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Halide-aided Controlled Fabrication of Pt–Pd/Graphene Bimetallic

Nanocomposites for Methanol Electrooxidation

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Fabrication of agglomeration-free Pt-based bimetallic nanoparticles (NPs) supported on carbon structures is extremely important for direct methanol fuel cells (DMFCs) applications. In this study, by introducing halide ions and ascorbic acid (AA) as a reducing agent in the synthesis recipe a controlled co-reduction of graphene oxide sheets, H<sub>2</sub>PtCl<sub>5</sub> and Na<sub>2</sub>PdCl<sub>4</sub> is achieved. The microstructure and morphological features of fabricated Pt-Pd bimetallic NPs deposited on reduced graphene oxide (RGO) sheets, herein after called as Pt-Pd/RGO bimetallic nanocomposites (NCs), are evaluated by X-ray diffraction and transmission electron microscopy. The results reveal that for the samples prepared in presence of halide ions (i.e. Pt-Pd/RGO-5KI and Pt-Pd/RGO-15KI) the uniformity and dispersion of Pt-Pd bimetallic NPs are significantly improved on RGO sheets over the sample prepared in absence of haide ions (i. e. Pt-Pd/RGO-0KI). The electrocatalytic activities of Pt-Pd/RGO bimetallic NCs towards methanol oxidation are investigated by cyclic voltammetric and chronoamperometric measurements. Among the various Pt-Pd/RGO bimetallic NCs prepared, Pt-Pd/RGO-15KI exhibits the best electrocatalytic activity and stability for methanol oxidation. The improved methanol oxidation on Pt-Pd/RGO-15KI is due to the enhanced uniformity, dispersion and lower size of Pt-Pd NPs, and synergistic roles played by Pt, Pd and RGO support. The present halide-aided fabrication strategy will be significantly helpful to the further design of Pt-based nanocomposites with desired properties relevant to DMFCs applications.

#### Introduction

Bimetallic nanoparticles (NPs), consisting of two different metallic components, are gaining greater interest than those of the corresponding bulk materials and monometallic NPs in nanoscience and nanotechnology disciplines.<sup>1</sup> This interest is largely stemmed from the ability of individual components present in bimetallic NPs to work synergistically in offering unique chemical, physical and electronic properties than their monometallic counterparts.<sup>2-4</sup> It is well-known that better exploitation of the bimetallic NPs for various scientific and technological applications is hugely reliant on the development of reliable and strategic preparation routes which can deliver monodisperse bimetallic NPs in good yields.<sup>5,6</sup> Since the bimetallic NPs are finely divided bulk materials they are typically more prone to thermodynamic instability which leads to agglomeration. With the agglomeration, surface area-to-volume ratio of bimetallic NPs decreases making them less suitable for catalytic applications. Hence, it is crucial to stabilize the bimetallic NPs to prevent the agglomeration and to achieve a better

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of NPs to circumvent the problems associated with surfactantremoval methods.<sup>31</sup> When metal NPs are produced by reducing the metal halide ion-based precursors, the reduction rate depends on the affinity of halide to metal cations. If a halide ion is more strongly bonded with the metal ions then its reduction ability is lowered causing controlled reduction.<sup>32</sup> For example, halide ions like bromide and iodide were utilized to fabricate Ag, Au, Pd and Pt nanocrystals by controlling the redox potentials of corresponding metal ions to yield lower-sized particles.<sup>33,34</sup> This kind of halide ligand replacement strategy is used for the fabrication of metal NPs with controlled growth rates.<sup>35</sup> Yin and co-workers based on a spectroscopic evidence reported that the addition of iodide ions to PtCl<sub>6</sub><sup>2-</sup> completely replaces Cl<sup>-</sup>. According to the Hard-Acid-Base-Theory the Ptl<sub>6</sub><sup>2-</sup> complex is fairly stable and exhibit slower reduction rate compared to PtCl<sub>6</sub><sup>2-34b</sup> Mirkin et al. also observed that presence of iodide lowers the reduction rate Aul<sub>2</sub> compared to AuCl<sub>2</sub> and AuBr<sub>2</sub>.<sup>36</sup>

Recently, there has been a sudden upsurge in the development of graphene-supported bimetallic nanoparticles due to their promising applications as electrocatalysts for direct methanol fuel cell (DMFC) reactions. In particular, graphene-supported Pt-based bimetallic nanoparticles are gaining much interest because of their promising electrocatalytic activity and stability than monometallic NPs.<sup>3</sup> Graphenewhich is a two dimensional monolayer of carbon atoms arranged in a hexagonal configurations offers promising properties like high charge carrier mobility, larger surface area, high mechanical, chemical and thermal stability and durability makes it an ideal electrocatalyst support material for fuel cell applications.<sup>38</sup> Zhao et al developed a supercritical route for the fabrication of PtRu bimetallic nanoparticles with a particle size of about 3.11 nm on functionalized graphene sheets (FGS). Compared with PtRu/C, PtRu/FGS catalyst reported to exhibit 2-3 times higher activity towards methanol electrooxidation.<sup>39</sup> The improved activity is related to the improved surface area of FGS and uniform dispersion of PtRu NPs on FGS support. A polyol method has been demonstrated by Dong et al. for obtaining PtRu NPs on graphene supports.<sup>40</sup> It is reported that the graphene-supported PtRu NPs exhibited 2-3 times superior activity towards methanol oxidation compared to carbon-supported and graphite-supported PtRu NPs. In addition, researchers have found promising methanol electrooxidation on graphene-supported Pt-Au<sup>41</sup> and Pt-Pd.<sup>42-44</sup>

In this study, by utilizing the advantages offered by the halide ligand replacement strategy we fabricated Pt-Pd bimetallic NPs on reduced graphene oxide (RGO) support. The simultaneous reduction of graphene oxide and metal precursors was achieved by using ascorbic acid as a reductant. Well-dispersed and more uniform nanoparticles were achieved by controlling the reduction ability of  $\mathrm{Pd}^{^{2+}}$  ions by adding KI in the synthesis process. As supported by transmission electron microscopy studies, it was found that more uniform dispersion was achieved if 15 mg of KI was introduced in the system (sample labeled as Pt-Pd/RGO-15KI) when compared to the nanoparticles prepared with 5 mg of KI (Pt-Pd/RGO-5KI) and in absence of KI (Pt-Pd/RGO-0KI). The structural features and composition of the as-prepared Pt-Pd/RGO nanocomposites were verified by X-ray diffraction and energy**RSC Advances Accepted Manuscript** 

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dispersive X-ray spectroscopy (EDS) inductively coupled plasma optical emission spectroscopy (ICP-OES) studies. Furthermore, electrochemical measurements on Pt-Pd/RGO NCs revealed that Pt-Pd/RGO-15KI showed the superior catalytic activity towards electro-oxidation of methanol in acidic medium when compared to the Pt-Pd/RGO-5KI, Pt-Pd/RGO-0KI and commercial Pt/CNPs. The generalized fabrication method demonstrated here for Pt-Pd/RGO nanocomposites can be extend to other bimetallic nanoparticle systems applicable for fuel cell applications.

#### Experimental

Chemicals. Graphite powder, H<sub>2</sub>PtCl<sub>6</sub> 6H<sub>2</sub>O, Na<sub>2</sub>PdCl<sub>4</sub> were purchased from Aldrich and used as-received. KI, KMnO<sub>4</sub>, NaNO<sub>3</sub>,  $H_2O_2$  and ascorbic acid were purchased from Merck India. All the chemicals used in the present study are of analytical grade and used without further purification.

Synthesis of graphene oxide from graphite powder. Graphene oxide was synthesized from natural graphite powder by using a modified Hummers and Offemanmethod.<sup>45,46</sup> Typically, 3 g of graphite powder, 6 g of sodium nitrate and 12 g of KMnO<sub>4</sub> were dissolved in 120 ml of H<sub>2</sub>SO<sub>4</sub> in a 250 ml three necked conical flask. The reaction mixture was initially maintained at 0 - 10 °C under icebath for 4 h and later the temperature is increased to 50 °C and kept constant for 4 h. Later, the reaction mixture is cooled down to 0 - 10 °C under ice-bath and 300 ml of water was added. To this, 15 mL of 30% (w/v)  $H_2O_2$  was added and stirred for 2 h. Later, the reaction mixture was washed with distilled water repeatedly until pH of washings reaches neutrality. Finally, the reaction mixture was centrifuged and dried at 80 °C overnight in hot-air oven.

Preparation of Pt-Pd bimetallic nanoparticles on reduced graphene oxide (Pt-Pd/RGO). In a typical procedure, 70 mg of GO was added to 50mL distilled water in a 100 mL beaker. The water and GO mixture was first ultrasonically treated for 1 h to ensure the GO being uniformly dispersed in water. To this, 2 mL of 0.05 M aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> 6H<sub>2</sub>O was added with continuous ultrasonication by a Labman ultrasonicator operated with an ultrasonic wattage of 300 W. Later, 29.26 mg of  $Na_2PdCl_4$  in 4 mL water with various amounts of KI (5 mg and 15 mg) was added. Precursor amounts of Pt and Pd were taken to get the final weight of 19 wt% Pt and 11 wt% Pd with a Pt-to-Pd atomic ratio as 1:1. The total mixture was stirred overnight in a beaker at room temperature. Separately, 120 mg of L-ascorbic acid was dissolved in 10 mL distilled water and taken in a 250 mL round bottomed flask and heated up to 100 °C for 30 min under nitrogen. To this solution, slowly the suspension containing metal halides and GO was added and the entire reaction mixture pH was maintained at 12 by adding an appropriate amount of NaOH and stirred at 140°C for 5 h. The final Pt-Pd on reduced graphene oxide (Pt-Pd/RGO) product was washed copiously with distilled water and dried in hot-air oven at 60 °C for 12 h. The products obtained by adding 5 mg KI and 15 mg in thesynthesis process were labelled as Pt-Pd/RGO-5KI and Pt-Pd/RGO-15KI, respectively. For comparison Pt-Pd/RGO in the absence of KI(labelled as Pt-Pd/RGO-OKI) was also prepared using the similar procedure. A schematic representation of Pt-Pd deposition on RGO is shown in Scheme-1.



Scheme 1.Schematic presentation of fabrication of Pt-Pd/RGO nanocomposites.

Physical Characterization.X-ray diffraction patterns of all the assynthesized catalysts were recorded using a Rigaku Miniplus-600 Xray diffractormeter with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) to identify the phase of as-synthesized catalysts and to estimate the particle size. The X-ray diffractogram was obtained at a scan rate of 5°/s for 20 values between 5 to 90°. Fourier Transformed infrared spectroscopy (FT-IR) measurements of catalysts powders were performed on a PerkinElmer Spectrum Two<sup>TM</sup> FT-IR spectrometer in the range  $500 - 4000 \text{ cm}^{-1}$ . Transmission electron microscopy (TEM) images were obtained with a JEOL 3010 operated at an accelerating voltage of 300 kV. For TEM analysis, catalyst powders were suspended in ethanol and exposed to ultrasonication. An aliquot of the suspension was then dropped on a carbon-coated grid and dried in air. The compositions of the bimetallic Pt-Pd/RGO catalysts were analyzed by energy dispersive X-ray spectrometry (EDX) analysis using a Quanta 200 FEG scanning electron microscope. The ratio of Pd-to-Pt was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Optima 5300 DV, Perkin Elmer, USA).

Electrode Preparation and Electrochemical Measurements.All electrochemical measurements were performed at room temperature in a standard three-electrode electrochemical cell connected to a CHI potentiostat (Model CHI 6002 E, USA). A silver/silver chloride (saturated KCI) ( $E^\circ = -0.197$  V vs NHE) and a Pt wire were used as the reference and auxiliary electrodes, respectively. The working electrode was fabricated on a glassy carbon disk (GCE) (3 mm in diameter with a geometric area of 0.0706 cm<sup>2</sup>). At first, the glassy carbon electrode was polished carefully with 1.0, 0.5, and 0.05 µm alumina powder, followed by ultra- sonication in ethanol and deionized water several times. Then, 2 mg of catalyst was dispersed in a mixed solvent including de-ionized water (500 µL), ethanol (500 µL) and 0.5 wt% Nafion solution (10 µL) under ultrasonication for 30 min. Finally, 4 µL of the solution was dropped on the surface of the GCE by using

micropipette and dried in the air for 24 h before performing the electrochemical experiments.

Cyclic voltammetry experiments were performed in N<sub>2</sub>-saturated freshly prepared 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by sweeping the electrode potential from -0.2 to 1.2 V vs Ag/AgCl (saturated KCl) at a scan rate of 50 mV/s for 20 runs. Electrochemical surface areas (ECSA) of catalysts samples were calculated from the stable voltammograms. All potentials in this work were reported against Ag/AgCl (saturated KCl). Methanol oxidation activity was studied by performing CV measurements in a mixture of 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution with the same scan rate from -0.2 to 1.2 V vs Ag/AgCl (saturated KCl).Chronoamperometric measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution at a fixed potential of 0.62 V vs Ag/AgCl (saturated KCl).

#### **Results and discussion**

*FT-IR*.FT-IR spectroscopy can provide insights into the extent of removal of oxygen groups from graphene oxide during the reduction process. FT-IR spectral scans of as-prepared Pt-Pd/RGO nanoparticles and graphene oxide are presented in Figure 1. As can be seen from Fig. 1, a spectral scan of graphene oxide exhibits absorption bands at  $3461 \text{ cm}^{-1}$  and  $1731 \text{ cm}^{-1}$  which were ascribed to the vibrations of O–H and C=O, respectively. In addition, the peaks at  $1382 \text{ cm}^{-1}$  and  $1260 \text{ cm}^{-1}$  were attributed to the vibrations of O–H of carboxylic acid functionality and C–OH functionality of graphene sheet, respectively. Furthermore, the peak appeared at  $1058 \text{ cm}^{-1}$  was related to the vibration of epoxide functionality. The appearance of all these peaks indicates the presence of rich oxygencontaining functionalities in graphene oxide. From fig. 1, it can also be seen the appearance of a peak at  $1626 \text{ cm}^{-1}$  which can be

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assigned to the skeletal vibrations of un-oxidized graphitic domains. Furthermore, a C–H stretching peak appeared at 2923 cm<sup>-1</sup> can also be observed in the spectra. When ascorbic acid is introduced in the synthesis process it can reduce both Pt and Pd metal precursors and graphene oxide simultaneously to generate Pt-Pd bimetallic NPs on reduced graphene oxide (RGO). A close inspection of FT-IR scans of all the three Pt-Pd/RGO bimetallic nanocomposites, i. e. Pt-Pd/RGO-15KI, Pt-Pd/RGO-5KI and Pt-Pd/RGO-0KI nanoparticles reveal that the intensity of peaks related to the carbonyl and epoxide functional groups are almost decreased indicating the partial reduction of graphene oxide. However, a small amount of carbonyl and epoxide functional groups are still retained by the RGO.



**Fig. 1** FT-IR spectra of graphene oxide and Pt-Pd/RGO bimetallic nanocomposites.

Further, the intensities of hydroxyl group appeared at 3461 cm<sup>-1</sup> and O–H of carboxylic acid functionality appeared at 1382 cm<sup>-1</sup> of graphene sheet is decreased indicating the extent of reduction of graphene oxide into partially reduced graphene oxide. The residual oxygen-containing functionalities present on graphene oxide are attractive since they will act as anchoring sites for metal deposition so that better dispersion of metal nanoparticles can be expected. The FT-IR results of graphene oxide and bimetallic-graphene nanoparticles well agreed with the literature studies.<sup>47</sup>

**XRD analysis.** Structural features of GO and RGO (Fig. 2a) as well as Pt/RGO, Pd/RGO and Pt-Pd/RGO nanocomposites (Fig. 2b) have been verified by X-ray diffraction analysis.The comparison of the XRD spectra of GO and RGO clearly shows that the typical C(002) peak of GO appeared between 2 $\theta$  values 10° and 15° shifts to higher angle after reduction by L-ascorbic acid. The broad peak between 2 $\theta$  values 20° and 30° is attributed to the diffraction of the C (002) plane of reduced graphene oxide suggesting that grapheme oxide was reduced by ascorbic acid and restacked into an ordered crystalline structure.<sup>48</sup> As can been seen from the XRD scans presented in Fig. 2b, Pt/RGO and Pd/RGO nanoparticles exhibit peaks that match well to those of fccPt (JCPDF 04-0802) and Pd (JCPDF 46-1043). All the three home-made Pt-Pd/RGO

nanocomposites exhibits diffraction peaks at  $2\theta$  values  $40.09^\circ$ ,  $46.41^\circ$ ,  $67.74^\circ$  and  $81.71^\circ$  which could be conveniently assigned to the diffraction from (111), (200), (220) and (311) planes, respectively of Pt-Pd NPs of Pt-Pd/RGO nanocomposites.



**Fig. 2** XRD patterns of (a) GO and RGO, (b)Pt-Pd/RGO bimetallic nanocomposites.

The presence of the (111) diffraction peak at 40.09° with its position lying in between (111) peak of Pt i. e. at 39.78° and (111) peak of Pd i. e. at 40.12° is taken as evidence for the formation of Pt-Pd NPs on RGO and has been reported in previous literature studies.  $^{42,49,50}$ Further, relative to the fcc-Pt reflections, the diffraction peaks of the Pt-Pd/RGO catalysts are shifted to higher 20 values revealing decreased lattice parameters and a high level of alloying.<sup>51</sup> The lattice parameter (a) of Pt-Pd nanoparticles in all three catalysts have also been estimated by carefully determining the position of the (111) Bragg peak seen in the diffraction pattern. For Pt/RGO we obtained a lattice parameter a = 3.920 Å which is shorter than that of bulk platinum (a = 3.970 Å). This could be due to the smaller size of Pt/RGO nanoparticles. Estimates of 'q' for Pt are 3.892 Å. 3.896 Å and 3.894 Å in Pt-Pd/RGO-0KI, Pt-Pd/RGO-5KI and Pt-Pd/RGO-15KI, respectively. The decrease in lattice parameter of Pt in Pt-Pd/RGO bimetallics compared to the lattice parameter of Pt/GO might result from the lattice contraction upon alloying by Pd. In addition, the average crystallite size of Pt-Pd/RGO composites is calculated using the Scherrer formula from the diffraction peak of (220) plane.<sup>52</sup> The results shows that the Pt-Pd/RGO-5KI and Pt-Pd/RGO-15KI composites exhibits particle size of about 6.4 nm and 3.2 nm, respectively which is consistent with the TEM analysis. For Pt-Pd/RGO-OKI, particle size is not calculated from the line broadening analysis since this sample has a bimodal distribution of particles as seen from the TEM images shown below.

**TEM analysis.** The morphological features, particle size and homogeneity of the as-prepared Pt-Pd/RGO nanocomposites were evaluated by transmission electron microscopy (TEM). Figure 3a-c displays the representative TEM images of Pt-Pd/RGO-0KI sample at various magnifications. It is clearly observed that Pt-Pd particles were deposited on RGO sheets with a bimodal distribution. Larger particles with a particle size of about 50 nm were well-attached to RGO sheets. Since this sample was prepared without the addition of KI during the synthesis process uncontrolled reduction rates of Pt and Pd metal chloride precursors resulted in agglomerated particles of Pt-Pd/RGO composites.



Fig. 3 TEM images of Pt-Pd/RGO bimetallic nanocomposites: (a-c) Pt-Pd/RGO-0KI, (d-f) Pt-Pd/RGO-5KI, (g-i) Pt-Pd/RGO-15KI at various magnifications.

In a recent study, Zhang et al. reported that the formation of bigger sized Pt-Pd particles could be possible due to stronger electron acquisition ability of Pt vs Pd in the precursors which controls the nucleation and final growth rates of Pt-Pd nanoparticles.<sup>42</sup> Interestingly, in this study when the Pt-Pd nanoparticles are prepared by introducing various amounts of KI during the synthesis process the particle sizes of final Pt-Pd nanoparticles are dramatically decreased. For example, in case Pt-Pd nanoparticles prepared by the addition of 5 mg KI during the synthesis process the particle size is decreased to about 6 nm and particles are homogeneously covered the surface of graphene sheets (Fig. 3d-f). Here, the addition of KI to Pd and Pt chloride precursors lowers their reduction potentials and more uniform nucleation and growth rates could be achieved. As a result, monodispered Pt-Pd nanoparticles are well-anchored on the surface of graphene sheets. Further, if the amount of KI introduced is increased to 15 mg as in the case of Pt-Pd/RGO-15 mg sample the dispersion and uniformity

of final Pt-Pd particles are even better on graphene sheets (Fig. 3 gi) with a particle size of about 3 to 4 nm further demonstrating the capability of iodide in lowering the reduction ability of metal chloride precursors.

**EDS analysis.** Energy dispersive X-ray spectroscopy (EDS) data as shown in Figure 4, reveals that for all the Pt-Pd/RGO bimetallic nanocomposites the elemental abundance of Pt and Pd is found to be 49:51 close to the theoretical composition of 1:1 demonstrating that both Pt and Pd are deposited on reduced graphene oxide sheets. Further, chemical composition of Pt-Pd/RGO bimetallic nanoparticles is evaluated by ICP-OES analysis. The ratio of chemical composition of Pt-to-Pd for Pt-Pd/RGO-15KI, Pt-Pd/RGO-5KI and Pt-Pd/RGO-0KI is found to be 51:49, 49:51 and 47:53, respectively. The results indicate that the as-synthesized Pt-Pd/RGO bimetallic nanocomposites have Pt-to-Pd ratio close to 1:1.



**Fig. 4** Energy dispersive X-ray spectroscopy (EDS) data of Pt–Pd/RGO bimetallic nanocomposites.

CV analysis. Cyclic voltammograms (CVs) of Pt/C, Pt-Pd/RGO-OKI, Pt-Pd/RGO-5KI and Pt-Pd/RGO-15KI nanocomposites in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions were collected to measure the electrochemically active surface area (ECSA) of the catalysts and shown in Figure 5. Cyclic voltammetry experiments were performed in N<sub>2</sub>-saturated freshly prepared 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by sweeping the electrode potential from -0.2 to 1.2 V vs Ag/AgCl (saturated KCl) at a scan rate of 50 mV/s before which 20 cycles of potential scanning were carried out in order to obtain stable voltammograms. The CV features of Pt-Pd/RGO-0KI, Pt-Pd/RGO-5KI and Pt-Pd/RGO-15KI composites exhibits typical features related to the Pt-Pd surfaces. More specifically, the CV profiles are distinguished in to three regions comprising of typical hydrogen adsorption/desorption region, the double-layer region and the surface oxide formation/reduction profiles of region. The CV graphene-supported Pt-Pdnanocomposites of this study exhibits irregular current peaks which are typical of graphene oxide supports and are normally caused by the residual oxygen-containing groups of graphene present after the partial reduction of graphene oxide.<sup>53</sup> By integrating the area under the hydrogen adsorption peak in the CV curves between -0.2 and 0.07 V, which represents the total charge of hydrogen adsorption, the ECSA is calculated after a double-layer correction.<sup>42,54</sup> For comparison, CV profile of a commercial Pt/C catalyst is also shown in Fig. 5 and its ECSA value is also calculated. The trends in ECSA values of commercial Pt/C and as-prepared Pt-Pd/RGO nanocomposites varied in the following order: Pt-Pd/RGO-15KI (81.2 m<sup>2</sup>/g) > Pt-Pd/RGO-5KI (78.5 m<sup>2</sup>/g) > Pt-Pd/RGO-0KI  $(65.1 \text{ m}^2/\text{g}) > \text{commercial Pt/C black} (59.05 \text{ m}^2/\text{g})$ . The observed higher ECSA for Pt-Pd/RGO-15KI is probably due to the smaller size and more uniform distribution of Pt-Pd on RGO sheets as supported by the TEM observations. The CV results reveal that better electron transfer through the electrode surface with more active sites for electrochemical reaction can be achieved on Pt-Pd/RGO-15KI nanocompositeelectrocatalyst. As a result higher electrocatalytic activity towards methanol oxidation can be anticipated on PtPd/RGO-15KI nanocompositeelectrocatalyst when compared to the Pt-Pd/RGO-0KI, Pt-Pd/RGO-5KI and commercial Pt/C catalysts.

![](_page_6_Figure_7.jpeg)

Fig. 5 Cyclic voltammograms (CVs) of Pt/C and Pt-Pd/RGO nanocomposites in 0.5 M  $H_2SO_4$  (Scan rate 50 mV/s).

CV analysis in CH<sub>3</sub>OH. The electrocatalytic properties of commercial Pt/C and as-prepared Pt-Pd/RGO nanocomposites towards methanol oxidation were investigated by measuring CVs in 0.5 H<sub>2</sub>SO<sub>4</sub> containing 1 M CH<sub>3</sub>OH solution and were shown in Figure 6. All the catalysts exhibit characteristic well-separated anodic peaks in the forward sweep and reverse scan due to the methanol oxidation. The peak appeared at 0.6 to 0.7 V is attributed to the oxidation of freshly chemisorbed species coming from methanol adsorption.<sup>55</sup> The peak appeared at 0.4 V in the backward scan is related to the faradic oxidation of residual carbonaceous species formed in the forward scan on Pt and Pd surfaces.<sup>56-58</sup> Further, a small cathodic wave peaking at 0.52 - 0.54 V appeared and is attributed to the traces of unalloyed Pd present in the sample. Comparison of methanol electro-oxidation activity on as-prepared Pt-Pd/RGO nanocomposites with a commercial Pt/C catalyst reveals that methanol electro-oxidation in terms of specific activity follows the order: Pt-Pd/RGO-15KI (0.52 mA/cm<sup>2</sup>-ECSA) > Pt-Pd/RGO-5KI  $(0.36 \text{ mA/cm}^2\text{-ECSA}) \sim \text{Pt-Pd/RGO-OKI} (0.35 \text{ mA/cm}^2\text{-ECSA}) > \text{Pt/C}$ (0.32 mA/cm<sup>2</sup>-ECSA). As can be seen from these results, asprepared Pt-Pd/RGO-15KI catalyst exhibit almost 1.62 times higher electrocatalytic activity than that of a commercial Pt/C. Further, the MOR mass activity (MA) of Pt-Pd/RGO-15KI is a two order higher (0.41 mA/ $\mu$ g<sub>Pt</sub>) compared to the commercial Pt/C (0.19 mA/ $\mu$ g<sub>Pt</sub>). The enhanced electrocatalytic activity observed in the case of Pt-Pd/RGO-15KI nanocomposites can be attributed to the higher ECSA, high and uniform dispersion of Pt-Pd nanoparticles on graphene surface and improved electron transport and higher surface area of graphene. Further, the ratio of the forward anodic peak current (I<sub>f</sub>) to the backward anodic peak current  $(I_b)$ ,  $I_f/I_b$ , can be used as an important index to evaluate the catalyst tolerance to the CO accumulation.43,59,60 Generally, higher tolerance to intermediate carbonaceous species can be expected for the catalysts having higher  $I_f/I_b$  values and subsequently, they can act as highly active CO-tolerant electrocatalysts for practical fuel cell applications. For commercial Pt/C, the  $I_f/I_b$  ratio is found to be 1.01. Though the

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particle size of as-synthesized Pt-Pd/RGO-15KI catalyst (3.2 nm) and a commercial Pt/C (3 nm) is of similar order the presence of second metal 'Pd' play a crucial role in enhancing the methanol oxidation activity. The presence of Pd which is relatively more oxophilic metal than Pt could be acted as a promoter for the oxidative removal of CO on Pt because nanoscale palladium is highly active for CO oxidation. Further, the Pd may alter the electronic structure of Pt to facilitate weakening of Pt–CO bond thereby facile CO removal could be expected. Recently, it has been reported that the presence of small amount of oxygen-containing groups on RGO can also enhance the tolerance of the catalyst to CO poisoning.<sup>41d</sup> So in the as-synthesized Pt-Pd/RGO-15KI catalyst, the presence of graphene also play a key role in the removal of CO-like species resulting in the high electrocatalytic activity towards methanol oxidation.

![](_page_7_Figure_4.jpeg)

Fig. 6 Cyclic voltammograms (CVs) of Pt/C and Pt-Pd/RGO nanocomposites in a solution of 0.5 M  $\rm H_2SO_4$  and 1 M CH\_3OH with a scan rate of 50 mV/s.

However, for Pt-Pd/RGO-0KI bimetallic nanocomposite this value is slightly raised to 1.17. Further, increase in  $I_f/I_b$  values are observed for the samples Pt–Pd/RGO-5KI and Pt–Pd/RGO-15KI with the values 1.527 and 1.709, respectively. The highest  $I_f/I_b$  value of Pt-Pd/RGO-15KI indicates its superior methanol electro-oxidation ability and lower extent of accumulation of carbonaceous species. Furthermore, the onset potential of the methanol oxidation for the Pt-Pd/RGO-15KI is significantly shifted towards more negative potentials than the Pt–Pd/RGO-5KI, Pt-Pd/RGO-0KI, and Pt/C. This result suggests enhanced dissociation of methanol on Pt-Pd/RGO-15KI.

Figure 7 displays current-time plots (Chronoamperograms) of Pt/C and different Pt-Pd/RGO nanocomposites which can reflect catalytic activity and durability of the electrocatalysts for methanol oxidation. Higher current densities are observed for all the catalysts during the initial period which can be attributed to the availability of more number of active sites on the surface of the catalysts.<sup>42</sup> However, a rapid decay in current densities can be seen particularly below 50s due to the accumulation of CO-like intermediates on the active sites of electrocatalysts hindering methanol from further oxidation.<sup>39</sup> Although the current decay is observed for all the electrocatalysts, Pt-Pd/RGO-15KI exhibits significantly higher current density than other Pt-Pd/RGO nanocomposites and Pt/C in the entire time period. As supported by the TEM observations, Pt–Pd/RGO nanocomposites fabricated in the presence of KI yields more uniform dispersion on the RGO sheets with least aggregation thereby producing more accessible Pt–Pd sites for efficient catalytic activity in comparison with Pt–Pd/RGO-0KI. These findings suggest that Pt-Pd/RGO-15KI catalyst has higher methanol oxidation activity and stability than other Pt-Pd/RGO nanocomposites and Pt/C consistent with voltammetric measurements (Figure 6). All the electrochemical results presented here demonstrate that Pt-Pd/RGO-15KI bimetallic nanocomposite fabricated via a halide-aided synthesis strategy can serve as an efficient anode catalyst for DMFC applications.

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![](_page_7_Figure_9.jpeg)

Fig 7 Current-time curves of Pt/C and Pt-Pd/RGO nanocomposites measured in 0.5 M  $H_2SO_4 + 1$  M CH<sub>3</sub>OH.

#### Conclusions

In conclusion, this work offers a facile halide-aided synthesis strategy to fabricate Pt-Pd bimetallic nanoparticles well dispersed and anchored on reduced graphene oxide (RGO) supports without using any polymeric surfactants. These graphene-supported Pt-Pd/RGO nanocomposites, particularly Pt-Pd/RGO-15KI exhibit considerably higher electrocatalytic activity and stability towards methanol oxidation than Pt/C which can be attributed to the uniform dispersion of PtPd particles on the high surface area of RGO support. This work demonstrated that addition of halides can yield controlled reduction of metal ions into metal particles on RGO supports and improve their electrocatalytic activity for practical applications.

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# **TOC content**

# Halide-aided Controlled Fabrication of Pt–Pd/Graphene Bimetallic Nanocomposites for Methanol Electrooxidation

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![](_page_10_Figure_6.jpeg)

Herein, Pt-Pd/RGO bimetallic nanocomposites were successfully synthesized through a halide-aided fabrication strategy. The Pt-Pd/RGO-15KI catalyst with its uniform dispersion exhibit the improved electrocatalytic activity towards methanol oxidation when compared to the Pt-Pd/RGO-0KI.