Noble metal nanocrystals have attracted much research attention for their use in photonics, sensing, thermal, and magnetic as well as catalytic properties [1-4]. Their physical and chemical properties can easily be tuned by controlling the size and shape. Size determines the ratio of surface to bulk atoms specifically, and surface area. Shape controls the facets and thus the surface structure of a nanocrystal, as well as the fractions of atoms at corners and edges. Moreover, shape has more importance than the size and other parameters and it offers greater versatility in tuning the catalytic properties of a nanocrystal, especially when the atoms at different facets possess different activities [5]. Although, for face-centered cubic (fcc) metals, the morphology and surface of their nanocrystals are closely related subjects of matter, however, their properties depend differently upon the morphology and surface structure of the nanocrystals [6-7]. For example, as a surface property, catalysis of noble metal nanocrystals are concerned more with the surface structure [8-9]. Previous studies have shown that the catalytic properties of nanocrystals can be controlled by changing the order of surface energies through selective adsorption and thus their growth rates [11]. Where, the product of a kinetically controlled synthesis can significantly deviate from the thermodynamically favored structure that includes high index facets or concave surfaces [12].

For Pd and Pt nanocrystals, recently, the surface adsorption method has also been established in which strong and specific surface adsorption of small adsorbates as reducing agents have appeared as a dominant approach to control the surface structure of their nanocrystals [13-14]. Specific adsorption of small adsorbates controls only the surface structure of Pd and Pt nanocrystals, other factors further than the specific adsorption have been employed to improve the morphology of noble metal nanocrystals. A wide range of reducing agents have been used to prepare noble metal nanocrystals [10].

1. INTRODUCTION

Noble metal nanocrystals have attracted much research attention for their use in photonics, sensing, thermal, and magnetic as well as catalytic properties [1-4]. Their physical and chemical properties can easily be tuned by controlling the size and shape. Size determines the ratio of surface to bulk atoms specifically, and surface area. Shape controls the facets and thus the surface structure of a nanocrystal, as well as the fractions of atoms at corners and edges. Moreover, shape has more importance than the size and other parameters and it offers greater versatility in tuning the catalytic properties of a nanocrystal, especially when the atoms at different facets possess different activities [5]. Although, for face-centered cubic (fcc) metals, the morphology and surface of their nanocrystals are closely related subjects of matter, however, their properties depend differently upon the morphology and surface structure of the nanocrystals [6-7]. For example, as a surface property, catalysis of noble metal nanocrystals are concerned more with the surface structure [8-9]. Previous studies have shown that the catalytic properties of nanocrystals can be controlled by changing the order of surface energies through selective adsorption and thus their growth rates [11]. Where, the product of a kinetically controlled synthesis can significantly deviate from the thermodynamically favored structure that includes high index facets or concave surfaces [12].

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Abstract: Palladium (Pd) octahedral and spherical nanocrystals (NCs) were successfully synthesized on crumpled graphene oxide (GO) by surface adsorption of H₂ and CO in the presence of capping agent poly(vinylpyrrolidone) (PVP). Their comparative studies as an anode material for direct methanol fuel cells (DMFCs) have been measured by hydrogen evolution reaction (HER) performance and methanol oxidation reaction (MOR) activity. The electrocatalytic properties of both the nanocrystals were studied in HClO₄ acidic media and compared with each other. Pd octahedral nanocrystals have shown the best performance as an anode material, their onset potential for evolution of hydrogen from the active sites of the catalyst is more towards zero than the spherical NCs. The observed specific activity (ca. 4.3 mA.cm⁻²) and mass activity (ca. 5300 mA.mg⁻¹) of Pd towards MOR is much higher for octahedral NCs than that of spherical NCs.

Keywords: Pd nanocrystals; Graphene oxide; Surface adsorption; Hydrogen evolution reaction; Methanol oxidation reaction
nanoparticles, including hydrogen, carbon monoxide, metal hydrides, hydrazine, hydroxyl amine, ascorbic acid, citric acid and vitamin B [15]. Hydrogen in particular is an effective reducing agent for noble metal salts in aqueous or non-aqueous solutions. Importantly, it provides a clean, reducing atmosphere with no harmful byproducts produced during the reactions [16]. Furthermore, the use of hydrogen decouples the effect of the reducing agent and stabilizing agent on the nucleation and any preferential directional growth of the particles. Recently, hydrogen has been used in aqueous media as a reducing agent in decorating different 2D nanostructures with Pd, Pt and Ru nanoparticles [17]. CO has also been employed as a powerful reducing and shaping agent in the last decade. Its adsorption properties have been determined on different surfaces of metal nanocrystals. In case of Pt, co-adsorption of CO and amine makes Pt[100] more energetically stable than Pt[111] and thus prompts the formation of Pt nanocubes [18-19]. CO favors to adsorb on Pd[111] surface and enables the growth of ultrathin Pd nanosheets having [111] as the main exposure surface and exhibiting catalytic properties as well as unique optical properties [20-21]. Two recent examples are, (1) the preferential growth of micrometer-long five-fold twinned Pd nanowires over Pd nanocubes under slow reduction and (2) the production of corolla-like Pd mesocrystals in the co-presence of FeCl₂ as the oxidative etchant and CO as the surface controller [22]. In these two examples, the control over the surface adsorption by reduction kinetics and introducing oxidative etching to disturb the growth of seeds enrich the morphology of noble metal nanocrystals. Gang Fu et al., demonstrated that, CO specifically adsorbs on Pd (111), the adsorption strength and coverage of CO on Pd can be essentially varied by introducing H₂ to facilitate the formation of single-crystalline Pd tetrapod and tetrahedral nanocrystals enclosed by (111) surfaces. They have found that in the co-presence of CO and H₂ prepared tetrapod and tetrahedral nanocrystals. Upon aging in air, the as-prepared nanocrystals released hydrogen and were converted gradually to Pd nanocrystals. They have calculated conclusion by density functional theory (DFT) calculations, the formation of palladium hydride in the presence of H₂ weakens the chemisorption of CO and therefore helps to lower the CO coverage to induce the formation of Pd tetrapod nanocrystals [23].

In this work, we have evaluated the surface adsorption behavior of CO and H₂ by their reduction kinetics separately in the presence of same capping agent PVP to synthesize Pd octahedral and spherical NCs. Their catalytic activity as anode materials for DMFCs have been measured comparatively. Two types of results have been evaluated here, first basic electrocatalytic characterization analysis such as HER performance to remove the adsorbed hydrogen on the active sites of catalyst surface and second the MOR activity. The electrocatalytic activity for HER and MOR analysis give interesting results with a shape difference of the two same facets. MOR activity is presented here with respect to both the scales such as specific activity and mass activity.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials

H₂PdCl₄ (99.9 % metal basis) was purchased from Alfa Aesar, Poly(vinylpyrrolidone) (PVP), MW = 58000, AR) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received without further purification.

2.2. Synthesis

2.2.1. Synthesis of Graphene Oxide

The catalyst support, reduced graphene oxide (GO), was prepared through the reduction of graphite by NaBH₄. The graphene oxide (GO) was prepared by the modified Hummers method [23]. In a typical experiment 2 g of graphite powder was first added into 100 mL concentrated H₂SO₄ at room temperature. Under stirring, the mixture was cooled to 5°C using an ice bath, and the temperature of the mixture was kept to be below 5°C for 30 min. 8 g KMnO₄ was then added gradually under stirring and cooling, so that the temperature of the mixture was not allowed to reach 10°C. 100 mL distilled water was added into the mixture, stirred for 1 h, and further diluted to approximately 300 mL with distilled water. After that, 20 mL of 30% H₂O₂ was added to the mixture to reduce the residual KMnO₄. The solid was filtered, washed with 5% HCl aqueous solution to remove metal ions and with distilled water until the pH was 6. The resulting graphite oxide was dried at 50°C for 24 h.

2.2.2. Synthesis of Pd Octahedral Nanocrystals on Graphene Oxide

Above synthesized GO powder was dispersed in water (1mg/1mL) and ultrasonicated for 30 minutes. Then 105 mg of PVP as capping agent and 1 mM of H₂PdCl₄ solution was added in GO dispersion. Reaction flask was sealed to create high vacuum environment and heated up to 95°C with continuous stirring and bubbling of H₂ as reducing agent for 30 minutes. The resulting products were collected by centrifugation and washed several times with ethanol and acetone to remove excess amounts of PVP from nanocrystals. Pd octahedral nanocrystals are demonstrated as GO/Pd-01 in all the figures.

2.2.3. Synthesis of Pd Spherical Nanocrystals on Graphene Oxide

For spherical nanocrystals the synthesis procedure is exactly the same as above for octahedral nanocrystals but only the difference is CO gas is used as a reducing agent instead of H₂. Pd spherical nanocrystals are demonstrated as GO/Pd-02 in all the figures.

2.3. Characterization Tools

2.3.1. Physical Characterization

After synthesis of GO, its characterizations were done to make sure the 2D structure of GO sheets, presence of C-C / C-H / C-OH bonds, characteristics of GO with transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy, respectively. Then after synthesis of Pd nanocrystals on GO, their physical characterizations were done by scanning electron microscopy (SEM), the powder X-ray diffraction (XRD) measurements were performed with an X’pert PRO instrument (PANalytical) using CuKα radiation (λ = 0.15418 nm) and UV-Vis spectroscopy within the range of 200 to 800nm.

2.3.2. Electrochemical Characterization

Before each electrochemical experiment, a glassy carbon (GC) electrode (0.196 cm² geometric surface area) was first polished with alumina slurries (Al₂O₃, 0.05 μm) on a polishing cloth to obtain a mirror finish, followed by sonication in 0.1 M HNO₃, 0.1 M H₂SO₄, and pure water for 10 min, successively. To prepare a cata-
lly coated working electrode, 15 µL of the 1 mg/mL suspension in pure water was drop-coated on the polished electrode surface by a microliter syringe, followed by drying in vacuum at room temperature. Afterward, the catalyst was covered with a thin layer of Nafton (0.1 wt % in water, 5 µL) to ensure that the catalyst was tightly attached to the electrode surface during the electrochemical measurements. Voltammetry measurements were carried out with a CHI750D electrochemical workstation. The electrode prepared above was used as the working electrode. The Ag/AgCl (in 3 M NaCl, aq.) combination isolated in a double junction chamber and a Pt coil were used as the reference and counter electrodes, respectively. All the measurements were performed in electrochemical experiments with respect to standard values of reversible hydrogen electrode (RHE). Electrochemical characterizations were done by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA).

3. RESULTS AND DISCUSSION

A facile synthetic route is applied to prepare GO/Pd hybrid composites with different shape Pd nanocrystals as illustrated in the schematic diagram in Figure 1. For this purpose, we initially prepare GO via the Hummer’s method and then reduce it by NaBH₄. Since GO contains a large number of oxygen-containing functional groups, which allow GO to be well dispersed in an aqueous solution [24,25]. Their functional group presence is analyzed from FTIR spectra given in Figure S1-b. The graph shows the stretching of hydroxyl group at 3450 cm⁻¹, the C=O carbonyl stretching at 1728 cm⁻¹, and the C-O epoxide group stretching at 1229 and 1061 cm⁻¹ [26]. The high intensity of the main peaks in GO confirms the presence of large amount of oxygen functional groups after the reduction process. The morphology of sheet structure of GO is analyzed from TEM shown in Figure S1-a. The reduced graphene oxide exhibit typical wrinkled structure that caused sheet folding [27]. This 2D structure of GO and presence of oxygen-containing functional groups not only increases the specific contact area, which facilitates the transport of the Pd ions and electrons into the inner region of the graphene sheets, but also provides more exposed active sites for the anchoring of Pd precursors and Pd nucleation [28].

The formation of GO/Pd hybrid composite is based on the nucleation and growth of spherical and octahedral Pd nanocrystals on the suitable surface sites of GO through a capping agent PVP and by the reduction of H₂PdCl₄ through H₂ and CO. As a typical surface-capping agent PVP is generally added at the start of the reaction or continuously during metal reduction. The role of the PVP is dual: it continuously during metal reduction. The role of the PVP is dual: it facilitates using the liquid solution approach.

In the case of Pd Octahedral nanocrystals, the mechanism of H₂ adsorption as reducing agent in the presence of a stabilizing agent (PVP) is a key point of discussion for this work. CO-H interaction on Pd (111) surface has attracted much attention for the researchers [38,39]. Fu et al., have discussed the co-adsorption of CO and H₂ on Pd (111) surface. Their main conclusion was that CO co-adsorption would cause adsorbed H atoms desorbing as H₂ or dissolving into a Pd lattice. Morkel et al., additionally pointed that for Pd nanoparticles, a hydride phase is more easily formed, and dissolved hydrogen starts to desorb only after a considerable amount of CO has been removed [40]. According to the neutron diffraction experiment [39,40], H atoms locate on the octahedral position in the bulky Pd lattice, with a saturation concentration of x=0.64. From H₂ interaction, two different hydrogen adspecies appear on the surface of Pd in the process of formation of PdHₓ. The negatively polarized atomic adspecies, being formed at the beginning of the process, denoted as β⁺, and the positively polarized atomic adspecies, arising with the increasing coverage, denoted as β⁻. However the β⁻ seems to be stable on the surface, the β⁺ incorporated quickly into the bulk forming hydrides. So upon bubbling with H₂, Pd nanosheets were converted into Pd hydride, PdHₓ. Pd (111) surface is partially saturated by the interstitial H atom, which...
become energetically stable. This creates the seed growth of the small nanosheets on the GO sheets. The increased thickness of the nanosheets resulted by the deposition of Pd atoms on Pd(111) surface by an atomic addition process allowed by the presence of H₂. As the H atoms occupy octahedral sites, so the atomic addition process eventually leads to the synthesis of Pd octahedral nanocrystals from initially grown Pd nanosheets of (111) facets.

FESEM images of the samples GO/Pd-01 and GO/Pd-02 are shown in Figure 2. The FESEM images revealed that Pd spherical and octahedral nanocrystals with a uniform size were well-dispersed on the surfaces of the GO. It was clearly shown in FESEM micrographs that spherical and octahedral Pd nanocrystals were the dominant phases. The high-magnification FE-SEM image shows that Pd octahedrons have well-defined shapes with a uniform size distribution (Figure 2a). It can be seen that the prepared Pd nanocrystals are uniformly distributed on the GO surface. It should be noted that almost no Pd nanocrystals can be observed outside the GO sheet, indicating that GO serves here as a template for the Pd nanocrystals formation. As shown in Figure 2b, spherical Pd nanoparticles were deposited onto the surface of GO with greater retention of the spherical characteristics of the nanocrystals.

The obtained GO/Pd composite was characterized by a UV-Vis absorption spectrum to confirm the existence of Pd nanocrystals loaded on GO as shown in Figure 3. In the absorption spectrum of reduced GO, the broad absorption peak centered around 270nm can be ascribed to the π-π* transitions of aromatic C=C bonds. For the GO/Pd hybrid composite, no obvious absorption peak was observed, showing a typical Mie exponential decay profile [41].

Figure 2. FE-SEM images of Pd nanocrystals on crumpled GO (left side), High magnifications images of Pd Octahedral and Pd Spherical nanocrystals on crumpled GO (right side).

Figure 3. UV-vis spectra of Pd Octahedral (GO/Pd-01) and Pd Spherical (GO/Pd-02) nanocrystals.
GO/Pd composite was further characterized by XRD to investigate the hybrid. As shown in Figure 4, the XRD pattern of Pd/GO-1 and Pd/GO-2 composites, diffraction peaks at 40.20°, 46.87°, 68.56° and 81.93° are ascribed to the (111), (200), (220) and (311) crystalline planes of the face centered cubic (fcc) structure of Pd, respectively. The diffraction peaks are consistent with a fcc crystalline structure of bulk Pd (JCPDS, card no. 46-1043). The relatively broad diffraction peak observed at 10° to 30° centered at $2\theta = 24.5^\circ$ corresponds to the (002) plane of graphene. It is an eminent fact that metallic Pd is catalytically active to split H$_2$ molecules to hydrogen atoms which can completely permeate into Pd to form metal hydride [42-44]. In fact, the powder XRD measurements (Figure 4) on the freshly prepared Pd nanocrystals confirmed that the as-prepared octahedrons and spherical nanocrystals are completely metallic and there is no evident peak observed for $\beta$-PdHx. This may be due to the high vacuum environment and temperature that all the transition phases of Pd are converted into a metallic phase Pd. The crystallite size of the particles was also calculated from XRD data by using Debye Scherrer’s formula (Table S1). The average crystal size calculated by XRD is closely co-related with the SEM measurements; hence both the results can strengthen each other’s accuracy.

The electrochemical properties of Pd/GO hybrid composites were examined by measuring cyclic voltammograms (CVs). Before observing the electrochemical behavior of the catalysts, they were cleaned by three different methods. Because the metal surface capped with organic ligands, which served as capping agents, largely reduce their catalytic activity when they are used as catalysts. In the past few years, various methods have been applied to clean or remove these surfactants, such as thermal annealing, acetic acid washing, oxygen plasma cleaning, and UV-ozone irradiation. However, these methods require either extremely high temperature or long treatment time. At the same time, the cleaning process may cause the change in particle size and morphology, especially for the shaped nanocrystals. Therefore, it is essential to develop a simple and effective strategy to clean the surface of nanoparticles and make them catalytically active. Here, we demonstrate that CO-stripping is an efficient method to clean the particle surface over oxygen plasma cleaning and simple electrochemical cleaning and thus improve the electrocatalytic activity of the PVP-stabilized Pd nanocrystals. Figure S2 and Figure S3 show the CVs of the Pd octahedral and spherical nanocrystals supported on a glassy carbon electrode respectively, after electrochemical, oxygen plasma and CO-stripping treatments. These base CVs are restricted in a small region between 0 to 1 V in order to avoid for the destruction of electrode at many scanes cycles. Compared to the all three treatments, the CO stripping-treated electrode exhibited clearer hydrogen region and oxygen region and eventually an increased electrochemically active surface area (ECSA), which further can enhance catalytic activity towards methanol oxidation. Finally, more surface atoms were exposed and became electrochemically active after CO stripping which is also characterized by CV at longer scale from 0.05 to 1.2V vs RHE where oxidation reductions peaks are clearly visible which is given in Figure 5. The present result is similar to that of another recent study where the CO treated cleaned Pt/Pd/RGO catalyst and surfactant-free Ag nanorods exhibited good characteristic CV and much enhanced electrocatalytic activity compared with the PVP-stabilized ones [45-47].

In order to calculate the electrochemical active surface area (ECSA), the cyclic voltammograms (CVs) curves of GO/Pd-01 and GO/Pd-02 presented in Figure 5. As shown in these voltammograms,
There is hydrogen adsorption/desorption region (0.05-0.3 V) and surface metal oxidation/reduction region (0.4-0.8 V) on the CV curves for all the catalysts. From these CVs, their ECSAs were determined by integrating the area bounded by the hydrogen adsorption curve and the baseline in the range of 0.05-0.4 V (Table 1). The detailed calculation with appropriate formula and method are also provided in Supplementary information (S1). The increase in ECSA of octahedral NCs than spherical NCs should be attributed to optimize dispersion and size distribution of the octahedral NCs on GO, which can further improve the electrocatalytic activity of octahedral NCs.

The enhancement factor for electrocatalytic activity of octahedral NCs over spherical NCs is also measured theoretically from surface area to volume (S/V) ratio concepts of bulk materials. As for the bulk material S/V values are slightly higher for octahedral crystals than the spherical crystals by a factor of 1.15, which can lead to the enhancement of surface properties of octahedral crystals than the spherical. In case of nanoparticles S/V values have significant effect on their properties. As the S/V values increases with the decrease in crystallite size of the material. Therefore as particle size decreases, a greater portion of the atoms are found at the surface compared to those inside. Therefore, nanoparticles have much greater surface area per unit volume compared with the larger particles. It leads to nanoparticles more chemically reactive. As growth and catalytic chemical reaction occurs at surfaces, therefore a given mass of nanomaterial will be much more reactive than the same mass of material made up of large particles. It is also found that materials which are inert in their bulk form are reactive when produced in their nanometric scale. It can improve their properties.

In our studies the granulometric data obtained from SEM is used to calculate S/V values of NCs, calculated in the Supplementary information (S2). The S/V value for octahedral NCs is higher than that of spherical NCs by a factor of 1.2 which is slightly higher and nearly equal to the bulk calculated value. This enhancement in S/V for octahedral NCs can explain the enhancement in their electrocatalytic properties and enhancement of S/V factor value over bulk material can explain the nano sized confirmation of NCs with higher surface catalytic properties over bulk materials.

HER performance is presented here in Figure 6. The onset potential is measured by tangent method. From the figure, it is clear that the onset potential for evolution of adsorbed hydrogen on the surface active sites of the catalyst is more near towards zero for octahedral NCs than that of spherical NCs. This confirms that octahedral NCs could show better performance as anode material for DMFCs. This argument is further proved by MOR measurements.

The electroactivity of Pd spherical and octahedral nanocrystals towards methanol oxidation in 0.1 mol L\(^{-1}\) HClO\(_4\) + 1 mol L\(^{-1}\) CH\(_3\)OH solution at a scan rate of 50 mV s\(^{-1}\) are demonstrated in Figure 7. The current density is normalized to the geometric surface area to make a comparison of the two catalysts loaded on same electrode surface metal oxidation/reduction region (0.4 V) on the CV curves. The current density is normalized to the geometric surface area to make a comparison of the two catalysts loaded on same electrode.

Table 1. Comparison of ECSA and current density values for both the catalysts w.r.t different parameters.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ECSA cm(^{-2})</th>
<th>ECSA cm(^{-2}) (\times 10^3)</th>
<th>(J^a)</th>
<th>(J^b)</th>
<th>(J^c)</th>
<th>(J^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/Pd-01</td>
<td>0.245</td>
<td>8.3</td>
<td>4.3</td>
<td>3.56</td>
<td>100</td>
<td>5300</td>
</tr>
<tr>
<td>GO/Pd-02</td>
<td>0.067</td>
<td>2.2</td>
<td>2.0</td>
<td>1.95</td>
<td>60</td>
<td>1800</td>
</tr>
</tbody>
</table>

\(J^a = mA\cdot cm^{-2}\) w.r.t GSA, \(J^b = mA\cdot cm^{-2}\) w.r.t ECSA, \(J^c = \mu A\cdot cm^{-2}\) w.r.t ECSA, \(J^d = mA\cdot mg^{-1}\) w.r.t mg of catalyst.
on the other hand, spherical nanocrystals became unable to oxidize the intermediate in the electro oxidation mechanism of methanol. The reason is that in Pd octahedral nanocrystals, which is characterized by CA measurements up to 300s at constant voltage 0.30 V, 0.40 V and 0.50 V demonstrated in Figure 8. This increase of oxidation current is also characterized by CA measurements up to 300s at constant potentials of 0.30 V, 0.40 V and 0.50 V demonstrated in Figure 8. This CA measurement clearly showing the increase of oxidation current from lower potential to higher potential with maximum stability for 300s for both the catalysts. The current work, not only gives a simple method to synthesize Pd nanocrystals with special facets on graphene oxide, but also offers a comparative analysis among both NCs. Together with the use of specific strong adsorbates to control the surface structure of Pd nanocrystals, the shape-control strategy, hydrogen evolution reaction activity and methanol oxidation reaction active catalyst reported here could provide a new research avenue to further enrich the Pd based nanocrystals.

5. CONCLUSIONS

In conclusion, palladium octahedral and spherical nanocrystals with uniform morphology were successfully synthesized in the presence of hydrogen and carbon monoxide, respectively. The as made Pd nanocrystals are bound with \{111\} facets. The electrocatalytic activity as an anode material for DMFCs with comparative study shows that Pd octahedral nanocrystals have good affinity towards methanol oxidation with an improved catalytic activity over that of Pd spherical nanocrystals of similar facets, which was formerly characterized and proved by HER performance for both the nanocrystals. The current work, not only gives a simple method to oxidize Pd nanocrystals with special facets on graphene oxide, but also offers a comparative analysis among both NCs. Together with the use of specific strong adsorbates to control the surface structure of Pd nanocrystals, the shape-control strategy, hydrogen evolution reaction activity and methanol oxidation reaction active catalyst reported here could provide a new research avenue to further enrich the Pd based nanocrystals.

6. SUPPLEMENTARY INFORMATION

S1. Measurement of Electrochemical Active Surface Area (ECAS)

\[ A = \frac{Q^e}{\eta} \] gives the electrochemically accessible area of Pd in the electrode

where \( Q^e = 212 \mu C/cm^2 \);

\[ Q_R = \frac{\int i \cdot dS}{v} \]

Scan rate (v) = 50mv/s

\( \int i \cdot dS \) is the area from the hydrogen desorption region given in the following figures.

Figure 8. CA results of MOR activity for Pd octahedral (GO/Pd-01) and Pd spherical (GO/Pd-02) nanocrystals in 0.1 M HClO4 + 1M CH3OH at constant voltage 0.30 V, 0.40 V and 0.50 V up to 300s time.
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**a. For GO/Pd-01 (Octahedral NPs)**

\[ \int 1 \cdot dE = \int A \cdot V \sim \int \frac{1}{\theta} \cdot dE \sim \int 0.95 \cdot V \sim 0.95 \cdot \theta \]

\[ A_{\text{real}} = \frac{0}{A} \cdot \left( \frac{0.883552}{(1.11/1.12)} \right) = 0.245 \text{ cm}^2 \]

\[ \theta = \text{Pd loading} \cdot \left( \frac{1}{\text{cm}^2} \right) \cdot \text{area of the electrode,} \frac{0.196}{(15\%)} \]

\[ E \text{SA} = 0.245 \cdot \text{cm}^2 \cdot \frac{\text{m}g}{\text{Pd}} \]

**b. For GO/Pd-02 (Spherical NPs)**

\[ \int 1 \cdot dE = 0.2 \cdot A \cdot V \sim \int \frac{1}{\theta} \cdot dE \sim \int 0.95 \cdot V \sim 0.95 \cdot \theta \]

\[ A_{\text{real}} = \frac{0}{A} \cdot \left( \frac{0.883552}{(1.11/1.12)} \right) = 0.067 \text{ cm}^2 \]

\[ \theta = \text{Pd loading} \cdot \left( \frac{1}{\text{cm}^2} \right) \cdot \text{area of the electrode,} \frac{0.196}{(15\%)} \]

\[ E \text{SA} = 0.067 \cdot \text{cm}^2 \cdot \frac{\text{m}g}{\text{Pd}} \]

**S2. Measurement of Specific Surface area to Volumen Ratio (and a Factor) from Granulometric Data of Octahedral and Spherical NPs**

**a. For GO/Pd-01 (Octahedral NPs)**

\[ S_{\text{eef}} = 2a^2 \sqrt{2} \]

\[ V_{\text{eef}} = \frac{1}{3} a^3 \sqrt{2} \]

\[ \frac{S_{\text{eef}}}{V_{\text{eef}}} = \frac{3\sqrt{6}}{a} \]

\[ a = 34 \text{ nm (average edge length obtained from SEM granulometric data)} \]

\[ \frac{S_{\text{eef}}}{V_{\text{eef}}} = 0.21 \]

**b. For GO/Pd-01 (Spherical NPs)**

\[ S_{\text{sphere}} = 4\pi a^2 \]

\[ V_{\text{sphere}} = \frac{4}{3} \pi a^3 \]

\[ \frac{S_{\text{sphere}}}{V_{\text{sphere}}} = \frac{3\sqrt{6}}{a} \]

\[ a = 33 \text{ nm (average edge length obtained from SEM granulometric data)} \]

\[ \frac{S_{\text{eef}}}{V_{\text{eef}}} = 0.17 \]

From above obtained values the specific surface area of octahedral NPs is slightly higher than that of spherical NPs (by a factor of 1.2).

**7. ACKNOWLEDGMENTS**

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**REFERENCES**


**Table S1: Measurement of crystallite size from XRD data using Debay-Sherrer Equation**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Width</th>
<th>2θ (deg)</th>
<th>(hkl)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/Pd-01</td>
<td>2.36</td>
<td>40.1</td>
<td>111</td>
<td>40.11</td>
</tr>
<tr>
<td>Octahedral NPs</td>
<td>1.98</td>
<td>46.7</td>
<td>200</td>
<td>34.37</td>
</tr>
<tr>
<td></td>
<td>1.40</td>
<td>68.1</td>
<td>220</td>
<td>34.37</td>
</tr>
<tr>
<td>GO/Pd-02</td>
<td>2.26</td>
<td>40.1</td>
<td>111</td>
<td>38.30</td>
</tr>
<tr>
<td>Spherical NPs</td>
<td>1.94</td>
<td>46.7</td>
<td>200</td>
<td>33.70</td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td>68.1</td>
<td>220</td>
<td>26.51</td>
</tr>
</tbody>
</table>

Average crystallite size for GO/Pd-01 = 33.78
Average crystallite size for GO/Pd-02 = 32.83
Figure S1: Characterizations of synthesized Graphene Oxide (a) TEM image, (b) FTIR spectrum, (c) UV-vis spectrum and (d) CV in 0.1 mol.L\(^{-1}\) HClO\(_4\) at a scan rate of 50 mV.s\(^{-1}\) vs RHE.

Figure S2: CVs of Pd octahedral (GO/Pd-01) nanocrystals after different cleaning treatments, in 0.1 mol.L\(^{-1}\) HClO\(_4\) at a scan rate of 50 mV.s\(^{-1}\) vs RHE.

Figure S3: CVs of Pd spherical (GO/Pd-02) nanocrystals after different cleaning treatments, in 0.1 mol.L\(^{-1}\) HClO\(_4\) at 50 mV.s\(^{-1}\) vs RHE.