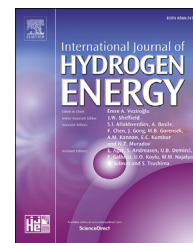




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# Facile synthesis of well dispersed Pd nanoparticles on reduced graphene oxide for electrocatalytic oxidation of formic acid

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## ABSTRACT

In present study, we report a facile synthesis of crystalline, small size Pd nanoparticles (NPs) on reduced graphene oxide (RGO) abbreviated as Pd/RGO for electrocatalytic oxidation of formic acid (FA). Here, first graphene oxide (GO) was reduced by the green method using L-ascorbic acid and citric acid and further Pd NPs were decorated on RGO by a facile method without using any reducing agents. The reduction of GO to RGO and synthesis of Pd NPs was confirmed by the X-ray diffraction (XRD) and X-ray photoelectrons (XPS) techniques. Surface morphology of Pd/RGO nanocomposite was evaluated by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The electrocatalytic behavior of Pd/RGO nanocomposite was tested by using of cyclic voltammetric (CV) technique for electro-oxidation of FA in mixed solution of 0.5 M HCOOH + 0.5 H<sub>2</sub>SO<sub>4</sub> at RT. Results shows that the higher electrocatalytic activity of Pd/RGO nanocomposite compare to Pd NPs.

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## Introduction

Recently, vast research is going on to develop alternatives to fossil fuels due to continuous depletion of proven petroleum reservoirs and concerning environmental threats based on

greenhouse gas emissions [1–4]. In such contest, presently research is focused on clean energy solutions [5]. Hydrogen (H<sub>2</sub>) is consider as choice of fuel for power generation due to its high energy density and clean combustion without emission of any harmful chemical by-products [6]. However, conventional storage technologies such as high pressure storage

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(350–700 bar) or cryogenic liquefaction (20.2 K) hinders it as a choice of fuel due to safety concerns and energy efficiency criteria [7].

In this quest, presently H<sub>2</sub> economy based on liquid hydrogen carrier (LHC) is an emerging field of interest due to its high gravimetric and volumetric content [8]. The examples includes are liq. ammonia, hydrazine and N-ethylcarbazole (NEC) [9–11]. However, to release the H<sub>2</sub>, the requirement of high temperature and safety concerns are two major apprehensions with LHC. Instead of them, formic acid (FA) is a convenient energy vectors for H<sub>2</sub> economy [12]. It is dense, viscous and has a high liquid boiling point. It contains 4.4 wt.% of H<sub>2</sub> with a volumetric capacity of 53.4 g/L which is higher than that of most other liquid H<sub>2</sub> storage materials due to its high density ( $d = 1.22$  g/L) [13,14]. However, due to its corrosive nature, diluted form (85%) of FA is more often used as energy carrier due to easy-to-handle and relatively nontoxic, noncorrosive, and nonflammable behavior [15]. Its electrochemical oxidation conveniently produces H<sub>2</sub> at RT, which makes it suitable for fuel cells application [16].

Fuel cells provide the high energy out-put without emitting harmful by-products, suitable for various kind of light weight, portable and flexible electronic device applications such as mobile phones, laptops, roll-up display and wearable devices [17,18]. For these reasons, in previous decades pioneering works have been carried out for the development of direct formic acid fuel cells (DFAFCs) based on Pt catalyst [19–23]. For instance, Jiang et al. demonstrated the FA electro-oxidation on nanostructured Pt [24]. However, Pt limited availability, high cost and vulnerability for CO poisoning restricts Pt application in fuel cells [25]. Recently, Pd nanoparticles (NPs) based electrocatalysts have emerged as alternatives to Pt for fuel cells application due to their affordable price, comparable higher abundance and greater resistance to CO poisoning during the electrocatalysis reactions [26,27]. Bai et al. reported the FA electro-oxidation on dendritic Pd nanostructure and investigated the superior CO tolerance capability of Pd catalyst [28]. Similarly, Zhang et al. exhibited the electrocatalytic activity of monodispersed Pd nanocrystals towards the FA oxidation [29]. Although, Pd is promising catalyst for electro-oxidation of FA although, it is desirable to further maximize the catalytic activity using the support materials.

The recent discovery of graphene has opened a new avenue as catalyst support due to their large surface area, high electrical and thermal conductivity and robustness during the catalytic reactions [30,31]. Huang et al. successfully demonstrated the high catalytic activity of Pd/RGO towards the FA electro-oxidation [32]. Apart of catalyst support the size and shape of the Pd NPs are also important aspect for electrocatalytic reactions where the small size, uniform morphology and monodispersion are some key features for their performance. Recently, Yang et al. exhibited the synthesis of cubic and spherical Pd NPs on graphene in presence of N-methyl-2-pyrrolidinone (NMP) using the solvothermal process at 140 °C [33]. In another work, Ghosh et al. synthesized the small sized Pd NPs using the Pd (acac)<sub>2</sub> precursor in presence of CO reducing environment via irradiation of <sup>60</sup>Co  $\gamma$ -rays [34]. However, involvement of expensive, toxic chemicals and specific instrumental tools for Pd NPs synthesis restricts them

for wide applications. In such contest, synthesis of Pd NPs without involvement of toxic and expensive chemicals, harsh reaction conditions such as high-temperature is appreciable for both research and industrial purposes. Here, we report a stepwise synthesis of Pd/RGO nanocomposite by a green and facile method. Pd NPs were synthesized on RGO by a facile method without using any external reducing agents in anhydrous methanol. The Pd/RGO nanocomposite was fully characterized by several techniques to confirm the structure and surface morphology. Additionally, the Pd/RGO nanocomposite electrocatalytic activity towards the FA electro-oxidation reaction was evaluated.

## Experimental

### Materials

Palladium (II) acetate (Pd content 47% assay basis, 99.98% purity), flake graphite powder, KMnO<sub>4</sub>, NaNO<sub>3</sub>, conc. H<sub>2</sub>SO<sub>4</sub> (95–98%), conc. HCl (36.5–38%), H<sub>2</sub>O<sub>2</sub> (30% v/v), NaOH, citric acid, L-ascorbic acid and methanol were purchased from Sigma-Aldrich Co. All other chemicals were of analytical grade and all aqueous solutions were prepared in Milli-Q water (>18.2 M $\Omega$ .cm).

### Synthesis

#### Synthesis of GO

GO was synthesized by modified Hummer's method as described in previous work [35]. Briefly, flakes graphite powder (1.5 g) was dispersed in 48 mL of conc. H<sub>2</sub>SO<sub>4</sub> by magnetic stirring (30 min) at low temperature (0–5 °C). Afterward, a calculated amount of NaNO<sub>3</sub> (0.75 g) was added and mixed. Then, 7.5 g of KMnO<sub>4</sub> was slowly added and continuously stirred for 2 h. Followed by, temperature was raised to 35 °C for 1 h. Then, 600 mL Milli Q water was slowly poured into the acidic mixture. Further, temperature was increased to 98 °C for 2 h. Finally, 20 mL of 30% v/v H<sub>2</sub>O<sub>2</sub> was slowly added to the reaction mixture to subside the further process. After completion of reaction, resultant suspension was centrifuged (3000 rpm) and washed (with Milli-Q water and dilute HCl) and finally, freeze-dried and stored in a vacuum oven at RT.

#### Reduction of GO to RGO

First, GO was reduced to RGO using the green and facile method. A well dispersed GO suspension was prepared in Milli Q water (1 mg/mL, 100 mL) using high power ultrasonication (4 h) at RT. Afterward, for GO reduction a mixed solution (1:1) of citric acid and L-ascorbic acid (1.5 M, 30 mL) was added into the GO suspension and mixed by magnetic stirring (3 h) at RT. Followed by, 5 g of NaOH was slowly mixed in above suspension (to increase the pH) and reaction was heated at 80 °C for 2 h. Then after, reduced product RGO was filtered and multiple washed with Milli Q water to remove the impurities and finally, the product RGO was dried at 250 °C for 8 h.

#### Synthesis of Pd/RGO nanocomposite

To synthesize the Pd/RGO nanocomposite, a dispersion of RGO was prepared in anhydrous methanol (0.5 mg/mL, 25 mL)

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