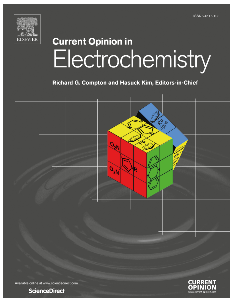

State-of-the-art in the electrochemical characterization of the surface structure of shape-controlled Pt, Au and Pd nanoparticles

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Abstract:	The application of shape-controlled metal nanoparticles in Electrocatalysis has improved significantly the activity, selectivity, and even the stability of many relevant electrocatalytic reactions. It is well-accepted that, by controlling the shape of the nanoparticles, it is possible to provide nanoparticles with a preferential surface structure. However, to fully understand the capabilities of these nanomaterials, it is extremely relevant to correlate shape, surface structure and electrocatalytic reactivity. Particularly, establishing the correlations between surface structure and reactivity is the key point to be studied and understood. Consequently, having tools to characterize the surface structure of these nanoparticles results of critical importance. In this short review, we discuss about the progress in the in-situ characterization of the surface structure of shaped Pt, Au, and Pd nanoparticles by electrochemical probes. The results here included clearly demonstrate the potentialities of the electrochemical tools to gain detailed information of the surface structure of these shaped nanomaterials.
Author Comments:	

State-of-the-art in the electrochemical characterization of the surface structure of shape-controlled Pt, Au and Pd nanoparticles

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Summary

The application of shape-controlled metal nanoparticles in *Electrocatalysis* has improved significantly the activity, selectivity, and even the stability of many relevant electrocatalytic reactions. It is well-accepted that, by controlling the shape of the nanoparticles, it is possible to provide nanoparticles with a preferential surface structure. However, to fully understand the capabilities of these nanomaterials, it is extremely relevant to correlate shape, surface structure and electrocatalytic reactivity. Particularly, establishing the correlations between surface structure and reactivity is the key point to be studied and understood. Consequently, having tools to characterize the surface structure of these nanoparticles results of critical importance. In this short review, we discuss about the progress in the in-situ characterization of the surface structure of shaped Pt, Au, and Pd nanoparticles by electrochemical probes. The results here included clearly demonstrate the potentialities of the electrochemical tools to gain detailed information of the surface structure of these shaped nanomaterials.

Keywords: Shaped metal nanoparticles, surface structure, Electrocatalysis.

Introduction

Developing advanced electrocatalysts with improved properties in terms of activity, selectivity and stability to be used in electrochemical applications, such as energy conversion and storage devices has been, is, and, will be the subject of countless works. Among other approaches, the use of shape-controlled metal nanoparticles (SNPs) has demonstrated to be one of the most interesting options to enhance the electrocatalytic properties of many nanomaterials. Since our pioneer publications dealing with the use of preferentially oriented {100} (cubic-shaped) platinum (Pt) nanoparticles towards ammonia electrooxidation in alkaline solution [1••, 2], many contributions have been published. To illustrate the progress in this field, we include here a brief collection of relevant and recent reviews about the application of different SNPs for most of the electrocatalytic reactions of interest [3-8].

Thanks to all this previous knowledge, it is well-established that, by controlling the shape of the nanoparticles, nanoparticles with a preferential surface structure, that is, with a well-defined arrangement of the atoms at their surface, can be produced. However, it is extremely important to take into consideration that these nanoparticles are far from being "perfect" and their surface structure is in fact very complex, and includes i) different surface domains of various dimensions and geometries, and ii) an important number of surface defects including corner, edge, step, vacancy and kink sites. As a consequence, the resulting electrocatalytic activity (for a particular reaction) is the sum of the specific contributions of each type of surface site present at the surface of the nanoparticles. Additionally, it is also worth noting that each nanoparticle (even those contained in the same batch and prepared with the most convenient methodology) has its own characteristics in terms of surface structure. Consequently, it is of outstanding importance to have experimental techniques able to characterize the surface structure of these nanoparticles. Here, it is worth noting again that the particle shape is not the key point controlling the electrocatalytic activity of the nanoparticles but their particular surface structure [9•] In addition, this surface characterization must provide statistically representative information of the whole sample and not only of some individual nanoparticles (as usually performed with advanced microscopy systems). In this regard, the use of electrochemical probes has demonstrated to be one of the most powerful approaches to gain detailed information about the surface structure of different types of nanomaterials [10••-19]. Interestingly, the electrochemical surface structure characterization presents two main advantages in comparison with other possible approaches: (i) the analysis is performed simultaneously with 10^{10}-10^{11}nanoparticles/cm^2, and therefore, the response is statistically representative of the whole sample, and (ii) the analysis is carried out in similar conditions than those that will be subsequently employed during the electrochemical reactions, that is, the analysis may be considered as in-situ, a situation not fulfilled in the usual microscopic characterization. It is necessary to recall that surface cleanliness is the most relevant requirement to correctly perform this electrochemical analysis. Most of the best methodologies to prepare SNPs are based on colloidal routes in which different surface capping agents are used to control the growth and induce the formation of specific particle shapes [20•, 21] Once the shaped nanoparticles are synthesized, and before being electrochemically characterized, it is indispensable to apply efficient decontamination procedures to completely remove the presence of these surface-regulating agents at the surface of the nanoparticles. Despite the importance of this point [22•], this issue is still underestimated and many contributions dealing with the electrocatalytic properties of shaped metal nanoparticles report voltammetric features of insufficiently cleaned shaped nanoparticles [23-26]. From our point of view, this is a critical point that must be unequivocally satisfied to properly establish the correct correlations between surface structure and electrocatalytic reactivity. In fact, contaminated nanoparticles supply wrong and misleading information about reactivity.

With these previous concepts in mind, in this short review we summarize and discuss about the use of different electrochemical probes to characterize the surface structure of shaped Pt, Au, and Pd nanoparticles

Shaped Pt nanoparticles

Obtaining the voltammetric response of the shaped Pt nanoparticles in the so-called hydrogen region (involving the hydrogen and anion adsorption-desorption states) is as recognised the most straightforward way to qualitatively characterize their surface structure. In fact, this response should be considered as fingerprint of their crystalline surface structure. The relative intensity of the different voltammetric features present in this hydrogen region directly reflects the distribution of all active sites present on the surface of the nanoparticles [10••]. In addition, the sharpness and reversibility (between desorption vs adsorption states) of the different voltammetric features and the overall charge involved in the so-called hydrogen region allows to guarantee the cleanness of the surface and thus evaluate the electroactive surface area. Interestingly, this analysis can be equally performed in different supporting electrolytes (H_2SO_4, $HClO_4$, or NaOH) although we consider that the analysis in 0.5 M H_2SO_4 is the most convenient one due to the better understanding and minor overlapping of the voltammetric features associated with the different surface sites. To exemplify this approach, figure 1 displays the voltammograms obtained in 0.5 M H_2SO_4, 0.1 M NaOH and 0.1 M $HClO_4$ with quasi-spherical, cubic, octahedral/tetrahedral and truncated octahedral Pt nanoparticles [27]. For a more detailed analysis of the different features present in the voltammmograms, readers are referred to Ref. 10••, 27, 28.

Despite the so-called hydrogen region provides very valuable information about the surface structure of the shaped Pt nanoparticles, it is always more interesting having tools to get a quantitative analysis of the real distribution of surface sites present at the surface of these nanoparticles. With this objective, we described a methodology, based on the redox behaviour of some adatoms (Bi and Ge) spontaneously adsorbed at the surface of different Pt single crystals, to quantify the {111} and {100} oriented domains at the surface of different shape-controlled Pt nanoparticles [2, 10••]. This methodology is being currently adopted by many research groups and has allowed adequately quantifying the {111} and {100} oriented domains on a large number of shape-controlled Pt nanoparticles [29-31]. It is worth comment that, once the sample is quantitatively characterized in terms of {111} and {100} oriented domains, it is possible to establish additional correlations between these {111} or {100} percentages and pure electrocatalytic measurements. Thus, for instance, as shown in figure 2, the ammonia electrooxidation has shown a linear correlation with the percentage of {100} domains [32], whereas the desorption-adsorption of hydroquinone-derived adlayers displayed a similar correlation for {111} domains [33].

Some attempts have been also carried out to use Cu underpotential deposition (UPD) as electrochemical probe to characterize the surface structure of some shaped Pt nanoparticles [29]. However, despite the Cu UPD features were affected by the surface structure of the nanoparticles, the electrochemical response showed an important overlapping of contributions from different surface sites, which limits its possible application.

Shaped Au nanoparticles

The so-called hydrogen adsorption desorption does not take place on Au surfaces and, therefore, different alternatives have been considered to evaluate the surface structure of shaped Au nanoparticles. For instance, and based on Au single crystal studies by Hamelin [34, 35], it is known that the voltammetric profile of the surface oxide region shows distinctive features which are attributed to specific surface structures. This approach has been used by Ke et al [36] to characterize some shaped Au nanoparticles (octahedral, truncated octahedral and truncated tetrahexahedral (THH) Au nanocrystals). The voltammograms obtained in 0.5 M H_2SO_4 solution showed an evident decrease of the {111} character in clear agreement with their particle shape (octahedral >truncated octahedral >truncated tetrahexahedral). Similarly, cubic and octahedral Au nanoparticles were characterized in 0.1 M NaOH and display characteristic features associated to a preferential {100} and {111} surface structure, respectively, in accordance with previous Au single crystal studies [15].

Interestingly, relevant contributions were made by El-Deab et al. [37-39] who reported that the reductive desorption of different thiol compounds such as cysteine, mercaptoacetic acid or cystamine can be employed to estimate the surface structure in some Au nanostructures.

However, Pb UPD on Au surfaces has been demonstrated to be a more convenient approach to qualitatively evaluate the different surface domains present at the surface of different shaped Au nanoparticles. This approach has been satisfactorily used for many different shaped Au nanoparticles [13, 16, 40]. Figure 3 shows the Pb UPD profile obtained with cubic and octahedral Au nanoparticles. As expected, the voltammetric profile suggests the existence of a preferential {100} and {111} surface structure, respectively.

It is worth noting that from the charge involved in the Pb UPD reaction, it is possible to calculate the electroactive surface area of the nanoparticles. To the best of our knowledge, a *quantitative* analysis of this Pb UPD voltammetric profile is still missing.

Shaped Pd nanoparticles

Similarly to shaped Pt nanoparticles, the so-called hydrogen region seems a convenient approach to qualitatively evaluate the surface structure of different shaped Pd nanoparticles. However, as previously shown with Pd single crystal studies [41, 42], the response obtained with Pd surfaces is not as well-defined as that obtained with Pt surfaces. In any case, as recently published by our group with the cubic, octahedral and rhombic dodecahedral Pd nanoparticles [43•], the so-called hydrogen/anion adsorption–desorption region obtained in 0.1 M H_2SO_4clearly shows characteristics features associated to the presence of a preferential {100}, {111}, and {110} surface structure, respectively. Again, note that from the charge involved in this hydrogen region, the electroactive surface area of the Pd sample can be easily obtained.

For shaped Pd nanoparticles, Cu UPD is particularly interesting because allows getting not only qualitative but also quantitative information about their surface structure. Based on previous studies with Pd single crystals [44-47] different contributions showed that Cu UPD may result very convenient to qualitatively characterize the surface structure of some shaped Pd nanoparticles [17-19]. This has been very recently confirmed by Garnier et al. [43•] who evidenced the potentialities of the Cu UPD to qualitatively and quantitatively characterize the surface structure of different shaped Pd nanoparticles. Interestingly, Cu UPD is shown to be sensitive not only to the {100}, and {111} surface domains but also to the {110} surface sites. Figure 4 shows the Cu UPD voltammetric profiles and the corresponding deconvolution obtained with cubic, octahedral and rhombic dodecahedral Pd nanoparticles. The results obtained clearly indicated the existence of a preferential {100}, {111}, and {110} surface structure, respectively.

Concluding remarks

This review briefly summarizes the potentialities of the electrochemical tools to characterise the surface structure of shaped Pt, Au and Pd nanoparticles. Despite the significant advances reported in this topic, more work is still required to adapt and apply these methodologies to shaped metal alloy nanoparticles which, nowadays, represent one of the most interesting electrocatalytic systems [48].

Acknowledgments

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Declaration of interest

None

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

• paper of special interest

•• paper of outstanding interest

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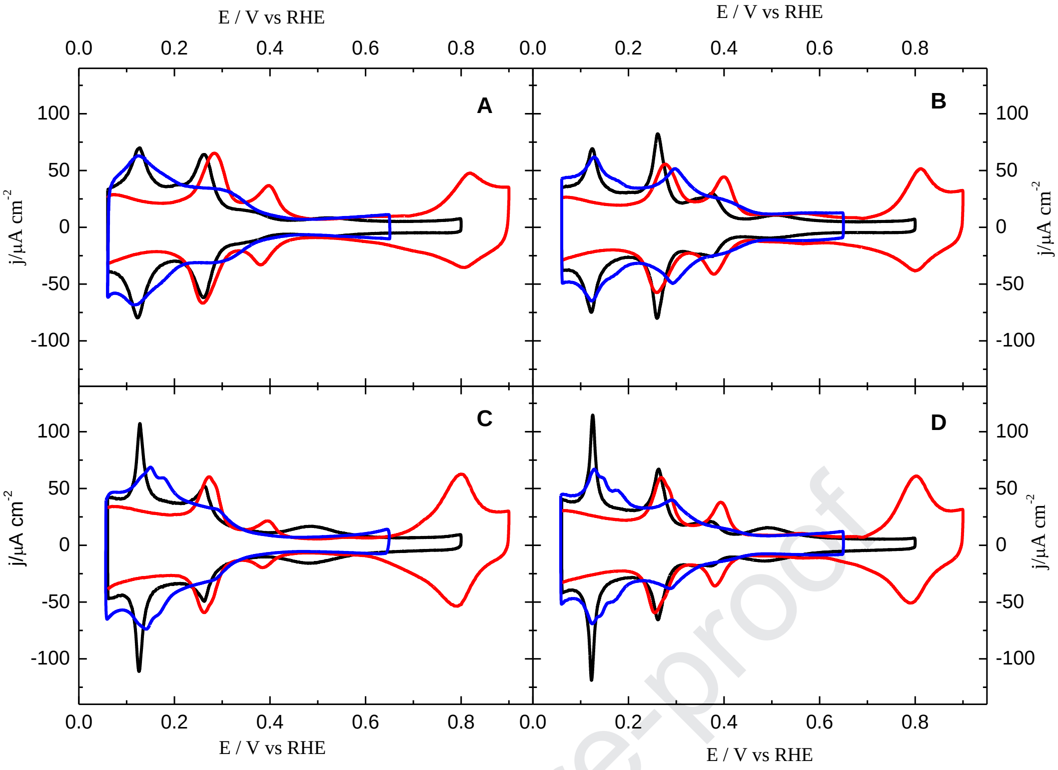


Figure 1. Representative voltammetric profiles of (a) quasi-spherical, (b) cubic, (c) octahedral/tetrahedral and (d) truncated octahedral Pt nanoparticles obtained in different supporting electrolytes (black line: 0.5 M H_2SO_4, red line: 0.1 M NaOH and blue line: 0.1 M $HClO_4$) at 50 mV s^{-1}. Data taken from ref. 46.

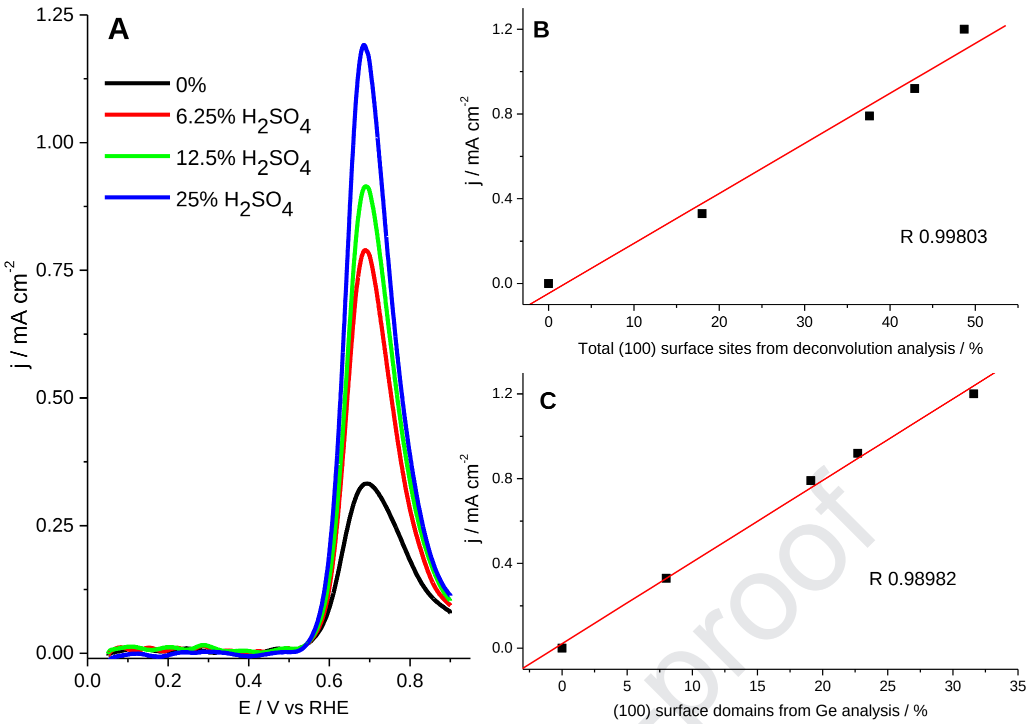


Figure 2. A) Voltammetric profiles for ammonia oxidation with Pt NPs prepared by using water-in-oil microemulsion in the absence and presence of different amounts of H_2SO_4. Electrolyte: 0.2 M NaOH+0.1M NH_3. Scan rate: 10 mVs^{-1}. B) Linear fitting between the peak current density and the total number of (100) surface sites and C) linear fitting between the peak current density and the number of (100) surface domains. Data taken from ref. 32.

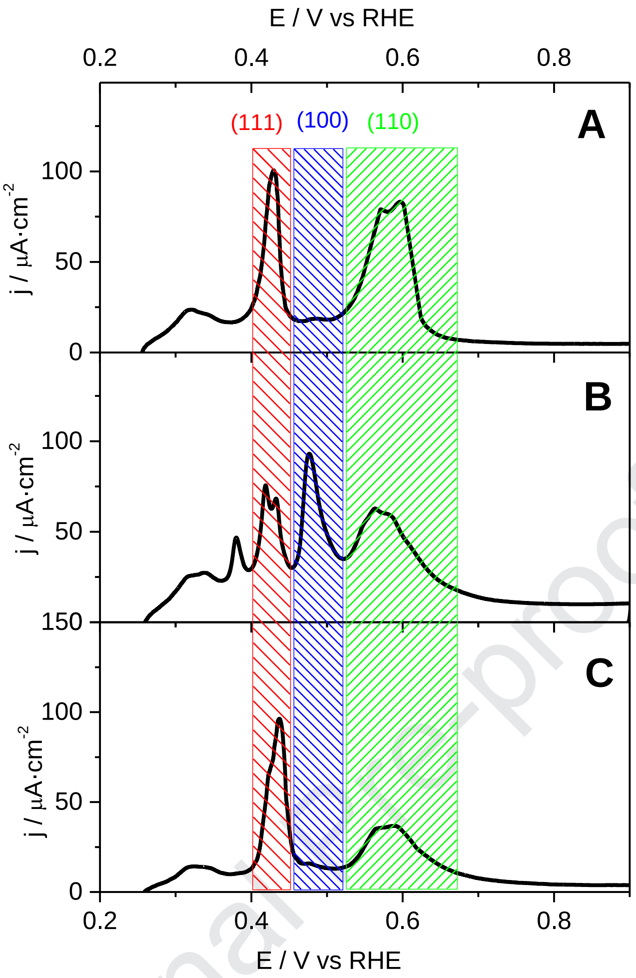


Figure 3. Pb UPD voltammetric profiles of the shaped gold nanoparticles in Ar-saturated 0.1 M NaOH containing 10^{-3} M $Pb(NO_3)_2$: (A) spherical (B) cubic and (C) octahedral nanoparticles. Scan rate: 50 mV s^{-1}.

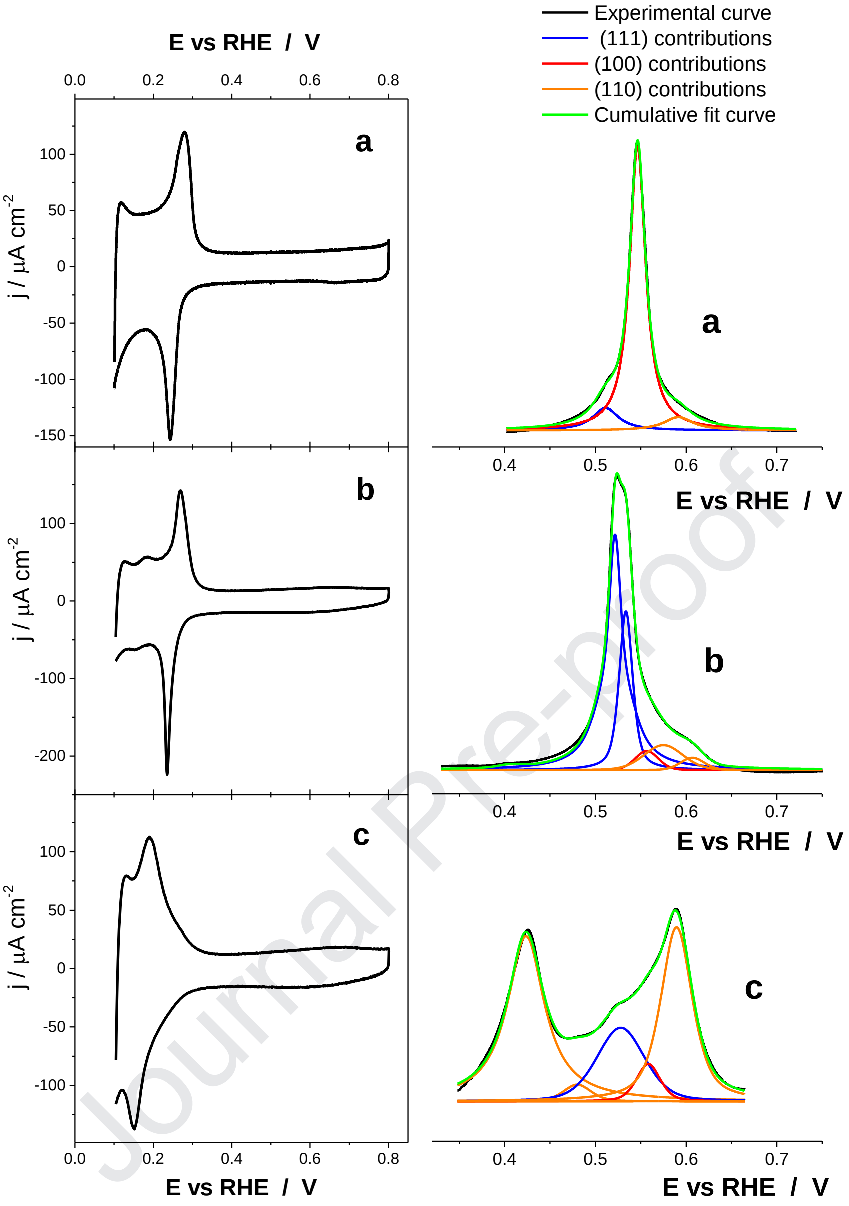


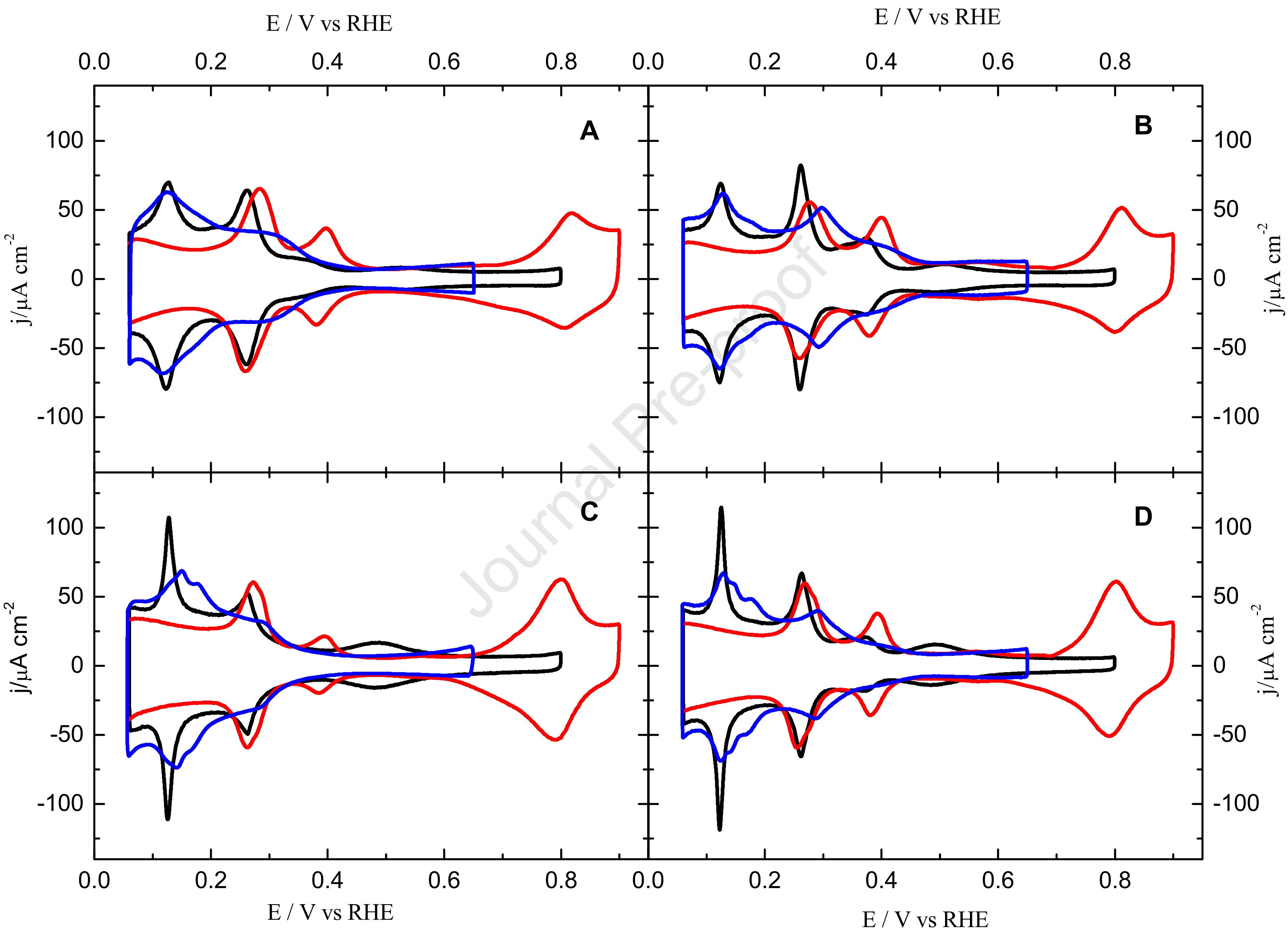
Figure 4. *Left panel*. Voltammetric profiles obtained with (A) cubic, (B) octahedral, and (C) rhombic dodecahedral Pd nanoparticles. Test solution 0.1 M H_2SO_4, scan rate 50mV s^{-1}. *Right panel*. Cu UPD deconvolution with pseudo-Voigt function for the (A) cubic, (B) octahedral, and (C) rhombic dodecahedral Pd nanoparticles. Test solution 0.1 M H_2SO_4 + 1 mM Cu^{2+} + 1 mM NaCl, scan rate 50mV s^{-1}. Data taken from ref. 43.

Declaration of interests

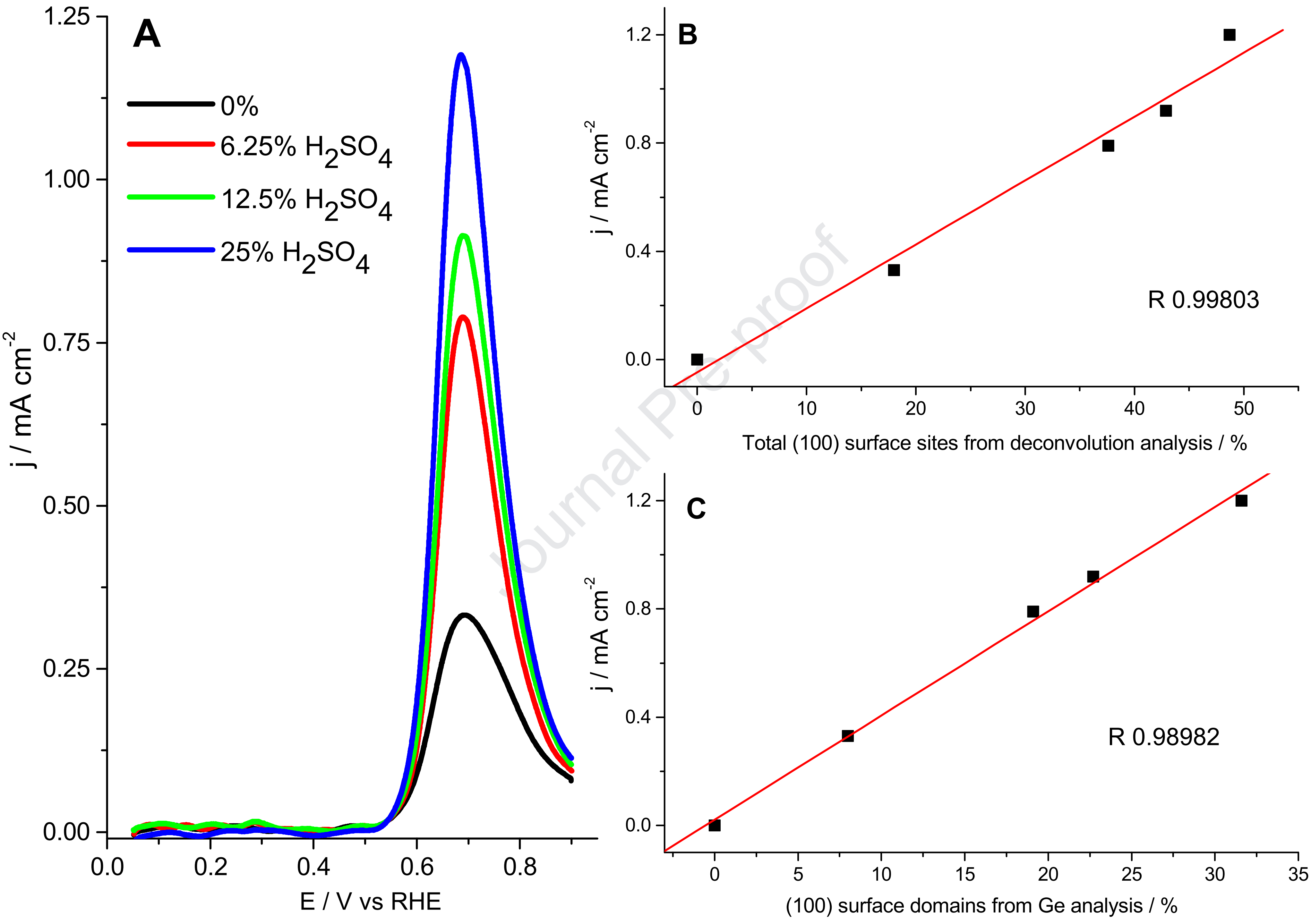
☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

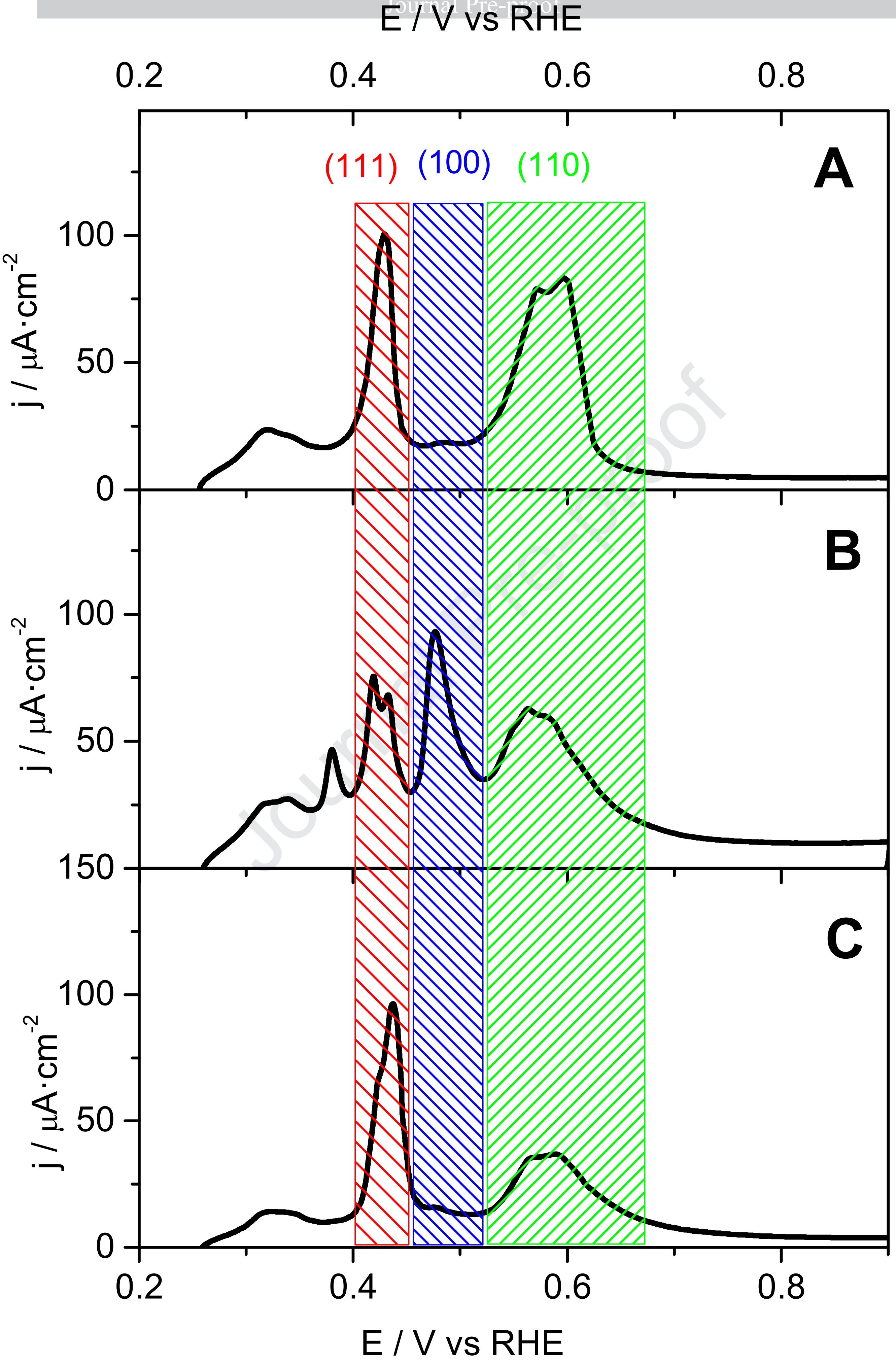
Figure



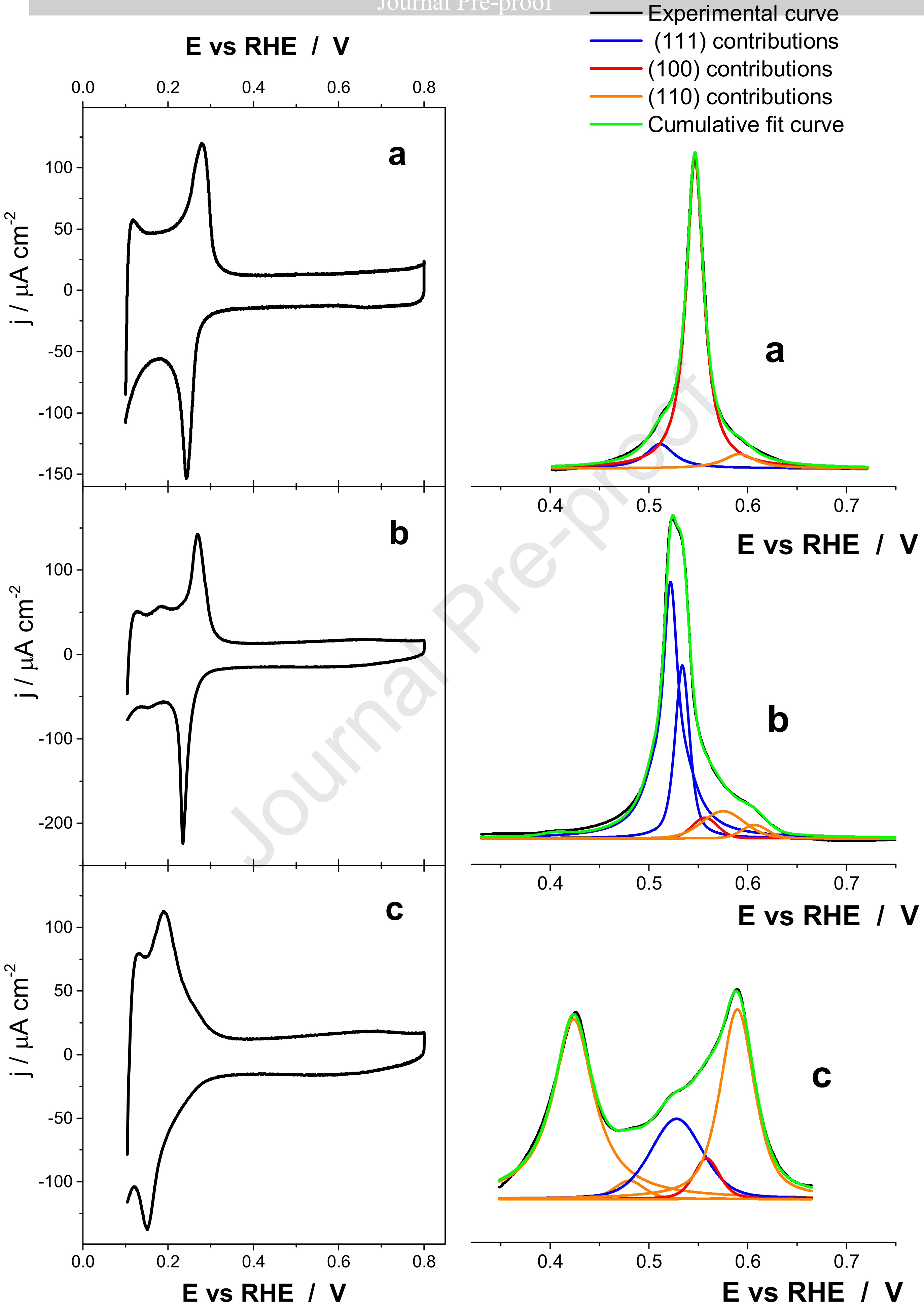
Figure


A
0%
6.25% H_2SO_4
12.5% H_2SO_4
25% H_2SO_4
j / mA cm^{-2}
1.25
1.00
0.75
0.50
0.25
0.00
0.0
0.2
0.4
0.6
0.8
E / V vs RHE
B
j / mA cm^{-2}
1.2
0.8
0.4
0.0
0
10
20
30
40
50
Total (100) surface sites from deconvolution analysis / %
R 0.99803
C
j / mA cm^{-2}
1.2
0.8
0.4
0.0
0
5
10
15
20
25
30
35
(100) surface domains from Ge analysis / %
R 0.98982

Figure


E / V vs RHE
0.2
0.4
0.6
0.8
(111)
(100)
(110)
A
B
C
j / μA·cm^{-2}
j / μA·cm^{-2}
j / μA·cm^{-2}
100
50
0
100
50
150
100
50
0
0.2
0.4
0.6
0.8
E / V vs RHE

Figure


Experimental curve
(111) contributions
(100) contributions
(110) contributions
Cumulative fit curve
E vs RHE / V
0.0
0.2
0.4
0.6
0.8
j / µA cm^{-2}
100
50
0
-50
-100
-150
-200
a
b
c
0.4
0.5
0.6
0.7