution and density of NPs were obtained by averaging over a large number of SEM micrographs for each sample.

3.2.1. Particle size distribution

The histograms for particle size distribution are shown in Fig. 6. It can be seen that for carbon foam samples with and without surface functional coatings (Fig. 6(a)–(c)), the process of two-coating cycles of Pd yields a narrower range of well-defined particle size distribution with average size peaking around 5 nm. For the one-coating cycle, there are detectable numbers of larger particles indicating broad size distribution.

The distribution of Pd-NPs is different in the CNT-grafted foam supports as shown in Fig. 6(d). In this case, average particle size is larger, and samples with one-coating cycle shows significantly better size distribution, compared to those with two-coating cycles. The two-coating cycle of Pd on CNT-grafted foam supports results in very broad size distribution indicating significant particle coalescence. This may be useful in few select applications requiring a wide range of nanoparticle sizes, but not very suitable for quantitative analysis. Therefore for all subsequent studies involving CNT-grafted foam, the sample with one-coating cycle of Pd was used.

3.2.2. Surface density estimate of Pd nano-particles

Fig. 7 is a schematic indicating a plan view (as seen by SEM) of Pd-NPs attached on the planar cell wall carbon foam (a), and the CNT-grafted carbon foam (b). The total number of NPs per area (\( \mu \text{m}^2 \)) on the planar carbon cell wall can be determined directly from such SEM images. On the other hand, the top view SEM micrographs of the thick CNT forest will show only the outer tips of the forest, and obviously shadows the interior as depicted in Fig. 7.

Therefore, in order to estimate nanoparticle counts per unit area, one needs to first take into account the length and the density of the nanotubes that now cover the cell walls. Assuming that the cell walls are covered with CNT forests, and vast majority of NPs are now attached to the CNT walls, the number of Pd-NPs per unit area (\( \mu \text{m}^2 \)) of the base foam is given by the following equation,

\[
N_{\text{Pd}} = N_{l_{\text{CNT}}}N_{\text{CNT}}
\]

where, \( N_{\text{Pd}} \): estimated total number of Pd-NPs per unit area (\( \mu \text{m}^2 \)) of the base substrate, \( N_{l} \): average number of Pd-NPs per unit length (\( \mu \text{m} \)) of CNT, \( l_{\text{CNT}} \): average length of CNT grafted on the support (\( \mu \text{m} \)), \( N_{\text{CNT}} \): estimated number of CNT per unit area (\( \mu \text{m}^2 \)) of the base substrate.

This model is somewhat simplified by assuming uniform distribution of nanotubes on the surface as well as NPs on the nanotubes. However, if average values are taken over large samples of micrographs, this can provide a reasonable estimate.

The average number of Pd-NPs per unit length of CNT (\( N_{l} \)) was obtained by analyzing SEM and STEM micrographs of Pd-NPs attached on CNT-grafted supports. Fig. 8 shows few typical micrographs used for this analysis. The results are tabulated in Table 1, and it can be seen that both the SEM and STEM analyses are in reasonably close agreement. Based on this data, the average number of Pd-NPs per length of CNT was estimated to be 30/\( \mu \text{m} \). The average number of CNT grown per unit area \( (N_{\text{CNT}}) \) and the average length of CNT-grafted on the support \( (l_{\text{CNT}}) \) for various growth conditions have been discussed in earlier studies [35]. Based on the growth conditions used in this study, the average length of CNT is estimated to be about 10 \( \mu \text{m} \) and average number of CNT per unit area is approximated to be around 240/(\( \mu \text{m}^2 \)). These numbers have been used to estimate the total number of Pd-NPs per unit area of the foam wall (\( \mu \text{m}^2 \)) and summarized in Table 1.
Table 1

Density of palladium nanoparticles in CNT-grafted foam.

<table>
<thead>
<tr>
<th>Mode</th>
<th>No. of Pd-NPs per micron length (µm) of CNT (Nl)</th>
<th>Estimated no. of CNT per µm² (N_CNT)</th>
<th>Average length of CNT (µm) (l_CNT)</th>
<th>Estimated no. of Pd-NPs/µm² 100% coverage of CNT (N_{pd} = N_l N_{CNT} l_{CNT})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>28</td>
<td>240*</td>
<td>10*</td>
<td>72000</td>
</tr>
<tr>
<td>STEM</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Estimated values obtained from Ref. [35].

3.2.3. Total available surface area of Pd

For use of these structures in advanced catalysis, estimates of available Pd surface area will be a key indicator of chemical activity. The particles are mostly spherical in shape, so the knowledge of radius and contact angle of the particles with the support can provide some estimates for available surface area of Pd-NPs. The contact angles of Pd-NPs on CNT samples were determined from microscopic images taken in the SEM (scanning) and the STEM (transmission) modes. The images were collected for particles that could be seen edge-on on the nanotubes (from SEM incident viewpoint) as shown in Fig. 9(a). The contact angle was measured for over 30 particles in the size range of up to 50 nm that were attached to CNT ranging from 10 nm to 25 nm in diameter. The obtained data reveals that the contact angle of particles on CNT depends on the particle-size, as plotted in Fig. 9(b). While getting exact angles from two-dimensional images can be somewhat tricky, the overall trend is clear: smaller particles have lower contact angles compared to the larger ones. Based on this observation, it has been assumed that...
particles having average sizes of 5 nm–6 nm as seen for carbon foam samples would have a contact angle close to 60°, and the particles on CNT having average size of about 15 nm would have a contact angle of about 120°.

The surface area of such particles is calculated using the formula for the surface area of a spherical cap as shown in the Fig. 10 [52,53]. It can be summarized in the following equations:

\[ S_{NP} = \pi \left( a^2 + h^2 \right) \]  \hspace{1cm} (2)

where,

\[ a = R \cos \beta \]  \hspace{1cm} (3)

\[ h = R(1 - \sin \beta) \]  \hspace{1cm} (4)

and

\[ \beta = 90° - \alpha \]  \hspace{1cm} (5)

where, \( S_{NP} \) is surface area of the particle; and as shown in Fig. 10, \( \alpha \) is the base radius, \( h \) is the height, \( R \) is the radius of the particle, and \( \alpha \) is the contact angle.

The surface area of individual Pd particles was estimated using the above equations. These can be converted to catalytic surface area per unit volume of foam as follows: the surface area of starting foam material can be obtained from analytical models developed for these types of microcellular foams [35]. Based on the microstructural parameters of the grade of foam used in this study, the total surface area in a cubic meter of foam can be estimated to be about 6.2 \( \times \) 10^3 m². The surface area of foam times the number of NPs per unit area of foam wall and the surface area of particles can provide a reasonable estimate of catalytic surface area offered by unit volume of the overall foam structure. These have been tabulated in Table 2. It must be pointed that this is the estimated total available surface area of the Pd catalyst. The surface catalytic
Table 2
Size distribution, density and estimated specific surface area of palladium nanoparticles obtained through different processing routes.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Type of foam</th>
<th>Number of coating-cycles of palladium</th>
<th>Particle size, (Mean ± SD), nm</th>
<th>Pd-NPs per unit area of support, #/µm²</th>
<th>Surface area of Pd per unit volume of the foam support m²/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Untreated</td>
<td>One</td>
<td>6.6 ± 5.2</td>
<td>765</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Two</td>
<td>5.3 ± 4.2</td>
<td>705</td>
<td>130</td>
</tr>
<tr>
<td>2</td>
<td>HNO₃ treated</td>
<td>One</td>
<td>5.9 ± 6.0</td>
<td>382</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Two</td>
<td>5.4 ± 3.8</td>
<td>987</td>
<td>186</td>
</tr>
<tr>
<td>3</td>
<td>Silica coated</td>
<td>One</td>
<td>6.1 ± 6.3</td>
<td>988</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Two</td>
<td>4.7 ± 3.2</td>
<td>2118</td>
<td>303</td>
</tr>
<tr>
<td>4</td>
<td>CNT grafted</td>
<td>One</td>
<td>15.1 ± 15</td>
<td>72000</td>
<td>239 × 10³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Two</td>
<td>30.3 ± 22</td>
<td>Clusters</td>
<td>Clusters</td>
</tr>
</tbody>
</table>

activity of nano-sized particles for specific reactions may have size dependant effects that are not yet understood clearly [54,55]. In the absence of such understanding, however, the total surface area of Pd per unit area of substrate does provide a useful estimate of the potential effectiveness of these supported catalyst structures.

It is very clear from these results that advanced surface modification techniques such as oxide functionalization can provide about 3-fold increase in available Pd surface per unit area of substrate. On the other hand, the nanotube attachment approach can increase this by over three orders of magnitude.

3.3. Chemical characterization with XPS

As mentioned earlier, the surface sensitive chemical characterization was carried out on a flat model support, HOPG. A detailed XPS analysis was performed on Pd-NPs fabricated on untreated graphite (Pd/HOPG) and CNT-grafted graphite (Pd/CNT/HOPG) samples. To obtain the chemical state of palladium, the fine scans of Pd 3d peaks were obtained as shown in Fig. 11. The Pd/CNT/HOPG has stronger Pd peak compared to Pd/HOPG as expected, but the peak positions are unchanged. The binding energy positions for Pd 3d₅/₂ and Pd 3d₃/₂ were 335.3 eV and 340.6 eV respectively with a 3d spin–orbital splitting of 5.3 eV. The energy values correlates well with the literature for the positions of metallic palladium, Pd⁰ (zero-valent Pd) [56–60]. If oxidized state of Pd were present, then the Pd 3d₅/₂ peak would have had peak component(s) between 336.5 eV and 337.5 eV [56–60]. Such peaks were absent from all samples tested. The XPS signal therefore indicates that the Pd formed by this process is completely reduced to its zero-valent state.

3.4. Crystal structure analysis using XRD

The XRD patterns of Pd-NPs fabricated on CNT Foam (Pd-CNT-Foam) and pristine CNT-Foam (CNT-Foam) are shown in Fig. 12. The XRD pattern of CNT-Foam exhibits peaks at 2θ values of 26°, 42°, 44°, 55°, 78°, 83°, and 87° which correspond to the graphitic structure of carbon. The strong peak at 26° corresponds to (0 0 2) plane, a characteristic peak of hexagonal structure of graphite and CNT. The XRD pattern of Pd-CNT-Foam exhibits additional peaks at 2θ values of 40°, 46°, 69°, 82°, and 86° corresponding with the (1 1 1), (2 0 0), (3 1 1), and (2 2 2) crystal planes. These peaks are in good agreement with those reported in the literature for the face-centered cubic (fcc) structure of palladium nanoparticles having a lattice constant, \( a = 3.91 \text{ Å} \) [61–63].

3.5. Durability and mechanical integrity

The durability and mechanical integrity of the supported Pd-NPs was tested by monitoring how they withstand rapid rotations (32 rpm) in water for long periods. Fig. 13 shows the SEM micrographs followed by EDAX spectrum of the Pd/CNT/Foam samples before (a), and after (b) 72 h of high speed rotation. It is observed from the SEM micrographs that the Pd-NPs have remained intact in all samples. The elemental data obtained by EDAX indicates reduction of other impurities, but no significant change in Pd content after these tests. This observation clearly shows that, for the time and intensity tested, these materials are robust and durable.

The successful fabrication and characterization of these materials opens up the possibility of creating carbon-supported
nano-catalysts that offer not only very high catalytic area in compact space, but also the mechanical integrity needed for long-term use of such devices. It must be reiterated that all earlier reported studies on CNT-supported catalysts involved isolated nanostructures that would be dispersed in the environment and not be recaptured easily. The supports used in this study provide the ease of handling, loading, and unloading of supported metal catalyst in the intended environments. These structures have also been tested in electrochemical cells and water de-chlorination systems, and have shown increased effectiveness. Such tests are beyond the scope of this paper and will be published elsewhere.

4. Concluding remarks

In this paper, palladium nanoparticles (Pd-NPs) have been successfully supported on hierarchical carbon structures having multi-scale architecture. The challenges of developing a supported Pd catalyst with high nanoparticles dispersion and loading have been addressed. X-Ray Photoelectron Spectroscopy shows that the carbon-supported Pd-NPs are reduced to stable metallic state. When attaching Pd-NPs directly on micro-porous carbon foam, a two-coating cycle of Pd deposition process was needed to get truly well dispersed nanoparticles having uniform particle sizes. In such cases, functionalizing the surface through an acid etch or plasma oxide coating can increase Pd loading to some extent, as much by 3 times. However, the increase can be boosted much more significantly, by orders of magnitude, if the surface geometry is altered by attaching carbon nanotubes, creating a hierarchical architecture. Crystal structure investigation using X-ray diffraction indicates FCC structure of Pd-NPs. This study also shows that Pd-NPs on these structures are highly durable and long-lasting. These types of hierarchical structures can provide very high surface activity within the compact volume for smaller and lighter components. Moreover, these nanocatalysts are anchored on larger robust solids, rather than being released into the environment making them reusable and eco-friendly.

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References