

Supporting Information

Oxygen Reduction Reaction and Peroxide Generation on Shape-controlled and

Polycrystalline Platinum Nanoparticles in Acidic and Alkaline Electrolytes

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1. Experimental Details

1.1 Materials

Dihydrogen hexachloroplatinate (H_2PtCl_6), potassium tetrachloro platinate (K_2PtCl_4), tetradecyl trimethyl ammonium bromide (TTAB) and sodium poly-acrylate (PAA) from Alfa Aesar; bismuth (III) oxide (Bi_2O_3) and germanium (IV) oxide (GeO_4) from Sigma Aldrich; sodium carbonate (Na_2CO_3), sodium bisulphite (NaHSO_3), sodium borohydride (NaBH_4) and solvents (acetone, ethanol, iso-propyl alcohol (IPA) and n-hexane) from Merck; and hydrogen peroxide (H_2O_2) from Loba Chemie were used as-received without any further purification for the catalyst synthesis. De-ionized (DI) water was obtained from Direct-Q Millipore de-ionizer.

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1.2 Synthesis of polycrystalline platinum (Pt-PC) nanoparticles

Pt-PC nanoparticles were prepared through a sulfito-complex route followed by conventional borohydride reduction. The procedure followed for preparing the sulfito-complex is reported in the literature.¹ Borohydride-reduction method for the synthesis of Pt-PC nanoparticles is as follows: 160 mg of platinum sulfito-complex was dissolved in 25 mL of 0.5 M H₂SO₄, and it was diluted with *ca.* 400 mL of DI water. To this solution maintained at 80°C, 25 mL of H₂O₂ (30 vol.%) was added drop-wise and it was continuously stirred for 45 min. till the effervescence ceased. Resulting colloidal solution was reduced by the addition of 25 ml of 1 wt.% NaBH₄ solution. The catalyst prepared was filtered, washed with DI water, and dried in an oven at 80°C.

1.3 Synthesis of tetrahedral platinum (Pt-TD) nanoparticles

Pt-TD nanoparticles were synthesized following the procedure reported in the literature which is briefly explained here:² 5.2 mL of 0.1 M sodium polyacrylate (PAA) was added to aged aqueous solution of H₂PtCl₆ (2.62×10^{-3} mol dm⁻³ (M)) taken in a 100 mL beaker. The solution was purged with argon (purity: 99.9%) at room temperature for 60 min. Then, the argon-purged solution was bubbled with hydrogen gas for the next 10 min. The setup was then sealed-off to maintain an ambient hydrogenated atmosphere and left overnight at room temperature (25°C). The reactor was wrapped with an aluminium foil to protect the solution from the exposure to surrounding light during the entire period of the synthesis.

1.4 Synthesis of cubic platinum (Pt-NC) nanoparticles

Pt-NC nanoparticles were prepared using the procedure reported by Inaba *et al.*³ They were obtained by the reduction of K₂PtCl₄ with hydrogen in the presence of sodium polyacrylate (PAA) (average molecular weight: 5100) as a capping agent. K₂PtCl₄ was dissolved in DI water to prepare a 1×10^{-4} mol dm⁻³ (M) solution. 100 mL of the aged K₂PtCl₄ solution was taken in a two-necked round bottom flask (RBF) and 1.0 M PAA solution was added to it; the

Pt:PAA (monomer unit) ratio was maintained at 1:12. The pH of the solution was adjusted to 7 by adding dilute hydrochloric acid. The solution was de-aerated by bubbling high purity argon gas for 90 min. The argon-saturated solution was then bubbled with H₂ gas for 10 min. to reduce Pt²⁺ ions. After the reduction, the vessel was sealed air-tight and was left overnight maintaining the vessel temperature at 25°C. The setup was wrapped completely with an aluminium foil to protect the solution from exposure to surrounding light during the entire period of the synthesis.

1.5 Synthesis of cuboctahedral platinum (Pt-CO) nanoparticles

Pt-CO nanoparticles were prepared by following the procedure reported in the literature.⁴ A 100 mL solution of 100 mM TTAB and 1 mM K₂PtCl₄ was taken in a 250 mL RBF and it was heated for 15–20 min. at 55°C until the solution turns clear. The reaction vessel was closed using a rubber septum. Then, 30 mM NaBH₄ was added drop-wise using a syringe and the reaction was maintained at the same temperature for 6 h to reduce the platinum precursor. The reduced nanoparticles were then washed thoroughly with ethanol by centrifuging at 15,000 rpm according to the procedure described below.

1.6 Cleaning procedure for shape-controlled platinum nanoparticles

Pt-NC and Pt-TD nanoparticles were washed and centrifuged with distilled water after adding 0.5 mg of sodium hydroxide to the raw solution obtained after the synthesis. These nanoparticles were centrifuged at 15000 rpm for 30 min. The collected sample was again washed repeatedly with excess of ethanol for 3–4 times. Similar cleaning procedures were adopted with Pt-PC and Pt-CO nanoparticles except for the addition of sodium hydroxide pellets. Finally, the cleaned Pt nanoparticles were used for physical and electrochemical characterizations.

1.7 Physical characterization

XRD patterns were obtained using a PANalytical X'Pert PRO machine (30 mA, 40 KV) with Cu K α radiation of wave length (λ), 1.506 Å and step size of 0.07 from 30° to 90° at a scan rate of 0.6° per minute. JEOL JEM 2100 F field emission electron microscope operated at 200 kV equipped with an energy dispersive X-ray spectrometer was used for recording the HRTEM images. The Pt-nanoparticles were dispersed in ethanol, drop-cast on a carbon-coated Cu-grid and finally dried under IR lamp prior to recording the TEM images.

1.8 Electrode preparation

The electrode was prepared following the method reported in the literature.⁵ 5 mg of the catalyst mixed with 5 mL of de-ionized water and 10 μ L of the Nafion[®] ionomer was sonicated for 15 min. Then, 10 mL of IPA was added to the above-solution and it was sonicated for the next 15 min. to form a fine free-flowing catalyst ink. The catalyst ink was drop-cast on the electrode and the metal loading was maintained at 30 μ g cm⁻².

1.9 Electrochemical characterization

Electrochemical measurements were performed in a conventional three-electrode electrochemical cell. The potential was controlled using a WaveDriver 20 Bipotentiostat/Galvanostat system from Pine Research Instrumentation, USA. Pt wire was used as counter electrode and Ag/AgCl (double junction with outer tube filled with saturated KCl) was used as reference electrode. Typically, cyclic voltammograms (CVs) were recorded at a scan rate of 50 mV s⁻¹ in argon-saturated 0.1 M HClO₄, 0.5 M H₂SO₄ and 0.1 M NaOH electrolytes. ORR voltammograms were recorded in oxygen-saturated electrolytes with a rotating ring disk electrode (RRDE) at a scan rate of 20 mV s⁻¹ with 1600 rpm. Hydrogen peroxide (H₂O₂) oxidation current was recorded parallel to ORR in oxygen-saturated electrolytes by holding the ring potential at 1.2 V for acidic and 1.15 V for alkaline electrolytes.^{6,7} Cu stripping voltammograms of different shape-controlled Pt nanoparticles

were recorded in argon-saturated 0.1 M HClO₄ and 0.5 M H₂SO₄ at 10 mV s⁻¹ using 12 mM CuSO₄ solution. The electrochemical surface area (ESA) of the synthesized Pt nanoparticles was calculated from the CVs. All potentials are recorded vs. Ag/AgCl but are reported vs. RHE throughout this manuscript.

1.10 Irreversible adsorption of bismuth (Bi) on cleaned platinum nanoparticles

Bi adsorption on cleaned Pt nanoparticles was carried out using the procedure reported by Clavilier *et al.*⁸ 10⁻³ M bismuth solution, prepared from bismuth (III) oxide (Bi₂O₃) calcined for 45 min. at 500°C, was dissolved in 0.6 M HClO₄ solution. The voltammograms were recorded in 0.5 M H₂SO₄ (test electrolyte) solution for all the synthesized Pt nanoparticles at a scan rate of 50 mV s⁻¹. The fraction of low-index crystal orientation {111} on synthesized Pt-nanoparticles was investigated. A clean voltammogram was recorded first with the test electrolyte and the catalyst surface on the electrode was cleaned with DI water. Then, the electrode was dipped in the bismuth solution for 1 min., rinsed again with DI water and transferred back into the test electrolyte cell at a controlled potential of 0.75 V to record background voltammograms. From the CVs recorded before and after Bi adsorption, the percentage of {111} orientation was estimated for different Pt nanoparticles.

1.11 Irreversible adsorption of germanium (Ge) on cleaned platinum nanoparticles

Ge adsorption on cleaned Pt nanoparticles was carried out following the procedure reported by Gómez *et al.*⁹ 10⁻² M Ge solution was prepared by dissolving germanium (IV) oxide (Ge₂O₄) in 1 M NaOH solution. It was noted that the adsorbed Ge was not stable as it can easily get oxidized, therefore, the adsorption was carried out as follows: First, the voltammogram was recorded in 0.5 M sulfuric acid (test electrolyte) at a scan rate of 50 mV s⁻¹. The electrode was rinsed with DI water and dipped into 1 M NaOH electrolyte containing Ge solution for 1 min. by holding the potential at 0.1 V. Then, the electrode was transferred back into the test electrolyte and a voltammogram was recorded restricting the potential to

0.6 V. From the voltammograms recorded before and after Ge adsorption, percentage of {100} orientations of Pt nanoparticles was estimated.

2. XRD patterns of polycrystalline and shape-controlled Pt nanoparticles

Fig. S1 shows the powder X-ray diffraction (XRD) patterns of the carbon-supported Pt-PC, Pt-NC, Pt-TD, and Pt-CO nanoparticles. The XRD patterns of the platinum nanoparticles have multiple peaks that are clearly distinguishable. The peaks at 2 theta values of 39.78°, 46.38°, 67.58°, 81.38° and 85.94° correspond to {111}, {200}, {220}, {311} and {222} crystal planes, respectively, of face-centered cubic (FCC) structure [space group: Fm3m] with a lattice constant of 0.3923 nm (JCPDS card No. 04-0802). The crystallite size of the synthesized Pt nanoparticles determined using the Debye Scherer equation, is ~8, ~12.5, ~6.5 and ~12 nm, respectively, for Pt-PC, Pt-NC, Pt-TD, and Pt-CO nanoparticles. From the XRD patterns of Pt-NC and Pt-CO, it is clear that the intensity of {200} peak is slightly higher when compared to that of Pt-PC and Pt-TD; the intensity ratio of {111} to {200} peaks in the XRD patterns of Pt-NC suggests that Pt nanoparticles are preferentially oriented with their {100} facets. The faceting in shape-controlled metal nanoparticles can be clearly observed from their XRD patterns when the particle size is greater than 60 nm.¹⁰ The same cannot be observed in this case, may be due to the comparatively smaller size, truncation at the edges and corners, less than 100% shape-selectivity, and the random orientations of nanoparticles on the carbon-support.¹¹

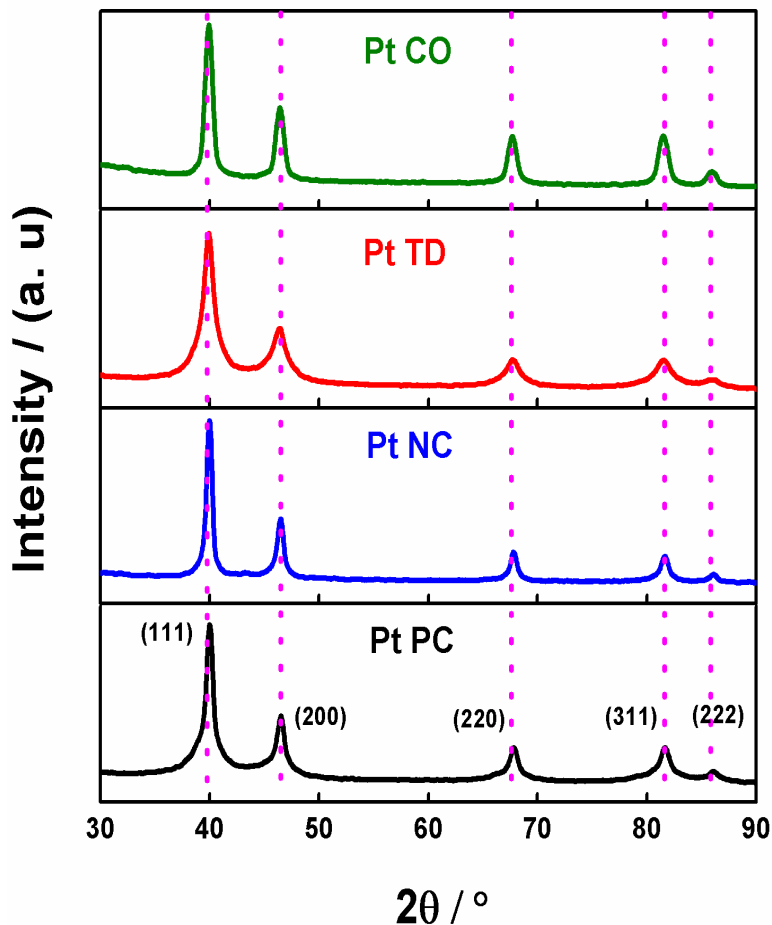


Fig. S1 XRD patterns of carbon-supported Pt-PC, Pt-NC, Pt-TD and Pt-CO nanoparticles.

3. Voltammetric characterization of the nanoparticles in acidic (0.1 M HClO₄) and alkaline (0.1 M NaOH) electrolytes

Fig. S2 shows the CVs of Pt-PC, Pt-NC, Pt-TD and Pt-CO in 0.1 M HClO₄ recorded at a scan rate of 50 mV s⁻¹. with Pt-PC, the initial peak at ~0.1 V is well-defined and a broad shoulder peak is observed in the potential region of 0.15–0.35 V. A characteristic peak at 0.27 V is observed and it is due to the presence of {100} step sites; the peaks at ~0.1 V and ~0.27 V have similar intensities. The H_{upd} region of Pt-TD does not show any peak center at ~0.27 V, and the CV is similar to that observed in case of Pt-PC, but in case of Pt-TD, the shoulder peak is comparatively higher than that observed with Pt-PC in the same potential region. The

Pt-CO voltammetric features are similar to that of Pt-NC, but the two peaks are more clearly defined. The peak at ~0.1 V is sharp, similar to that of Pt-PC, and the second peak center is slightly shifted to higher voltage when compared to that of Pt-NC. The CVs recorded in 0.1 M HClO₄ electrolyte do not show the {111} ordered bi-dimensional terrace sites in the double layer region as that observed in H₂SO₄. All these voltammetric features are in agreement with the Pt single-crystal electrodes.^{6,12,13}

Table S1. Electrochemical surface area (ESA) of the catalysts in 0.5 M H₂SO₄ and 0.1 M HClO₄.

<i>Pt nanoparticles</i>	<i>ESA (m² g⁻¹)</i>	
	<i>0.5 M H₂SO₄</i>	<i>0.1 M HClO₄</i>
<i>Pt-PC</i>	28	24
<i>Pt-NC</i>	24	21
<i>Pt-TD</i>	30	27
<i>Pt-CO</i>	25	23

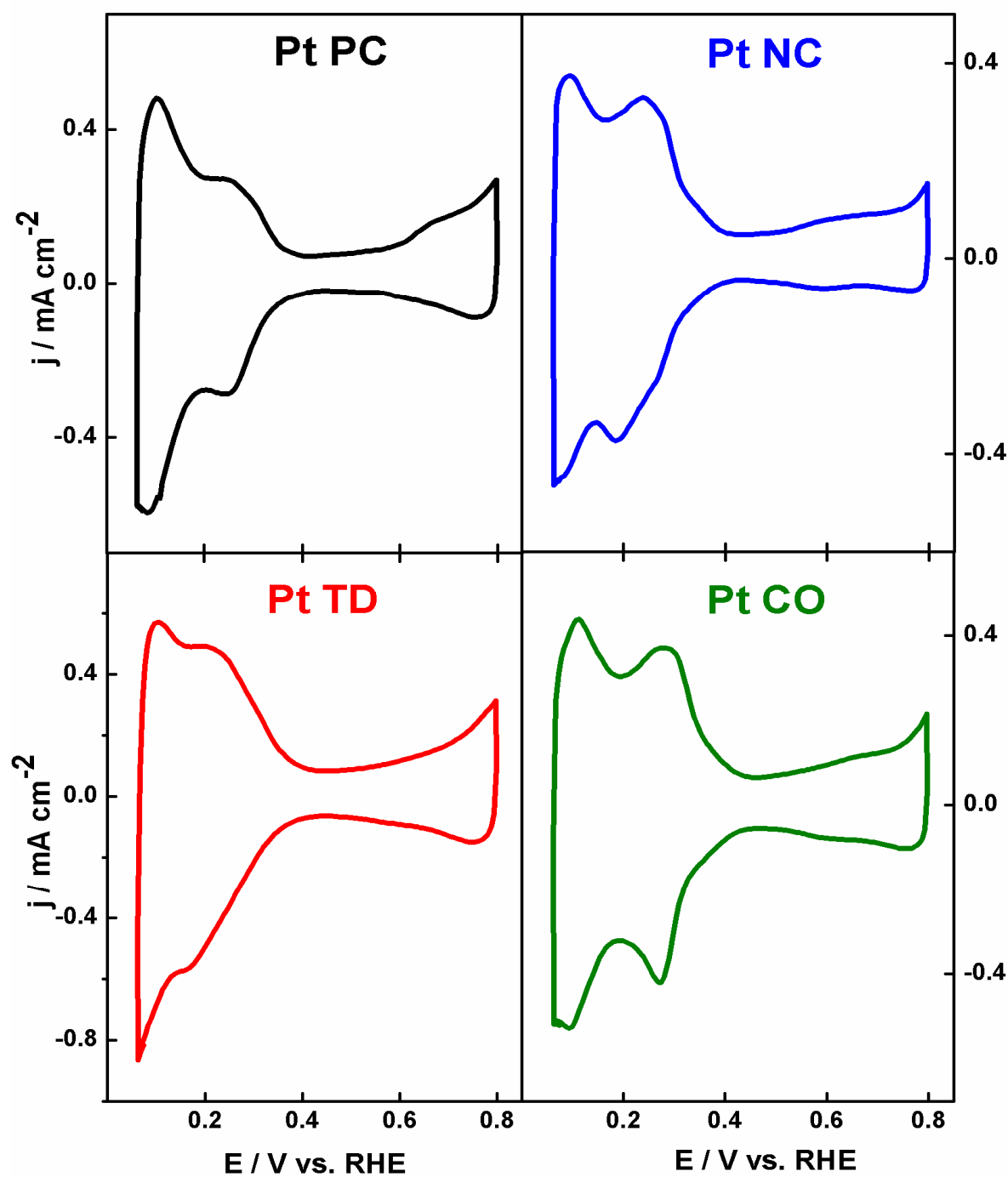


Fig. S2 CVs of Pt-PC, Pt-NC, Pt-TD and Pt-CO catalysts in argon-saturated 0.1 M HClO_4 solution recorded at a scan rate of 50 mV s^{-1} .

Fig. S3 shows the voltammograms recorded in 0.1 M NaOH solution. As that of the CVs of Pt in HClO₄ electrolyte, there is a lack of specific adsorption capability of Pt in the alkaline electrolyte as well. The features observed in the CVs are broad and well-spread over a range of potential from 0.06 to 0.4 V in the H_{ads/des} region. In general, it is observed that {110} sites give characteristic peaks at 0.27 and 0.75–0.80 V due to the adsorption of hydrogen (H_{ads}) and oxygen-containing species (OH_{ads}), respectively.^{7,13} {100} sites contribute at four different potentials (0.27, 0.35, 0.45 and 0.55 V). The contribution from the {111} sites gives the characteristic peak at 0.8 V due to the adsorption of oxygen-containing species (OH_{ads}). The double layer region is between 0.4–0.65 V. In case of shape-controlled Pt nanoparticles, it is obvious that 100 % faceting is not possible hence all features can be seen with varying relative intensities with each catalyst.

With Pt-PC nanoparticles only two features, at potentials ~0.27 and ~0.35 V, are predominant even though there is a small broad peak due to OH_{ads} at ~0.75 V which is not so evident from the CV. This is because the fraction of {111} sites are relatively less. In Pt-NC three characteristic features are observed at ~0.27, ~0.35 and ~0.55 V corresponding to the presence of {100} sites. Along with these features, there is a peak at ~0.8 V due to the presence of {111} sites on the Pt-NC nanoparticles; but, the contribution of this orientation is low relative to that of {100} sites. In Pt-TD, the features are almost similar to that of Pt-PC nanoparticles, but as expected, the characteristic feature at ~0.8 V due to OH_{ads} corresponding to the {111} is relatively higher. Similar kind of voltammetric features were reported by Vidal-Iglesias *et al.* for shape-controlled Pt nanoparticles.¹³ In Pt-CO four characteristic features are observed at ~0.27, ~0.35, ~0.55 V and ~0.8 V corresponding to the presence of both {100} and {111} sites. With {100} single crystal electrodes, a small shoulder peak due to H_{ads/des} is observed at 0.45 V along with the other three features in the H_{upd} region.^{7,14} This shoulder peak is not noticed on Pt-NC and Pt-CO even though these nanoparticles possess

{100} terrace sites, since it is suppressed by the presence of {111} terrace sites at 0.75 V. The double layer region has a minor hump for Pt-NC and Pt-CO nanoparticles *i.e.*, in the potential range 0.4–0.65 V due to $\text{OH}_{\text{ads/des}}$ on {100} terraces. However, with Pt-TD and Pt-PC nanoparticles, there is no such adsorption at 0.55 V resulting in a normal double layer region.

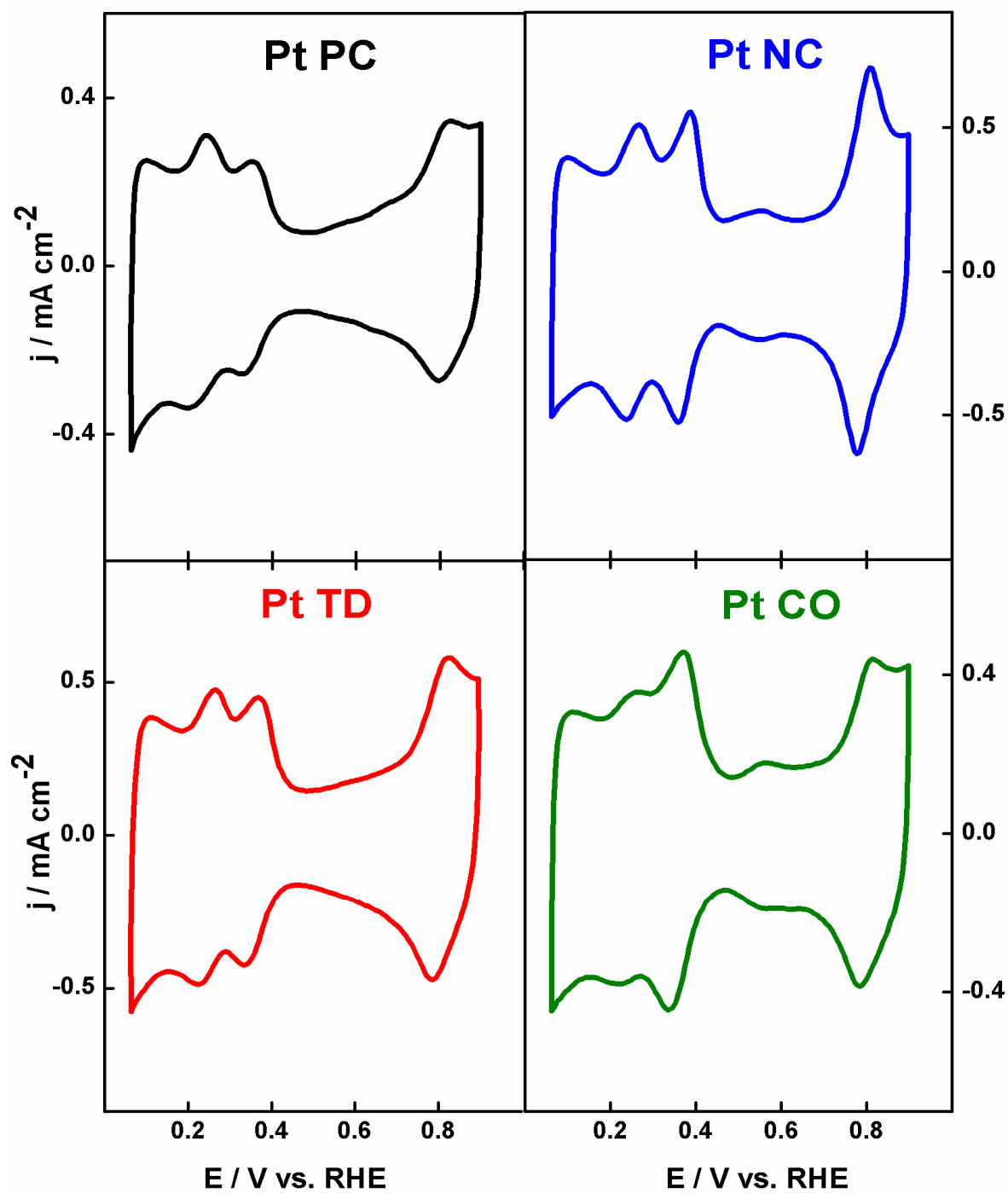


Fig. S3 CVs of Pt-PC, Pt-NC, Pt-TD and Pt-CO catalysts in argon-saturated 0.1 M NaOH solution recorded at a scan rate of 50 mV s^{-1} .

4. Reversible adsorption of copper (Cu^{+2}) ions on shape-controlled Pt nanoparticles in 0.1 M HClO_4 electrolyte

Fig. S4 shows the background-corrected Cu stripping voltammograms of Pt-PC, Pt-NC, Pt-TD and Pt-CO nanoparticles with 12 mM of CuSO_4 in 100 mL of 0.1 M HClO_4 electrolyte recorded at a scan rate of 10 mV s^{-1} . The stripping voltammogram shows three peaks corresponding to stripping of adsorbed Cu monolayer from the three low-index crystallographic planes. Similar to the Cu stripping voltammograms in 0.5 H_2SO_4 , it is difficult to assign a particular peak position to a specific facet in 0.1 M HClO_4 as well and this is due to the reversibility associated with the slow kinetics of the process. The Cu stripping voltammograms of Pt-PC and Pt-TD have $\{111\}$ peak ($\sim 0.62 \text{ V}$) as the most intense peak, and for Pt-CO, the peak at 0.75 V due to $\{100\}$ plane is the most intense one. In case of Pt-NC, the peak at 0.75 V is more intense when compared to that observed on Pt-PC and Pt-TD. This difference in the intensity of various peaks in Cu stripping voltammograms can be attributed to the faceting of platinum surface to a particular low-index crystallographic orientation due to the shape of the nanoparticle. In Pt-NC and Pt-CO, the nanoparticles surface is dominated by the $\{100\}$ sites and in Pt-TD the surface is dominated with $\{111\}$ sites. These results are in accordance with the *ex-situ* TEM analysis and the observed voltammetric features in both 0.5 M H_2SO_4 and 0.1 M HClO_4 .

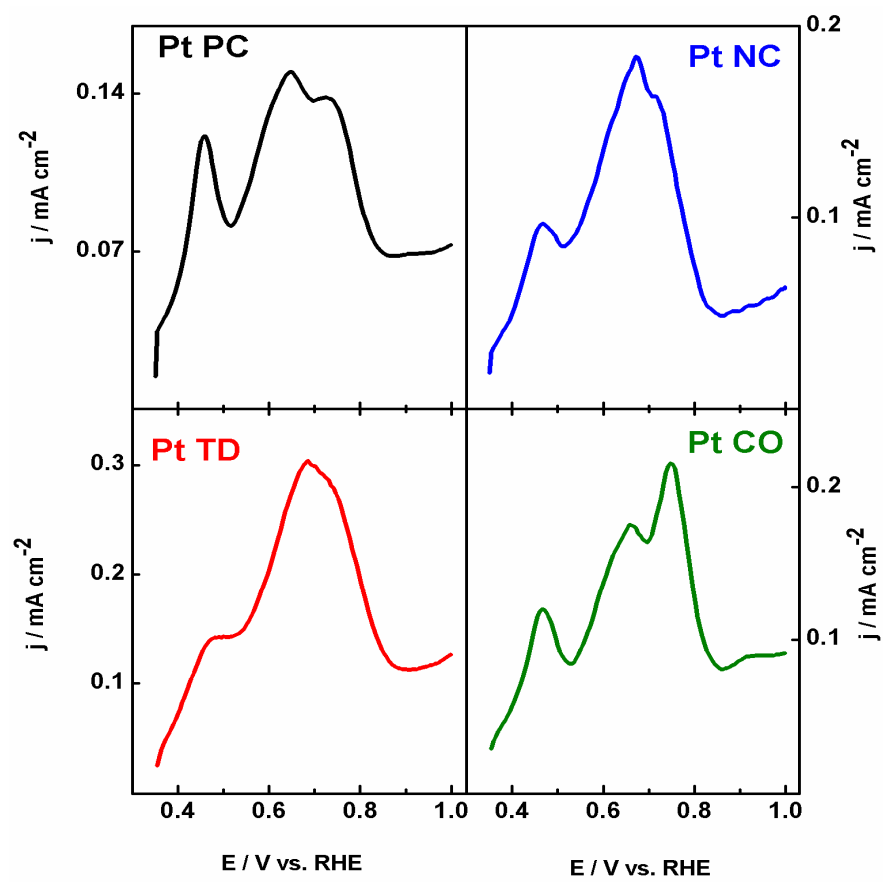


Fig. S4 Cu stripping voltammograms of Pt-PC, Pt-NC, Pt-TD and Pt-CO with 12 mM CuSO_4 solution in argon-saturated 0.1 M HClO_4 solution at a scan rate of 10 mV s^{-1} .

5. Specific and mass activities of polycrystalline and shape-controlled Pt nanoparticles in 0.5 M H₂SO₄ electrolyte.

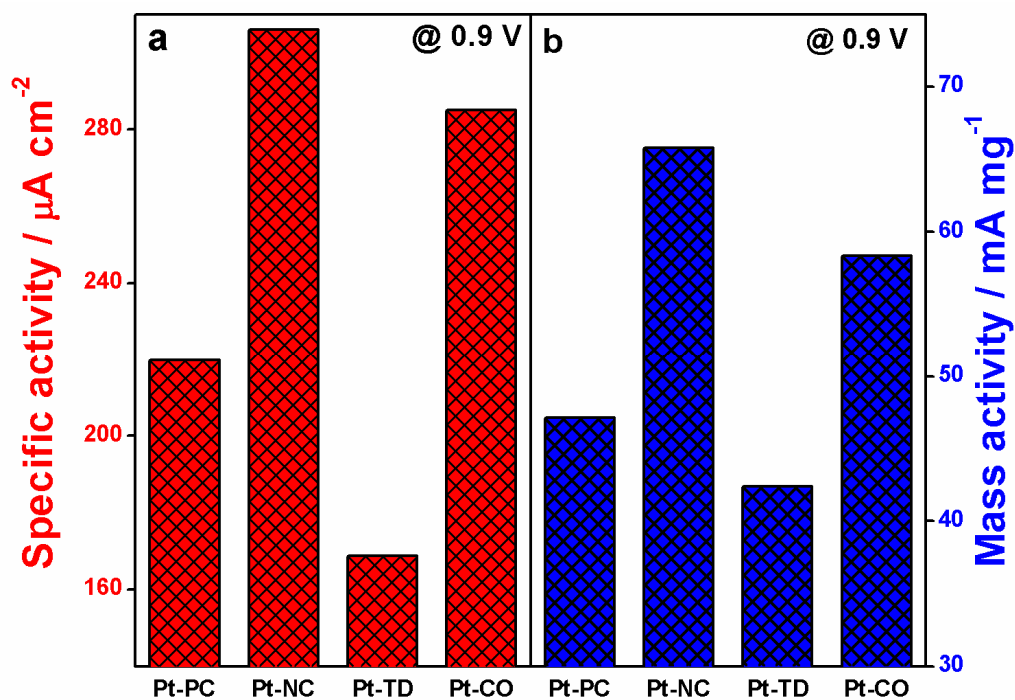


Fig. S5 Specific activity (a) and mass activity (b) of Pt-PC, Pt-NC, Pt-TD and Pt-CO catalysts at 0.9 V in 0.5 M H₂SO₄ electrolyte.

Table S2. MAs and SAs in 0.5 M H_2SO_4 electrolyte.

<i>Catalyst</i>	<i>Potential</i>	<i>MA (mA mg⁻¹)</i>	<i>SA (mA cm⁻²)</i>
<i>Pt-PC</i>	0.8	421	1.4
	0.85	155	0.56
	0.9	48	0.21
<i>Pt-NC</i>	0.8	347	1.44
	0.85	170	0.70
	0.9	66	0.31
<i>Pt-TD</i>	0.8	180	0.75
	0.85	86	0.37
	0.9	42	0.17
<i>Pt-CO</i>	0.8	300	1.19
	0.85	155	0.61
	0.9	64	0.28

6. ORR activity and peroxide formation in 0.1 M HClO₄ electrolyte

From Table. 2, the fraction of {111} sites present is higher in case of Pt-TD when compared to that on Pt-NC, Pt-PC and Pt-CO nanoparticles; it is expected that the Pt shape-controlled nanoparticles with more active {111} sites show higher ORR activity in 0.1 M HClO₄ electrolyte.

Fig S6a and **b** show the ORR voltammograms of Pt-PC, Pt-NC, Pt-TD and Pt-CO and the corresponding peroxide oxidation currents in 0.1 M HClO₄ electrolyte. A difference of ~100 mV in the ORR activity (in terms of shift in half-wave potentials of ORR) is reported between {111} and {100} single crystal electrodes in 0.1 M HClO₄ (Markovic *et al.*).^{15,16} Therefore, among shape-controlled nanoparticles, {111} dominated Pt-TD should be the most active and the {100} dominated Pt-NC the least active. But, the ORR activity difference (in terms of half-wave potential of ORR (Fig. S6a)) of shape-controlled nanoparticles (Pt-TD and Pt-NC) is lower than that observed with the single crystal electrodes (Pt {111} and Pt {100}).

This may be due to the less than 100% shape-selectivity, crystal imperfections, and truncations at the edges and corners of the shape-controlled nanoparticles. Table 1 shows the presence of only about 60 % {111} facets in Pt-TD and about 52% {100} facets in Pt-NC. The sum of these orientations in each case averages to ~70 % and the remaining 30 % would be {110} sites or the other high-index sites that are difficult to estimate (see the discussion on the role of defects on ORR in page 12 of the main manuscript). Thus, there exists at least two different dominant facets in any given sample. In Pt-TD nanoparticles, along with predominant {111} facets, {100} facets are also present. Similarly, in Pt-NC nanoparticles, along with predominant {100} facets, {111} facets are also present. The presence of least active {100} facets along with {111} dominated Pt-TD nanoparticles will downshift the half-wave potential of ORR from that of the ideal Pt-TD nanoparticles and the presence of the

most active {111} facets along with {100} dominated Pt-NC nanoparticles will upshift the half-wave potential of ORR from that of ideal Pt-NC nanoparticles. Thus, the difference in the ORR activity (in terms of half-wave potentials) among shape-controlled nanoparticles will shrink and the minimal difference is inevitable as compared to that reported among single crystal electrodes (essentially only one orientation is present on a given single crystal electrode). The roughness factor (ratio of Pt surface area to geometric disk surface area) for the all the bulk single crystal electrodes is close to ~ 1 .^{16,17} Therefore, it is fair to compare the activity among various single crystal electrodes from the ORR voltammograms in terms of half-wave potentials of ORR. With nanoparticles, roughness factor is in the range of 6.5–8.5. Thus, it is more appropriate to compare the intrinsic activities (mA mg^{-1}) at higher potentials (kinetic region) with nanoparticles. The intrinsic activities in 0.1 HClO_4 , given in Table S3, are in the order of $\text{Pt-TD} > \text{Pt-PC} > \text{Pt-NC} \sim \text{Pt-CO}$; this activity order is in line with that reported by Markovic *et al.*, though the variation in activity at 0.8 to 0.9 V is relatively small between the three low index faces on single crystal electrodes.¹⁶

The specific, and mass activities of Pt-PC are comparable with the those reported in the literature.¹⁷ At 0.9 V the SA of Pt-NC and Pt-CO are 320 and $310 \mu\text{A cm}^{-2}$, respectively, and are slightly lower when compared to that of Pt-PC *i.e.*, $331 \mu\text{A cm}^{-2}$, but there is a significant rise in SA for Pt-TD ($400 \mu\text{A cm}^{-2}$). This is due to the presence of more active {111} terrace sites in Pt-TD nanoparticles when compared with that on the other shape-controlled Pt nanoparticles. **Fig. S7** shows the MA and SA of Pt-PC, Pt-NC, Pt-TD and Pt-CO catalysts at 0.9 V in HClO_4 electrolyte.

Fig. S6b shows the H_2O_2 oxidation current (ring current) on Pt-PC, Pt-NC, Pt-TD and Pt-CO corresponding to the ORR voltammograms shown in Fig. S6a; solid line shows the forward scan and dotted line shows the reverse scan. The fraction of peroxide formation is shown in

inset to Fig. S6b. From the single-crystal study, it is understood that the adsorbed-hydrogen on Pt{hkl} surfaces has an enhancing effect on peroxide formation. Apart from this, the trend in peroxide formation and the peroxide features depend on the active site density, thickness of the catalyst layer, reaction mechanism and surface blocking by the adsorbed impurities; similar to that observed in H₂SO₄ electrolyte. Thus, the peroxide formation order is Pt-CO>Pt-NC>Pt-TD≈Pt-PC, which is in the reverse order of the ORR activity.

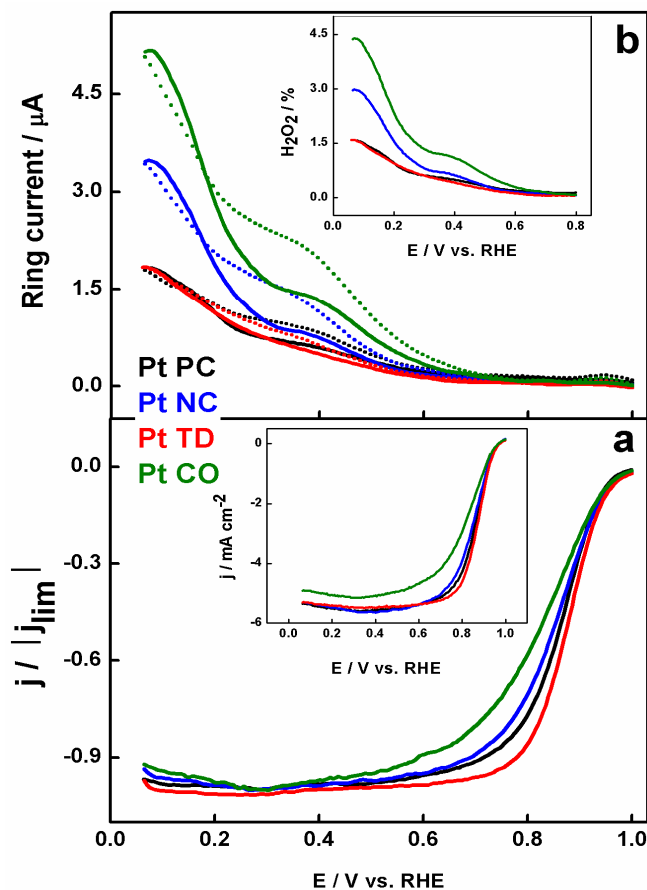


Fig. S6(a) ORR voltammograms ($|j_{lim}|$ normalized) of Pt-PC, Pt-NC, Pt-TD and Pt-CO in 0.1 M HClO₄; inset to Fig. S6a shows ORR voltammograms without normalization. **(b)** H₂O₂ oxidation current (ring current) recorded parallel to ORR voltammograms shown in Fig. S6(a); solid line indicates positive sweep and dotted line indicates negative sweep; inset to

Fig. S6(b) shows the fraction of H_2O_2 formation as a function of potential during O_2 reduction.

7. Specific and mass activities of polycrystalline and shape-controlled Pt nanoparticles in 0.1 M $HClO_4$ electrolyte.

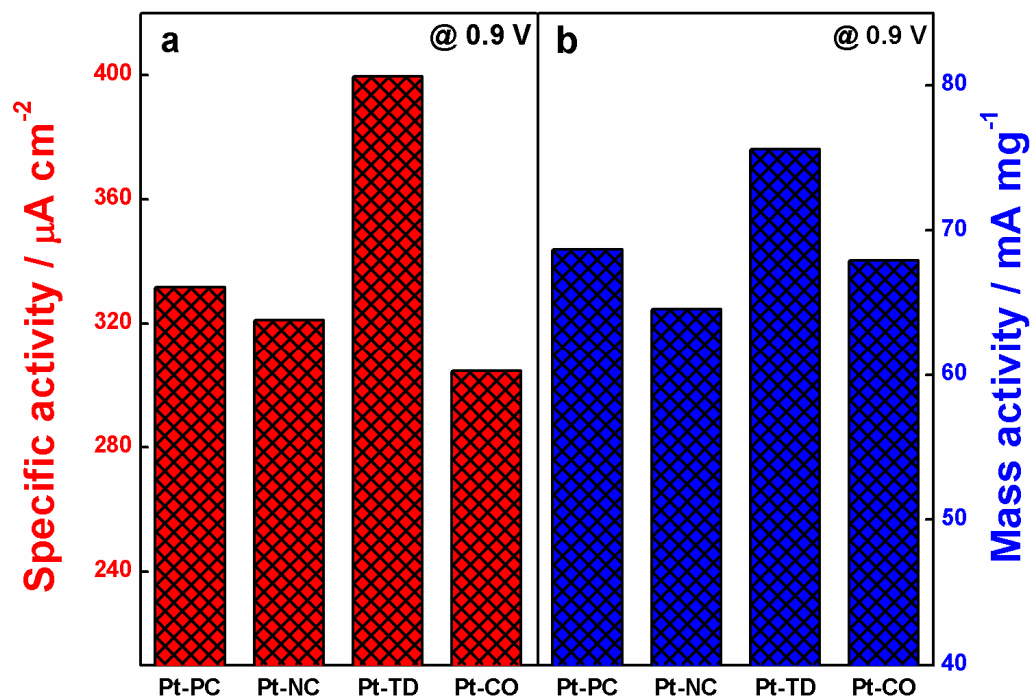


Fig. S7 Specific activity (a) and mass activity (b) of Pt-PC, Pt-NC, Pt-TD and Pt-CO catalysts at 0.9 V in 0.1 M $HClO_4$ electrolyte.

Table S3. MAs and SAs in 0.1 M HClO₄ electrolyte.

<i>Catalysts</i>	<i>Potential</i>	<i>MA (mA mg⁻¹)</i>	<i>SA (mA cm⁻²)</i>
<i>Pt-PC</i>	0.8	627	2.61
	0.85	246.	1.02
	0.9	68.68	0.33
<i>Pt-NC</i>	0.8	451	2.6
	0.85	190.7	0.95
	0.9	64.6	0.32
<i>Pt-TD</i>	0.8	1093	4.6
	0.85	348	1.5
	0.9	88	0.4
<i>Pt-CO</i>	0.8	234	1.2
	0.85	114	0.56
	0.9	67	0.31

8. ORR activity and peroxide formation in 0.1 M NaOH electrolyte

In 0.1 M NaOH electrolyte, ORR kinetics depends on the structure-sensitivity of (OH^-) adsorption on $\text{Pt}\{\text{hkl}\}$ along with its site blocking effect.⁷ From **Fig. S8a**, it can be seen that the half-wave potential of Pt-PC is 839 mV, and on Pt-TD it is shifted to higher potential by ~ 25 mV, *i.e.*, 864 mV, whereas, the half-wave potential on Pt-NC and Pt-CO is shifted to lower potentials by ~ 5 and ~ 20 mV, respectively. The ORR activity is in the order of Pt-TD>Pt-PC $\approx$ Pt-NC>Pt-CO, and it can be attributed to the relative changes in the availability of various active low-index sites on the shape-controlled Pt nanoparticle. The ORR activity order with our shape-controlled Pt nanoparticles in 0.1 M HClO_4 , 0.5 M H_2SO_4 and 0.1 M NaOH electrolytes are in accordance with that of the single-crystal electrodes reported in the literature.^{6,7,12}

Fig. S8b shows the H_2O_2 oxidation current (ring current) on Pt-PC, Pt-NC, Pt-TD and Pt-CO corresponding to the ORR voltammograms shown in Fig. S8a; solid line shows the forward scan and dotted line shows the reverse scan. The fraction of peroxide formation is shown in inset to Fig. S8b. The order of formation of H_2O_2 on different catalysts is Pt-CO>Pt-PC>Pt-TD>Pt-NC, which is in accordance with the order observed in the case of extended surface reported in the literature.⁷ The order of peroxide oxidation current is attributed to the adsorbed hydrogen which inhibits the adsorption of oxygen and irreversible (OH^-) adsorption favoured by $\{100\}$ sites, and hence results in the formation of more peroxide on Pt-CO nanoparticles which contains both the $\{100\}/\{111\}$ sites.

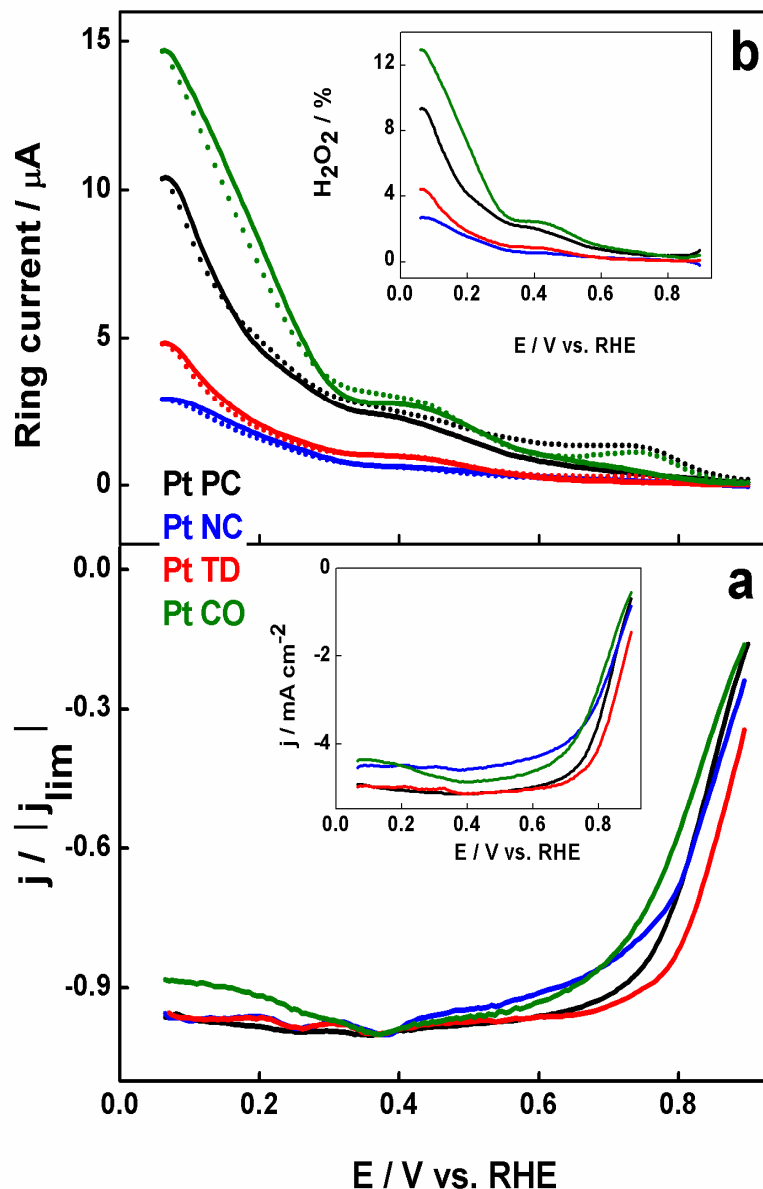


Fig. S8(a) ORR voltammograms ($|j_{lim}|$ normalized) of Pt-PC, Pt-NC, Pt-TD and Pt-CO in 0.1 M NaOH; inset to Fig. S8(a) shows ORR voltammograms without normalization. **(b)** H_2O_2 oxidation current (ring current) recorded parallel to ORR voltammograms shown in Fig. S8(a); solid line indicates positive sweep and dotted line indicates negative sweep; inset to Fig. S8(b) shows the fraction of H_2O_2 formation as a function of potential during O_2 reduction.

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