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Regular Article

Green synthesis of palladium nanoparticles mediated by black tea leaves (*Camellia sinensis*) extract: Catalytic activity in the reduction of 4-nitrophenol and Suzuki-Miyaura coupling reaction under ligand-free conditions

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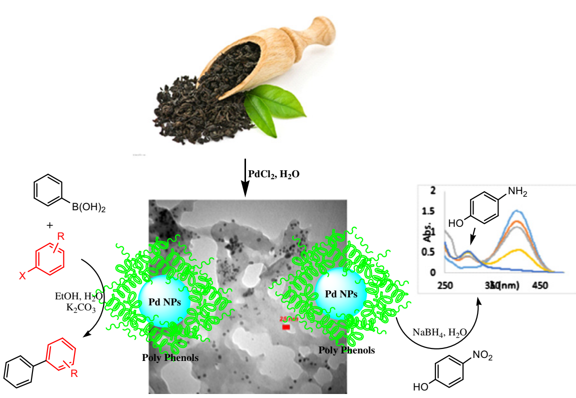
GRAPHICAL ABSTRACT



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ABSTRACT

The present study was conducted to synthesize palladium nanoparticles (Pd NPs) through a facile and green route using non-toxic and renewable natural black tea leaves (*Camellia sinensis*) extract, as the reducing and stabilizing agent. The as-prepared Pd@B.tea NPs catalyst was characterized by UV–vis spectroscopy, X-ray diffraction (XRD), fourier transformed infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The Pd@B.tea NPs catalyst could be used as an efficient and heterogeneous catalyst for Suzuki coupling reactions between phenylboronic acid and a range of aryl halides (X = I, Br, Cl) and also the reduction of 4-nitrophenol (4-NP) using sodium borohydride in an environmental friendly medium. Excellent yields of products were obtained with a wide range of substrates and the catalyst was recycled 7 times without any significant loss of its catalytic activity.

1. Introduction

The reaction of aryl halides and aryl boronic acids results in formation of wide variety of unsymmetrical biaryls is Suzuki-Miyaura [1]. Biaryls which are also known as the fourth state of matter are

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significant groups used in liquid crystal materials [2a,2b]. Moreover, there have been many successful examples of total synthesis of biological and medicinal molecules through the approach of constructing new carbon-carbon bonds [2c,2d]. Such molecules generally can be synthesized by C—C bond formation reaction of Suzuki. However, there is still a significant challenge as this reaction suffers from some limitations and drawbacks. One of these is the necessity of inert atmosphere [2e], because the moisture may oxidize the catalyst or its reactive intermediates in the procedure. Furthermore, the ligands might be sensible to air and the existence of air which may diminish the efficiency [3]. Therefore, progress of Suzuki reaction in aqueous media and air condition is of remarkable importance.

Biosynthesis of metal nanoparticles using plant materials is currently under exploration. It has received more attention as a suitable alternative to chemical and physical methods [4]. The development of new, efficient, and practical catalysts for organic transformation to synthesize valuable target molecules is an important research area in the pharmaceutical and chemical industries [5,6]. Although various methodologies have been developed for the synthesis of palladium nanoparticles, including chemical and electrochemical reduction [7,8], ion exchange [9], vapor deposition, thermal decomposition [10,11] and polyol method [12], preparation of metal nanoparticles is usually based on the reduction of a metal salt in the presence of a reducing agent such as sodium borohydride, hydrazine, dimethyl formamide and hydrogen, and a stabilizer like polymeric materials, dendrimers, surfactants, organic ligands and polyoxometalates [13,14].

It is important to note that bioinspired, eco-friendly greener methods for the synthesis of metal nanoparticles are among the most attractive aspects of today's nanoscience and nanotechnology [15,16]. There are few reports available for the synthesis of palladium nanoparticles that effectively utilize *Diopyros kaki. leaf* [17], *Cinnamom zeylanicum bark* [18], *C. Camphora leaf* [19], *Curcuma longa tuber* [20], *banana peel* [21], *Hippophaerhamnoides Linn* [22], *Pistacia atlantica kurdica gum* [23], *Rosa canina fruit* [24], *pectin* [25], *Stachys lavandulifolia* [26], and *Oak gum* [27]. The black tea which grows in many parts of world, is used as an herbal tea and Drinking. *Camellia sinensis* leaves (black tea) have been reported to contain considerable amounts of tannin products [28]. This is motivated us to explore the possible bio-reduction of palladium ions into nanoparticles. Hence, the present work deals with biological (green) synthesis of palladium nanoparticles by black tea extract at ambient conditions. The bioreduction process was monitored by the UV–Visible, XRD, TEM, FESEM, WDX and EDX. Also, the catalytic activity of Pd@B.tea NPs for the Suzuki-Miyaura coupling reaction was studied.

2. Experimental section

2.1. Materials

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. Melting points were determined in open capillaries using a BUCHI 510 melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Avance DRX spectrometer at 400 MHz. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer (Bruker, Karlsrohe, Germany) using pressed KBr pellets. Lahijan black tea leaves (*Camellia sinensis*) were supplied from the Lahijan Tea Research Center, Lahijan, Iran. X-ray diffraction (XRD) measurements were carried out using a Philipspowder diffractometer type PW 1373 goniometer (Cu Ka = 1.5406 Å). The scanning rate was in the 2θ range of 10–80°. UV–visible spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900) to ensure the formation of nanoparticles. Morphology and particle dispersion was investigated by field emission scanning electron microscopy (FE-SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM. TEM images were obtained using a Philips-EM-2085 transmission electron microscope with an accelerating voltage of 100.0 kV.

2.2. Green synthesis of palladium nanoparticles using black tea leaves (Camellia sinensis)

Lahijan black tea leaves (*Camellia sinensis*) were supplied from the Lahijan Tea Research Center, Lahijan, Iran. 10 g of the black tea was added to 100 mL of deionized water and was boiled for 5 min in a water bath. The mixture was then cooled down and was filtered through Whatman filter paper No. 1 to obtain aqueous extract. The filtered extract was stored in refrigerator at 4 °C for further use. The extract was used as reducing as well as stabilizing agent. For preparation of Pd NPs, 10 mL of the prepared plant extract was added drop wise to 100 mL of 1 mM aqueous $PdCl_2$ solution and refluxed at 100 °C for 1 h. The color of the reaction mixture gradually turned over 60 min and indicated the formation of Pd NPs, to which acetone was added to precipitate the catalyst (Pd@B.tea NPs). After addition of acetone (anti-solvent) the precipitated catalyst was then centrifuged at 1000 rpm for 10 min followed by re-suspension of the pellet in Milli-Q water. The Pd loading of the prepared catalyst was measured to be 1.7 mmol/g by ICP and EDX.

2.3. Suzuki-Miyaura coupling reaction

In a typical experiment, to a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), and K_2CO_3 (2.0 mmol) in (4.0 mL, 1:1) water-ethanol, 6.0 mg of the Pd@B.tea NPs catalyst (containing 0.1 mol% of Pd) was added and heated at 60 °C. The progress of the reaction was followed by thin layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled down to room temperature and (10 mL) EtOAc was added and the catalyst was separated from the reaction mixture by centrifuge and extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and evaporated in a rotary evaporator under reduced pressure. The product was purified by column chromatography (hexane-ethylacetate, 1:5) to obtain the desired purity. All of the products are known and were identified by comparison of their physical and spectral data with those of authentic samples.

2.4. General procedure for the reduction of 4-nitrophenol

In a typical experiment, 2.0 mg of the Pd@B.tea NPs catalyst was added to an aqueous solution that contained 4-nitrophenol (2.5 mM, 25 mL), freshly prepared aqueous $NaBH_4$ solution (250 mM, 25 mL) and stirred for 80 s at room temperature. The rate of 4-nitrophenol reduction was evaluated using UV–vis spectroscopy at room temperature. After completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation, washed with doubly distilled water and then dried for the next cycle.

3. Results and discussion

Biological methods for the synthesis of Pd nanoparticles are gaining importance in the field of nanoparticle synthesis. As a result of the growing success and simple processes for the