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Electrodeposition of sizeable and compositionally tunable rhodium-iron nanoparticles and their activity toward hydrogen evolution reaction

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ABSTRACT

Rh-Fe nanoparticles (NPs) with variable Rh/Fe ratios have been obtained by direct current electrodeposition onto Au-metalized Si/Ti substrates from an electrolyte containing Rh(III) and Fe(III) chloride salts. NP mean diameter could be varied in the range of 20–80 nm by playing with the applied current density ($-j = 0.5–2\ \mathrm{mA\,cm^{-2}}$) and deposition times ($t = 200–3200$ s). NPs were very well adhered to the substrate and became progressively enriched in Fe as the absolute value of the current density increased. X-ray photoelectron spectroscopy analyses revealed that the NPs are mostly metallic. The oxygen signal detected at surface level is relatively high but reduces down to less than 1 at% after 1 min Ar ions sputtering. The as-deposited Rh-Fe NPs are active toward hydrogen evolution reaction in alkaline medium. Different values of the onset potential for water reduction have been observed depending on the j and t values applied for NPs growth. Cycling stability tests reveal that NPs do not suffer from excessive deterioration of their electrocatalytic activity with time.

1. Introduction

Nanoparticles (NPs) exhibit a wealth of physical and chemical properties associated with their crystal structure, chemical and electrochemical reactivity or electrical and magnetic properties at the nanoscale [1]. For this reason, NPs have become the cornerstone for the development of next generation of sensing, energy conversion, electronic, optoelectronic, and magnetic devices [2–4]. Among the synthesis methods to produce substrate-supported NPs, electrochemical deposition is one of the least expensive, highly productive and readily available methods [5–7]. Electrodeposition enables not only directly growing the NPs onto the substrate, but also to tune on-demand the NPs composition, the crystallographic structure, the size, and the shape by playing with the electrodeposition parameters [8–10].

Rhodium (Rh) is a precious transition metal with intriguing properties including chemical inertness towards mineral acids, outstanding catalytic properties for a variety of organic transformations [11–14] and electrocatalytic properties [15]. For those reasons, Rh has been broadly employed in fuel cells, solar energy conversion devices and for environmental remediation [16].

However, one of the main drawbacks associated with Rh is its high price, which makes it necessary to partially replace Rh by more abundant and less expensive elements. Iron (Fe), as one of the most earth-abundant elements, is a suitable candidate. For example, Haider and co-workers synthesized Fe-promoted Rh catalysts by incipient wetness impregnation. They showed that the addition of Fe to the catalyst significantly improved the catalytic activity and the selectivity of the material toward ethanol and other oxygen-containing compounds [17]. Likewise, Nakamula et al. synthesized bimetallic Rh/Fe NPs by stepwise complexation for the hydrogenation of olefins and nitroarenes. They showed improved catalytic performance toward these hydrogenation reactions, under relatively mild conditions, in comparison with previously reported hydrogenation reactions using pure Rh NPs [18].

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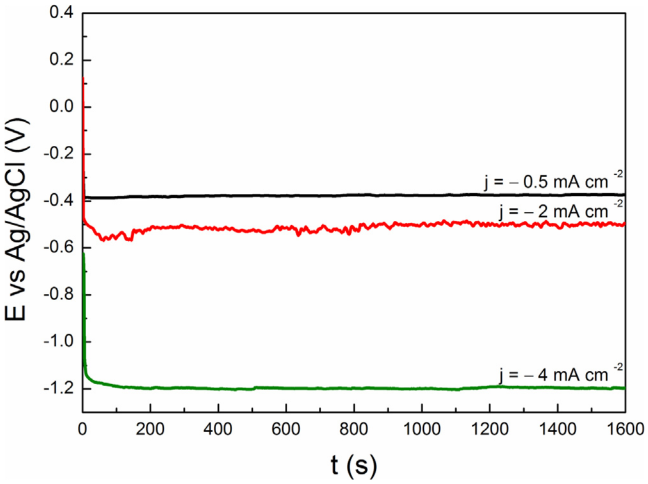

Fig. 1. Representative E–t transients for NPs deposition onto Au/Ti/Si substrates at the indicated current densities.

Hydrogen evolution reaction (HER) is a cathodic reaction in the electrolysis of water that allows producing hydrogen as a key energy carrier [19]. HER is of uttermost importance in electrochemical energy conversion devices such as electrolysers, fuel cells and solar hydrogen devices [20]. Although Rh cannot compete with Pt in terms of HER in alkaline medium, Rh still shows a reasonable activity [21,22]. For example, Smiljanic et al. found that bimetallic catalysts composed of Rh nanoislands on Pt exhibited enhanced HER performance with respect to bare Pt [23]. Meanwhile, Fe and its compounds (e.g. hydro(oxy) oxides) have been developed as highly efficient HER electrocatalysts under acidic or alkaline conditions [24,25]. Due to their large surface area, NPs are expected to outperform thin films in HER.

The present work aims to demonstrate that Rh- and Fe-containing NPs can be successfully prepared by electrodeposition. Although there are studies on either the electrodeposition of Rh [26,27] or Fe [28], little attention has been paid to the codeposition of these two elements [29,30], and certainly not in the form of NPs. It will be shown that the here-presented deposition scheme renders Rh-Fe NPs whose chemical composition and size can be adjusted by simply changing the current density and deposition time. The HER characteristics of the deposited NPs have been investigated in alkaline media and the trends observed have been outlined.

2. Experimental

2.1. Electrochemical synthesis of Rh-Fe NPs

NPs were synthesized by direct current electrodeposition in a thermostatized three-electrode cell using a PGSTAT 302 N Autolab

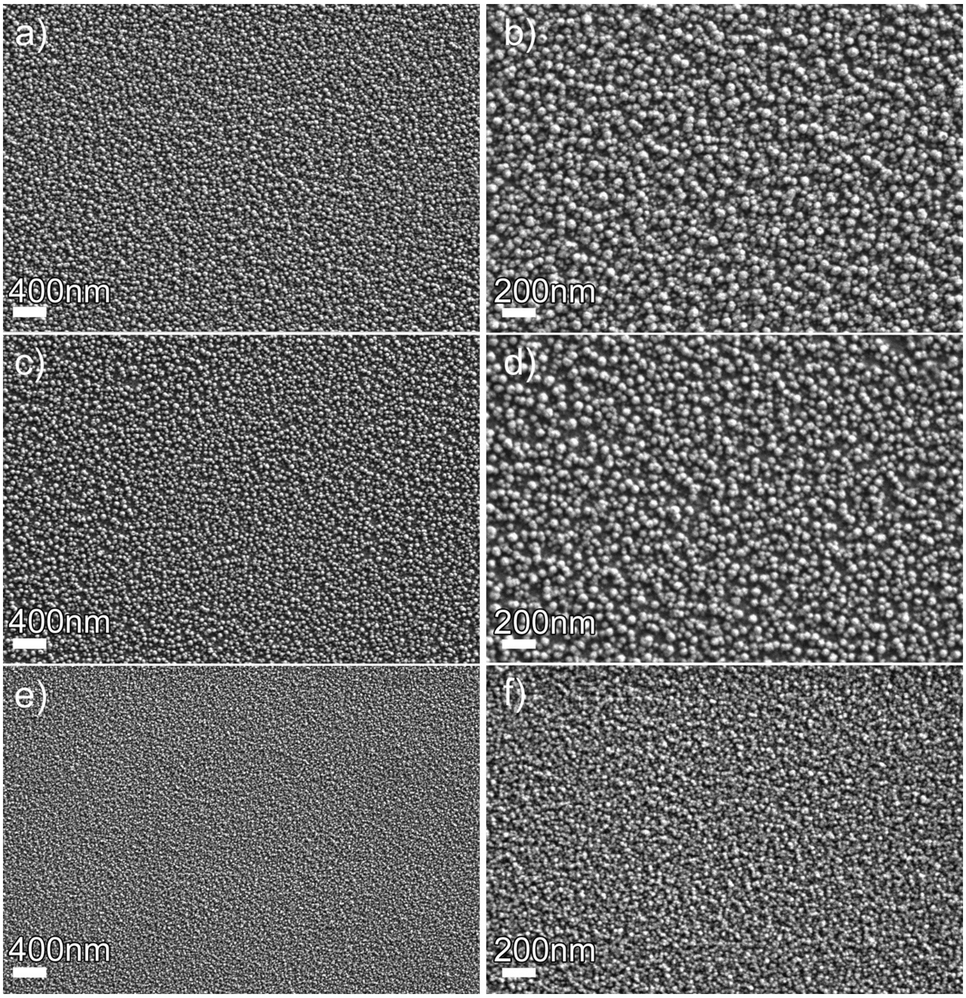

Fig. 2. FE-SEM images of NPs obtained at fixed deposition charge: (a, b) j = –0.5 mA cm^{-2}, 1600 s, (c, d) j = –2 mA cm^{-2}, 400 s and (e, f) j = –4 mA cm^{-2}, 200 s.