



Hybrid Pd/Fe₃O₄ nanowires: Fabrication, characterization, optical properties and application as magnetically reusable catalyst for the synthesis of *N*-monosubstituted ureas under ligand-free conditions



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ABSTRACT

This paper reports the synthesis and use of Pd/Fe₃O₄ nanowires, as magnetically separable catalysts for ligand-free amidation coupling reactions of aryl halides with benzylurea under microwave irradiation. Then, the in situ hydrogenolysis of the products was performed to afford the *N*-monosubstituted ureas from good to excellent yields. This method has the advantages of high yields, simple methodology and easy work up. The catalyst can be recovered by using a magnet and reused several times without significant loss of its catalytic activity. The catalyst was characterized using the powder XRD, SEM, EDS and UV–vis spectroscopy. Experimental absorbance spectra was compared with results from the Gans theory.

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1. Introduction

N-Monosubstituted urea compounds constitute a very important class of organic compounds playing a significant role in a number of natural products and bioactive molecules [1–4].

The classical approaches to substituted ureas are based on the reaction of primary amines with toxic phosgene or its derivatives [5,6], reaction of primary or secondary amines with isocyanates or reaction with sodium or potassium cyanate in aqueous solution in the presence of one equivalent of HCl [7,8], insertion of CO or CO₂ into amino compounds in the presence of different catalysts in organic solvents (at high pressure and temperature) [9–12], acid or base-catalyzed hydration of cyanamides or reaction of *S,S*-dimethyl dithiocarbonate with ammonia in water-dioxane [13–16].

However, each of these methods suffer from different drawbacks such as employing expensive, toxic, hazardous and moisture sensitive reagents, harsh reaction conditions, tedious work-ups,

long reaction times, low yields, several-step methods, environmental pollution caused by formation of side products [13–16]. Thus, due to safety considerations, it is desirable to develop a more efficient and convenient method for the synthesis of *N*-monosubstituted ureas that reduce or eliminate the use and generation of hazardous compounds is essential.

Palladium-catalyzed C–N cross-coupling reactions have evolved into a highly versatile and synthetically attractive technique for targeting pharmaceutically useful intermediates [17–19]. While a number of C–N cross-coupling methods to synthesize symmetrical and unsymmetrical diarylureas exist, methods for the formation of monoarylureas are sparse [20,21]. As an alternative approach, we believed a mild and efficient cross-coupling method might be utilized to greatly expand the inventory of available monoarylureas.

Nanotechnology is emerging as a cutting edge technology interdisciplinary with biology, chemistry and material science. Metal nanoparticles have been used widely in recent years due to their unique electronic, optical, mechanical, magnetic and chemical properties which differ greatly from the bulk substances [22]. For these reasons, metallic nanoparticles have been found to be of use in many applications in different fields, such as catalysis, photonics, and electronics. Palladium (Pd) is able to catalyze a wide variety of chemical reactions that are homogeneous and heterogeneous under conditions and therefore it is one of the most

Abbreviations: XRD, X-ray Powder Diffraction; SEM, Scanning Electron Microscopy; EDS, Energy Dispersion X-ray Spectroscopy; FT-IR, Fourier transform infrared spectroscopy; NMR, Nuclear Magnetic Resonance.

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widely used metal catalysts [23]. Due to a higher available catalytic surface, use of heterogeneous catalysts in the form of nanoparticles is increasing. Recently, a variety of magnetic nanoparticles that are amenable for easy separation and recovery have been synthesized and applied as heterogeneous catalysts to a range of chemical reactions [24–27].

In the course of our researches on the applications of heterogeneous catalysts [28–35], herein we report a simple, inexpensive and two-steps protocol for the preparation of Pd/Fe₃O₄ nanowires by arc discharge of Fe in deionized (DI) water and electroless deposition of palladium. The main advantage of the present method is the direct formation of Fe nanowires from discharge of iron electrodes in water. The catalyst is heterogeneous and reusable, which provides an advantage over the homogeneous Pd-catalyst.

Several methods for preparation of Fe nanowires have been reported. Classical methods for the synthesis of Fe nanowires have involved epitaxy [36], chemical deposition [37], self-assembly [38] and electrochemical methods [39]. In spite of these methods, there are no reports on the preparation of iron nanowires by the electrical arc discharge method. The early works on arc discharge method in liquids were based on the production of carbonaceous nanostructures such as MWCNTs, SWCNTs, SW-CNHs and nano onions [40–43]. In general, electrical arc discharge in water has the advantage in this regard as it produces self-crystallized nanoparticles due to the high temperature caused by joule heating. Moreover, compared with other techniques, electrical arc discharge in water is an attractive method because of the simplicity of the experimental set up, lack of complicated equipment, low impurity and less production steps leading to a high-throughput and cost-effective procedure to generate high yields of nanoparticles.

In the next step, we hereby describe the development of Pd/Fe₃O₄ nanowires as a novel and stable heterogeneous catalyst for the amidation of aryl halides with benzylurea (Scheme 1). The amidation of aryl halides with benzylurea, followed by hydrogenolysis, provides the corresponding *N*-monosubstituted ureas in high yields.

During this study, we also introduce the effective medium optical constant for decorated nanowires (Fe₃O₄ nanowires decorated by Pd nanoparticles) thin films by comparing the experimental data and calculation results in the spectral range of 300–700 nm. Gans theory and these effective optical constants were used for calculation of extinction cross section of dispersed above nanostructures in water. Our simulation results show that this approach can be used for prediction of optical spectra of decorated nanowires.

2. Experimental

2.1. Instruments and reagents

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by different spectroscopic methods (FT-IR and ¹H NMR spectra), elemental analysis (CHN) and melting

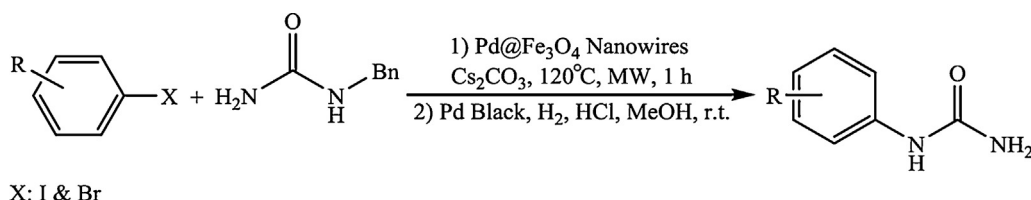
points. The NMR spectra were recorded in acetone and DMSO. ¹H NMR spectra were recorded on a Bruker Avance DRX 250, 300 and 400 MHz instrument. The chemical shifts (δ) are reported in ppm relative to the TMS as internal standard. *J* values are given in Hz. IR (KBr) spectra were recorded on a PerkinElmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. The elemental analysis was performed using Heraeus CHN-O-Rapid analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates. X-ray diffraction measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the 2 θ range (10–60) with scanning speed of 2° min. Morphology and particle dispersion were investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS performed in SEM. UV–vis spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900).

2.2. Preparation of Pd/Fe₃O₄ nanowires

Fe nanowires were prepared using a system consisting of two main parts: a high current DC power supply and a reactor including an anode, cathode and a micrometer, which moves the anode in contact with the cathode. In this method, an 8 V DC voltage and 5 A current are applied between two metallic iron electrodes; it was found that the voltage dropped to 5 V during arcing but the current remained constant. Both the anode and cathode were Fe, wire shaped, 2 mm in diameter and 99.99% in purity. Initially we brought the two electrodes into contact, leading to a small contact cross section and thus to a high current density. As more iron was ablated from the anode, the plasma expanded and pushed the liquid away, and a gaseous bubble was formed. Melted species can react with plasma and then condense into the liquid. In order to extract the dispersed wires, the solution was dried at a pressure of 10⁻¹ Torr and centrifuged several times and then dispersed on a glass substrate. Deposition of Pd on the surface of Fe nanowires was accomplished via a simple drop-drying process by dropping PdCl₂ solution onto Fe nanowires films and drying them at room temperature. This solution was prepared by ultrasonically solving 0.02 g of PdCl₂ powder (5 N), 99.9 mL DI water and 0.1 mL HCl. After Pd deposition, samples were washed with DI water several times and then dried in air. However, Fe nanowires are very air-sensitive and easily oxidize to Fe₃O₄ nanowires in water.

2.3. General experimental procedure for the synthesis of *N*-monosubstituted ureas

A Smith process vial was charged with 1.0 mol% Pd/Fe₃O₄ nanowires, 1.0 mmol of phenylurea, 1.0 mmol of aryl halide and Cs₂CO₃ (1.5 mmol). After sealing the cap and twice purging with N₂, the vial was irradiated by microwave at 120 °C for 1 h in the Smith Synthesizer. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled to room temperature, and a small volume of MeOH (4 mL) was added; the catalyst was



Scheme 1. Synthesis of *N*-monosubstituted ureas.

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