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Aerobic oxidation of benzyl alcohols through biosynthesized palladium nanoparticles mediated by *Oak fruit bark* extract as an efficient heterogeneous nanocatalyst

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ABSTRACT

In this study, green synthesis of Pd nanoparticles (NPs) is outlined through application of *Oak fruit bark* extract as a reducing, capping and stabilizing agent. The characteristics and properties of the biosynthesized Pd NPs were revealed by FESEM, EDX, XRD, TEM, UV–Vis, and FT-IR spectroscopies. So that, UV–Vis spectroscopy of the Pd colloidal solution confirmed reduction of Pd ions, and XRD and TEM analysis identified fcc unit cell structure forming 5–7 nm spherical Pd NPs. Furthermore, catalytic activity of the prepared catalyst was investigated through aerobic oxidation of alcohols, as model reactions. Catalytic evaluations demonstrated achievement of good yields from primary and secondary benzyl alcohols. In general, the devised synthesis method is advantageous from several perspectives. For example, the synthesized catalysts give high product yields and are efficient, they eliminate the need for surfactant, chemical reductants, ligand and organic solvents, the approach is economically inexpensive, it results in cleaner reaction profiles, application of the simply prepared heterogeneous catalyst is convenient, and the catalyst is recoverable and reusable for at least six times without any significant loss of its catalytic activity.

Introduction

Production of carbonyls through oxidation of alcohols is one of the essential organic transformations[1] since carbonyls can be employed as intermediates in manufacturing dyes and pharmaceuticals.[2] Such organic transformations can be facilitated by catalysts. In this respect, transition metal based catalysts can conduct selective oxidation of organic compounds as interesting alternatives to conventional waste-producing oxidation procedures, which demand for stoichiometric amounts of toxic inorganic salts.[3,4]

Recently, aerobic oxidation processes have gained more attention as utilizing oxygen has considerable benefits, from both economic and green chemistry points of view. In fact, molecular oxygen is inexpensive and produces just water as its byproduct. Consequently, extensive catalytic studies have concentrated on finding suitable active metals for homo- and heterogeneous catalytic oxidation with molecular oxygen, e.g. Fe,[5] Ru,[6] Co,[7] Cu,[8] Mn,[9] Os[10] and Pd.[11] Also, solid supported transition metal nanoparticles (NPs) have attracted immense interest in development of new catalysts due to their high catalytic activity and reusability properties.[12] So that, few recent reports have shown that heterogeneous palladium NPs can undertake aerobic oxidation of aromatic alcohols.[13,14]

To date, different chemical, physical and biological methods have been employed for production of Pd NPs. However, physical methods require expensive equipment and involve high vacuum technology. Also, chemical methods are not completely favorable since they need capping agents to avoid agglomeration of the produced particles, due to their high surface reactivity. Meantime, using the necessary toxic chemicals is a major concern and presence of non-polar solvents and toxic chemicals limit application of chemical synthesis of Pd NPs, in clinical fields. Therefore, researchers have shifted to ecofriendly NP synthesis through microorganisms and plant extracts. Green synthesis of Pd NPs is consisted of three main steps, which should be evaluated according to green chemistry perspectives and include (i) solvent medium selection, (ii) choosing an ecofriendly reducing agent and (iii) finding nontoxic NP stabilizers. Therefore, biosynthesis approach of Pd NPs through green chemistry reduction has been explored, in this study.

It is noteworthy that bio-inspired, ecofriendly and greener synthesis methods of metal NPs are among the most interesting

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aspects of nanoscience and nanotechnology, nowadays.[15,16] There are limited number of available works on biosynthesis of Pd NPs and *Diospyros kaki. leaf,*[17] *Cinnamomum zeylanicum bark,*[18] *C. Camphora leaf,*[19] *Curcuma longa tuber,*[20] *banana peel,*[21] *Hippophae rhamnoides Linn,*[22] *Pistacia atlantica kurdica gum,*[23] *Rosa canina fruit,*[24] *pectin,*[25] *Stachys lavandulifolia*[26] and *Oak gum*[27] have been employed, to date. Oak tree is widely spread throughout Zagros Mountains, West of Iran, East and North of Iraq, Southern Turkey, Northern Syria and, also, in many other parts of the world. Tough acorns have had an important role in human diet for thousands of years, they are not widely used today as food or food ingredients, despite their noticeable availability. Moreover, many cultures have used acorns as a main staple and food, historically, and even many modern Asian countries are still using them. Acorns are rich in calorie, because of their high fat levels, protein and phenolic compounds.[28] These facts motivated us to investigate possible bioreduction of Pd ions to Pd NPs. Therefore, this study continues our previous work[29] and reports a facile and green method for biosynthesis of Pd NPs by *Oak fruit bark* extract (Fig. 1). In this regard, the bio-reduction process is monitored by UV–Visible, FT-IR, XRD, TEM, FESEM and EDX spectroscopies. Also, catalytic activity of Pd NPs in oxidation of benzyl alcohols to the associated aldehydes and ketones by molecular oxygen is studied. Primary and secondary benzyl alcohols are found out to give the corresponding products in good yields. Moreover, recyclability of the catalyst system is explored to show that the NPs can be recycled up to six times without significant loss of activity.

Experimental

Preparation of plant extract

The *Oak fruit bark* was obtained from Zagros Mountains, Kermanshah, Iran. The isolated barks were washed thoroughly several times with deionized water and then air dried under sunlight to remove the moisture completely. The barks were chopped and powdered in a ball mill. The final sieved powder was used for all the further studies. 2 g of powder were weighed, boiled for 20 min in 20 ml deionized water and the extracts were filtered through Whatman filter paper No. 1. The filtered extract was stored in refrigerator at 4 °C. This extracts were used as reducing as well as stabilizing agent.

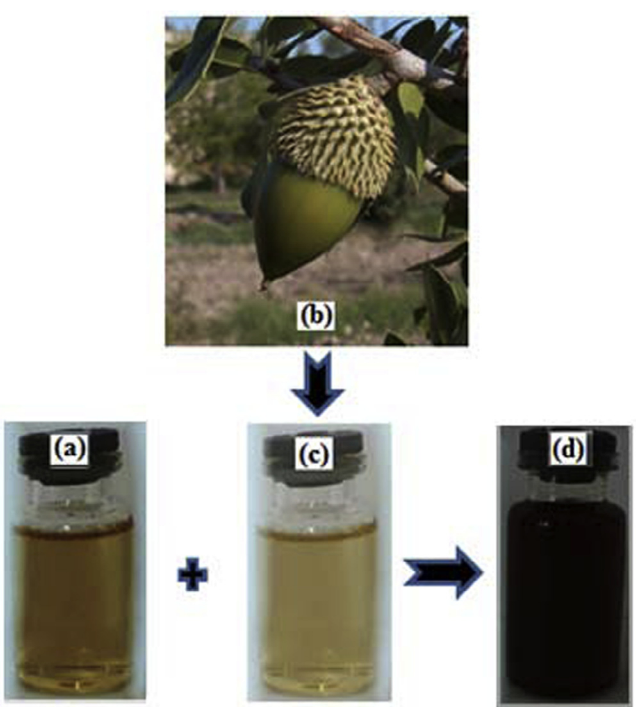

Fig. 1. Schematic synthesis procedure of green Pd nanoparticles (a) $PdCl_2$ solution, (b) collected *Oak fruit bark*, (c) solution of *Oak fruit bark* extract and (d) biosynthesized Pd.

Bioinspired synthesis of palladium nanoparticles

20 ml of 1×10^{-3} M aqueous solution of $PdCl_2$ were taken in Erlenmeyer flask and 10 ml of *Oak fruit bark* extract was added to it and refluxed at 100 °C. After 90 min the solution turns yellow to black indicating the formation of Pd nanoparticles. Then the solvent was evaporated. The dark gray solid achieved during this process was dried by the flow of air over a night and then under vacuum for 48 h.

Aerobic oxidation of alcohols

A mixture of K_2CO_3 (1 mmol) and the catalyst (10 mg) in toluene (5 mL) was prepared in a two necked flask. The flask was evacuated and refilled with pure oxygen. To this solution, the alcohol (1 mmol, in 1 mL toluene) was injected and the resulting mixture was stirred at 80 °C under an oxygen atmosphere. After completion of reaction, the reaction mixture was filtered off and the catalyst rinsed twice with CH_2Cl_2 (5 mL). The excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds.

Procedure for reusing the catalyst

After the reaction time, 5 mL of CH_2Cl_2 was added to the reaction mixture and stirred for 5 min. After this time, the catalyst was separated by centrifugation. In the next step, the recovered solid was washed using EtOH and dried under vacuum. Then, the recovered catalyst was used for another run.

Results and discussion

Reduction of Pd ions to Pd NPs in the presence of the plant extract could be followed by color change and spectroscopic techniques, such as UV–Vis spectroscopy. As the *Oak fruit bark* extract was poured in the aqueous solution of $PdCl_2$, the solution color started changing from yellow to black (Fig. 1). Surface Plasmon resonance phenomenon confirmed formation of Pd NPs. As NP formation continued, intensity of the color increased. In addition to optical tracking of the changes, UV–Vis spectra of the reaction solution was recorded and characterized a significant change as the peak about 400 nm disappeared (Fig. 2). This observation is a hallmark of Pd(II) conversion to Pd(0). This also verified noticeable reduction potency of the extract.

Involvement of the available functional groups of *Oak fruit bark* extract in reduction and capping of the Pd NPs was well demonstrated by Fourier transform infrared spectroscopy (FTIR). Using FT-IR spectroscopy, the major factors responsible for biological reduction of palladium ions (Pd^{2+}) to Pd NPs (Pd^0) in oak fruit extract were defined. Fig. 3 displays the FT-IR spectra of aqueous *Oak fruit bark* extract with strong bands at 3423 cm^{-1} (O—H stretch), 2924 and 2853 cm^{-1} (C—H stretch), 1649 cm^{-1} (—C=O stretch), 1460 and 1386 cm^{-1} (C—C stretch) and 1024 cm^{-1} (C—N stretch). Therefore, based on the FT-IR data, it can be inferred that phenolic hydroxyl groups of flavones, terpenoids and tannins that