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DECIPHERING THE DYNAMICS OF GALVANIC REPLACEMENT REACTION TO DESIGN METALLIC CAGES AS FREE-STANDING ELECTROCATALYSTS

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Summary:

Galvanic replacement reaction (GRR) occurs spontaneously when the atoms of one metal are in contact with the ions of another metal that has a higher redox potential in solution. Owing to its versatility, GRR has far-reaching technological implications beyond physical chemistry in catalysis, chemistry, physics, biology, and medicine.^[1,2]

In the bulk state, silver with $E^\circ(\text{Ag}^+/\text{Ag}) = 0.8 \text{ V vs SHE}$ (standard hydrogen electrode) can be replaced by gold with $E^\circ(\text{AuCl}_4^-/\text{Au}) = 1.0 \text{ V vs SHE}$ according to: $3\text{Ag}_{(s)} + \text{AuCl}_4^-(\text{aq}) \rightarrow 3\text{Ag}^+(\text{aq}) + 4\text{Cl}^- + \text{Au}_{(s)}$. Given that the introduction of 1 atom of Au requires the replacement of 3 atoms of Ag (Ag and Au atoms have similar size), GRR generates porous and alloyed structures with unique physicochemical properties.^[1-3] Fundamentally, the exact driving force is quantitatively unknown as from a physical chemistry point of view, the understanding of the dynamics of such a redox process, which mixes electrochemical kinetics and mass transport (diffusion), remains a puzzle. Historically, both the synthesis of the initial Ag particles and the GRR are done in solution, making electroanalytical monitoring impossible.

We will discuss our recent methodology allowing to grow surfactant-free Ag particles on GDE and then perform GRR with Au while monitoring the dynamics via the open circuit potential (OCP, **Fig. 1a**).^[3] It allows to capture in real time the formation of metallic cages of Ag-Au alloys after a '3by1' atomic exchange. This strategy has led to the fabrication of high performance electrocatalysts where the formation of an alloy phase, the creation of nanoporosity within it and the self-supporting nature amplify, through synergistic and electronic effects, the electrocatalytic activity (**Fig. 1b**).^[1]

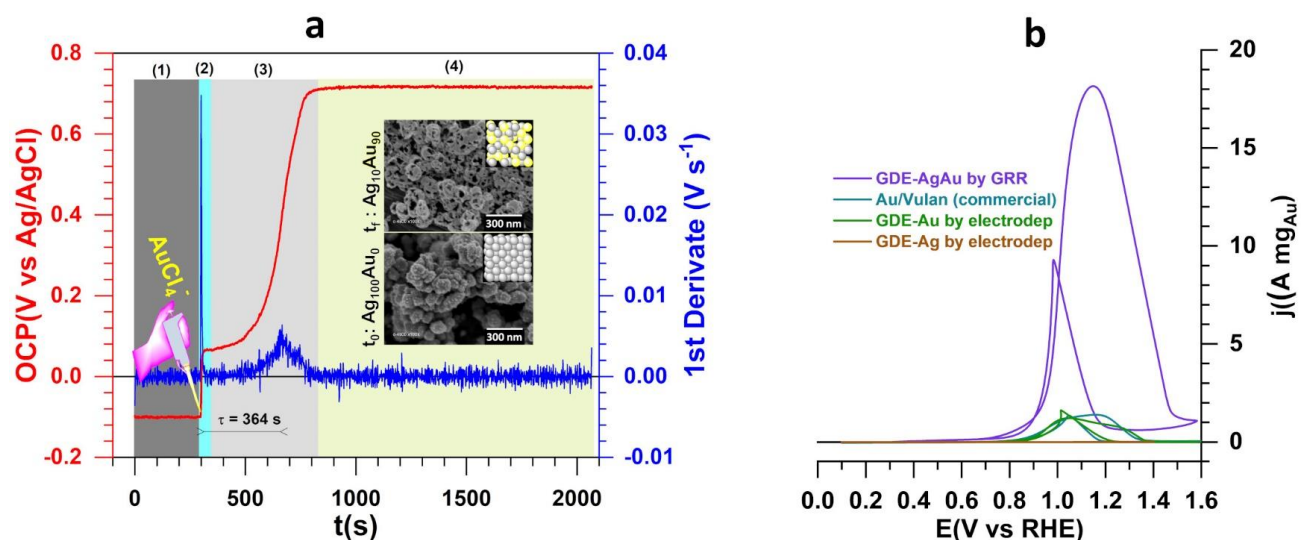


Fig. 1. (a) Open circuit potential (OCP) during GRR (3.5 M NaCl, rt, gentle stirring): inset shows SEM images of the initial GDE-Ag and final GRR-Au₉₀Ag₁₀ electrodes. (b) Comparative performance (CVs at 50 mV s⁻¹ in 1 M KOH+0.1 M glycerol at 25 °C).

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