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Short communication

Biogenic synthesis of cellulose supported Pd(0) nanoparticles using hearth wood extract of *Artocarpus lakoocha* Roxb — A green, efficient and versatile catalyst for Suzuki and Heck coupling in water under microwave heating

Diganta Baruah [a], Ram Nath Das [a], Swapnali Hazarika [b], Dilip Konwar [a,*]

[a] Synthetic Organic Chemistry Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India
[b] Chemical Engineering Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India

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ABSTRACT

A simple, convenient and green protocol has been developed for the synthesis of cellulose supported Pd(0) nanoparticles (NPs) using hearth wood extract of *Artocarpus lakoocha* Roxb-as a bioreductant. Novel one-step method for the isolation of active bioreductant oxyresveratrol (2, 3′, 4, 5′-tetrahydroxy-trans-stilbene) present in the hearth wood extract of *A. lakoocha* Roxb is also disclosed. Synthesized cellulose supported Pd(0) NPs have been used as an efficient catalyst for Suzuki and Heck coupling reactions in water under microwave irradiation. The prepared Pd(0) NPs were characterized by Ultraviolet–visible (UV–vis), Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The catalyst can be recycled up-to ten times without losing its activity significantly.

1. Introduction

Palladium nanoparticles (NPs) have diverse applications in the field of both homogeneous and heterogeneous catalysis [1]. Suzuki and Heck reactions are the most important coupling reactions in the synthesis of great variety of simple to complex molecules which have tremendous application in the field of drugs, pharmaceuticals, agrochemicals and advanced materials [2]. Homogeneous Pd catalysts always exhibit better reaction rate, activity and selectivity but heterogeneous catalysts have many advantages over their homogeneous counterparts such as recycling, cost effectiveness and ease of catalyst/product separation [1–2]. Nowadays, much attention have been paid to investigate biocompatible solid support to provide thermo and air stable metal NPs as the synthetic solid support (carbon [3], zeolites [4], metal oxides [5], sol–gel [6], clays [7], dendrimers [8], polymers [9]) or the stabilizing ligands (phosphine, etc. [10]) are expensive, toxic, and in large-scale applications they may become more tedious for solid waste disposals.

In recent years, biogenic synthesis of metal NPs using different plant extracts received much attention both from environment and economy points of view. It was assumed that different flavonoids and polyphenols present in these plant extracts act as bio-reductant and stabilizing agent in NPs' synthesis. Biogenic synthesis eliminates the use of toxic, expensive and non-biodegradable chemical reagents ($N_2H_4 \cdot H_2O$, $NaBH_4$, DMF, etc.) as well as high temperature and pressures. Hence economically viable, environmentally safer plant based biogenic synthetic protocols for NPs synthesis are more advantageous [11–13]. Numerous metal NPs such as Au, Ag, Pd, Pt, Cu and bimetallic Ag–Au, Au–Pd, and Cu–Au can successfully be synthesized by different plant extracts [14]. These NPs have potential application in the field of catalysis [15]. In this research work, we report the successful isolation of oxyresveratrol, the active bio-reductant present in the hearth wood extract of *Artocarpus lakoocha* Roxb, a medicinal plant available in NE region of India in the synthesis of Pd(0) NPs. To enhance the surface area per volume, the NPs should be anchored on a suitable solid support so as to increase the catalyst robustness as well as reusability of the catalyst. In this endeavour, in continuation of our earlier works [16–20], we used microgranullar cellulose as a sustainable solid support for Pd(0) NPs to make the catalyst more stable and recyclable in the study on Suzuki and Heck coupling reaction in aqueous media under microwave heating. Cellulose consists of anhydroglucose units joined by β-1–4 glycosidic linkage to form a molecular chain. The intra-chain hydrogen bonding between hydroxyl groups and oxygens of the adjoining ring molecules stabilizes the linkage and results in the linear configuration of the cellulose chain. Cellulose contains microfibrils up to 30 nm width that are three dimensionally connected to each other. The metal NPs can be stabilized in these cavities via oxygen–metal electrostatic interaction. Depending upon the pore size of cellulose microfibrils the size of the metal NPs also varies. That is how cellulose can act as a solid support for the metal

* Corresponding author.
E-mail address: dkonwar@yahoo.co.uk (D. Konwar).

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NPs' synthesis [21]. Biogenic synthesis of cellulose supported Pd(0) NPs using hearth wood extract of *A. lakoocha* Roxb and their application as a versatile and efficient catalyst in Suzuki and Heck coupling is the first protocol that we depicted herein (Scheme 1). We performed all the reactions under microwave heating. As being energy efficient, microwaves can enhance the rate of reactions and improve product yields [22].

2. Experimental section

2.1. General remarks

Cellulose (CAS: 9004-34-6, microcrystalline, 20 μm, pH: 5–7), $PdCl_2$ (99.9%), all arylbromides, all phenylboronic acids, methyl acrylate, acrylonitrile, bases, and all solvents were purchased from Sigma Aldrich, USA and were used without any further purification. X-ray diffraction (XRD) analysis was performed with a scanning rate of 3° min^{-1} and two theta values ranging from 5 to 100° using a Rigaku X-ray diffractometer (model: ULTIMA IV, Rigaku, Japan) with a Cu Kα X-ray source (λ = 1.54056 Å) at a generator voltage of 40 kV and a generator current of 40 mA. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEM-2100 electron microscope (Transmission Electron Microscope, NEHU, Shillong, India) operated at an accelerating voltage of 60–200 kV. UV–visible spectra were recorded using Specord 200 and Spectrum 100 FTIR-Spectrometer (resolution: 4 cm^{-1}) was used for recording IR data. All microwave (MW) reactions were carried out in CEM, Discover microwave reactor. All NMR (^1H, ^{13}C) spectra were recorded on a Bruker Avance DPX 500 MHz spectrometer. Chemical shifts were reported on the δ scale (ppm) downfield from TMS (δ = 0.0 ppm) using the residual solvent signal at δ = 7.26 ppm (^1H) or δ = 77 ppm (^{13}C) as an internal standard. All products were purified by column chromatography using silica gel (200–300 mesh) and petroleum ether (60–90 °C).

2.2. General procedures

2.2.1. Synthesis of Pd(0) NPs on cellulose [Pd(0) NPs@cellulose] using hearth wood extract of A. lakoocha Roxb

200 mg nanoporous cellulose and 10 mg palladium(II) chloride were added to a 250 mL round bottom flask containing 100 mL hearth wood extract of *A. lakoocha* Roxb. The hearth wood extract of *A. lakoocha* Roxb was prepared by grinding the dry heart wood of *A. lakoocha* Roxb and extracted with water. The mixture was stirred for 30 min at room temperature and then warmed (50 °C) for 15 min until the light brown solution turned into black colour. No further colour change was observed after 15 min. The black precipitate was filtered, washed, vacuum dried, and finally stored under N_2 atmosphere in a dessicator. The synthesized Pd NPs were characterized by UV–visible spectroscopy, FT-IR spectroscopy, XRD and TEM analysis.

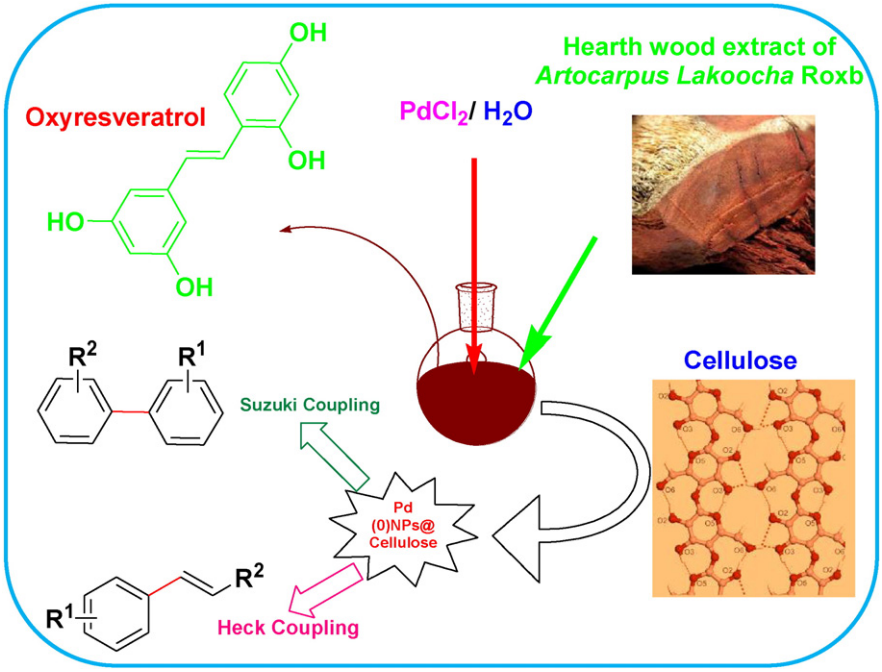
2.2.2. Isolation of active bio-reductant present in hearth wood extract of A. lakoocha Roxb

2.2.2.1. Method A. 10 g of dried and ground hearth wood of *A. lakoocha* Roxb was treated with 100 mL petroleum ether (40–60 °C) and kept overnight for removing fatty materials. After filtration, these wood materials were taken in 100 mL water, refluxed for 6 h, filtered off at hot condition, concentrated to one fourth of the volume under reduced pressure, and kept in a refrigerator for overnight. Separated deep brown solid materials were filtered, washed with cool water (50 mL) and vacuum dried. These solid materials are identified as oxyresveratrol (2, 3′, 4, 5′-tetrahydroxy-trans-stilbene), yield: 500 mg (5%), melting point: 200 °C, (Lit. Mp 201 °C [23–25]).

2.2.2.2. Method B. 10 g of dry and powdered wood material was taken in 100 mL acidic water solution (pH = 4) and 20 mL *accelerase* enzyme [Aldrich] was added to the solution. The mixture was heated for 5 h at 40 °C, hot filtered, extracted with ethyl acetate (3 × 50 mL), the organic layer washed with 5% $NaHCO_3$ solution and dried over anhydrous sodium sulphate for 5 h. The solvent was distilled off under reduced pressure to give deep brown solid oxyresveratrol (2, 3′, 4, 5′-tetrahydroxy-trans-stilbene), yield: 600 mg, (6%). The compound was analysed and found as above.

2.2.3. Reaction of arylbromides with phenylboronic acids using Pd(0) NPs@cellulose under microwave heating [Suzuki coupling]

In a 10 mL microwave glass vial 0.5 mol% (0.028 g) Pd(0) NPs@cellulose, 0.5 mmol arylbromides, 0.75 mmol phenylboronic acid and 1.5 mmol K_2CO_3 were mixed in 5 mL water. The mixture was stirred at



Scheme 1. Schematic diagram of fabrication of Pd(0) NPs on cellulose by biogenic method and its catalytic activity towards Suzuki and Heck coupling reaction.