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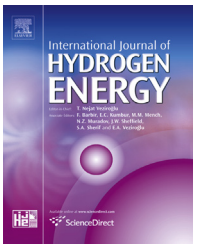

Short Communication

Sustainable application of pecan nutshell waste: Greener synthesis of Pd-based nanocatalysts for electro-oxidation of methanol

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ABSTRACT

Palladium-based electrocatalysts are widely used in alkaline direct alcohol fuel cells. The synthesis and characterization of carbon-supported bimetallic nanoparticles (NP) of AuPd and AgPd is described using pecan nutshell extract (*Carya illinoinensis*) which serves as both, reducing and the stabilizing agent. This environmentally friendly route generates bimetallic NP for a wide range of applications, including electrocatalysis; since particularly AuPd NP proved to be a potentially suitable electrode material for alkaline direct methanol fuel cells. The electrocatalytic activity of these nanomaterials was comparable to commercially available Pd/C 1% in the electro-oxidation of methanol in alkaline media.

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Introduction

Abiding by the Green Chemistry Principles, waste prevention and sustainable utilization of resources rank very high due to the global challenge faced by society and industry. As an example, the agroindustry sector generates billions of metric tons of waste every year worldwide, causing, among other environmental issues, a major disposal problem. Therefore, it is imperative to find sustainable pathways to exploit the availability of rich biorenewable and biodegradable biomass resources, rather than simply using them for only fuel value [1].

Annually, Mexico produces over a hundred thousand tons of pecan nuts, *Carya illinoinensis* (Fig. S1), which generates approximately forty thousand metric tons of nutshell waste, a residue with no apparent economic value [2–4]. Valorisation of this residue has been attempted as a carbonaceous precursor for activated carbon [5,6], and the production of carbon electrodes for Na-ion batteries [7]. In view of the fact that aqueous extracts of pecan nutshell are rich in polyphenols and tannins with good antioxidant activity [8,9], we envisioned to exploit this property to reduce metal salts to generate high-value nanomaterials [10].

Although Mexico is top ten producer of gold and silver, very little attention is paid to the generation of valuable metallic nanoparticles [11]; such nanoparticles are now well known to have important applications in the fields of biotechnology, bioengineering, textile engineering, water treatment and catalysis [12].

Overall, the conventional synthesis of metal nanoparticles (NP) often involves the use of toxic and hazardous reagents, which comprise solvents, and reducing and stabilizing agents. Although the potential adverse effects of these metallic NP in the environment is debated, their proven advantages over other materials is unquestionable. Thus, the use of environment-friendly and biocompatible reagents to produce these NP's should be fostered to curtail the potential toxicity and environmental impact of the ensuing byproducts [13]. Greener synthesis of metal NP's using relatively benign and abundant natural products is a good alternative to achieve such objectives; this burgeoning research field mainly focuses on exploiting natural extracts either obtained from plants or waste residues [10,14,15]. However, there are two major drawbacks in this strategy: a) food residues are rich in nutrients, if not for human consumption, perhaps still suitable for an animal diet [16]; and b) as has been known historically in the case of herbal medicines, the widespread utilization of plant extracts sometimes leads to plant devastation [17]. In this context, exploitation of pecan nutshell residues, as a viable feedstock, circumvents these two issues because there is no human or animal consumption known for pecan nutshell waste.

Among others, catalysis is one of the mature applications for some of these nanoparticles. Indeed, zerovalent metals can act as active phases in carbon-supported electrocatalysts for fuel cells. Specifically, Pd-based NPs have been explored as a suitable candidate to replace Pt, as the catalyst in alkaline direct alcohol fuel cells. In fact, it has been amply proven that there is a synergetic effect in Pd bimetallic alloys in presence of either Au or Ag, when oxidizing alcohols in alkaline media [18–20].

Based on the aforementioned rational, we decided to pursue an integrated approach wherein supported catalysts encompass metallic nanoparticles (NP) which could be supported on ensuing carbonaceous material generated from the solid waste residues. In this paper, we report the synthesis of supported bimetallic nanoparticles, AuPd/C and AgPd/C, which are evaluated as potential electrocatalysts for methanol oxidation in alkaline media.

Materials and methods

Preparation of AuPd/C and AgPd/C electrocatalysts

Carbon-supported AuPd and AgPd NP with equiatomic compositions were synthesized by simultaneous chemical reduction of $HAuCl_4$, $AgNO_3$ and Na_2PdCl_4, as applicable, in the presence of an aqueous pecan nutshell extract as a reducing and stabilizing agent. Further, we wanted to exploit the use of alternate energy systems, such as microwave irradiation to generate uniformly small size NPs [21–23]. The AuPd and AgPd colloidal dispersions were prepared by dissolving appropriate amounts of commercial high purity (99.998% or better) individual precursors salts, $HAuCl_4$ (35.0 mg), $AgNO_3$ (17.5 mg) and Na_2PdCl_4 (29.7 mg) in 10 mL of deionized water. Then 1 mL of each of the corresponding aqueous solutions containing the precursors were added to 5 mL of aqueous pecan nutshell extract and manually homogenized. The resulting admixture was then irradiated, in a CEM Discover Benchmate Microwave system (300 W); for AgPd (30 s, 90 °C) and for AuPd (30 s, 130 °C) to generate two colloidal dispersions: AuPd and AgPd, respectively. In order to obtain either of the supported bimetallic electrocatalysts, AuPd/C or AgPd/C, an appropriate amount of Vulcan XC72, previously oxidized with H_2O_2 (30 wt%), was weighed to achieve 5 wt%, poured into the corresponding colloidal dispersion and kept under sonication for 15 min. Later, the dried powder was rinsed with deionized water, dried again at 120 °C for 2 h and then thermally treated in a tubular furnace at 340 °C under an argon atmosphere for 1 h and finally for another hour in air, to promote alloy formation and to remove the impurities on the electrocatalyst surface.

Characterization methods

Metallic NP formation was preliminarily confirmed using a Perkin Elmer UV–visible spectrophotometer (Lambda 35). Metal loading of the supported electrocatalysts was determined via thermogravimetric analysis (TGA Q500, TA Instruments). The metallic composition of the nanocatalysts was assessed by X-ray fluorescence (S2 Picofox, Bruker). Crystallite size and alloying degree were estimated through X-ray diffraction (D5000, Siemens; $\lambda = 1.541877$ Å). The dispersion and size of the bimetallic particles, within the electrocatalytic support, were examined by scanning electron microscopy (JSM-7401F, JEOL) and transmission electron microscopy (TEM, JEM-2200FS, JEOL). Finally, the electrocatalytic performance of AuPd/C and AgPd/C was assessed at room

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