Electrochemical synthesis of CoPt nanoparticles over carbonaceous substrates for electrocatalysis

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Abstract

The electrochemical technology is demonstrated as a useful procedure to fabrication of micro or nanostructures of metals and alloys, approaching to the Nanoscience and Nanotechnology field. In our laboratory, we develop different electrochemical strategies for the synthesis of nanoparticles, from a few nanometers to tens of nanometers, core@shell nanoparticles, nanowires with modulated aspect-ratio, nanotubes or nanometric films. Herein we describe the fabrication of CoPt nanoparticles with two different structures: CoPt alloy nanoparticles over glassy carbon or carbon cloth, and core@shell Co@Pt nanoparticles over glassy carbon (GC) substrate. These structures can be useful as electrocatalyzers for methanol oxidation in acidic or basic medium.

We have demonstrated that it is possible to fabricate CoPt alloy nanoparticles of a few (3-4 nm) nanometers and variable composition, from chemical reduction in water-in-oil microemulsions [1]. These NPs show a discrete electrocatalytic behavior respect to oxalic electro-oxidation, especially those corresponding to Pt_3Co. We demonstrate now that the electrochemical methods allows preparing CoPt alloy nanoparticles of greater size on different carbonaceous substrates, as the manner that the resulting structures could be directly used for electro-catalytic activity.

By direct electrodeposition from electrolytic baths containing Co(II) and Pt(IV) salts, we have fabricated dense distributions of CoPt alloy NPs over both glassy carbon and carbon cloth substrates. The strict control of the deposition technique (continuous or pulsed electrodeposition), applied potential, and deposition charge permit to control the size, distribution and composition of the NPs (Figure 1). The best electrocatalytic behavior respect to methanol oxidation in acidic medium (H_2SO_4) is for Pt_3Co.

Co@Pt NPs have been fabricated electrochemically on glassy carbon substrates, by means cobalt deposition with a strict control of the deposition charge and deposition potential to induce the formation of homogeneously distributed isolated cobalt particles (Figure 2). The cobalt particles formed has been immersed in platinum (IV) solution in order to induce the displacement between the superficial cobalt or cobalt oxide and the platinum. The control of the shell of platinum formation has been performed electrochemically, by following the electrochemical profile of the materials in a blank solution. This CoPt particles present better electrocatalytic behavior for methanol oxidation in basic media that pure platinum particles of the same size supported over glassy carbon.

References

[1] J. Solla-Gullon, E. Gómez, E. Vallés, A. Aldaz, J.M. Feliu, Journal of Nanoparticles Research 12 (2010) 1149

Figure 1: CoPt (Pt_3Co) nanoparticles electrodeposited on GC substrate**,** and their electro-catalytic activity respect to methanol oxidation in acidic medium

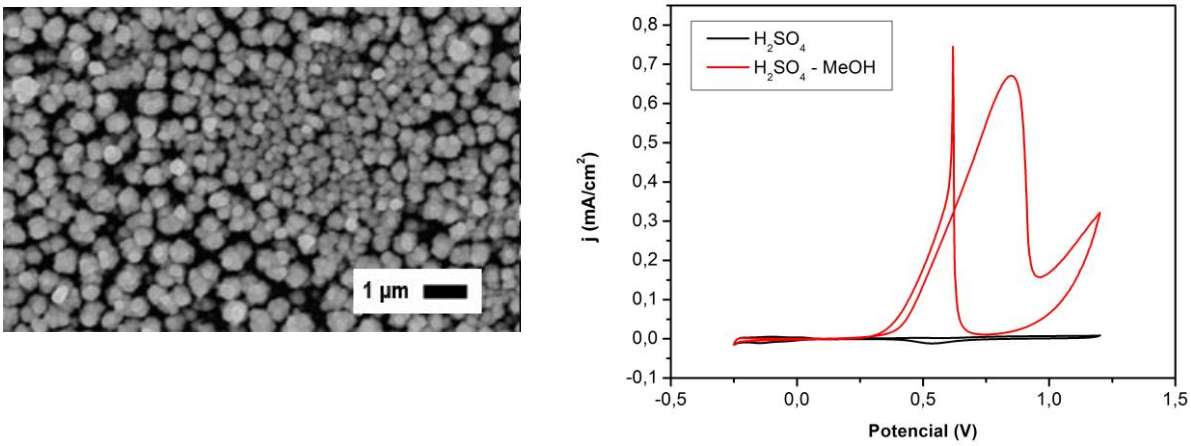

Figure 2: Co nanoparticles electrodeposited on GC substrate and voltammetric response, at 50 mV s^{-1}, of the Co@Pt core@shell nanoparticles in NaOH 0.1 M + Methanol 0.4 M solution (solid line) and NaOH 0.1 M + Methanol 0.8 M solution (dashed line). Recovery of the nanoparticles with a shell of Pt. Dotted line: NaOH 0.1 M