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Graphene-supported palladium phosphide PdP₂ nanocrystals for ethanol electrooxidation

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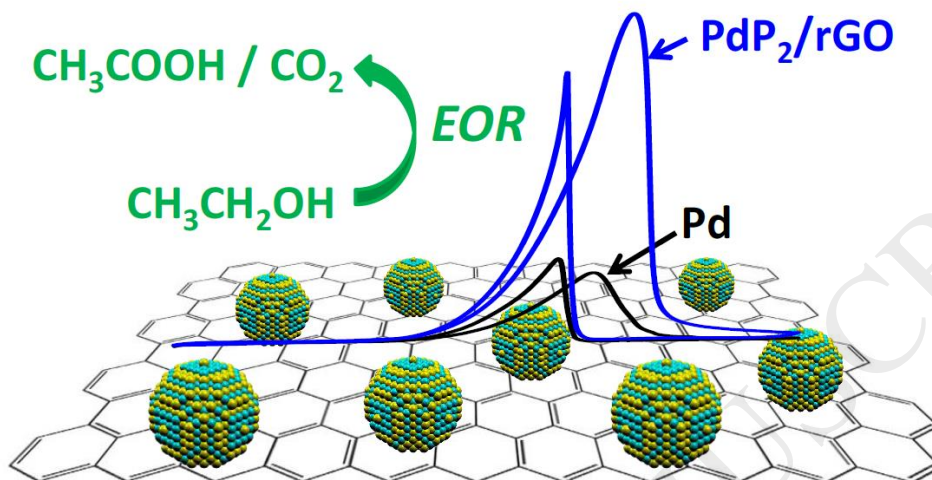
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Graphical abstract



Highlights

- A new procedure was developed to produce single-phase PdP₂ crystals in the nanometer size region.
- PdP₂ nanocrystals were applied as electrocatalysts for ethanol oxidation reaction for the first time.
- PdP₂ nanocrystals supported on reduced graphene oxide showed excellent performances, comparable to the best Pt- and Pd- based catalysts.
- PdP₂ and PdP₂/rGO nanocrystal-based catalysts demonstrated improved stability when compared with Pd and Pd/rGO.

ABSTRACT

We present a procedure to produce single-phase PdP₂ nanocrystals (NCs). The approach involves the reaction of palladium(II) acetylacetonate and hexamethylphosphorotriamide to nucleate defective Pd₅P₂ nanoparticles that subsequently, with further phosphorous incorporation,

crystallize into PdP₂. The synthesized PdP₂ NCs were supported on reduced graphene oxide (rGO) and applied as electrocatalysts for ethanol oxidation. The activity of PdP₂ toward the ethanol oxidation reaction (EOR) was over a threefold higher than that of Pd NCs prepared under similar conditions. Even better performance was obtained from PdP₂ NCs supported on rGO, which showed current densities up to 51.4 mA cm⁻² and mass activities of 1.60 A mg⁻¹_{Pd}, that is 4.8 and 15 times higher than Pd NCs. Besides, PdP₂ NCs and PdP₂/rGO catalysts showed improved stability during EOR than Pd NCs and Pd/rGO.

Keywords: Palladium diphosphide; colloidal synthesis; electrocatalysis; ethanol oxidation

1. Introduction

Direct liquid fuel cells are electrochemical devices able to directly convert chemical energy stored within liquid fuels into electricity. Among the possible liquids, ethanol has a high energy density (8.01 KW h kg⁻¹) [1,2], low toxicity, a relatively high boiling point for safe storage and transportation, and the potential to be bio-sourced in large quantities from the fermentation of biomass. Owing to these advantages, direct ethanol fuel cells (DEFCs) have become one of the most appealing alternatives to electrochemical batteries and conventional fossil fuel-based combustion engines in numerous fields of application. However, the high price and limited performance of current fuel oxidation electrocatalysts is limiting their deployment. These limitations, extensive to most fuel cell technologies, are particularly severe in DEFCs since the complete ethanol oxidation reaction (EOR) involves the release of 12 electrons per molecule and the cleavage of a C-C bond.

Extensive research on electrocatalysts for DEFCs has been carried out on acidic conditions, which allow taking advantage of convenient proton exchange membranes for the device fabrication. However, the slow reaction kinetics and low stability of electrocatalysts in these conditions are very tough barriers to be overcome [3,4]. As an alternative, effort has been moved toward developing electrocatalysts for alkaline-type DEFCs. The enhanced kinetics of the catalytic

reaction in alkaline solution increases the efficiency in the use of precious metals and even permits the use of less expensive catalysts.

Pt and Pt-based alloys have been extensively studied as the most active catalysts for DEFCs. Alternatively, Pd is a more abundant and less demanded element, what currently translates in significantly lower costs. Pd [5] and Pd-based electrocatalysts, such as PdNi [6,7], Pd₂Ru [8], PdCu [9-11], PdAu [12] and Pd₂Sn [4,13], have demonstrated electrocatalytic activities in the electrooxidation of different types of liquid fuels and particularly ethanol comparable to those of Pt-based catalysts. Pd and Pd-based materials are also excellent catalysts for the Suzuki coupling reaction [14-16] and oxygen reduction reaction [17]. An especially interesting case is that of Pd-based phosphides, which have shown excellent activity toward hydrogen evolution, oxygen reduction, formic acid oxidation and hydrodesulfurization [18,19]. Additionally, palladium phosphides are characterized with high electrical conductivities and show improved corrosion resistance with respect to Pd. However, surprisingly, palladium phosphides have not been investigated as electrocatalysts for the EOR.

Actually, few attempts have been done to produce palladium phosphide NCs at all. Most attempts to produce palladium phosphides were based on the reaction of premade Pd with a phosphorus precursor such as trioctylphosphine (TOP) or white phosphorous at relatively high temperatures [18,20-22]. Following this strategy, quasi amorphous palladium phosphide particles with irregular shapes and broad size distributions were obtained [21,22]. The synthesis of crystalline palladium phosphide NCs have proved to be very challenging. Single-phase Pd₅P₂ crystallites with a few hundred nanometers were prepared using Pd(acac)₂ as metal precursor and TOP as phosphorus precursor [19]. Using the same strategy, Pd₅P₂ nanoparticles encapsulated within mesoporous silica were also prepared [19].

Herein, we report a procedure to produce single-phase colloidal PdP₂ NCs. Compared with previous synthesis strategies based on the reaction of premade metallic Pd with a phosphorous source, our protocol involved the nucleation of Pd₅P₂ and their subsequent crystallization and growth into PdP₂ NCs with the incorporation of additional P. After ligand exchange, PdP₂ NCs were uniformly deposited on reduced graphene oxide sheets and tested as electrocatalysts for the EOR.

2. Experimental

2.1. Chemicals

Hexamethylphosphorotriamide (HMPT, 97 %), and palladium(II) acetylacetonate ($\text{Pd}(\text{acac})_2$, Pd 34.7 wt%) were purchased from Alfa Aesar. Oleylamine (OAm, approximate C18 content 80-90 %) was purchased from ACROS Organics. TOP (97 %), methylamine hydrochloride (MAHC, 98 %), ammonium thiocyanate (NH_4SCN , 99 %), ammonium chloride (NH_4Cl , 99.5 %), potassium hydroxide (KOH, 85 %), Nafion (5 wt% in a mixture of low aliphatic alcohols and water), graphite, potassium permanganate (KMnO_4 , 99 %), sodium nitrate (NaNO_3 , 99 %), sulfuric acid (H_2SO_4 , 95-98 %), hydrochloric acid (HCl, 37 %), hydrogen peroxide (H_2O_2 , 30 wt% in H_2O) were obtained from Sigma-Aldrich. Chloroform, ethanol and acetone were of analytical grade and obtained from various sources. MilliQ water was obtained by using a PURELAB flex from ELGA. All chemicals were used as received without further purification.

2.2. Synthesis of PdP_2 NCs

Caution: Because this procedure involves the use and high-temperature decomposition of HMPT that can liberate toxic and flammable phosphine gas or toxic phosphorus oxides, the reaction should only be carried out by appropriately trained personnel using rigorously air-free conditions and the Schlenk line should be connected with gas absorption solutions.

In a typical synthesis, 60.9 mg (0.2 mmol) of $\text{Pd}(\text{acac})_2$, 67.5 mg (1 mmol) of MAHC or 53.5 mg (1 mmol) ammonium chloride, and 10 mL of OAm were mixed in a 50 mL three-neck flask. The reaction system was purged with argon at 120 °C for 1 h. Then 0.1 mL (0.57 mmol) of HMPT was injected into the solution and the temperature was further increased to 300 °C in 20 min. During the heating up, the solution became black at around 250 °C. The flask was maintained at 300 °C for 1 h before the solution was allowed to cool to room temperature. The isolation of the resultant black precipitate was achieved with excess ethanol followed by centrifugation at 5000

rpm (3200 g). Purification was achieved by multiple dispersion/precipitation steps using chloroform and ethanol. Finally the powder was suspended in 5 mL of chloroform in a vial.

2.3. Synthesis of Pd NCs

Reference Pd NCs were prepared in a similar way as PdP₂ NCs, i.e. by mixing the same amounts of Pd(acac)₂, MAHC and OAm and at the same condition as in the synthesis of PdP₂ NCs, but without injection of HMPT. The reaction was kept at 300 °C for 1 h and then washed following the same procedures as in the synthesis of PdP₂ NCs.

2.4. Synthesis of rGO

Graphene oxide was produced by a modified Hummers method as originally presented by Kovtyukhova [23]. Briefly, in a 500 mL flask, 2.0 g of graphite, 1.5 g of NaNO₃ and 96 mL of concentrated H₂SO₄ were vigorously stirred in ice-water bath. Then, 9.0 g of KMnO₄ was slowly added to the flask over 30 min. Stirring was continued for 1.5 h in the ice-water bath and then followed by another 2 h at 35 °C. Afterward, 280 mL of H₂O was added into the mixture. During the process, the solution was heated to 98 °C and kept at this temperature for 2 h. 5 mL of 30 wt% H₂O₂ were added to the solution after the temperature was decreased to 60 °C. To remove ionic impurities, the obtained solution was washed by vacuum filtration and rinsing with aqueous 3 wt% HCl for 3 times, followed by H₂O for another 3 times. The resulting product was dried under vacuum at 60 °C and then calcined in a tube furnace at 500 °C for 2 h in flowing argon. As a result, the reduced graphene oxide (rGO) was obtained.

2.5. Ligand exchange

The ligand exchange procedure used here was similar to that previously reported by Fafarman et al. [24]. In a typical procedure, 0.5 mL of 130 mM NH₄SCN in acetone was added to 1 mL of a dispersion of as-synthesized PdP₂ NCs in chloroform (~10 mg in 1 mL). The resulted solution was agitated for 1 min; a complete flocculation was observed within seconds. The slurry was centrifuged at 3000 rpm (1200 g) for 1 min and the supernatant discarded. Another 1 mL of acetone was added to the precipitate; the mixture was sonicated for 1 min and followed by centrifuge at

3000 rpm for 1 min. The washing steps were repeated another time and the obtained precipitate was dried at room temperature.

2.6. Catalyst preparation

The catalyst ink for electrochemical measurements was prepared by mixing 5 mg of PdP₂ NCs and 5 mg of rGO in 5 mL of deionized water. The mixture was sonicated for 1 h to form a homogeneous catalyst ink. For comparison, catalysts of Pd, Pd/C, Pd/rGO and PdP₂ were also prepared through dissolving 10 mg of as-synthesized Pd, Pd and rGO (1:1 weight ratio) or PdP₂ NCs in 5 mL of deionized water by sonication for 1 h.

The working electrode was prepared using a glassy carbon electrode (GCE, 5 mm in diameter) which was previously polished using diamond paper and 0.05 μm alumina slurry sequentially, followed by ultrasonication in ethanol first and water later, for 1 min each. The cleaned GCE was dried under argon flow at room temperature. The electrode was modified by drop casting 10 μL of the catalyst ink and posterior drying at room temperature. To immobilize the catalysts on the electrode, 10 μL of a 0.5 wt% Nafion solution was dropped on the surface of the electrode.

2.7. Electrochemical measurements

Electrochemical measurements were conducted at room temperature on a BioLogic electrochemical workstation using a standard three-electrode cell with the modified GCE as working electrode, a Pt mesh as counter electrode and Hg/HgO (1 M KOH) as reference electrode. All the cyclic voltammetry (CV) measurements were conducted at room temperature. The electrolyte solutions were purged with argon for 30 min before use. The background was obtained by CV measurement in 0.5 M KOH solution from -1.0 to 0.3 V vs. Hg/HgO at 50 mV s^{-1} . Afterward, for EOR measurement, the working electrodes were tested in 0.5 M KOH with 0.5 M ethanol solution under the same conditions. The chronoamperometry measurements were conducted at -0.1 V vs. Hg/HgO for 10000s in the electrolyte of 0.5 M KOH and 0.5 M ethanol in order to evaluate the stability of the catalysts.

2.8. Characterization

Transmission electron microscopy (TEM) characterization was carried out using a ZEISS LIBRA 120, operating at 120 kV and a JEOL 1011 operating at 100 kV. Carbon-coated TEM grids from Ted-Pella were used as substrates. High-resolution TEM (HRTEM) studies were conducted using a field emission gun FEI™ Tecnai F20 microscope at 200 kV with a point-to-point resolution of 0.19 nm. Annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai F20, by using a GATAN QUANTUM filter. Scanning electron microscopy (SEM) analyses were done in a ZEISS Auriga microscope with an energy dispersive X-ray spectroscopy (EDS) detector operating at 20 kV. Powder X-ray diffraction (XRD) patterns were collected directly from the as-synthesized NCs dropped on Si (501) substrate on a Bruker-AXS D8 Advanced X-ray diffractometer with Ni-filtered (2 μm thickness) Cu K radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. A LynxEye linear position-sensitive detector was used in reflection geometry. X-ray photoelectron spectroscopy (XPS) was done on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos 150 MCD-9 detector. The pressure in the analysis chamber was below 10^{-7} Pa. The area analyzed was about $2 \text{ mm} \times 2 \text{ mm}$. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). Binding energy values were centered using the C 1s peak at 284.8 eV. Fourier transform infrared spectroscopy (FTIR) was performed on an Alpha Bruker FTIR spectroscopy with a platinum attenuated total reflectance (ATR) single reflection module. FTIR spectra data were recorded from 400 cm^{-1} to 4000 cm^{-1} .

3. Results and discussion

3.1. NC synthesis

PdP₂ NCs were produced within OAm from the reaction of Pd(acac)₂ with HMPT in the presence of MAHC (see details in the experimental section). All elements were introduced in the reaction flask at a low temperature and the mixture was heated up to 300 °C. During the heating up process, the solution became black at around 250 °C, indicating the precursor reaction at this temperature.

Figure 1a shows a TEM micrograph of the NCs obtained after 1 h reaction at 300 °C. NCs showed elongated, tear drop-like geometry and had an average size of its longer axis of 12 ± 2 nm. XRD patterns showed the NCs to have a PdP₂ monoclinic phase, with I2/c space group (**Figure 1b**). No additional XRD peak corresponding to secondary crystal phases was detected. HRTEM analysis confirmed the monoclinic phase of the NCs and allowed determining the lattice parameters: $a = 6.207$ Å, $b = 5.857$ Å and $c = 5.874$ Å (**Figure 2a**). Annular dark field scanning TEM (ADF-STEM) and STEM-EELS elemental composition maps revealed all NCs to contain Pd and P and to have both elements uniformly distributed throughout each NC (**Figure 2b**). SEM-EDS analysis showed the NCs to have an atomic ratio of P/Pd = 2.0 (**Figure S1**).

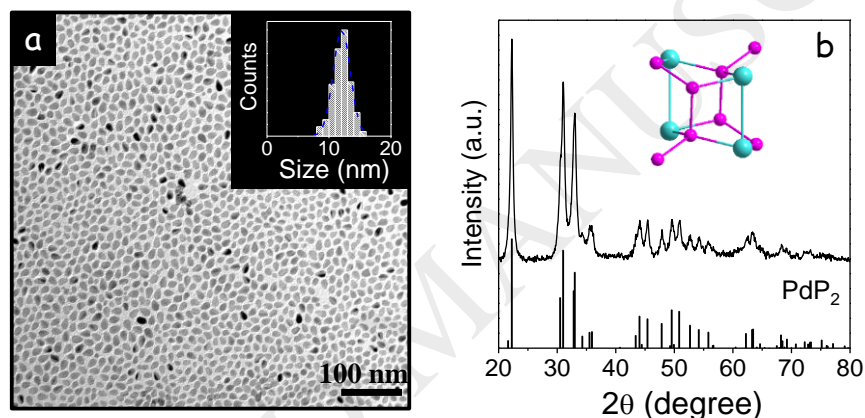


Figure 1. a) Representative TEM micrograph of PdP₂ NCs. Inset shows their size (long axis) distribution histogram. b) XRD pattern of PdP₂ NCs including the JCPDS 77-1421 reference. Inset shows a unit cell of the PdP₂ monoclinic phase (Pd in blue and P in pink).

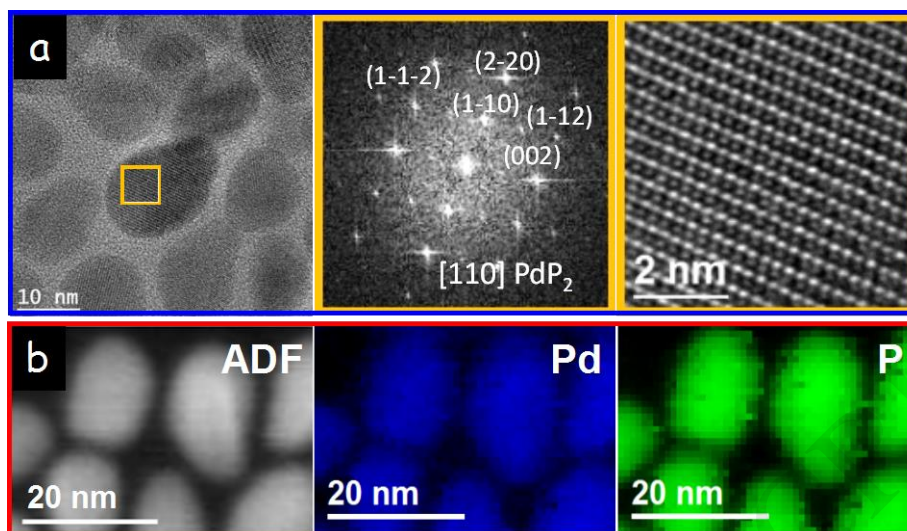


Figure 2. a) HRTEM image of several PdP₂ NCs and power spectrum fitting with the PdP₂ phase of one of them. b) ADF-STEM image of several PdP₂ NCs and EELS compositional maps for Pd (blue) and P (green).

To gain inside of the NC growth mechanism, aliquots were extracted at different reaction times. Spherical nanoparticles with a highly defective/disordered Pd₅P₂ phase, as deduced from the XRD band at about $2\theta = 40^\circ$, and an average size of 7 nm were recovered from aliquots extracted after 1 min reaction at 300 °C (**Figure S2 and S3**). As the reaction time increased, additional P was progressively incorporated into the Pd₅P₂ nanoparticles, which crystallized into elongated PdP₂ NCs (**Figure S2 and S3**).

To determine the role of MAHC in the synthesis, the reaction was performed in the absence of this compound. In these conditions, before adding the P precursor, the solution changed to black at 120 °C, during the heating up process. XRD analysis of the recovered solid showed that it consisted of Pd (**Figure S4**). We conclude that in the absence of MAHC, the Pd precursor is reduced by OAm at low temperature, resulting in the formation of Pd NCs. Once HMPT was injected in the solution containing the reduced Pd precursor, Pd NCs reacted with P to produce very small Pd-P nanoparticles, which after reaction at 300 °C for 1 h resulted in a mixture of small Pd₅P₂ and PdP₂ NCs (**Figure S5**).

In the presence of 0.2 mmol of MAHC, the precursors reacted at higher temperature, about 250 °C, indicating that the presence of MAHC prevented the reduction of the Pd precursor by OAm. After reacting at 300 °C for 1 h, teardrop shaped PdP₂ NCs with some spherical Pd₅P₂ particles were obtained. With larger amounts of MAHC, the shape of the NCs became uniform and less spherical Pd-P quasi-amorphous particles were observed in the products (**Figure S6**). This last point was followed by the decrease of the XRD band at about $2\theta = 40^\circ$ assigned to a disordered/defective Pd₅P₂ phase (**Figure S7**), which was observed to decrease with the amount of MAHC introduced. This band completely disappeared when 1 mmol MAHC was present in the reaction system. At this point, pure phase PdP₂ NCs were obtained.

To elucidate the role of chlorine and the amine group of MAHC, the synthesis was carried out in the presence of NH₄Cl instead of MAHC. In these conditions, a similar reaction temperature with respect to the presence of MAHC, as observed from the color change of the solution, and a similar product was obtained (**Figure S8**). This experimental result pointed toward Cl⁻ ions having a main role on the stabilization of the Pd precursor in solution, preventing its reduction with OAm and yielding pure phase PdP₂ when reacting with the P source. This result also demonstrates that ammonium chloride could be used instead of MAHC for the synthesis of PdP₂ NCs. However, all the following results were obtained using PdP₂ NCs produced in the presence of MAHC.

To determine the role of the P precursor, HMPT was replaced by TOP. Using TOP, no NCs were obtained at 300 °C, which we associated to the much lower reactivity of TOP when compared with HMPT. When reacting at 350 °C for 1 h, irregular and large-size NCs were produced (**Figure S9**). XRD and EDS showed these NCs to consist of a mixture of Pd₅P₂ and PdP₂ phases (**Figure S10**). In this case, the produced NCs were irregular in shape and highly polydisperse in size.

Figure 3 shows the Pd 3d and the P 2p XPS spectra of the PdP₂ NCs. Two doublets were fitted to the Pd 3d states. The main Pd component, accounting for 64 % of the total Pd detected, was found at a Pd 3d_{5/2} binding energy 335.9 eV. This binding energy was slightly above that of Pd(0) in pure Pd (335.1-335.5 eV) [25,26], which is consistent with the chemical environment of Pd within a Pd phosphide. A more oxidized component, accounting for 36% of the Pd detected, was

found at a Pd 3d_{5/2} binding energy of 337.7 eV. This component was assigned to Pd(II) species at the surface of the air-exposed NCs that had undergone oxidation [27].

Two P chemical states were also identified from XPS analysis of the P 2p electronic states. A main P 2p_{3/2} peak at 130.3 eV matched well with P in a metal phosphide environment. This component accounted for 64 % of the detected P. The second component, accounting for 36 % of the P detected, was found at a higher binding energy, P 2p_{3/2} peak at 134.1 eV, and it was assigned to a phosphate environment. We believe this phosphate to result from the partial oxidation of the PdP₂ surface due to air exposure [28-30].

The atomic ratio of Pd and P at the NC surface detected by XPS was approximately 1, which points toward a Pd enriched surface compared to the PdP₂ core.

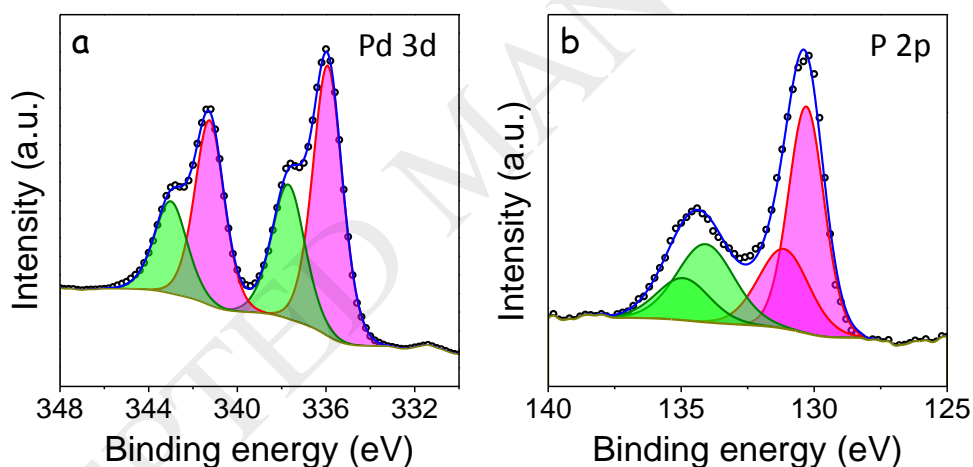


Figure 3. XPS spectra of PdP₂ NCs in the Pd 3p (a) and P 2p (b) regions.

3.2. NC surface treatment and catalyst preparation

FTIR spectra of as-produced PdP₂ NCs displayed peaks at 2920 and 2852 cm⁻¹ attributed to the C-H stretching vibration of the alkyl group of OAm (**Figure 4**). Additionally, peaks attributed to the bending vibration of C-H in alkyl and alkenyl part of OAm, at 1457 and 968 cm⁻¹, and to the bending vibrations of N-H and C-N, at 1551 and 1059 cm⁻¹, were also identified. These features were slightly shifted compared with pure OAm, consistently with its binding to the NC surface.

While the presence of OAm at the NC surface rendered the NCs colloidally stable in non-polar solvents and limited their growth, OAm might also block catalytic sites and hinder charge transfer. Thus, it had to be removed prior to NC catalytic application.

OAm was displaced from the NC surface using a short inorganic ligand, ammonium thiocyanate, following the procedure reported by Fafarman et al. (see experimental section for details) [24]. FTIR spectra of the NCs after ligand displacement with ammonium thiocyanate showed the presence of peaks at 2045 and 1596 cm^{-1} , assigned to the $\text{C}\equiv\text{N}$ antisymmetric and asymmetric vibration, and a broad peak at ca. 1400 cm^{-1} corresponding to the N-H stretching vibration of the amino group of ammonium thiocyanate (NH_4SCN).

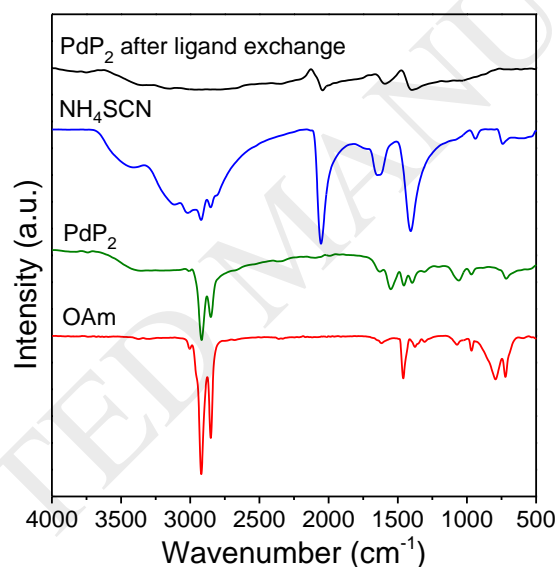


Figure 4. FTIR of OAm, NH_4SCN , as-synthesized PdP_2 NCs and PdP_2 after ligand exchange by NH_4SCN .

Electrocatalysts were prepared by supporting the colloidal PdP_2 NCs onto reduced graphene oxide (rGO). Graphene is considered an ideal electrocatalyst support owing to its excellent electric conductivity, large surface area, superior mechanical flexibility and chemical stability [31]. The use of graphene as the support material not only improves the electrical conductivity of the nanocomposite catalyst, but also increases the dispersion of the active components, which helps to

prevent their aggregation during the catalytic reaction. Graphene oxide (GO) sheets were prepared here by a modified Hummers method as presented by Kovtyukhova [23], and then reduced to rGO at high temperature (**Figure S11**). rGO exhibited a rippled and crumpled morphology and paper-like structure with single or few layers (**Figure 5**), offering a large surface area to support the PdP₂ NCs. PdP₂ NCs were supported by mixing the proper amount of rGO and PdP₂ NCs in water (see experimental section for details). As shown in **Figure 5**, PdP₂ NCs were homogeneously distributed on the rGO sheet after solvent removal. The nanocomposite was drop-casted onto GCE and then dried at room temperature. On top of it, Nafion was deposited to immobilize the catalysts on the electrode (see details in the experimental section).

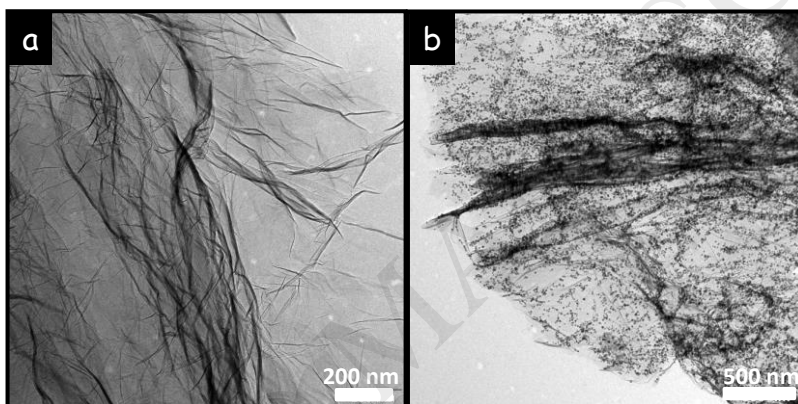


Figure 5. TEM images of as-prepared rGO (a) and PdP₂/rGO (b) catalyst.

3.3. Cyclic voltammetry in base solution

CV of PdP₂/rGO, unsupported PdP₂, 12 ± 3 nm Pd (**Figure S12**) and Pd/rGO electrocatalysts was initially investigated in a 0.5 M KOH aqueous solution (**Figure 6a**). The same total amount of catalyst was used to produce each of the tested electrodes, which translated into significantly lower amounts of Pd in the PdP₂ and especially on the PdP₂/rGO catalysts.

All catalysts showed similar coulombic features, but with small differences in relevant regions of the voltammograms. The peaks in the region between -0.6 V and -0.8 V vs. Hg/HgO were attributed to the adsorption (cathodic scan) and desorption (anodic scan) of hydrogen. In the anodic scan, the PdP₂ catalyst showed a positive shift of peak potentials compared to Pd, while in the

cathodic scan, the PdP₂ showed a slight negative shift of the peak potential. The distinct anodic and cathodic behaviors of PdP₂ and Pd catalysts were related to their different electronic structure involving partial electron donation from Pd to P sites, consistent with XPS results [32].

The peaks in the anodic scan region from -0.4 to -0.2 V vs. Hg/HgO were attributed to the formation of palladium oxide on the NC surface. Subsequently, a PdO reduction peak appeared at about -0.2 V vs. Hg/HgO during the negative scans. The electrochemically active surface area (ECSA) of the catalysts was estimated from the coulombic charge for the reduction of PdO, i.e. from the area over the voltammetry curve in the PdO reduction peak region [13]:

$$ECSA = \frac{Q (\mu C \cdot cm^{-2})}{Q_{PdO} (\mu C \cdot cm_{Pd}^{-2}) \times Pd_{loading} (mg \cdot cm^{-2}) \times 10} \quad (1)$$

where $Q_{PdO} = 405 \mu C \text{ cm}^{-2}$ is the charge value given for the reduction of a PdO monolayer, the coulombic charge Q is calculated by integrating the area of the PdO reduction peak, and $Pd_{loading}$ is the Pd mass on the working electrode.

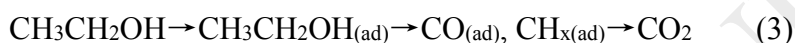
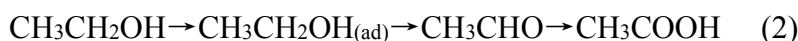
ECSA values obtained for Pd, Pd/rGO, PdP₂, and PdP₂/rGO catalysts were 49.4 m² g⁻¹, 63.8 m² g⁻¹, 97.9 m² g⁻¹, and 105.1 m² g⁻¹, respectively. The Pd utilization effectiveness was estimated taking into account that the active surface area for full utilization of 1 g of Pd would be 448 m² [13,33]. Thus, the Pd utilization efficiencies of PdP₂, PdP₂/rGO, Pd/rGO and Pd were 21.8 %, 23.4 %, 14.2 % and 11.0 %, respectively (**Figure 6e**).

Besides slight differences related to the dissimilar geometry and size of PdP₂ and Pd NCs, the larger ECSA and Pd utilization efficiency of PdP₂ over Pd demonstrated PdP₂ to have a highly Pd-rich surface, as observed from XPS measurements. The oxidation of PdP₂ beyond the surface monolayer could also partially explain the higher ECSA obtained for PdP₂. Besides, the slightly improved Pd utilization efficiency of PdP₂/rGO over unsupported PdP₂ might be attributed to the high surface area of rGO which allowed a better dispersion of the PdP₂ NCs.

3.4. Cyclic voltammetry in ethanol solution

The EOR electrocatalytic activities of Pd, Pd/rGO, PdP₂ and PdP₂/rGO catalysts were investigated in a 0.5 M KOH and 0.5 M ethanol aqueous solution (**Figure 6b**). CVs from all catalysts showed the two well defined anodic peaks associated with the ethanol oxidation in alkaline media, one in the forward and one in the reverse scan. The oxidation peak in the forward scan was associated with the oxidation of freshly chemisorbed species coming from ethanol adsorption. The oxidation peak in the reverse scan was related to the removal of carbonaceous species that were not completely oxidized in the forward scan.

The ethanol oxidation process may take place through two parallel pathways [8]:



In the path schematized in equation 2 (C2 pathway), the ethanol is first oxidized to acetaldehyde and subsequently to acetic acid or acetate in alkaline solution. The C-C bond is not broken during this pathway. In the path of equation 3 (C1 pathway), the C-C bond is broken and intermediate species such as CO and CH_x fragments are produced, which can be further oxidized to CO₂ or carbonate in alkaline solution.

During the positive scan, to reach a current density of 1 mA cm⁻², overpotentials of -0.48 V and -0.45 V vs. Hg/HgO were required for PdP₂/rGO and PdP₂, respectively, which was less than the overpotential required for Pd/rGO (-0.43 V vs. Hg/HgO) and Pd NCs (-0.41 V vs. Hg/HgO), indicating a lower activation energy for ethanol oxidation on PdP₂. The forward oxidation current peaked at around -0.12 V vs. Hg/HgO for Pd, -0.09 V for PdP₂, -0.07 V for Pd/rGO and -0.04 V for PdP₂/rGO (Table 1). Higher potentials resulted in a decrease of current density associated with the oxidation of the Pd surface. In the forward scan, peak current densities for the EOR in Pd, Pd/rGO, PdP₂ and PdP₂/rGO were 10.6, 16.9, 22.1 and 51.4 mA cm⁻², respectively (Table 1). When the values were normalized to reflect the amount of Pd, the mass peak current density of PdP₂ and PdP₂/rGO were 0.344 and 1.60 A mg⁻¹_{Pd}, respectively, which is ca. 3.3 and 15 times higher than that of Pd (0.104 A mg⁻¹_{Pd}), and 1.03 and 4.8 times higher than that of Pd/rGO (0.332 A mg⁻¹_{Pd})

(**Figure 6f**). Overall, PdP₂/rGO showed very high specific and mass activities toward the EOR, comparable to the best Pt- and Pd-based catalysts reported to date (**Figure 7**).

In terms of loading, while bare rGO showed no activity toward EOR (**Figure S13**), with the increasing amount of PdP₂ on rGO from 25% to 75%, the catalyst showed increasing specific activity and decreasing mass activity. A 50 wt% loading of PdP₂ on PdP₂/rGO was considered the best compromise and was the composition selected to carry on all measurements.

The ratio of the forward (J_F) and reverse (J_R) peak current densities was calculated to get insight of the reaction pathway: the higher the J_F/J_R ratio, the more efficient oxidation of ethanol and the less accumulation of carbonaceous species on the catalyst [4]. As calculated from **figure 6b**, the J_F/J_R ratios for Pd, Pd/rGO, PdP₂ and PdP₂/rGO were 0.82 and 1.00 to 0.99 and 1.22, respectively (**Table 1**). The increased ratio suggested more efficient ethanol oxidation process for PdP₂ and especially PdP₂/rGO than Pd.

To evaluate the stability of the catalysts, chronoamperometry (CA) measurements were carried out in a solution of 0.5 M KOH + 0.5 M ethanol with a constant applied potential of -0.1 V vs. Hg/HgO. As displayed in **figure 6c**, initial rapid decreases in current density were observed for all the catalysts, followed by a sluggish decrease until a pseudo-steady state. The sharp initial decrease was ascribed to the adsorption and accumulation of strongly adsorbed reaction intermediates on the surface of free active sites. Subsequently, the adsorption of ethanol depends on the liberation of the active sites resulting from the oxidation of ethanol or the intermediates that form during the initial state. After 10000 s activity, the current obtained from PdP₂ (0.90 mA cm⁻²) and PdP₂/rGO (1.56 mA cm⁻²) was much higher than that of Pd (0.15 mA cm⁻²) and Pd/rGO (0.57 mA cm⁻²). When comparing by mass activities, PdP₂/rGO (48.5 mA mg⁻¹_{Pd}) and PdP₂ (14.0 mA mg⁻¹_{Pd}) showed about 32 and 9.5 times higher values than Pd (1.47 mA mg⁻¹_{Pd}), and 4.3 and 1.3 times higher values than Pd/rGO (**Figure 6g**). Notice that no morphological or structural change of the NCs was observed to take place during EOR (**Figure S14**).

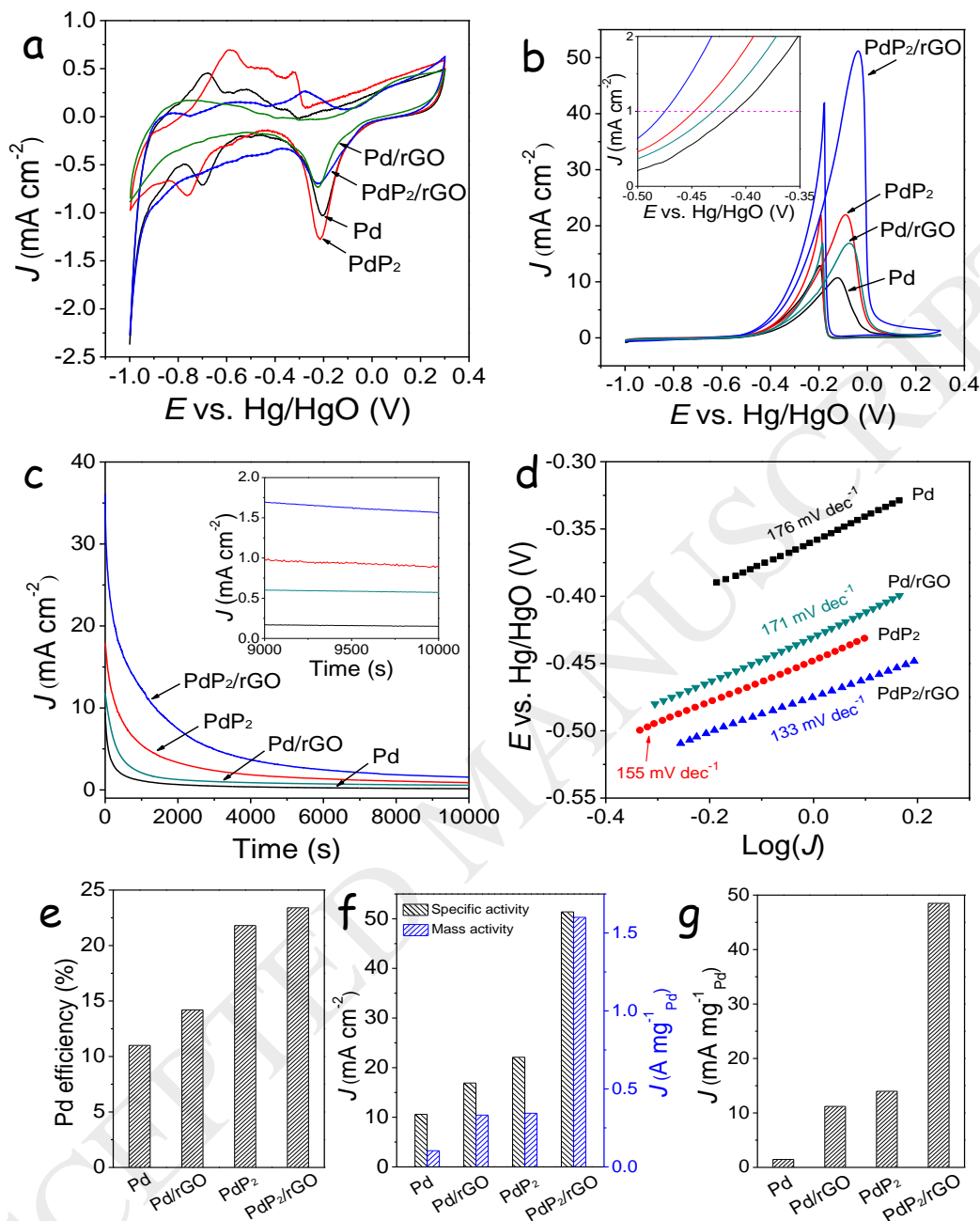


Figure 6. a) Cyclic voltammetry measurements of Pd, Pd/rGO, PdP₂ and PdP₂/rGO in a 0.5 M KOH solution and b) in a 0.5 M KOH + 0.5 M ethanol solution. c) Chronoamperometric measurements of Pd, Pd/rGO, PdP₂ and PdP₂/rGO in a 0.5 M KOH + 0.5 M ethanol solution at -0.1 V vs. Hg/HgO. d) Tafel plot of the Pd, Pd/rGO, PdP₂ and PdP₂/rGO. e) Comparison of Pd utilization efficiencies. f) Comparison of specific activity and mass activity of the Pd, Pd/rGO, PdP₂ and PdP₂/rGO. g) Mass activity after chronoamperometric measurement for 10000 s.

Table 1. Current density and potential at the forward and reverse peak and ratio of the peak current density between the forward and reverse oxidation peaks J_F/J_R .

Catalysts	Forward Scan		Reverse Scan		J_F/J_R
	E_F (V vs. Hg/HgO)	J_F (mA cm ⁻²)	E_R (V vs. Hg/HgO)	J_R (mA cm ⁻²)	
Pd	-0.12	10.6	-0.194	12.9	0.82
Pd/rGO	-0.07	16.9	-0.185	16.9	1.00
PdP ₂	-0.09	22.1	-0.192	22.3	0.99
PdP ₂ /rGO	-0.04	51.4	-0.178	42.1	1.22

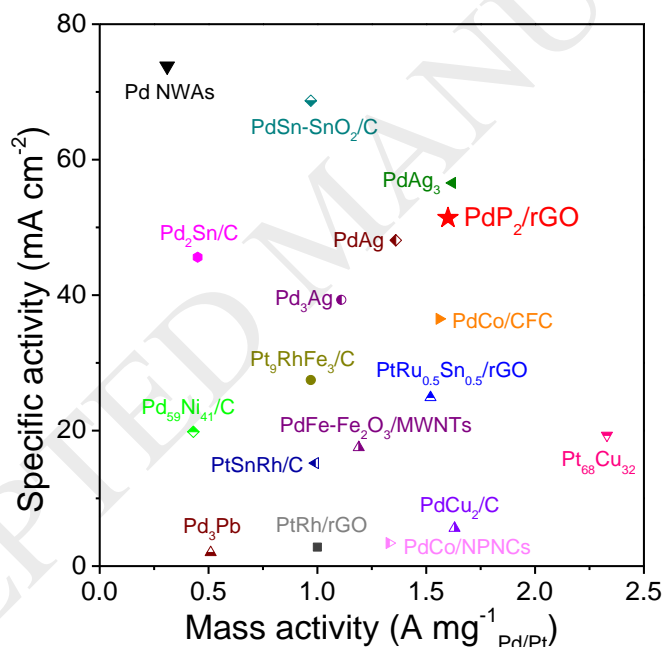


Figure 7. Specific and mass activities of the PdP₂/rGO electrocatalysts tested in the present work compared with reported best performing catalysts: PtRh/rGO [34], Pt₉RhFe₃/C [35], PtRu_{0.5}Sn_{0.5} [36], Pd₂Sn/C [4], Pd₅₉Ni₄₁/C [37], Pd₃Pb [38], PdCo/NPNCs [39], PdCu₂/C [40], PdFe-Fe₂O₃/MWNTs [41], Pt₆₈Cu₃₂ [42], Pd NWAs [43], PtCo/CFC [44], PdAg₃, PdAg and Pd₃Ag [45], PtCu [46], PtSnRh/C [47] and PdSn-SnO₂/C [48]. Abbreviations: reduced graphene oxide (rGO),

N-doped porous carbon nanocapsules (NPNCs), multiwalled carbon nanotubes (MWNTs), nanowire arrays (NWAs) and carbon fiber cloth (CFC).

Figure 6d shows a linear region of the Tafel plots obtained from the CV curves in the range from -0.5 to -0.3 V vs. Hg/HgO. As the potential further increased above -0.2 V, the Tafel plot became curved, indicating a change in the factor limiting the reaction rate. As shown in **figure 6d**, Pd NCs and Pd/rGO showed a Tafel slope of 176 and 171 mV dec⁻¹, well above that of PdP₂ and PdP₂/rGO, with Tafel slopes of 155 and 133 mV dec⁻¹, respectively. These values were close to the theoretical value for the EOR as calculated by Liang (120 mV dec⁻¹) [49]. The lower Tafel slopes indicated that the charge-transfer kinetics of the EOR on the PdP₂ and especially PdP₂/rGO catalysts were faster than that on Pd in the alkaline medium, which can be ascribed to the positive effect of P on the electronic state of Pd, the enhanced electron conductivity of rGO and the uniform dispersion of PdP₂ NCs on rGO.

4. Conclusions

In summary, single-phase PdP₂ NCs were produced in the presence of chlorine ions and using a highly active P precursor, HMPT. PdP₂ NCs showed high mass activity and long-term stability toward the EOR in alkaline media. The enhanced properties were attributed to the effect of P on the electronic structure of Pd and the Pd-rich surface of the produced PdP₂ NCs. The activity and stability of the PdP₂-based catalyst were further improved by supporting PdP₂ NCs onto rGO, taking advantage of an enhanced electrical conductivity and a high dispersion of the PdP₂ NCs. Additionally, the slower current decay over time combined with the higher measured activity for PdP₂ and PdP₂/rGO electrocatalysts when compared with Pd and Pd/rGO, indicated a higher tolerance to the carbonaceous species formed.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version.

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