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# **Galvanic Replacement Mediated Synthesis of Hollow Pt Nanocatalysts: Significance of Residual Ag for the H<sub>2</sub> Evolution Reaction**

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## **Abstract**

With the increasing popularity of the galvanic replacement approach towards the development of bimetallic nanocatalysts, special emphasis has been focused on minimizing the use of expensive metal (e.g. Pt), in the finally formed nanomaterials (e.g. Ag/Pt system as a possible catalyst for fuel cells). However, the complete removal of the less active sacrificial template is generally not achieved during galvanic replacement, and its residual presence may significantly impact on the electrocatalytic properties of the final material. Here, we investigate the hydrogen evolution reaction (HER) activity of Ag nanocubes replaced with different amounts of Pt, and demonstrate how the bimetallic composition significantly affects the activity of the alloyed nanomaterial.

Keywords: Galvanic replacement, Ag/Pt nanocubes, electrocatalysis, hydrogen evolution reaction

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## 1. Introduction

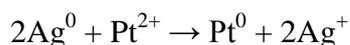
The chemical synthesis of nanomaterials with well defined size, shape and composition is critical for their applications as electrocatalysts, sensors, in surface enhanced Raman spectroscopy (SERS), and biological labelling [1-5]. The most active electrocatalysts are generally expensive noble metal based materials, in particular platinum, which is important for fuel cells [6]. Recent efforts have focused on minimizing the use of platinum, while retaining its activity, through an elegant galvanic replacement approach [7-11]. This has become popular for the controlled synthesis of bimetallic hollow nanomaterials such as Ag/Pt, Ag/Au and Ag/Pd by utilizing sacrificial metal nanoparticles as a template ( $\text{Ag}^0$ ) and suitable metal ions as a selective etchant ( $\text{AuCl}_4^-$  and  $\text{PtCl}_4^{2-}$ ) [7-12]. However, during replacement reactions, the less active sacrificial template is not generally fully removed [9, 10, 13] and its residual presence may significantly impact on the electrocatalytic properties of the final material. In particular, the Ag/Pt system has received attention as an electrocatalyst for fuel cell relevant processes [7, 8], however, in many cases residual Ag is still present and its role often neglected [10].

The hydrogen evolution reaction (HER) is regarded as a model system where it is known that the hydrogen-metal bond strength dictates HER efficiency [14, 15]. This influence is likely therefore to impact on the activity of Ag/Pt nanomaterials synthesized through the replacement method. Here, we investigate the HER activity of Ag nanocubes replaced with different amounts of Pt and demonstrate an often neglected issue that the Ag content in a nanosized Ag/Pt bimetallic system can drastically affect its activity. Also, the electrochemical removal of Ag from galvanically replaced nanomaterials significantly enhances their activity for the HER.

## 2. Experimental

### *Ag/Pt Nanocube Synthesis*

Ag nanocubes were synthesized using a polyol-mediated process as reported previously [16]. The Ag cubes were dialyzed against MilliQ water for 3 days, concentrated by centrifugation, and their concentration determined using atomic absorption spectroscopy (AAS). 83.4 mg of  $K_2PtCl_4$  in 4.5 mL of MilliQ water was then reacted with 1.5 mL of 100 mM  $AgNO_3$  to allow AgCl to precipitate out. The Pt concentration in the supernatant containing  $Cl^-$  ions-free Pt(II) nitrate was determined using AAS. The conversion of  $K_2PtCl_4$  into  $Cl^-$  free Pt salt is important, to avoid insoluble AgCl formation, which might interfere with electrocatalytic performance. This  $Pt^{2+}$  solution was then reacted with 150 mM Ag nanocubes for 24 hours. Reaction products were dialyzed for 3 days against MilliQ water to remove any free  $Ag^+$  ions. Given, the galvanic replacement between  $Pt^{2+}_{(aq)}$  and Ag nanocubes is described by



the final Pt to Ag molar ratios in the reaction products were 0 % (no platinum salt), 0.8 %, 2 %, 4 % and 20 %, referred to as samples A, B, C, D and E respectively.

### *Electrochemical Measurements*

10  $\mu$ L of the relevant Ag/Pt nanoparticles solution was drop casted onto a glassy carbon (GC) electrode surface and allowed to dry at room temperature after which 10  $\mu$ L of a 0.2 % Nafion solution was spread over the surface and allowed to dry. For Ag stripping experiments, Nafion was not used to ensure that  $Ag^+$  ions diffused from the sample. It should be noted that the presence of Nafion did not affect the current magnitudes for the HER. Voltammetric experiments were conducted with a CH Instruments (CHI 760C) electrochemical analyzer. A modified 3 mm GC (BAS) with Ag/Pt nanocubes was used as the working electrode, which prior to modification, was polished with an aqueous 0.3  $\mu$ m alumina slurry on a polishing cloth (Microcloth, Buehler), sonicated in deionized water for 5 min, and dried with a flow of nitrogen gas. A Ag/AgCl (3 M KCl) reference and Pt wire counter

electrode were used. Electrochemical experiments were commenced after degassing the electrolyte solutions with nitrogen for 10 min prior to any measurement.

### *Nanomaterials Characterization*

Samples for transmission electron microscopy (TEM) analysis were prepared by drop-casting the samples onto a carbon coated copper grid and performed using a JEOL 1010 TEM instrument operated at an accelerating voltage of 100 kV. UV-visible spectroscopy measurements of solutions were performed using a Cary 50 Bio-spectrophotometer.

## **3. Results and Discussion**

TEM images of Ag nanocubes galvanically replaced with different ratios of  $\text{Pt}^{2+}_{(\text{aq})}$  are shown in Figure 1. The as-synthesized Ag nanocubes were monodispersed with an average size of 20 nm (Figure 1A). The replacement reaction of Ag nanocubes with increasing  $\text{Pt}^{2+}_{(\text{aq})}$  concentration (0.8, 2, 4 and 20 molar % in Figure 1B-E respectively) results in dissolution of Ag nanocubes and the simultaneous reduction of  $\text{Pt}^{2+}_{(\text{aq})}$  onto preexisting Ag nanocubes. This leads to the formation of a hollow shell consisting of a Ag/Pt alloy, where the shell thickness is dependent on the  $\text{Pt}^{2+}_{(\text{aq})}$  concentration (Figure 1C and D), as observed previously for spherical Ag nanoparticles [7]. Upon reaction with higher concentration of  $\text{Pt}^{2+}_{(\text{aq})}$  (20 molar %), the hollow framed structures break down into open Ag/Pt alloyed nanostructures, with the coexistence of 2-3 nm sized nanoparticles (Figure 1E).

The UV-visible absorption spectrum (Figure 1F) for cubic Ag nanoparticles shows a narrow surface plasmon resonance (SPR) peak at ca. 426 nm (curve A). Upon reaction with 0.8 %  $\text{Pt}^{2+}_{(\text{aq})}$ , the SPR reduces in intensity, along with a red-shift towards ca. 450 nm (curve B). These two changes can be respectively attributed to the dissolution (oxidation) of Ag from preexisting Ag nanoparticles, and simultaneous formation of Ag/Pt alloy on their surface. When an increased amount of  $\text{Pt}^{2+}_{(\text{aq})}$  (2 %) is reacted with Ag nanoparticles, Ag/Pt alloying is clearly evident from a further red-shift to ca. 536 nm (curve C), along with peak broadening

indicative of changes in nanostructure composition [2]. A further increase of  $\text{Pt}^{2+}_{(\text{aq})}$  to 4 % results in an SPR peak at significantly longer wavelengths (668 nm – curve D). Our TEM and UV-vis results corroborate well with Mie theory and discrete dipole approximation (DDA) calculations, wherein such strong red shifts were assigned to metal nanoshell formation, and decreasing shell thickness [17]. Moreover, formation of a Ag/Pt alloy, instead of a Ag/Pt core/shell structure is supported by DDA calculations that predicted an SPR peak at 680 nm for alloyed Ag/Pt nanoboxes, in close agreement with curve D [2]. Finally, reaction with 20 % of  $\text{Pt}^{2+}_{(\text{aq})}$  results in a broad SPR, arising from disintegrated Ag/Pt nanoboxes (curve E).

Figure 2X illustrates linear sweep voltammograms (LSVs) for the HER on Ag nanocubes and those replaced with Pt from 0.8 to 20 molar %. Ag nanocubes do not show any activity for the HER under the potential range of interest. As expected, on increasing the amount of Pt the current magnitude increases accompanied by a shift to less negative potentials for the HER. However, normalizing the data with respect to the mass of Pt (inset Figure 2X) reveals a significant increase in the mass activity after addition of 4 molar %  $\text{Pt}^{2+}_{(\text{aq})}$  (sample D). Notably, the morphology of samples C and D, replaced respectively with 2 and 4 molar % Pt, is quite similar (Figure 1C and D), and differs only in shell thickness; however their activity, especially after accounting for the amount of Pt, is significantly different. This shell is expected to consist of a Ag/Pt alloy with more Ag present in sample C compared to D. It is also noted that upon a further significant increase in Pt content to 20 %, only a marginal increase in the HER activity was observed at higher overpotential, attributed to breakdown of Ag/Pt nanoshells, leading to greater accessibility to the Ag/Pt alloy (sample E). These observations are supported by DFT calculations reported by Nørskov wherein a negative influence of increasing Ag content within a Ag/Pt alloy on the free energy of hydrogen adsorption ( $\Delta G_{\text{H}}$ ) was observed, which, for an optimal HER catalyst, was calculated to be 0 eV [15]. They found that increasing the surface solute concentration of Ag in Pt from 1/3 of a monolayer (ML) ( $\Delta G_{\text{H}} = -0.15$  eV) to 2/3 ML ( $\Delta G_{\text{H}} = -0.20$  eV) to a full overlayer

( $\Delta G_H = 0.55$  eV) should significantly decrease the alloy's catalytic activity for the HER. The presence of an overlayer introduces significant strain effects that lead to significant shifts in d-band centers, resulting in  $\Delta G_H$  values far from zero [18]. Our experimental results therefore suggest that at the early stages of galvanic replacement (samples B and C), the alloy may consist of a surface layer with significant Ag content which inhibits the HER, when compared to a hollow shell with a thinner wall (sample D), that is expected to be a more Pt rich Ag/Pt alloy.

Electrocatalysts are often activated by repetitive potential cycling [8] which for Ag/Pt catalysts may result in Ag removal further impacting on their electrocatalytic performance. Figure 3 shows CVs performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> that demonstrate characteristic Ag stripping peaks for samples D and E, which indicates that Ag must be present at the surface of these nanomaterials. The magnitude of the stripping peak clearly shows the greater amount of Ag in sample D compared to E. Also, the hydrogen adsorption/desorption region is more prominent in sample E when compared to sample D, where the latter shows a marked decrease in H interaction with the Ag/Pt surface. To verify the inhibitory effect of Ag for the HER in a nanoscale Ag/Pt alloy, Ag was electrochemically removed from these samples. The stripping of Ag was carried out at 0.60 V for 60 sec, which ensures that an oxide does not grow on the exposed Pt surface. Repetitive cycling was not employed to avoid re-deposition of Ag onto the nanomaterial in the reverse sweep (Figure 3). LSV measurements were performed for the HER on samples after Ag removal in fresh electrolyte to avoid any possibility of Ag re-deposition. It is clearly evident that the magnitude of the HER current increases significantly after Ag is removed (Figure 2Y dashed lines), which is also accompanied by a shift in the onset for hydrogen evolution to less negative potentials. These results clearly demonstrate that the residual Ag left in the nanostructures after galvanic replacement of Ag nanoparticles template with Pt<sup>2+</sup><sub>(aq)</sub> has a negative influence on HER reactions.

#### **4. Conclusions**

We propose that given the extensive interest in the galvanic replacement method to create nanocatalysts, the influence of the sacrificial template can be significant for electrocatalysis applications, in particular for the Ag/Pt system, and therefore must be taken into account when assessing the performance of the final nanomaterial. The electrochemical pretreatment of the catalyst must also be considered, more so if it results in the removal of one of the components such as Ag. This is an often neglected, but critical parameter for the performance of catalysts for hydrogen evolution, and may also be important for reactions such as methanol oxidation, which occur at potentials where the removal of Ag may simultaneously occur.

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**Fig. 1:** TEM images of Ag nanocubes (A) before, and after galvanic replacement with (B) 0.8, (C) 2, (D) 4 and (E) 20 molar % of  $\text{Pt}^{2+}_{(\text{aq})}$ . Scale bar in each case corresponds to 20 nm. (F) UV-vis absorbance spectra showing the galvanic replacement of Ag nanoparticles with  $\text{Pt}^{2+}_{(\text{aq})}$ , wherein curves A-E correspond to the samples A-E respectively.

**Fig. 2:** (X) LSVs for the HER obtained at  $10 \text{ mV s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  for samples A to E. The inset in X is the data normalized for mass of Pt. (Y) shows the same data as shown in X, but before (solid line) and after (dashed line) electrochemical removal of Ag (the inset in Y shows results for samples B and C).

**Fig. 3:** CVs recorded at  $50 \text{ mV s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  for sample D (dashed line), and sample E (solid line).

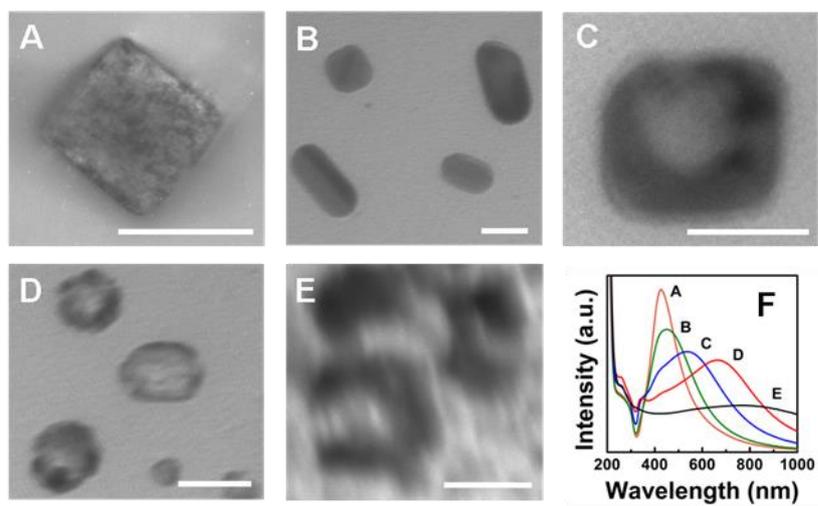


Fig. 1

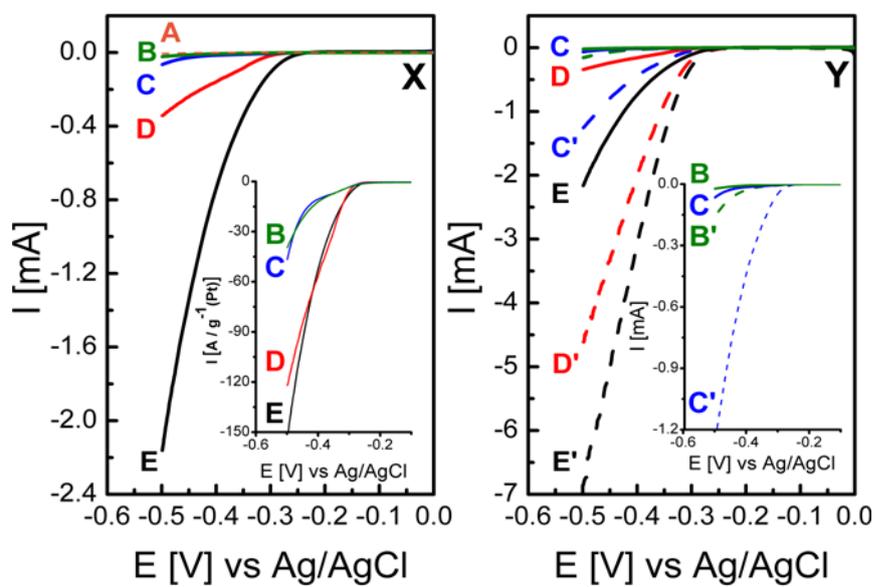
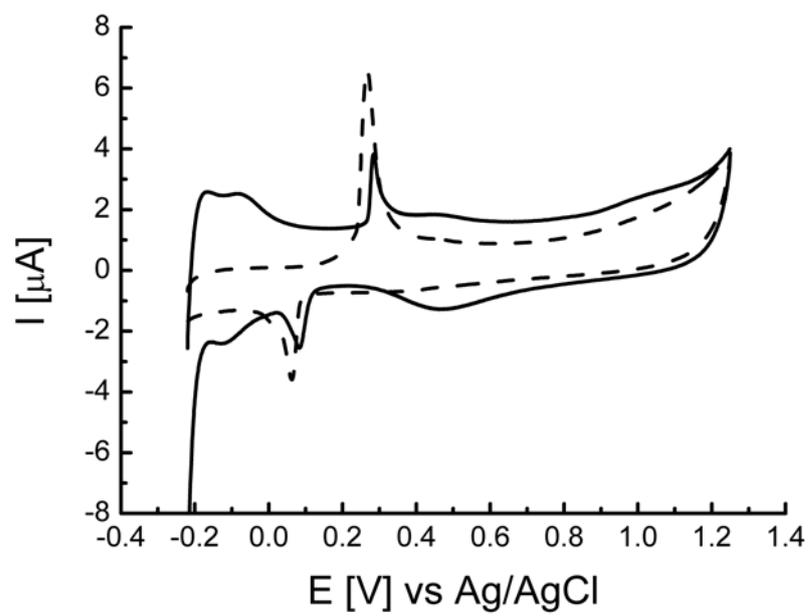


Fig. 2



**Fig. 3**