



# Carbon nitride supported palladium nanoparticles: An active system for the reduction of aromatic nitro-compounds



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## ABSTRACT

Synthesis of carbon nitride supported highly dispersed ultrafine palladium nanoparticles has been reported for the reduction of aromatic nitro-compounds using hydrazine hydrate as a reducing agent. As a demonstration, the as-synthesized carbon nitride-palladium composite was shown to be a highly active and chemo-selective for the title reaction. Utilizing the optimized reaction conditions a set of aromatic nitro compounds have been converted to their corresponding amine derivatives with good to excellent yield ranging from 80% to 99%. The catalyst can be used for multiple times without affecting the catalytic performance and can also be stored for a long time at ambient condition maintaining the high catalytic efficiency.

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## 1. Introduction

Development of a high performance catalyst has attracted extensive attention in the field of synthetic organic chemistry. Metal nanoparticles are used as an efficient catalyst and it is well documented that a small particle size with a high surface area with accessible surface can greatly improve the catalytic performance [1]. However, nanoparticles with high surface area have an inherent tendency to minimize their energy through agglomeration [2]. To prevent the agglomeration, the nanoparticles are generally capped with various stabilizers. Palladium nanoparticles have served, in various industries and academic synthetic chemistry laboratories, as a powerful catalyst for various organic transformation reactions. Commonly used stabilizers for palladium nanoparticle are ligands [3], polymers [4–6], dendrimers [7] and surfactants [8] and these stabilizers severely limit the accessibility of the reactant molecule toward the catalyst surface and thus lowering the catalytic performance. To overcome this issue, metal nanoparticles are dispersed on various solid supports that can stabilize nanoparticles as well as increase the accessibility of the metallic surface. The stabilizing of the nanoparticles to a solid support offers additional advantage towards the catalyst recovery and recyclability process. Solid supports such as carbon nanotubes [9], metal oxides [10], zeolites [11], clays [12] and naturally occurring porous diatomite [13] have been used to immobilize palladium nanoparticles.

It has been reported that palladium nanoparticle in metal-organic framework has been used for the Sonogashira cross-coupling reaction of aryl and heteroaryl bromides with various alkynes under copper-free conditions [14]. A magnetically separable palladium nanoclusters, supported on iron based metal-organic framework, exhibited excellent catalytic activity towards the reduction of 4-nitrophenol with high recyclability performance [15]. Polymer supported nanosized palladium catalyzed Sonogashira reaction has been reported in an environmental-friendly reaction system with ethanol as the solvent and potassium carbonate as a base [16]. *In-situ* synthesized conjugated polymer stabilized palladium nanoparticles has also been reported for Heck and Suzuki coupling reactions where the metal particles within the size range of 2–3 nm are stabilized within the polymer matrix [4–6]. Polypyrrole stabilised palladium nanoparticles showed good catalytic efficiency for the chemoselective transfer hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds with high specificity and selectively for the olefins or acetylenes only, without affecting the carbonyl moiety, for a wide range of substrates [17]. Carbon nanotube-palladium nanoparticle system was evaluated for the Suzuki and Stille coupling reactions and the hybrid material showed a significant catalytic activity for both the reactions [18]. The carbon nanotube supported palladium catalyst was applied for the hydrogenation of commercial polystyrene under mild reaction conditions. The catalyst characterization showed that the active metal deposited on the external surface of the nanotube with a good dispersion [19].

The selective reduction of nitroarenes to anilines is an important reaction in pigment, agrochemical and pharmaceutical industry.

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The traditional process for the reduction of nitroarenes using metallic iron generates large amounts of waste. Thus, hydrogenation of nitroarenes catalyzed by transition metals is now the system of choice for the successful transformation of anilines [20]. The source of reducing agents, such as, hydrogen, sodium borohydride, formic acid, hydrazine hydrate along with the metal catalysts can be considered as the suitable combination for the reduction of nitro groups.

Hydrazine hydrate can be considered as an efficient transfer hydrogenation reagent as it is easy to handle and generate only nitrogen as a product. In the past few years, several reports have been published for the reduction of nitroarenes employing the combination of hydrazine and the metal catalyst. Titanium oxide supported gold nanoparticle catalyzed transfer hydrogenation reaction has been reported for the reduction of the aryl and alkyl nitro compounds to the corresponding amines in the presence of hydrazine hydrate [21]. Graphene oxide supported iron oxide nanoparticles showed the performance as a catalyst for alkene hydrogenation to the corresponding alkanes using hydrazine hydrate as the source of hydrogen [22]. Hydrazine has also been used as a reductant of aromatic and heteroaromatic nitro compounds in the presence of several metal catalysts [23–27]. Traditionally for catalytic hydrogenation reaction, the metal catalysts based on Ru [28], Rh [29], Ni [30], Fe [31], Au [32], Pt [33], and varieties of reducing agents have been employed. The advantages of using nanoparticulate palladium as catalyst for a variety of organic reactions have been widely recognized and attention has also been paid for palladium based catalyst as it performs an excellent role for many organic hydrogenation reactions [34–39].

In this current study, we report a simple and effective method for the synthesis of graphitic carbon nitride (gCN) stabilized palladium nanoparticle catalyst, Pd-gCN, for the reduction of nitroarene compounds. The advantages of using gCN, as a support system, are (a) inexpensive raw material (urea) has been used for synthesis, (b) highly recyclable for heterogeneous catalysis reaction and (c) moderately accurate metal loading ability. For the current aromatic nitro reduction reaction, the combination of gCN supported palladium catalyst and hydrazine hydrate (a mild reducing agent) have several beneficial features including the chemo selective and regioselective product formation and the reaction is very effective for the reduction of a wide range of nitroarene compounds to aromatic amines. Other than that, an environmentally benign process as only nitrogen is the bi-product from the reaction. Motivation for this synthetic protocol is also attributed to an increased purity in the final product and also no catalyst degradation process has been noticed even after several times of recycling process. The catalyst was characterized by means of various optical and microscopic techniques, which offered the information about the structural properties and also the size and distribution of the metal nanoparticles.

## 2. Experimental

### 2.1. Materials

All the chemicals and the solvents used for this experiment were of analytical purity and used without further purification. Ultra-pure water (specific resistivity >17 M $\Omega$  cm) was used in this experiment wherever required.

### 2.2. Material characterization

Fourier transform infrared spectroscopy (FTIR) spectra were collected utilizing a Shimadzu IRAffinity-1 with a spectral resolution of 0.5 cm<sup>-1</sup>. Transmission electron microscopy (TEM) studies

of the nanocomposite were carried out at 200 kV on a JEOL-200. An energy-dispersive X-ray analyser (EDX) attached to the TEM was used to determine the chemical composition of the samples. The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer operating at 20 kV using Cu-K $\alpha$  radiation ( $k=0.1542$  nm). The measurements were performed over a diffraction angle range of  $2\theta=20-70^\circ$ . X-ray photoelectron spectra (XPS) were collected in a UHV chamber attached to a Physical Electronics 560 ESCA/SAM instrument. Nitrogen adsorption-desorption isotherms were measured with a Quadra-Sorb S1 apparatus at 77 K. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated from the desorption branch using the Barrett–Joyner–Halenda (BJH) theory. NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were recorded on a Bruker AVANCEIII-400 spectrometer. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) were registered in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in  $\delta$  units (ppm). All coupling constants (*J*) are reported in Hertz (Hz).

### 2.3. General procedures for the preparation of Pd-gC<sub>3</sub>N<sub>4</sub>

In a typical experiment, 15 g of urea was kept in a covered crucible at 80 °C under ambient pressure for 12 h. After that the dried urea was put in a Muffle Furnace for 4 h at 550 °C. The lemon yellow coloured product was washed several time with distilled water to remove the residual alkaline species (e.g. ammonia) on the sample surface and again dried at 80 °C for 24 h under vacuum. In the second stage of the synthesis, 0.5 g of the resultant product was dispersed in 10 mL of water and 0.1 M of K<sub>2</sub>PdCl<sub>4</sub> (2.34 mL) was added drop wise (5 wt% loading of Pd). After that, 5 mL of  $1 \times 10^{-3}$  M NaBH<sub>4</sub> solution was added dropwise for the reduction of palladium salt. At the end, the material was filtered, washed with water and dried. The resultant material, Pd(O)-gCN, was characterized using different techniques and applied as catalyst for the reduction of nitroarene compounds.

### 2.4. General procedure for the reduction of nitroarenes

In a typical reaction, 5.0 mg of Pd-gCN (5.0 wt% of Pd) catalyst was added to the solution of 1.0 mM of nitroarene in ethanol (2 mL) and 2 mM (1.2 equiv. 0.07 mL) of 60% of hydrazine hydrate. The mixture was placed into a 10 mL round-bottom flask at the reflux temperature (70 °C) for the 4 h and then allowed to cool at room temperature. The resultant material was filtered and the filtrate was subjected to column chromatography over silica gel to obtain the corresponding products. For di-nitroarenes substrates 4.0 mM (2.4 equiv. 0.14 mL) of 60% of hydrazine hydrate solution was used.

### 2.5. General procedure for the Ullmann reaction

In a 50 mL round-bottom flask, pyrrole or pyrazole or indole (2.0 mM), 4-iodonitrobenzene (4.4 mM, 1.2 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (2.5 mol%) and K<sub>2</sub>CO<sub>3</sub> (2.2 equiv.) were added under continuous stirring condition. To this, 5.0 mL of dry DMA was then added under reflux condition at 110 °C for 20 h. After completion of the reaction (monitored by thin-layer chromatography), the reaction mixture was allowed to cool at room temperature and diluted with distilled water. After that the solution was extracted with ethyl acetate and the organic layer was dried over anhydrous MgSO<sub>4</sub>, which was subjected to column chromatography to obtain the corresponding products.

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