



A green chemical route for synthesis of graphene supported palladium nanoparticles: A highly active and recyclable catalyst for reduction of nitrobenzene

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ABSTRACT

A facile green chemical reduction approach is developed to synthesize palladium (Pd) nanoparticles (NPs) supported on reduced graphene oxide (RGO) using exfoliated graphite oxide as a precursor with various reducing agents, including salicylic acid, oxalic acid, ascorbic acid, NaOH and hydrazine hydrate. The as-prepared catalysts were characterized by X-ray diffraction (XRD), Raman spectroscopy, Fourier transfer infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The catalytic performance has been examined for the reduction of nitrobenzene using sodium borohydride as a reducing agent under mild conditions. Our findings indicated that most of oxygen functionalities are removed using green chemical reduction approach associated with the good catalytic performance. The catalytic activity depends particularly on target concentration, catalyst loading and reaction time. The results of this research would develop a new one-pot synthesis avenue for the preparation of Pd/RGO nanocomposite materials and provides the application of Pd/RGO into the heterogeneous catalysis.

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1. Introduction

Graphene can be defined as one atom thick in a closely packed honeycomb two-dimensional (2D) lattice. Graphene possesses unparalleled physical properties, such as excellent electronic conductivity, high thermal stability and good mechanical strength. In addition, due to its high specific surface area (2630 m²/g) and high adsorption capacity, graphene has attracted a great interest for supporting catalytic nanoparticles [1–6].

Graphene sheets can be decorated with different functional groups or nanomaterials to form graphene composites. The incorporation of graphene into the composites can offer unexceptional characteristics providing a new opportunity for designing and developing next-generation catalysts [7]. Combination of these unparalleled properties of graphene, and the nanoparticle on its surface led to improvement of the composites performance. In fact, the use of graphene as a support for metal nanoparticles led to a

measurable enhancement of the electronic properties and synergistic interactions between the metal and graphene.

Recently, the synthesis of metal nanoparticles on graphene through the reduction of the metal precursors in the presence of exfoliated graphene oxide or pristine graphene suspensions is reported [8]. For instance, Scheuermann et al. [5] prepared Pd nanocatalysts supported on graphene sheets using hydrogen bubbles in graphene oxide suspension in ethanol containing Pd²⁺ ions. The prepared catalysts exhibited extremely high catalytic performance for the Suzuki coupling reaction. Zhang et al. [9] also introduced a green method for incorporation of nanodots metals on graphene sheets through a sonolytic and hydrothermal method. Carbonaceous nanomaterials decorated with noble metals that currently attract a great interest owing to their remarkable properties in gas sensing and catalysis [10,11]. Palladium nanoparticles are essentially important among the noble metals as efficient catalysts in organic reactions [12], which resulted in a combination of activity and selectivity [13–16].

Nitro compounds as multilateral synthetic intermediates have found widespread utility in industrial applications [17–19]. Amines and their derivatives are widely used in industrial chemicals as dye intermediates for azo dyes and pigments as well as in

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biologically active compounds, pharmaceuticals, agrochemicals and optical brighteners, as intermediate for photographic chemicals [20–25].

The reduction of nitro compounds to the corresponding amines is indispensable process in chemical, petrochemical, pharmaceutical and food industries [26]. Moreover, nitro compounds are highly toxic and do not undergo biodegradation easily and thus the elimination of nitro groups can be achieved by the reduction of amines with low toxicity and easily biodegradable [27,28]. The reduction of nitrobenzene has been typically carried out under homogeneous conditions [29]. These homogeneous catalysts suffer from several disadvantages as a difficult separation procedure, insufficiency recyclability and a powerful contamination from residual metals in the reaction product [30]. To overcome these disadvantages a significant effort has been devoted to progress the design of catalysts where the palladium nanoparticles is deposited on a solid support such as carbon material [31]. The design of nitrobenzene reduction catalysts where the palladium is deposited on solid support with good catalytic performance, stability of the catalyst and efficient recyclability is likely to have considerable influence on the chemical industries in the future.

Chemically converted graphene was prepared through the chemical reduction of exfoliated graphene oxide using hydrazine hydrate (H.H.) to produce ultrathin chemically converted graphene sheets in large quantities [32–34]. Unfortunately, it has a powerful health risk to individuals or environment, highly flammable and the graphene is often agglomerated in it. To avoid using H.H., the development of a green chemical reduction approach for the synthesis of graphene sheets in large quantities using salicylic acid, oxalic acid, ascorbic acid or NaOH is our challenge.

In this work, we report on the synthesis of Pd nanoparticles supported on reduced graphene oxide (Pd/RGO) by a commonly strategy used to prepare well-dispersed NPs on the graphene sheets using various reducing agents. Also, the activity of Pd nanoparticle catalysts supported on RGO for the catalytic hydrogenation of nitro-benzene under mild conditions was studied. Moreover, our ultimate objective is to maximize the catalytic performance of the catalyst and to reuse, recycle the catalyst without or with a minimal degradation under mild operating conditions.

2. Experimental

2.1. Preparation of graphene oxide nanosheets

Graphene oxide (GO) was synthesized from graphite powder (Fisher Scientific, 99%) by the modified Hummers and Offeman method [35]. Collect the cake, wash it with hot water for several times, filtrated and then dried at 25 °C for 24 h in vacuum oven.

2.2. Preparation of Pd/RGO catalyst

The synthesis of Pd/RGO composite with well-dispersed NPs based on the adopting of different reducing agents is conducted. To prepare Pd/RGO, dried graphite oxide (2.5 mg ml⁻¹) was sonicated in 10 ml deionized water until a homogeneous yellow dispersion was obtained. Then, a certain amount of Pd (II) acetate [(CH₃COO)₂ Pd] (Aldrich, 99.9% purity) was added to the GO suspension, followed by the addition of the reducing agents such as (salicylic acid, oxalic acid, ascorbic acid, NaOH and H.H. for comparison). The suspension was refluxed for 6 h at 98 °C. The final product was filtrated, washed followed by drying in a vacuum oven at 25 °C for 24 h.

2.3. Characterization of Pd/RGO catalyst

The X-ray diffraction patterns were recorded with (Bruker axs D8 Advance, Germany) which was equipped with Cu- α radiation

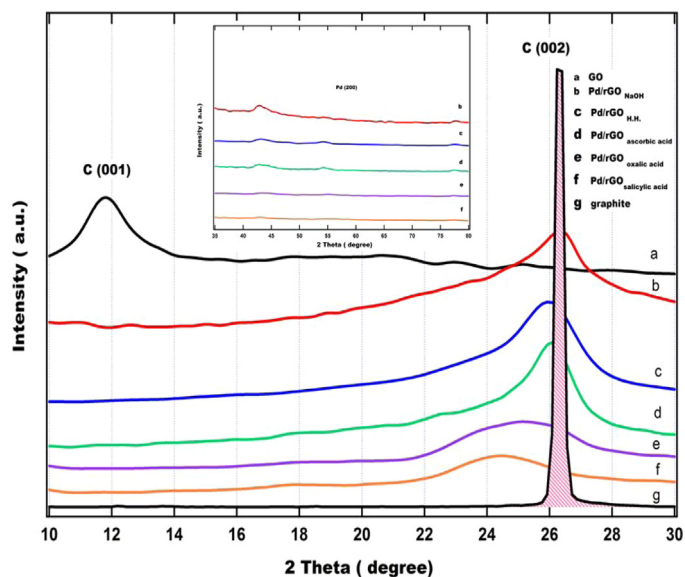


Fig. 1. XRD patterns of (a) GO, (b) Pd/RGO-NaOH, (c) Pd/RGO-H.H., (d) Pd/RGO-ascorbic acid, (e) Pd/RGO-oxalic acid, (f) Pd/RGO-salicylic acid and (g) pristine graphite. The inset is related to the pattern of Pd.

(40 kV, 40 mA) ($\lambda = 1.5406 \text{ \AA}$), the diffractogram in the 2θ range from 10 to 80°. For the FT-IR spectra, a KBr disk containing the Pd/RGO was prepared and scanned from 4000 to 500 cm⁻¹ using (Jasco FT-IR-6300 pulse, Japan). The Raman analysis was carried out on (a Senterra Dispersive Micro Raman, Bruker, Germany) using a doubled Nd:YAG laser ($\lambda = 532 \text{ nm}$) 10 mW as the excitation source. The XPS analysis was performed on Thermo VG Multilab 2000. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2010 electron microscope operating at 200 KV.

2.4. Hydrogenation reactions

For the catalytic reduction experiments, 1 mmol of biphenyl as a standard with a certain weight of sodium borohydride were dissolved in 20 ml ethanol followed by adding a known volume of nitrobenzene. The Pd/RGO catalyst was then added with a continuous stirring for 3 h at room temperature. The mixture was decanted and extracted by dichloro methane then analyzed by Agilent GC 7890A model: G3440A Gas Chromatography using 19,091 J-413 capillary column (30 m \times 320 μm \times 0.25 μm). The chromatographic conditions applied for the hydrogenation of nitrobenzene are summarized in (Supporting information, Table S1). The recyclability of Pd/RGO catalyst was examined by removing the catalyst from the reaction mixture followed by immiscible in dichloro methane where the organic products were extracted and removed by a simple decantation from the catalyst. After each run, the catalyst removed by the same method and reused for the subsequent runs. The palladium content was analyzed by an inductively coupled plasma-optical emission spectrometer (ICP-OES) model Perkin/Elmer Optima 2000.

3. Results and discussion

3.1. XRD analysis of Pd/RGO catalyst

Fig. 1 depicts the XRD patterns of pristine graphite, GO and Pd/RGO synthesized by different reducing agents. The XRD data displayed in Fig. 1 confirmed the formation of GO and the reduction of the GO as well as the formation of Pd/RGO using various reducing agents. As depicted in Fig. 1g, the graphite powder exhibits a

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