# Cubic PdPtRu Trimetallic Nanocomposite: Electrocatalytic Application As Anode Material for Direct Methanol Fuel Cell

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Palladium Nanocubes based tri-metallic nanocomposite has been synthesized by electrochemical codeposition of PtRu on Pd-NCs. Structural and morphological characterizations of PtRu@Pd-NCs nanocomposite material were performed using X-ray diffraction, X-ray photoelectron spectroscopy analysis and transmission electron microscopy. The electrocatalytic activity for methanol oxidation reaction (MOR) is studied in HClO<sub>4</sub> aqueous solution. A significant improvement in the MOR activity is observed by increasing the atomic ratio of Pt in PtRu co-deposition on Pd-NCs up to an optimum value. Among all prepared catalysts, Pt<sub>3</sub>Ru@Pd-NCs has shown highest mass activity (ca.10500 mA mg<sup>-1</sup><sub>Pd</sub> and 75mA mg<sup>-1</sup><sub>Pt</sub>) and specific activity (ca. 7.85 mA cm<sup>-2</sup>) for MOR at lower peak potential ca. 0.70V. The as-developed catalyst has also shown lower onset potential with enhanced durability and stability towards MOR. The results can be attributed to the collective effect of PtRu nanoparticles and the enhanced electron transfer of Pd-NCs in tri-metallic nanocomposite material.

**Keywords:** Pd nanocubes; Tri-metallic nanocomposite; Electrochemical co-deposition; Methanol oxidation reaction.

# **1. INTRODUCTION**

Direct methanol fuel cells (DMFC) have been attracted as potentially useful power sources in past and recent era, due to the high energy density of methanol [1]. However, the slow kinetics for methanol oxidation reaction (MOR) at the anode electrocatalysts remains one of serious challenges which hinder the industrial scale commercialization of the DMFCs. Pt materials exhibit facile adsorption and decomposition of methanol on their surfaces [2]. The strongly adsorbed  $CO_{ads}$  molecules on the Pt sites block the active sites for further mechanism of CH<sub>3</sub>OH chemisorptions. That is the major origin for the sluggish kinetics for MOR [3]. Addition of Ru onto Pt electrocatalysts is

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found to facilitate CO oxidation through both bi-functional and ligand effect [4]. However, the scarcity and high cost for both Pt and Ru calls for further efforts to develop new catalysts to modify and enhance the MOR reaction kinetics along with reduction of noble metal loading. Developing core-shell nanocatalysts with a choice of cheap metals as the core is a facile way to achieve the above goals [5-8].

Palladium based materials have been widely used as electrocatalysts for oxidation of different fuels such as different alcohols (CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, COOH and formaldehyde) due to similar properties of Pd with platinum [9]. Significant enhancement in electro-oxidation for methanol has been reported for various bimetallic alloys combinations such as PdPt, PdRu, PdSn, PdAu and PdMo [10]. Pd nanocubes (NCs) exhibit quite relevant electrochemical behavior to Pt monometallic catalysts due to the presence of fcc 100 crystallographic plane. Even so, Pd NCs have been frequently used for formic acid oxidation reaction (FOR) and less work has been reported on modification of Pd NCs for methanol oxidation reaction (MOR). Yizhong Lu *et al.* reported PdPt NCs supported on rGO for MOR [11] and later Fangwei Zhan *et al.* has modified unsupported PdPt alloy NCs with different compositions of Pd and Pt for MOR [12].

As for nano sized electrocatalysts, the catalytic activity, selectivity, and stability highly depend on the granulometric morphologies, composition and the dispersion of the catalyst nanoparticles. Due to a highly active shape of Pd nanocubes (fcc 100), comparable properties of Pd with Pt and to reduce the cost of catalyst. In this work, we have used Pd NCs and modify them by introducing Pt and Ru to develop Pd based trimetallic catalyst with well-defined shape (fcc 100). We have succeeded to get our goal and provided multiple contributions in the field of electrocatalysis with present work. Such as, reduced the cost of catalyst with optimum composition of precious metals PtRu on Pd based material, tuning of Pd NCs for excellent MOR activity, co-deposition of PtRu on Pd NCs by electrochemical method to synthesize trimetallic catalyst and finally provided an excellent MOR catalyst with lower onset potential vs RHE, higher current density at lower potentials and enhanced durability. This successful and new achievement informs us a Pd 100 facets based material has highly improved its activity by combining with low amount of PtRu metals. Which could be further adopted, to produce more active and low cost MOR catalysts with lower optimized PtRu composition by using active Pd based materials.

## 2. EXPERIMENTAL

#### 2.2. Chemicals and Materials

 $H_2PdCl_4$  (99.9% metal basis, from Alfa Aesar),  $H_2PtCl_6$  (40% from Fluka),  $Ru(NO)(NO_3)_2$  (40% w de Ru from Fluka), Hexadecyltrimethyl ammonium bromide (C<sub>16</sub>TAB), Ascorbic Acid, HClO<sub>4</sub> (from Sigma Aldrich) and CH<sub>3</sub>OH (99.9% from J.T. Baker). All reagents were used without further purification.

## 2.3. Synthesis of Pd Nanocubes

To synthesize Pd nanocubes initially, 500  $\mu$ l of a 5mM H<sub>2</sub>PdCl<sub>4</sub> aqueous solution was added to 10 ml of a  $1.25 \times 10^{-2}$  M C<sub>16</sub>TAB aqueous solution at temperature of 95 <sup>0</sup>C. After 15 minutes 80  $\mu$ l of a 0.1 M ascorbic acid was gradually added to the mixed solution of C<sub>16</sub>TAB and H<sub>2</sub>PdCl<sub>4</sub> with stirring. The resulting solution obtained 25 nm nanocubes.

#### 2.4. Electrochemical Experiments

Prior to each electrochemical experiment, a glassy carbon (GC) electrode (0.196 cm<sub>2</sub> geometric surface area) was initially polished with alumina powder (Al<sub>2</sub>O<sub>3</sub>, 0.05 mm) on a polishing cloth to obtain a mirror liked finish. To prepare a working electrode for electrochemical experiments, 15 mL of the 1 mg/mL Pd-NCs dispersed in pure water was drop-coated on the above polished electrode surface by a microliter pipit, let it drying in a vacuum at room temperature. Afterward, a thin layer of Nafion (0.1 wt % in water, 5 mL) was dropped over the surface of electrode to ensure that the catalyst was tightly attached to the electrode surface during the electrochemical experiments. Electrochemical measurements were carried out with a CHI750D electrochemical workstation. The Ag/AgCl (in 3MNaCl, aq.) reference electrode was isolated in a double junction chamber, and a Pt coil was used as the counter electrode. All the measurements were performed in electrochemical experiments with respect to standard values of the reversible hydrogen electrode (RHE). Electrochemical experimental work was done by potential cycling method.

#### 2.4. Synthesis of PtRu@Pd-NCs

PtRu@Pd-NCs catalyst was synthesized by electrochemical deposition of PtRu on Pd-NCs. Which was carried out at room temperature in  $H_2PtCl_6 + Ru(NO)(NO_3)_2 + 0.1M$  HClO<sub>4</sub> (PtRu compositions were varied according to demonstrated results) solution by chronoamperometric method at constant potential of 0.30V vs RHE up to 15 minutes. After the electro deposition, the electrode was rinsed with Mili-Q water and afterwards tested in 0.1M HClO<sub>4</sub> solution with in the potential range from 0.05V to 0.70V at 50 mV/s vs RHE. The obtained catalyst loaded on GCE is demonstrated as PtRu@Pd-NCs.

### 2.5. Physical Characterizations

The crystallographic structure, granulometric morphology and atomic composition of the synthesized catalyst were studied by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) (the measurements were carried out using SPeCS system (PHOIBOS 150, Germany) with Al Ka radiation (hv <sup>1</sup>/<sub>4</sub> 1486.6 eV).

# **3. RESULTS AND DISCUSSION**



**Figure 1.** TEM images of (a) Pd-NCs, (b) Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs (inset is given its SAED), (c) HRTEM image for Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs and (d) EDX spectra for Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs (inset table is given for Pd:Pt:Ru atomic composition)

The morphology and structural features of Pd NCs and  $Pt_3Ru_1@Pd-NCs$  composite were investigated by TEM. Fig. 1(a) shows the representative TEM image of synthesized Pd NCs with an average size of 27 nm. The Pd NCs have well-defined shape with a precise distribution. The formation of  $Pt_3Ru_1@Pd-NCs$  composite has been confirmed by TEM and HRTEM. Fig. 1(b) shows that Pt and Ru have been coated on the surfaces of Pd NCs making a uniform and smooth shell. Selected area electron diffraction (SAED) image displays a successive dotted pattern (insert in Fig. 1(b)), demonstrating  $Pt_3Ru_1@Pd-NCs$  composite is polycrystalline. HRTEM image of  $Pt_3Ru_1@Pd-NCs$ composite shown in Fig. 1(c) confirms a structurally uniformed shell of Pt on the surfaces of Pd NCs. The periodicity of the lattice fringes obtained for the core is d = 0.227 nm, corresponding to the (111) planes of the fcc Pt. Besides the crystalloids phase, there are some islands with no lattice fringes which may be ascribed to Ru.

The elemental composition of the Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs composite was carried out using EDX integrated with TEM instrument as expected in Fig. 3(d). From EDX measurements, it could be shown that Pd, Pt and Ru are present in the core-shell nanocomposite. The composition of Ru and Pt in the Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs composite are 6 and 41 at.% of the total elements. The identified and as shown carbon and copper elements came from the amorphous carbon coated copper grids. The composition of the PtRu was tuned to evaluate a catalyst with higher activity at optimized composition, by the amounts of H<sub>2</sub>PtCl<sub>6</sub> and Ru added in the electrochemical deposition cell as shown in Table 1. In our experimental setup for the synthesis of Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs tri-metallic catalyst, the solution containing H<sub>2</sub>PtCl<sub>6</sub> and Ru as precursor salts. The cathodic potential for the electro deposition experiments was selected to be 0.3 V (vs RHE), where H<sub>2</sub> evolution beginning on the PtRu particles synthesized during the deposition process. The deposition at constant potential favoured the successful formation of PtRu particles in the form of clusters/islands over the surface of Pd-NCs. Pletcher and co-workers [16] believe that electro chemical deposition is completely explained by slow nucleation of Pt centres, where the solution contains a considerable amount of  $PtCl_6^{2-}$  and two kinds of species resulting from the hydrolysis reaction such as  $PtCl_5(H_2O)^-$  and  $PtCl_4(H_2O)_2$ , where each species is reduced to metallic Pt with zero oxidation state. This explanation highly coincides with the electrochemical characterizations (base CVs) observed in the fig. 1b, although the presence of  $Pt^{2+}$  as a stable intermediate cannot be discarded. Along with, Ru deposition from Ru precursor ions could begin in the similar potential zone of  $PtCl_5(H_2O)^{-}$  specie reduced. As it is already believed that the overpotential of Ru nucleation is rather high on carbon, but it is much lower on Pt in electrochemical deposition process, so Ru can be co-deposited with Pt on the surface of Pd-NCs at a lower over potential favoured kinetically by Pt nuclei formed [17].



Figure 2. XRD pattern of Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs compared with Pd-NCs (base material).

The crystal structure of Pd NCs and  $Pt_3Ru_1@Pd$ -NCs was characterized by X-ray diffraction (XRD). Fig. 2 shows the X-ray diffraction patterns of Pd NCs. The diffraction patterns can be observed at  $2\theta = 39.9^{\circ}$  (111),  $45.5^{\circ}$  (220) and  $67.8^{\circ}$  (220). The reflection peaks are consistent with those of a face-centered-cubic (fcc) crystalline structure of bulk Pd (JCPDS, Card No.46-1043). In the XRD pattern of  $Pt_3Ru_1@Pd$ -NCs composite, diffraction peaks at  $2\theta = 39.4^{\circ}$  (111),  $46.2^{\circ}$  (220) and  $68.3^{\circ}$  (220) corresponding to the fcc crystalline structure of Pd, Pt and its alloys, while additional peak at  $2\theta = 77.3^{\circ}$  (301) clearly indicate the existence of Ru. Additional peaks of  $RuO_2$  were not detected in the XRD Spectra. Figure shows the XRD scans in where the (220) of  $Pt_3Ru_1@Pd$ -NCs composite shifted to higher angles than that of pure Pd NCs, indicating lattice contraction due to alloy formation, while the (111) peak is shifted lower than that of Pd (111). This shifting indicates that the nucleation of Pt atoms on the Pd surface was reasonable.



Figure 3. XPS spectra of (a-c) Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs sample. Observed bands were (a) Pt4f, (b) Pd3d and (c) Ru3p.

XPS was employed to determine the surface elemental composition of  $Pt_3Ru_1@Pd-NCs$  composite. As shown in Fig. 3, the Pt 4f, Pd 3d and Ru 3p spectra of the trimetallic  $Pt_3Ru_1@Pd-NCs$  composite. The Pt 4f spectra can be deconvoluted into two pairs of peaks doublets, in which the more intense doublet (at 71.4 and 74.6 eV, respectively, with an asymmetric nature) corresponded to the metallic  $Pt^0$  state. Similarly, Fig. 3 also shows that the spectrum of  $3d_{5/2}$  and  $3d_{3/2}$  electrons for Pd appears at 334.4 eV and 340 eV, respectively, corresponding to the metallic Pd(0) state. Since the other metal in a Pt-based alloy could modify the electronic structure of Pt, the binding energy of Pt 4f shifted to higher energy values while Pd 3d shifted to lower energy values. Hence, the electrons move from Pt to Pd band. On the other hand, the  $3p_{3/2}$  and  $3p_{1/2}$  peaks for the  $Pt_3Ru_1@Pd-NCs$  composite were shown at 464.4 eV and 487 eV, respectively, corresponding to the metallic Ru(0) state.



**Figure 4.** Base CVs for the catalysts in 0.1M HClO<sub>4</sub> solution at 50 mV/s, in order to determine the effect of increase of Pt and Ru concentrations.

To obtain PtRu@Pd-NCs tri-metallic catalyst, different experiments have done to evaluate optimum composition of Pt and Ru in co-deposition synthesis. The co-deposition of PtRu was started with Pt<sub>1</sub>Ru<sub>1</sub>@Pd-NCs catalyst. Then after wards to improve the activity of starting catalyst, the concentration of Pt and Ru were increased separately in the above starting catalyst. Those are demonstrated as Pt<sub>2</sub>Ru<sub>1</sub>@Pd-NCs and Pt<sub>1</sub>Ru<sub>2</sub>@Pd-NCs in figures. Fig. 4 shows the base CVs for above three catalysts in 0.1 M HClO<sub>4</sub> electrolyte. The presence of Ru in the catalysts cause changes in the shape of the CVs, i.e. the tri-metallic catalysts do not display a well-defined hydrogen adsorption/desorption zone, conversely to the case of Pt and the pseudo capacitance in the "double layer region" is larger than on pure platinum. In tri-metallic system movement of electrons is carried out from base metal Pd. This behavior is distinctive of Pt-based catalysts containing oxophilic transition metals as Ru, Sn and Os [18,19]. Also an increase in the Ru content leads to a small negative shift of the Ru oxides reduction peak position as well as an increase of the peak area on the cathodic branch of the CVs. However, a quantitative comparison of CVs is complicated by the influence of the material support in the pseudo capacitive zone. As shown in Fig. 4 the base CVs for all the catalysts, there is hydrogen adsorption/desorption region (0.05-0.3 V) and surface metal oxidation/reduction region (0.4-0.70 V) in the CV curves. 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 to 0.4 V. The ECSA value can be calculated by  $Q_H$ =mq, where  $Q_H$  is the total electric charge of hydrogen adsorption and desorption on the catalyst, m is the catalyst loading on the glassy carbon electrode in g and the charge of each actual active area assumed to be 210 mCcm<sup>-2</sup> [20,21]. Current densities (i) are also given along with current (i) values for MOR activity, which were obtained by normalizing current with electrochemical active surface area (ECASA) obtained from their base CVs for all the catalysts.



**Figure 5.** MOR activity measurements for the catalysts in 0.1M HClO<sub>4</sub> +1M CH<sub>3</sub>OH solution at 50 mV/s, in order to determine the effect of increase of Pt and Ru concentrations.



**Figure 6.** Chronoamperometric (CA) results for the catalysts in 0.1M HClO<sub>4</sub> +1M CH<sub>3</sub>OH solution at 0.30V, 0.40V and 0.50V up to 300s, in order to determine the effect of increase of Pt and Ru concentrations.

Fig.5 shows the CVs recorded at  $50 \text{mVs}^{-1}$  in 1M CH<sub>3</sub>OH+ 0.1M HClO<sub>4</sub> solution at room temperature. For all the catalysts the onset potential of the methanol electro-oxidation is near 0.30 V. This is also confirmed by chronoamperometric (CA) measurements at constant potentials of 0.30V, 0.40V and 0.50V (Fig. 6). The beginning of methanol chemisorptions can be associated with the formation of OH<sub>ads</sub> species on Ru sites initiating due to the water dissociation that occurs at more negative potentials than that on Pd/Pt atoms through the so-called tri-functional mechanism. At ambient temperature, CH<sub>3</sub>OH is adsorbed only on Pt and Pd sites, while water molecules dissociate on Ru giving OH<sub>ads</sub> and the adsorbed species on Pt/Pd and Ru combine together forming CO<sub>2</sub>. In order to understand the mechanism as Ru concentration exceeded. The active sites responsible for chemisorption of methanol decreased, which reduce the activity of the catalyst. This result can be easily explained assuming a randomly distributed Pt and Ru atoms on the surface. The presence of Ru islands compared to Pt, on the Pd-NCs highly affect the activity of methanol oxidation. Hoster *et al.* 

[22] has also observed in the bimetallic system, that the activity of methanol starts to decrease as soon as intermediates adsorption at the free Pt sites is hindered by very high Ru coverage.

According to the results of methanol oxidation activity of the above three catalysts,  $Pt_2Ru_1@Pd-NCs$  has shown higher activity, and  $Pt_1Ru_2@Pd-NCs$  has shown lower activity than the  $Pt_1Ru_1@Pd-NCs$  catalyst. This is giving a clear message that increase of Pt concentration favoured the chemisorption of methanol and increase of Ru cause negative effect on activity. On the basis of the given results, the activity of catalyst was further improved in order to get optimum concentration of Pt in PtRu system. Then, the concentration of Pt was increased up to optimum composition of PtRu in  $Pt_3Ru_1@Pd-NCs$  and  $Pt_4Ru_1@Pd-NCs$  catalyst.



Figure 7. Base CVs for the catalysts in 0.1M HClO<sub>4</sub> solution at 50 mV/s, in order to determine the effect of increase of Pt concentration.

The base CVs for these catalysts are shown in fig. 7. The trend of hydrogen adsorption/desorption zone and double layer region increment is already explained in previous paragraph, that is also similarly interpretable for these CVs.



Figure 8. MOR activity measurements for the catalysts in  $0.1M \text{ HClO}_4 + 1M \text{ CH}_3\text{OH}$  solution at 50 mV/s, in order to determine the effect of increase of Pt concentration.

In fig. 8, as the concentration of Pt is increased in  $Pt_3Ru_1@Pd-NCs$ , the chemisorption of methanol is highly increased. This mechanism could be explained as the alloying of Pt with Pd base materials caused a shift of d-band centres of Pd towards down and itself Pt high. That improved the adsorption of CH<sub>3</sub>OH on maximum Pt sites. Due to the shift of d-band centres of Pd towards down the bond between poisoning species  $CO_{ads}$  at Pd sites become weaker, which eventually enhanced the chemisorption of methanol on rest of blocked sites. But in case of a further increase of Pt concentration in  $Pt_4Ru_1@Pd-NCs$  catalyst, the sites for water dissociation (Ru) covered by excess of Pt on Pd surface. Formation of OH<sub>ads</sub> is slowed down and further oxidation of CO<sub>ads</sub> into CO<sub>2</sub> in the absence of OH<sub>ads</sub> is stoped. Due to which activity is decreased.



**Figure 9.** Chronoamperometric (CA) results for the catalysts in  $0.1M \text{ HClO}_4 + 1M \text{ CH}_3\text{OH}$  solution at 0.30V, 0.40V and 0.50V up to 300s, in order to determine the effect of increase of Pt concentration.

The stability in the current is important for the catalyst, so their CA measurements are also given in fig. 9. Among all the catalyst  $Pt_3Ru_1@Pd$ -NCs has shown highest specific activity towards MOR with a value of about 7.85 mA cm<sup>-2</sup>. This was higher than that of recently reported activities of modified catalysts with same base material (Pd-NCs). The MOR activity of as synthesized  $Pt_3Ru_1@Pd$ -NCs is compared with different reported excellent results at 0.70 V vs RHE. Our catalyst has shown about 4 time's higher activity than Yizhong Lu *et al.* [11] catalyst (0.39 mA cm<sup>-2</sup>) and 2 time's higher activity than Fanhwei Chang *et al.* [12] catalyst (3.1 mA cm<sup>-2</sup>) which was further 3 time's higher than the of commercial Pt/C (1.1 mA cm<sup>-2</sup>). The mass activity is also presented here in fig. 10 with respect to loading Pd NCs, Pt and PtRu loading in  $Pt_3Ru_1@Pd$ -NCs catalyst, which is ca. 10500 mA mg<sup>-1</sup><sub>Pd</sub>, 75 mA mg<sup>-1</sup><sub>Pt</sub>, 66 mA mg<sup>-1</sup><sub>PtRu</sub> at 0.70V. Furthermore, the onset potential for chemisorption of methanol is at lower potential vs RHE than the above compared reported catalysts. As the durability of electrocatalyst is one of the important issues for their applications in fuel cells. To evaluate the electrochemical durability of catalyst accelerated durability test (ADTs) was also performed in 0.1M HClO<sub>4</sub> + 1M CH<sub>3</sub>OH solution by applying a CV test between 0.05V to 0.70V vs RHE at a scan rate of 100mV/s up to 1000 cycles given in fig.11 (a).



**Figure 10.** Mass activity representation with respect to  $mg^{-1}$  of Pd, Pt and PtRu loading for for  $Pt_3Ru_1@Pd-NCs$  the catalyst with highest activity, in 0.1M  $HClO_4 + 1M CH_3OH$  solution at a scan rate of 100mV/s.

Stability test was also performed by chronoamperometric measurements before and after 1000 cycles of ADTs at 0.40V and 0.50V up tp 300s in order to find the stability in current after ADTs given in fig.11 (b).





Figure 11. (a) Accelerated durability test (ADTs) for  $Pt_3Ru_1@Pd-NCs$  the catalyst with highest activity, in 0.1M  $HClO_4 + 1M CH_3OH$  solution at a scan rate of 100mV/s up to 1000 cycles, inset is given base CVs before and after 1000 cycles, (b) Stability test i-t curves for  $Pt_3Ru_1@Pd-NCs$  the catalyst with highest activity, in 0.1M  $HClO_4 + 1M CH_3OH$  solution at 0.40V and 0.50V up to 300s.

The durability was analyzed by comparing the ECSA from base CVs and peak currents densities from MOR activity before and after methanol oxidation reaction. As shown in Fig. 11(a), the Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs experienced a loss of only 1.5% and 1.2%, respectively, of the initial ECSA and peak current after 1000 cycles of methanol oxidation. Such results indicate that as synthesized Pt<sub>3</sub>Ru<sub>1</sub>@Pd-NCs exhibit enhanced durability towards methanol oxidation. This was very significant improvement in tuning the Pd-NCs by alloying with other two metals for methanol oxidation and to develop a trimetallic nanocomposite electrocatalyst as anode material in DMFCs. Our catalyst has fulfilled all the required parameters for a good anode material in DMFCs such as highest activity at lower potentials, lower onset potential, enhanced durability and stability.

## 4. CONCLUSIONS

In conclusion, we have presented here a green approach to develop a tri-metallic PtRu@Pd-NCs catalyst for MOR. In our work, Pd-NCs have been used initially as base material to deposit PtRu by electrochemical method. Different catalysts have been prepared in order to get optimum compositions of metals with optimum activity. Physical characterizations have completely described the crystallographic structure, morphology and compositions of the three metals for optimized catalyst with highest activity and enhanced durability. This work could provide useful information about key aspects for researchers such as, how to design a systematic experimental work to develop a good catalyst with highest activity and as well provided an excellent tri-metallic catalyst with high activity, durability and optimum precised compositions of precious metals. These can save time as well cost of the catalysts in the field of electrocatalysis.

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