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TEM and EELS studies of microwave-irradiation synthesis of bimetallic platinum nanocatalysts

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Abstract: Microwave-irradiation (MW) synthesis of nanostructured materials provides for the synthesis of metal nanoparticles, using fast and uniform heating rates. This procedure affords better control of the shape and size of the nanoparticles when compared to conventional methods. In this work, microwave-irradiation was used to produce platinum-cobalt (Pt-Co) and platinum-nickel (Pt-Ni) nanoparticles for use as electrocatalysts in the methanol oxidation reaction. High resolution TEM imaging and EELS studies revealed that these bimetallic nanoparticles form islands or hetero-structures.

1. Introduction

Nanoparticles are of interest due to their enhanced electronic, magnetic and catalytic properties compared to bulk structures, mainly due to their relatively larger surface to volume ratio and consequent increased surface activity [1]. The preparation of nanoscale metal clusters and colloids with desirable properties presents a significant scientific challenge. In order to understand the architecture in bimetallic nanoparticles, it is important to synthesize the different structures, i.e. heterostructures, alloys and core-shell structures. Conventional synthesis procedures involve the use of volatile organic solvents with harmful effects on the environment and human health [2]. Therefore, the search for alternative synthesis procedures using uniform heating methodologies has become a high priority.

New synthesis approaches include microwave (MW)-irradiation [3]. Microwave heating results from dipole-dipole interactions between the polar molecules in the solution, and the electromagnetic field. The main advantages of the microwave-assisted reactions over conventional methods are; (a) the kinetics of the reaction can be increased by the 1 – 2 orders of magnitude, (b) novel phases can be formed, (c) the initial heating rate is rapid and can lead to energy saving, and (d) the selective formation of specific phases [4]. This MW synthesis approach is a versatile, cost-effective, energy efficient {Grace, 2007 #1} method with potential for mass production. In terms of the use of MW irradiation for nanoparticles, Bensebaa et al.[5], synthesized polymer-stabilized Pt-Ru nanoparticles using this approach. In this work, Pt-Ni and Pt-Co nanoparticles were synthesized using a MW process, which have both shown good activity towards the methanol oxidation reaction (MOR) in fuel cells.



2. Synthesis Procedure

Materials: The samples were prepared using metal precursor salts ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{M} = \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and ethylene glycol as both the solvent and reducing agent. Polyvinylpyrrolidone (PVP) was used as the capping agent and Pt:M was added at a molar ratio of 1:1.75. All the chemicals were obtained from Sigma Aldrich^(R), and used as received.

Synthesis: Microwave synthesis was performed using an Anton Paar M300 reactor (temperature = 200 °C, power = 750 W, time = 30 min). The Pt-Co nanoparticles were synthesized using a seeding method, i.e. Pt seeds were synthesized first, filtered and dried. Then the Co shells were grown on the surface of the platinum. Pt-Ni nanoparticles were synthesized using a co-reduction procedure in the microwave oven, i.e. the two metals salts are reduced simultaneously in solution.

Characterization: The morphology of the Pt-Co and Pt-Ni nanoparticles were determined using transmission electron microscopy (TEM) on JEOL JEM-2100 microscope. Electron energy loss spectroscopy (EELS) and scanning transmission electron microscope (STEM) were performed on a JEOL ARM 200F, both at 200 kV.

3. Results

3.1. TEM analysis

In the lower magnification TEM images (figure 1 a-b), the Pt-Co nanoparticles have a homogeneous, spherical structure with observed lattice fringes. However, as indicated by the arrows in figure 1(b), lattice information was observed on the material underneath the nanoparticles. This “layer” structure was suggested as Co sheets, also observed by Shin et al. [6] for Co nanoparticles synthesized in supercritical methanol. The crystalline nature of the nanoparticles is seen in figure 1c, with the cubic lattice structure confirmed by the Fast Fourier Transform (FFT) spectrum; figure 1(d), of a single nanoparticle (dashed box in figure 1(c)).

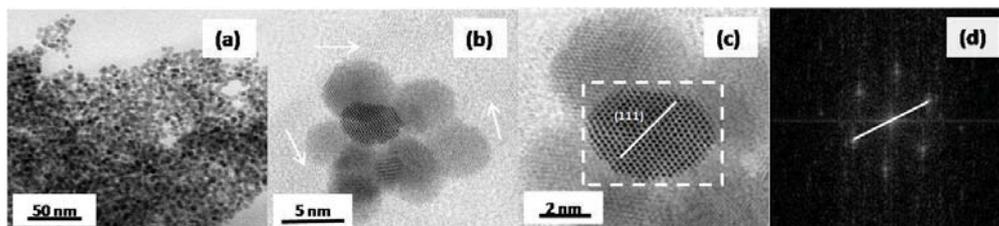


Figure 1. TEM images of microwave synthesized Pt-Co nanoparticles using Pt-seeds, (a) low magnification, (b) STEM images and (d) the FFT spectrum of a single nanoparticle.

The absence of any contrast in the particles indicates that the structure is not an intermetallic, as the difference in electron densities between the two metals was not observed. Further, the d-spacing of 2.30 Å is typical of the (111) direction of a Pt fcc crystal.

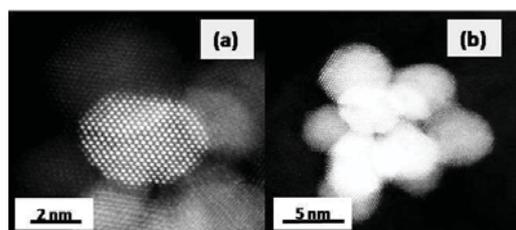


Figure 2. HAADF images of microwave synthesized Pt-Co nanoparticles, (a) single and (b) cluster of nanoparticles.

As shown in figure 3a, the Pt-Ni nanoparticles are crystalline (figure 3b) with two distinctive shapes, i.e. spherical and hexagonal. The FFT spectrum of figure 3a (dashed box), is illustrated in figure 3b, showing a crystalline pattern with a calculated d-spacing of 2.38 Å for fcc (111). Figure 3d indicates a possible hexagonal structure (from figure 3c) with a d-spacing of 2.24 Å for the hcp (100) direction. This could represent Ni because it can form a combination of fcc (NiO) and hcp (Ni) structures [7].

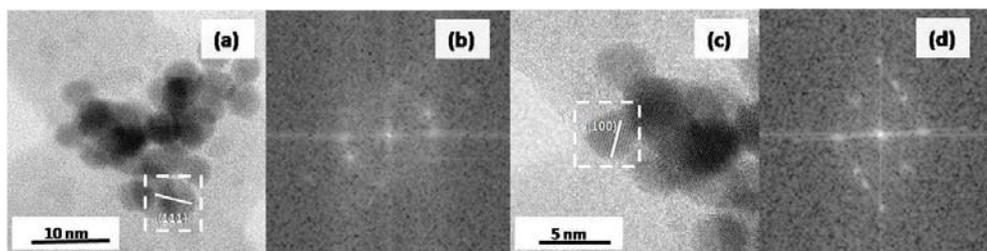


Figure 3. STEM images of microwave synthesized Pt-Ni nanoparticles (a,c) taken at different magnifications and (b,d) FFT spectra of single nanoparticles.

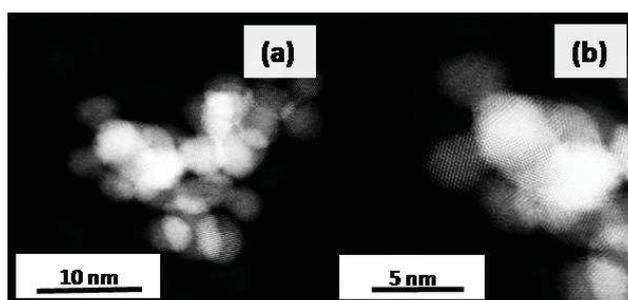


Figure 4. HAADF images of the Pt-Ni nanoparticles.

The dark-field images of the Pt-Ni nanoparticles (figure 4) also showed no clear phase in the nanoparticles. Therefore to confirm this observation, EELS was performed on both samples.

3.2. EELS analysis

EELS maps of Pt-Co nanoparticles synthesized by adding the CoCl_2 precursor solution to Pt seed nanoparticles followed by microwave heating, are shown in figure 5.

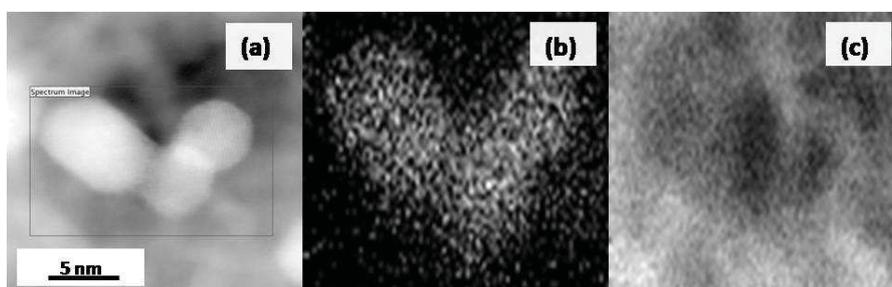


Figure 5. Energy-filtered EELS maps;(a) survey image,(b) Pt map and (c) Co map Pt-Co nanoparticles.

For the Pt and Co sample, contrast was observed in the images of the maps in figure. 5b, c. Furthermore the Pt seeds remain unaffected by the microwave process and the Co form sheets/layers of material underneath the Pt instead of growing as a shell around the Pt seeds. This is illustrated particularly in figure 5c where the Co is present as a homogeneous layer, whereas in figure 5b the Pt map illustrates the presence of Pt only in the nanoparticle structure.

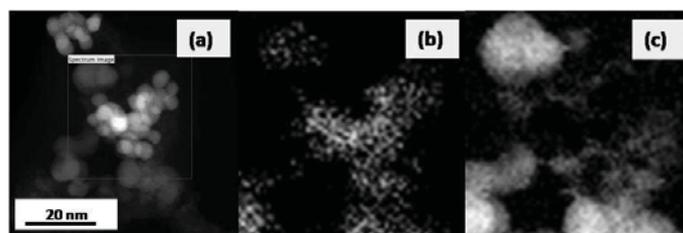


Figure 6. Energy-filtered EELS maps; (a) survey image, (b) Pt map and (c) Ni map, of microwave synthesized Pt-Ni nanoparticles.

The EELS maps of Pt-Ni nanoparticles (figure 6) illustrate the presence of two types of structures in the nanoparticles mixture, i.e. Pt-rich (figure. 6b) and Ni-rich (figure. 6c) areas. This suggests that an island/heterostructure is formed instead of an alloy structure. The Pt has been shown to grow independently from the alloying metal under certain conditions[8], therefore there is a possible island structure for this bimetallic systems.

4. Conclusion

The structures of the Pt-Co and Pt-Ni nanoparticles produced by microwave irradiation were investigated using electron microscopy. It was determined that for Pt-Co and Pt-Ni, the structures are not intermetallic or core-shell as expected, but that heterostructures were formed. In the case of Pt-Co, Pt nanoparticles are supported on Co layers, while in the Pt-Ni there is a presence of Pt-rich and Ni-rich areas. It has thus been shown that the seeding approach does not offer a route to the creation of core-shell structures, but instead results in hetero- or island structures. This stems from the differences that exist in the thermal decomposition rates of the Pt, Co and Ni.

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