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Biogenic Synthesis of Palladium Nanoparticles modified graphene using *Ficus carica* fruit extract and Study Its Catalytic Activity in Organic synthesis

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Abstract: Biogenic synthesis of metal nanoparticles is one of the green methods for production of nanoparticles in a large scale. Here we present a simple method for the synthesis of palladium nanoparticles modified graphene sheet in a single pot method using Ficus Carica fruit juice as reducing agent. Graphene oxide was first synthesized by modified Hummer method and then subsequently the simultaneous reduction of graphene oxide and the surface modification of palladium nanoparticles on graphene were carried out in a single step using FC fruit juice as a reducing agent. The as-prepared Pd NPs were characterized using ultraviolet-visible (UV-vis) spectroscopy, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform-infrared spectroscopy (FT-IR). Furthermore, as-synthesized Pd NPs decorated reduced graphene oxide have shown an enhanced catalytic activity towards the Suzuki coupling reaction in both aqueous and aerobic conditions. The progress of the catalytic reaction monitored by using GC and NMR studies confirmed that the reaction completed within 1 hr then previous reported method. The present method is considered as one of the greener approach for the synthesis of various organic intermediates using Pd doped graphene catalyst. The schematic diagram of the reaction is shown below:



Keywords: Biogenic Synthesis, Palladium Nanoparticles, grapheme, *icus carica*, Catalytic Activity.

1. Introduction

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Graphene has been a subject of intense recent studies from both experimental and theoretical points of view because of its unique structural and electronic properties that include the highest intrinsic carrier mobility at room temperature, very high mechanical strength and thermal stability as well as high surface area. These properties inspire many new applications in a wide range of application including nanoelectronics, supercapacitors, photovoltaic, solar cells, fuel cells, sensors, and catalysis [1-6]. Due to the large surface area ($2600 \text{ m}^2\text{g}^{-1}$, theoretical value) and its high thermal and chemical stability of graphene provide an excellent solid supporting for loading of Palladium based catalyst [7–15] of metal nanoparticles on graphene sheets could provide a large surface area and high anchoring thermally stability system for potential applications in catalysis, fuel cells, chemical sensors, and hydrogen storage. It is possible to tailor as graphene sheet to achieve new surface functionality which could enhance the interactions between anchored metal nanoparticles and layer graphene sheet[16-17]. Recently many research groups have been developing graphene based metal nanoparticles in various catalytic applications [19–21].

The development of palladium catalyzed cross-coupling reactions represents one of the most significant advancements in contemporary organic synthesis. This area of chemistry has increased the accessibility to molecules of greater chemical complexity, particularly in the area of pharmaceutical drug discovery and development [21-22]. These reactions have typically been carried out under homogeneous reaction conditions, which require the use of ligands to stabilize the catalyst and broaden its window of reactivity [23]. However, the use of these catalysts under homogeneous conditions has limited their commercial viability because of product contamination as a direct result of an inability to effectively separate the catalyst from the reaction product [24–27]. The issue of product contamination is of particular importance in pharmaceutical applications where this chemistry is practiced extensively.

Recently, there is a renewed interest in using green chemistry principles to synthesize metal nanoparticles [28]. Green chemistry is the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment [29]. Strategies to address mounting environmental concerns with current approaches include the use of environmentally benign solvents, biodegradable polymers and non-toxic chemicals. In the synthesis of metal nanoparticles by reduction of the corresponding metal ion salt solutions, there are three areas of opportunity to engage in green chemistry: (i) choice of solvent, (ii) the reducing agent employed, and (iii) the capping agent (or dispersing agent) used. In this area, there has also been increasing interest in identifying environmentally friendly materials that are multifunctional. It is interesting to note that fruit extract and green tea extract have been utilized for the synthesis of metal nanoparticle without using any harmful reducing agents. Here polyphenols play a vital role on reducing of metal salt to yield uniform size metal nanoparticles. For example, the *Ficus carica* fruit extract is used as both reducing agent and as well as capping agent for the synthesis Pd nanoparticles. This fruit extract initially form a complex with metal salt and then reduce them to achieve the corresponding metal nanoparticles. This approach therefore addresses several key requirements from a green chemistry perspective. The results demonstrate the successful application of this method to prepare active Pd/GO nano catalyst using fruit extract as a reducing agent with tunable catalytic activities for Suzuki cross-coupling reactions.

2. Experimental Section

2.1 Materials

All of the reagents and solvents are commercially available and are used as purchased, without any further purification. Compounds were purified on axially compressed columns, packed with Silica, and eluting with *n*-hexane/AcOEt mixtures. H^1 NMR and C^{13} NMR were recorded on Brüker Avance 200 or 300 MHz, in CDCl3 using TMS as the internal standard, chemical shifts were reported in parts per million (ppm) downfield from the tetramethylsilane. UV-Vis absorption spectra were recorded between 200–900 nm with Perkin Elmer Lambda 900 spectrophotometer.

2.2 Preparation of Pd/RGO

In the experiments, GO was prepared by the oxidation of high purity graphite powder according to the method of Hummers and Offeman.³⁰ After repeated washing of the resulting yellowish-brown cake with hot water, the powder was dried at 60 °C in an oven overnight. Typically, 3 ml of 0.1 mM noble metal precursors

solution $PdCl_4$, 0.03g of PVP, 10 mg of RGO was mixed homogeneously. Then 0.8 ml of 0.1 mM NaBH₄ aqueous solution was added to the above solution quickly. After that, mixture was stirred for 5 h and the resulting solution of Pd was obtained.

2.3. Suzuki Coupling reaction with Pd/RGO

For the cross-coupling catalysis experiments, Iodobenzene (1) dissolved in 4 ml of H₂O: EtOH (1:1). To this mixture, 3,4,5 trimethoxy phenyl boronic acid (2) in the presence of potassium carbonate, palladium catalyst solution is added (0.01 mol %), and the reaction mixture stirred to room temperature for 1 h. The characterization of the isolated products were carried out using ¹H NMR (300 MHz, CDCl₃), and ¹³C NMR (75.5 MHz, CDCl₃).



3. Result and Discussion:

3.1 UV-Vis spectra

In this work, we chemically synthesized GO using Hummers and Offeman Powder sample of GO was observed in brown color and of graphene were observed in black color. Chemical analysis of Pd, GO, Pd/*Ficus Carica*(F.C) fruit extract, Pd/GO, Pd/GO/Ficus *Carica*(F.C) fruit extract was carried out by using UV-Vis spectroscopy The UV-Vis spectra of obtained analysis as shown in Figure 1(A) shows band in the wavelength region of 225-237 nm for Pd, Figure 1(B) shows band in the wavelength region of 234 nm for GO, Figure 1(C) shows band in the wavelength region of Pd/*Ficus Carica*(F.C) fruit extract for 282 nm Figure 1(D) shows band in the wavelength region of Pd/GO for 237 nm and Figure 1(E) shows band in the wavelength region of Pd/GO/*Ficus Carica*(F.C) fruit extract for 282 nm Figure 1(D) shows band in the wavelength region of Pd/GO for 237 nm and Figure 1(E) shows band in the wavelength region of Pd/GO/*Ficus Carica*(F.C) fruit extract for 283 nm.





3.2. Synthesis of 3,4,5 trimethoxy biaryl compound:

3,4,5 methoxy biaryl compound (3) was synthesised from Iodobenzene (1) and 3,4,5 trimethoxy phenylboronic acid (2) Scheme 1 in the presence of Potassium carbonate and Palladium nanoparticles modified graphene sheet in a single pot method using *Ficus Carica* fruit juice as reducing agent in aqueous medium. PdNPs mediate synthesis afforded a good yield of 3,4,5 methoxy biaryl compound and suppress the formation of Biphenyl. 3,4,5 methoxy biaryl compound was obtanined in 88% yield and characterized using ¹H and ¹³C NMR. In ¹H NMR spectra of 3,4,5 methoxy biaryl compound shows peak around 7.85-6.90 and 4.79 ppm corresponding to the aromatic and methoxy groups respectively. Aromatic carbons of biaryl compound resonate around 109.7-164.2 ppm and aromatic carbons of methoxy groups resonate around 55.2 ppm in ¹³C NMR spectrum.

Scheme - 1



This product was confirmed by NMR spectrum.

In ¹H NMR: (300MHz, CDCl₃): δ H 7.85 (dd, 2H, Ar-H), 7.45 (d, 1H, Ar-H), 7.42 (s, 1H, Ar-H), 7.4 (d, 1H, Ar-H), 6.92(d, 2H, Ar-H), 4.7 (s, 9H, OCH₃).



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In¹³C NMR: (75MHz, CDCl₃): δc 55.2 (OCH₃), 109.7, 120.8, 132.2, 136.5, 164.2 (Ar-C).

4. Conclusion

In summary, we have synthesized palladium nanoparticles modified graphene sheet in a single pot method using *Ficus Carica* fruit juice as reducing agent. The Pd/PRGO catalyst exhibit exceptional catalytic activity and good recyclability for Suzuki cross coupling reaction under aqueous and aerobic condition. Specifically, we describe an environmentally friendly one-step method to synthesize noble nanoparticles, such as Pd, by reduction of corresponding metal solutions using fruit extract without usage of any special capping agents at room temperature. This green approach may find various medicinal as well as technological applications.

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