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Ultra-Small Platinum Nanoparticles with High Catalytic Selectivity Synthesized by an Eco-friendly Method Supported on Natural Hydroxyapatite

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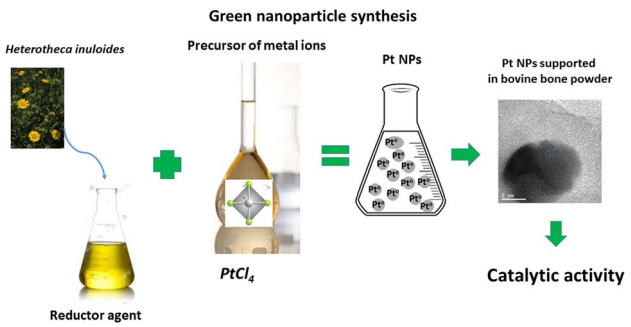
Abstract

The biosynthesis of Pt-nanoparticles (Pt NPs) supported on bovine bone powder was conducted by an environmentally friendly method that consists on immersing bovine bone powder into a Pt^{4+} metal ion solution at room temperature, atmospheric pressure and subsequent reduction by *Heterotheca inuloides*. It is worth pointing out that a calcination process is not required for the synthesis of this catalyst by the method reported herein. The nanocomposite was characterized by transmission electron microscopy (TEM), which revealed uniformly dispersed platinum nanoparticles with quasi-spherical form and average particle size of 7.1 nm. The XPS studies exhibited the presence of 47.62% Pt° and 51.84% PtO. The catalyst activity was tested in the selective hydrogenation of 2-butyne-1,4-diol towards 2-butene-1,4-diol. The nanocomposite exhibits a reasonable catalytic performance with nearly 100% conversion of the alkyne and 96% selectivity towards 2-butene-1,4-diol.

Graphic Abstract



Keywords Platinum nanoparticles · Green nanosynthesis · Bionanotechnology · *Heterotheca inuloides* · Selective catalyst

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1 Introduction

In the last decades, the study of nanostructured systems has been conducted by different research groups. This is because such systems exhibit unique properties that allow them to be applied in different areas like catalysis, health care and others [1–4].

In the context of nanoparticles synthesis, special attention has been given to the use of environmentally friendly reagents and materials in order to increase the sustainability of the synthesis process [4]. Actually, it can be said that green chemistry is the goal of many researchers around the globe [1, 3–10]. It is of special interest the supports where nanoparticles are dispersed [5, 11–17]. Support materials such as silica [14], amorphous titania, cellulose [2], nylon, hexylamine and calcite ($CaCO_3$), among others, have been used [2, 11, 13]. The use of bio-supports such as cork [15], cotton [11, 16], bone [12] and shells, results in a relatively low-cost, renewable and environmentally friendly way of supporting metal nanoparticles [12–16]. For example, the one-step synthesis of platinum nanoparticles supported on wood has been reported. This was conducted by using hydroxyl groups (OH^-) as reducing agent. The synthesized nanomaterial exhibited a high and relatively stable activity in the catalytic reduction of *p*-nitrophenol [17]. In the present investigation, bovine bone powder was used as support. This material is constituted by 60–70% hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. This is advantageous since the OH^- and PO_4^{3-} groups work as binding sites for the metal nanoparticles. In addition, bovine bone powder is a low-cost, easy-to-treat, biodegradable and renewable material. Furthermore, hydroxyapatite importantly contributes to the mechanical strength, chemical stability at extreme pH and thermal stability of the synthesized composite. At the same time, hydroxyapatite works as a nanoreactor and provides of stability to nanoparticles, improving the catalytic effect.

Different methods (laser ablation or chemical methods) have been used to obtain metal nanoparticles. In this sense, several investigations have reported biological methods to reduce metal nanoparticles using bioreducers such as honey [18], saffron [19], tannins [20], nopal [21], caliandra [21], *Camellia sinenses* [22], fruits [23], chili, bacteria, alfalfa, among many others [4, 18, 19, 22–24]. In this sense, plant extracts containing bioactive particles such as alkaloids, phenolic acids, polyphenols, benzoic acid, coffeic acid and proteins, have been reported [11, 20, 21, 25–27] to play an important role in reducing and stabilizing metallic ions. It is also well known that the use of typical chemical methods leads to toxic products for both, environment and humans [4, 28]. On the other hand, the known advantages of biosynthesis or green synthesis are economic viability, environmentally friendly, easily scalable, and that can be performed at room temperature and atmospheric pressure. In this research, *Heterotheca inuloides* (Mexican arnica) was assessed as reducing agent to synthesize platinum nanoparticles on bovine bone in order to prove that this biosynthesis is low-cost, simple, friendly to the environment (the only used solvent is water and strong reducing agents are not required). In addition, the catalytic activity of the as-prepared material was assessed in the hydrogenation of 2-butyne-1,4-diol towards 2-butene-1,4-diol.

2 Materials and Methods

2.1 Pt/Bovine Bone Biosynthesis

The precursor compound of platinum nanoparticles was $PtCl_4$. A 1 mM solution was prepared with 50 mL of deionized water (solution 1). Solution 2 was prepared by boiling during 5 min in an Erlenmeyer flask, 1 g of dried *H. inuloides* with 100 mL of distilled water. In order to prepare the support, a bovine femur was washed, cleaned and immersed in a 0.01 M HCl solution. Later, the support was dried in an oven at 40 °C for 24 h, then it was crushed and sieved by using a 170 mesh. 975 mg of the so obtained powder was added to solution 1 and after 30 s, the powder was filtered. The reduction of Pt(IV) ions was carried out with solution 2 during 1 h and then filtered. The resulting material was dried at room temperature overnight. Calcination is a common practice in the synthesis of heterogeneous catalysts, in this case, however, it is worth noticing that the synthesized composite was not calcined at any time. A micellar activity might also be expected since the micelle formation of sepia cartilage collagen solutions has been previously reported [29].

2.2 Characterization

Transmission electronic microscopy (TEM) and selected area electron diffraction (SAED) studies were carried out using a JEOL JEM-2100 microscope operating at 200 kV accelerating voltage. The platinum-impregnated bovine bone powder was suspended in 2-propanol and then ultrasonically dispersed for 5 h at room temperature. A drop of this suspension was then placed on a Cu-grid coated with a holey carbon film. Also, the supported platinum nanoparticles were analyzed by SEM technique.

The X-ray photoelectronic spectroscopy (XPS) analysis was carried out in a JEOL JPS-9200 equipped with a Mg source (1253.5 eV), operating at 200 W and vacuum of 1×10^{-8} Torr. For all samples, the analysis area was 1 mm^2. The specsurf™ software was used to analyze the results.

Charge correction was done based on the adventitious carbon signal (C 1s) at 284.5 eV. Shirley method was used for background adjustment, whereas Gauss-Lorentz method was used for curve fitting.

2.3 Hydrogenation of 2-Butyne-1,4-diol

The hydrogenation of 2-butyne-1,4-diol was carried out in a 300 mL stainless-steel Parr reactor equipped with a temperature control system, a mechanical stirrer, pressure indicator, an inner heating/cooling coil system and sampling valve. A reservoir for H_2 gas was used along with a constant pressure regulator to supply hydrogen at a constant pressure to the reactor.

In a typical hydrogenation experiment, 150 mL of 20% w/w aqueous 2-butyne-1,4-diol solution and 0.215 g of Pt-supported catalyst were loaded into the reactor. The initial concentration of the alkyne was 0.1 mol/L. The reactor was first flushed with nitrogen and then with hydrogen. After the desired temperature (328 K) was reached, the system was pressurized with hydrogen at the required pressure (6 bar) and a 550 rpm stirring speed was set at all experiments. Samples were obtained every 30 min.

Samples were analyzed by gas chromatography with a flame ionization detector using a 456 SCION GC (DB-WAX 52 column, length 32 m, inner diameter = 0.3 mm) and helium (30 mL/min) as a carrier gas, according to previously reported analysis methods [30–33]. Reaction samples were injected into the GC and analyzed under the following conditions: temperature detector was set at 518 K, injector temperature at 513 K, the initial oven temperature was 353 K and this was raised up to 493 K at a rate of 10 K/min. This final oven temperature was kept constant for 3 min.

3 Results and Discussion

3.1 Characterization

3.1.1 Transmission Electron Microscopy (TEM) Analysis

Figure 1a–c shows BF-STEM images where the platinum nanoparticles supported on bovine bone dust are clearly observed. The difference in electronic density allows to differentiate the platinum from the support that is constituted by hydroxyapatite (carbon, calcium, phosphorus and

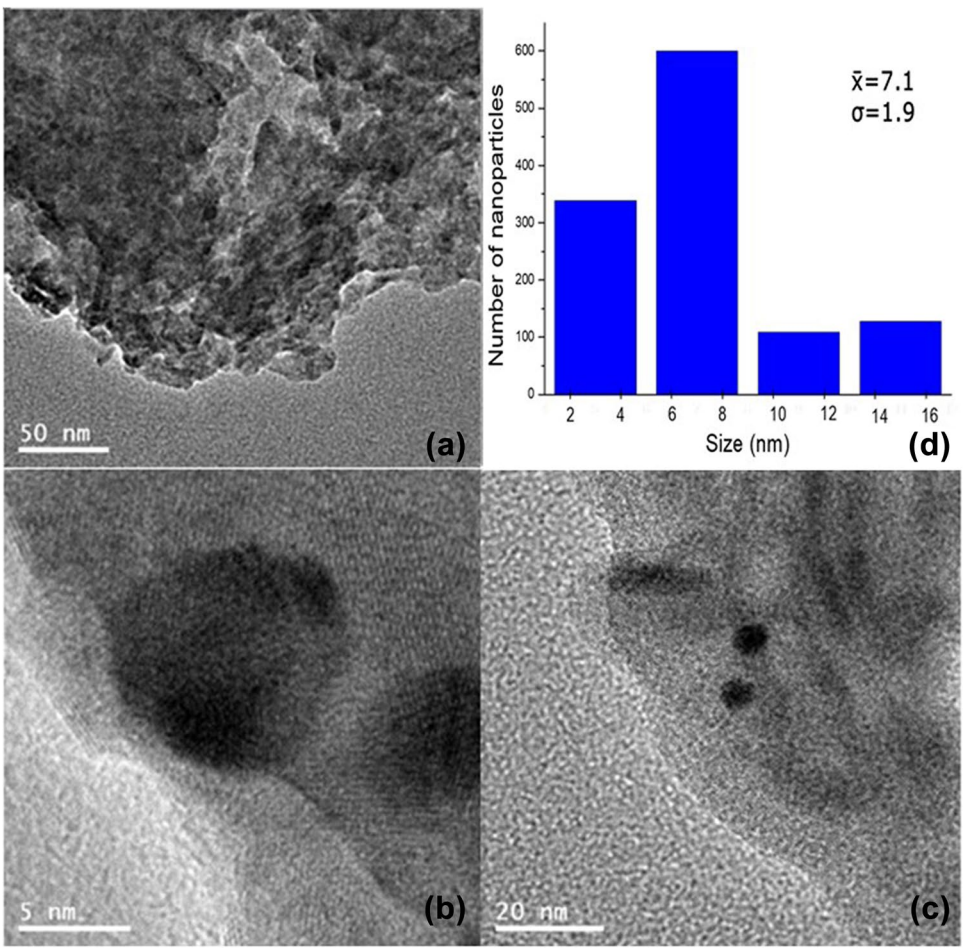


Fig. 1 **a–c** BF-STEM images of Pt nanoparticles on bovine bone powder, at different magnifications, **d** size distribution of platinum nanoparticles

oxygen), BFSTEM shows metallic particles in a darker color. The particle size is in the range of 3 to 40 nm, with few exemptions that are out of the particle size distribution. The images reveal that quasi-spherical Pt NPs with low size and low polydispersity are obtained into the bovine bone surface. These images correspond to a randomly chosen part of the substrate and can be considered as representative of the overall size and shapes of the particles.

These images correspond to Pt nanoparticles on the bovine bone powder after 5 h of ultrasonication. The average diameter of synthesized nanoparticles was found to be 7.1 nm, taking into account 600 nanoparticles approximately (Fig. 1).

The use of bovine bone as catalytic support and *H. inuloides* as reducer is rather novel. This synthesis method is relatively low-cost and environmentally friendly since the reducer and the support are easily biodegradable, the solvent is water and the calcination step followed by reduction with hydrogen is eliminated. Moreover, the chemical structure of hydroxyapatite can form stable compounds and anchor the metal ions.

Figure 2 shows two images of HRTEM where two particles of platinum supported on bovine bone powder can be observed, one of the platinum particles has an interplanar distance of 2.25 Å which corresponds to the plane (111) for metallic platinum FCC. In the other micrograph, two interplanar distances are identified, one with 2.25 Å that corresponds to the plane (111) of FCC metallic platinum (JCPDS card 00-004-0802) and the other with 2.66 Å that corresponds to the plane (101) of tetragonal platinum oxide (JCPDS card 00-043-1100). Therefore, it can be concluded that the platinum nanoparticles are polycrystalline.

By observing the shape and chemical composition of nanoparticles, a fast reduction appears to rule the synthesis of platinum nanoparticles with *H. inuloides* as reducing agent since polycrystalline isotropic particles are obtained [34].

In addition, XPS was used to determine the oxidation state of the platinum nanoparticles. The narrow spectra in the Pt 4f region and its curve fitting, show two oxidation states for platinum (Fig. 3). The components at 70.9 eV (4f7/2) and 74.4 eV (4f5/2) can be attributed to metallic platinum in around 47.62% of the total platinum, the energy separation of 4f7/2 and 4f5/2 is 3.5 eV corresponding to that reported for platinum, the ratio proportion intensity of the orbitals 4f7/2 with respect to 4f5/2 is 4:3 as it could be corroborated. The signals at 72.5 eV (4f7/2) and 76.7 eV (4f5/2) correspond to 51.84% of the total platinum and can be ascribed to platinum oxide. The energy separation of 4f7/2 and 4f5/2 is 3.1 eV corresponding to that reported for platinum, the ratio proportion intensity of the orbitals 4f7/2 with respect to 4f5/2 is 4:3 as it could be corroborated.

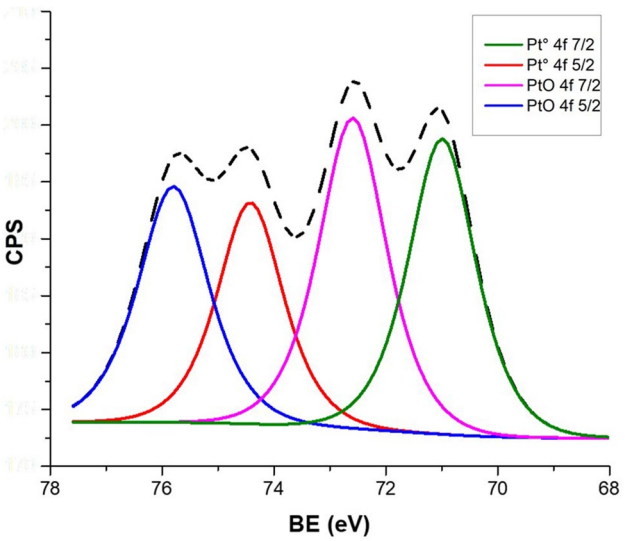


Fig. 3 XPS spectra corresponding to the 4f5/2 (pink line) and Pt 4f7/2 (dark green line) regions of the platinum nanoparticles supported on bovine bone dust

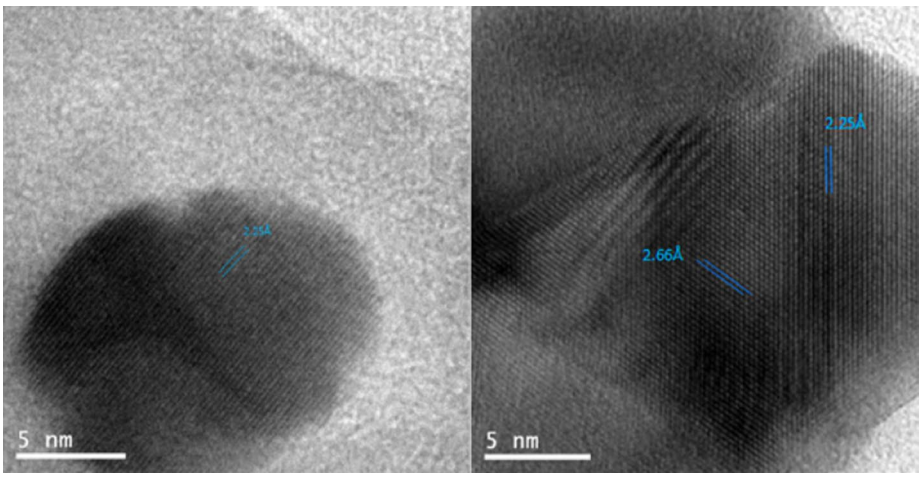


Fig. 2 HRTEM micrograph Pt-nanobiocomposite

These results indicate that the reduction of Pt(IV) to Pt° indeed took place and that Pt nanoparticles were supported onto the bovine bond powder in controlled size and shape.

3.2 Catalytic Activity

The catalytic activity of the synthesized powder was established in the hydrogenation of 2-butyne-1,4-diol. This reaction has been reported to be catalyzed by metallic Pt or Pd [32, 33, 35]. Therefore, the exhibited catalytic activity can be taken as an additional proof of the presence of metallic nanoparticles obtained by employing the bio-reducer *H. inuloides*. Nevertheless, the XPS results shows the presence of oxidized Pt and the catalytic contribution of this specie should not be discarded [36]. The referenced reaction has been reported to proceed as depicted in Scheme 1. According to this scheme, the consumption of the first hydrogen mole leads to the production of the usually desired intermediary, 2-butene-1,4-diol. The further consumption of H_2 produces the saturated diol (butanediol) and by-products like crotyl alcohol and/or butanol. Thus, in the context of this reaction, achieving a high selectivity towards 2-butene-1,4-diol, represents a challenge that has been usually addressed by adding chemical bases or by modifying the reactor hydrodynamics [32]. Figure 4 is the evidence that the synthesized material not only exhibits catalytic activity but also a high selectivity (0.96) towards the alkene.

The kinetics of the 2-butyne-1,4-diol hydrogenation was established by the integral method. A linear relationship between 2-butyne-1,4-diol concentration and reaction time was found when plotting the former versus the latter. By doing this, the specific rate constant was found to be $k_o = 0.001$ mol/dm^3 min. Thus, it can be concluded that under the studied conditions, the hydrogenation rate is independent of the alkyne concentration (zero order reaction regarding 2-butyne-1,4-diol). This reaction has been reported to follow a Langmuir–Hinshelwood mechanism when using Pd as active phase [32, 33, 37].

This mechanism suggests that both H_2 and the alkyne, are chemisorbed and compete for the same type of sites. It has been demonstrated [32] though, that the alkyne chemisorbs stronger than hydrogen and that olefins. This implies that the adsorption equilibrium constant for the alkyne is much higher than that of the other compounds. Therefore, the adsorption of hydrogen and the products can be neglected

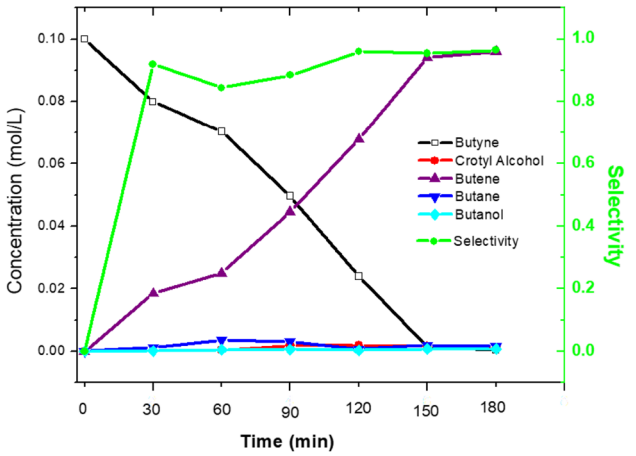
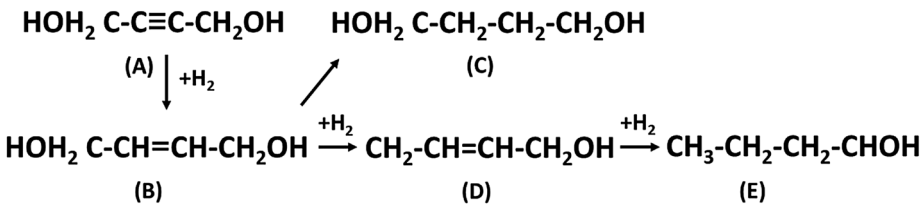


Fig. 4 Concentration and selectivity profiles for the hydrogenation of 2-butyne-1,4-diol. Reaction conditions: temperature, 328 K; pressure, 6 bar; initial concentration, 20% aqueous solution of 2-butyne-1,4-diol; active concentration of the catalyst, 0.215 mg; stirring speed, 550 rpm; total volume, 1.5×10^{-4} m^3

when the surface coverage by the alkyne is relatively high. This results in the zero-order kinetic equation regarding 2-butyne-1,4-diol [37].

Finally, it is worth noticing that the synthesized catalyst consisting on platinum nanoparticles supported on bovine bone powder, eliminates the use of base addition to obtain a selectivity above 90% in the hydrogenation of 2-butyne-1,4-diol. For the same reaction, Telkar et al. indicate that with 1% Pt/$CaCO_3$ they obtained a selectivity of 83% and when adding ammonia in the hydrogenation reaction, 100% selectivity is obtained [35]. This suggests that the attained high selectivity in this work might be ascribed to an enhanced basicity of the biosynthesized catalyst. A heterogeneous catalyst selectivity, however, might be influenced by other factors like particle size and shape [38]. In this case, as we are dealing with nanoparticles, it is very likely that the observed high selectivity might also be related to the average nanoparticle size (7.1 nm). In this regard, it has been demonstrated [38] that nanoparticle size might change the activation energy of a specific reaction and thus selectivity. In the same work [38], it was shown that platinum nanoparticles shape (cubes or cuboctahedra) leads to complete different products distribution in the hydrogenation of benzene. Therefore, the fact of having obtained semi-spherical



Scheme 1 2-butyne-1,4-diol hydrogenation scheme [33]. A: 2-butyne-1,4-diol, B: 2-butene-1,4-diol, C: butane-1,4-diol, D: crotyl alcohol, E: n-butanol

Pt nanoparticles in this work, might also be influencing the selectivity towards the alkene. At the end, it can be said that the observed high selectivity is the result of the combined effect of support, Pt nanoparticle size and shape. A special research work should be dedicated to establishing which of these factors affects selectivity the most.

4 Conclusions

Metallic platinum nanoparticles supported on bovine bone powder were synthesized by using as reducing agent *H. inuloides* (Mexican arnica). The average diameter of synthesized nanoparticles was found to be 7.1 nm. The resulting bio-nanocomposite exhibits catalytic activity to conduct hydrogenation reactions with high selectivity (96.5%) towards the intermediary in a consecutive hydrogenation reaction.

In addition, it can also be concluded that bovine bone powder is an efficient, low-cost support of platinum nanoparticles.

This synthesis method presented here is relatively low-cost and environmentally friendly since the support is a waste material, the solvent is water, the calcination step is eliminated and the reducing agent is environmentally friendly.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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