

Characterization Microstructural and Electrochemical of AgPd Alloy Bimetallic Nanoparticles

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ABSTRACT

Bimetallic nanoparticles are of special interest for their potential applications to fuel cells, among the bimetallic systems, AuPd bimetallic nanoparticles have received great interest as they can be widely used as effective catalysts for various electrochemical reactions. Monodisperse AgPd alloy nanoparticles were synthesized by polyol method using silver nitrate and potassium tetrachloropalladate(II) in ethylene glycol as the reducing agent at 160 °C. Structural, compositional and electrochemical characterizations of synthesized bimetallic nanoparticles were investigated. High-angle annular dark field scanning/transmission electron microscopy (HAADF-STEM) images and parallel beam X-ray diffraction (XRD) of the bimetallic nanoparticles were obtained. XRD and the contrast of the HAADF-STEM images show that the bimetallic nanoparticles have an alloy structure. Cyclic voltammetry was carried out in order to confirm the electrochemical responses of the AgPd/C electrocatalysts for methanol oxidation. Thanks to the narrow size distribution of the AgPd alloy bimetallic nanoparticles (9.15 nm) the supported AgPd/C electrocatalysts have high catalytic activity toward methanol electro-oxidation.

INTRODUCTION

Bimetallic nanoparticles systems are very interesting materials due to their notable properties in comparison to the monometallic systems [1]. The combination of different metals and different particle sizes offer a wide range of possible applications in different fields as catalysis, optoelectronics, biology, medicine and electronics [2], [3]. In this sense bimetallic nanoparticles with alloy nanostructure are of great significance because of the modification of properties observed, compared with their counterpart monometallic, not only due to size effects, but also as a result of the combination of different metals [1]. Because the properties of

monometallic nanoparticles are a manifestation of their size and structure, the elemental distribution and morphology of bimetallic nanoparticles give an explanation of their chemical and physical properties [4].

Among the various bimetallic nanoparticles, palladium (Pd) based alloys are always under investigation due to better permeability of hydrogen than the pure Pd and highly active for the oxidation of a large variety of alcohols [5]. Specially AgPd alloy is under research investigation due to the high permeability for hydrogen [6], [7]. AgPd alloy nanoparticles have been widely explored as catalytic materials for a variety of reactions [8], and also they have great potential in developing as a hydrogen storage material for fuel cells [8]. The structure of the alloy is controlled by parameters such as reduction kinetics of each metal, mole ratios and presence of external ligands. They all can play important roles in terms of whether or not alloy structures are realized. Recently much effort has been devoted to fabricate Ag-Pd nanostructures with well-defined morphology because the grain size and morphology have a great impact on the chemical and/or physical properties of metal nanomaterials. For example, Ag-Pd nanorings, hollow triangular nanoplates and dendrites were successfully prepared by a simple galvanic replacement reaction using Ag nanoparticle, triangular nanoplates and wires as template, respectively [9], [10]. Despite all these efforts, it remains a challenge to synthesize Ag-Pd nanostructures with novel shapes and controllable molar composition by a simple and inexpensive method.

In this work, AgPd alloy bimetallic nanoparticles were synthesized by polyol method. The structural characterization was carried out by parallel beam X-ray diffraction and scanning/transmission electron microscopy, indicating that AgPd bimetallic nanoparticles are formed with alloy structure. Finally, methanol electro-oxidation reaction of the supported bimetallic nanoparticles was measured using cyclic voltammetry.

EXPERIMENTAL PROCEDURE

Chemicals

Silver nitrate (AgNO_3), potassium tetrachloropalladate(II) (K_2PdCl_4), ethylene glycol (EG), hexane and methanol were purchased from Sigma-Aldrich and used as received.

Preparation of AgPd NPs

AgPd nanoparticles were prepared by oil-bath heating in EG using a two-step reduction method. For the synthesis of Ag nanoparticles, 3 ml of EG were preheated until the temperature stabilizes at 160 °C in a 3 neck round bottom flask. Over the stirred EG, 1.5 ml of 62.5 mM AgNO_3 in EG and 3 ml of 0.375 mM PVP in EG was added slowly in aliquots of 200 μl and 400 μl respectively each 2.5 minutes until the volume of the precursor and surfactant finished, then kept stirred at 160 °C for 2 hours. Without cooling, another 1.5 ml of 62.5 mM K_2PdCl_4 in EG was added to the flask followed by 3 ml of 0.375 M PVP, repeating the previously mentioned

aliquot quantities and addition time, as well as the growth wait of 2 hours. The cleansing of the nanoparticles were realized with several hexane and deionized water ultrasound baths.

Structural characterizations

Scanning/transmission electron microscopy (STEM) images were obtained using a JEOL JEM-ARM200F microscope (200 kV) with a field-emission electron source and spherical corrector in the illumination system. X-ray diffraction (XRD) patterns were recorded on Rigaku Ultima IV diffractometer with Cu K α radiation (40 kV, 15 mA, 1.54051 Å) over a 2 θ range from 30° - 80° at room temperature.

Electrochemical characterizations

Cyclic voltammetry (CV) was carried out on a VSP-Biologic® potentiostat/galvanostat containing a traditional three-electrode cell including a mercury-mercurous sulfate as reference electrode (Hg/Hg₂SO₄), a graphite rod as counter electrode, and a glassy carbon electrode (GCE, 3 mm in diameter BASI) as working electrode. The GCE electrode was loaded with catalysts as follows. The prepared 2 mg catalyst (AgPd/C) was mixed with Nafion solution and suspended in 1 mL distilled water. The mixture (10 mL) was pipette onto the GCE electrode and allowed to dry under ambient conditions. These steps were repeated three times. The electrodes were finally dried at room temperature for 2 h.

RESULTS AND DISCUSSION

Shape and size of the bimetallic nanoparticles are strictly dependent on the synthesis methods [ref], even more, combination of two metals results in more possibilities in shape and structure due to distribution of each metal within a particle [11]. Therefore a structural characterization of these bimetallic nanoparticles is essential. Figure 1 show the X-ray diffraction pattern of the bimetallic AgPd nanoparticles synthesized by polyol method. The well-defined diffraction peaks of the nanoparticles is between the peaks of Ag and Pd, as can be observed in the inset, where the (111) reflections of the Ag (JCPDS, No. 89-3722) and Pd (JCPDS, No. 46-1043) are showed, further indicating that AgPd is formed as an alloy structure. The bimetallic nanoparticles displayed a face centered cubic (fcc) crystal structure as shown by the characteristic (111), (200) and (220) reflections in the XRD spectrum (JCPDS, No. 03-7261). Scherrer equation was used to calculate the crystallite size and the analysis was performed on the (111) reflection. The obtained value of crystallite size was 8 nm.

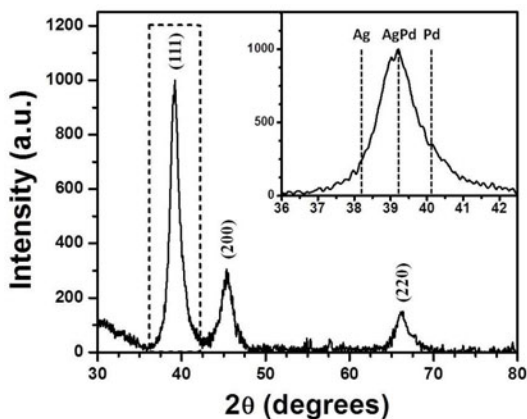


Figure 1. XRD pattern of the AgPd alloy nanoparticles.

The composition and elemental distribution of the bimetallic AgPd nanoparticles was characterized by scanning/transmission electron microscopy (STEM). As shown in Figure 2a, the nanoparticles have a narrow size distribution with an average particle size of 9.15 nm (size distribution plot inset) that is very close to calculate by XRD using the Scherrer equation. Figure 2b shows a bimetallic nanoparticle where energy dispersive spectrum (EDS) was obtained. The elemental distribution between Ag and Pd atoms was confirmed using energy dispersive X-ray spectroscopy (EDS). Representative EDS mappings are presented in Figure 2d, where the red and green plot correspond to the contribution from Ag and Pd, respectively. EDS mapping confirmed the mixing of Ag and Pd forming an alloyed structure.

The microstructure of the AgPd bimetallic nanoparticles also was obtained by STEM with aberration corrected. Representative high-resolution high-angle annular dark field (HAADF)-STEM image of AgPd is shown in Figure 3. As is known images with Z-contrast and high-resolution can be acquire using HAADF-STEM with spherical aberration corrected [12]. Figure 3a shows a high-resolution HAADF-STEM image of the AgPd bimetallic nanoparticle; as mention, the contrast in the HAADF-STEM images is associated with the atomic number Z of the elements in the sample [13], however the atomic difference between Ag and Pd is only one ($Z_{Ag}=47$ and $Z_{Pd}=46$), therefore to observe different contrast in the image associated to the elements of the sample is very difficult, however it is clear from this image that the contrast of the image is homogeneous therefore the nanoparticle has an alloy structure, where the atoms of Ag and Pd have a random distribution. From the Figure 3b and the fast Fourier transform (FFT, inset) d-spacings 0.1974 and 0.2289 nm were obtained, which corresponding to the (111) and (200) lattice spacing of face centered cubic (fcc), respectively, suggesting that AgPd is formed as an alloy structure.

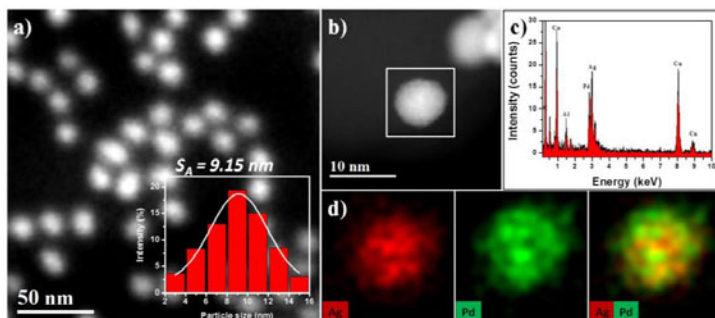


Figure 2. a) HAADF-STEM image of the AgPd bimetallic nanoparticles and its corresponding size distribution plot, b) HAADF-STEM of a single particle, c) EDS analysis, and d) elemental mapping of Ag, Pd and AgPd.

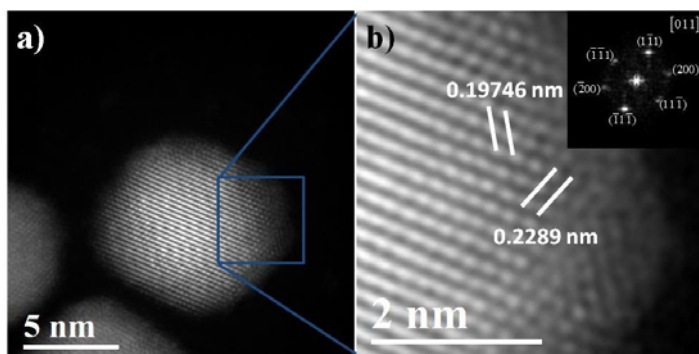


Figure 3. a) HAADF-STEM images of AgPd alloy nanoparticles, respectively, and b) lattice fringes of the AgPd alloy are marked.

AgPd nanoparticles were supported on Vulcan carbon black to analyze their electrocatalytic behavior, mainly methanol electro-oxidation reaction (MOR). Figure 4a and b show BF and HAADF-STEM images of the support AgPd/C catalyst, respectively. After that the nanoparticles were supported on the carbon black, it is evident that the nanoparticles with homogeneous size were uniformly dispersed, and agglomeration was not observed. Figure 4c shows the MOR cyclic voltammogram of the AgPd/C catalyst at different concentrations (0.1 and 1 M). An important factor that has been using in the evaluation of the electrocatalyst is the tolerance to CO poison species formed during the MOR [14]. To determine the tolerance to the accumulation of

carbonaceous species, were used the criterion of the ratio of the peak current in the forward sweep (I_f) and the peak current in the reverse sweep (I_b) [15], [16]. A higher value of the I_f/I_b ratio better oxidation of methanol and less poisoning of the electrocatalysts by the CO species are obtained [17]. It can be observed from the figure, at higher concentration of methanol (1 M), higher is the I_f/I_b ratio, that is, I_b is much smaller than I_f . Such high I_f/I_b ratio indicates that most of the intermediate carbonaceous species were oxidized to CO_2 during the forward scan.

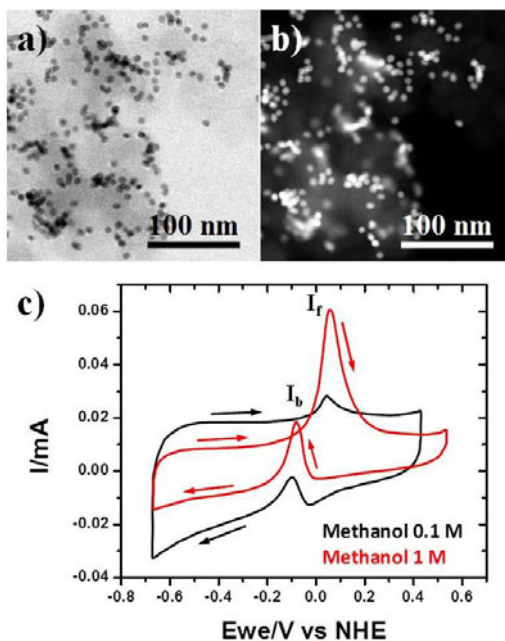


Figure 4. a) and b) BF and HAADF-TEM images of the AgPd/C catalyst respectively, c) cyclic voltammogram towards methanol electro-oxidation of the catalyst.

CONCLUSIONS

Using the described polyol method, AgPd bimetallic nanoparticles with alloy structure and good control on the particle size with a narrow distribution were synthesized. Such bimetallic nanoparticles have a smaller diameter and without agglomeration. The average size of the nanoparticles was around 9.15 nm. They have been characterized using parallel X-ray diffraction and STEM images which show the alloy structure. The electrocatalysts exhibited excellent I_f/I_b ratio, indicating the exceptional anti-poisoning strength and potential to be used in fuel cell conditions.

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