



Surfactant-free Ir nanoparticles synthesized in ethanol: Catalysts for the oxygen evolution reaction

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ABSTRACT

The development of highly active catalysts relies on the development of simple synthesis methods. Ir based materials are state of the art catalysts for the oxygen evolution reaction (OER), the anode reaction for water electrolysis, a key technology for more sustainable energy supply. Here, metallic Ir NPs ca. 2 nm in diameter are simply obtained by reducing IrCl₃ in ethanol only, without any additives. The colloidal dispersion is used to obtain Ir NPs supported on a carbon material at different metal loadings which can be employed as OER catalysts.

1. Introduction

For a more sustainable energy supply, water electrolysis is a promising technology [1], where the key reaction is the oxygen evolution reaction (OER). This reaction is typically performed by iridium (Ir) based oxides [2]. For large-scale implementation, a careful use of Ir resources is needed, e.g. by developing highly active and stable Ir nanocatalysts [3], like nanoparticles (NPs). As the mode of production of the NPs influence their performance [4], NP synthesis must be thought out to minimize energy, resources, time and so overall costs of production. In colloidal syntheses, a molecular complex comprising Ir atoms in an oxidized state is reduced to Ir NPs. The main drawback in these approaches come from the multiplicity of chemicals needed, including the Ir source, solvent(s), reducing agent(s) and often additives like surfactants to stabilize the NPs. Limiting the number of chemicals in the synthesis is desirable to avoid impurities, improve reproducibility, limit hazards, limit cleaning/activation steps, to ultimately make the synthesis more cost efficient [4,5].

Surfactants are typically used in colloidal syntheses but need to be removed by time and energy consuming steps [6]. Surfactant-free alternative approaches often still require several chemicals [7]. Examples of colloidal surfactant-free syntheses are the polyol [8,9] or mono-alcohol [10] syntheses performed in alkaline conditions where the mono-alcohol synthesis is promisingly simpler [7,11]. The need for alkaline conditions for NP syntheses in these solvents is largely stressed

[8,12] but in the case of ethylene glycol (EG), there is actually no need for a base for the synthesis to proceed [13,14]. It is here shown that alkaline conditions are also not needed when ethanol is used as solvent and reducing agent. The benefits of this synthesis approach is illustrated for the OER.

2. Materials and methods

2.1. Synthesis

Ir NPs were obtained in ethanol following the procedure previously reported but without using a base [10,15,16]. See details in *Supplementary information (SI)*.

2.2. Electrochemical characterization

The electrochemical characterization followed the procedure extensively detailed in [16]. The activity of the catalyst was assessed using 10 μg_{Ir}·cm⁻² of catalysts in 0.1 M HClO₄ at 1.5 V_{RHE}. See also *SI*.

2.3. Physical characterization

Details on the transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) measurements and analysis are given in *SI*.

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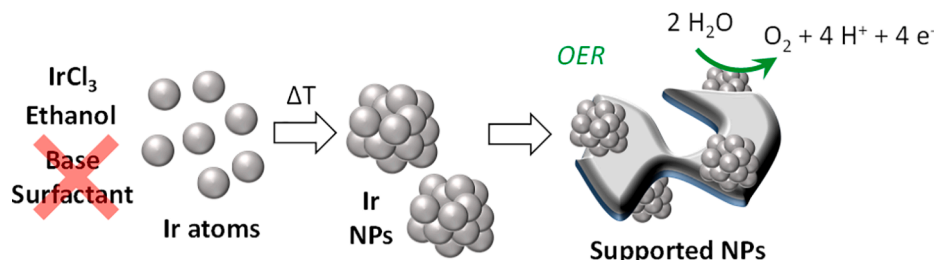


Fig. 1. Schematic representation of the synthesis, supporting and catalytic testing of Ir-based NPs.

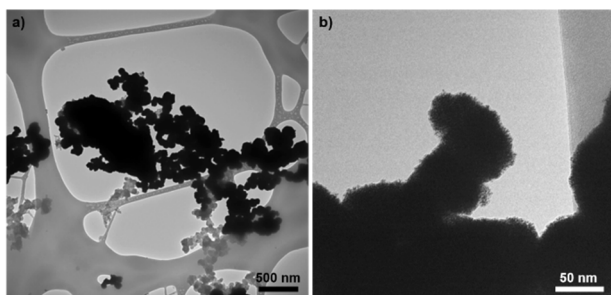


Fig. 2. Illustrative TEM of Ir NPs supported on carbon, here for a 50 wt% Ir loading.

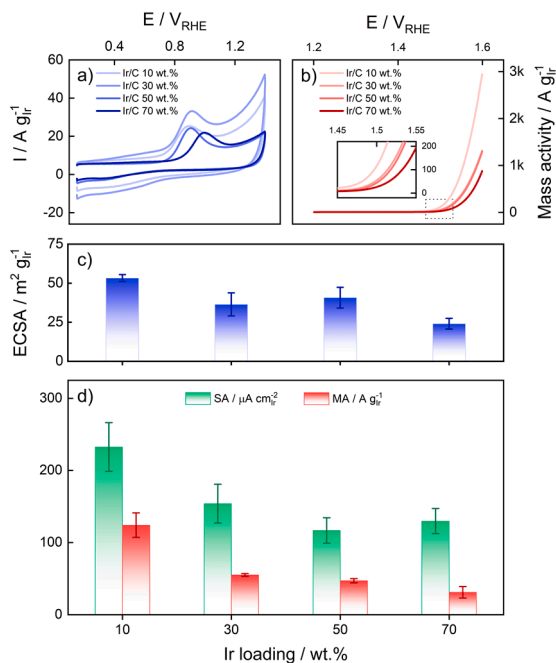


Fig. 3. Electrochemical characterization of samples prepared with Ir NPs obtained in ethanol without using base for different loading on carbon support: a) displays the CO oxidation, b) the OER activity, c) the ECSA and d) the SA and MA. All measurements are performed in 0.1 M HClO₄ at 25 °C.

3. Results and discussion

In various precious metal colloidal syntheses, e.g. performed in EG [8], methanol or ethanol [10], the need for alkaline conditions is often stressed. Without base, no Ir NPs are obtained using methanol as solvent. In contrast, NPs ca. 2 nm in diameter are obtained in ethanol without base, Fig. 1. This is a slightly smaller size compared to Ir NPs obtained in EG without base, ca. 2.5 nm in diameter [13]. Since the Ir NPs are obtained in a low boiling point solvent, they are easily supported on high

surface area carbon by mixing the colloidal Ir NPs and the support followed by ethanol removal, Fig. 1. This is a much simpler approach than strategies involving surfactant-removal and/or energy or time intensive steps [13,17,18]. By adjusting the mass ratio between the NPs and support, samples with different Ir loadings are prepared, Fig. 2.

The electrochemically active surface areas (ECSAs) are 53 ± 7 , 36 ± 7 and $41 \pm 7 \text{ m}^2 \text{ g}^{-1}$ for the samples with 10, 30 and 50 wt% Ir loading, respectively, see Fig. 3. These are a relatively high values for Ir NPs - e.g. compared to $25 \text{ m}^2 \text{ g}^{-1}$ reported for unsupported Ir NPs obtained in EG without base [13], or $40 \text{ m}^2 \text{ g}^{-1}$ for commercial materials [13,19] - but relatively low compared to $200 \text{ m}^2 \text{ g}^{-1}$ for Ir NPs prepared in alkaline ethanol [16].

The specific activity (SA) of the Ir NPs for the OER is 232 ± 34 , 154 ± 27 and $117 \pm 18 \text{ } \mu\text{A cm}^{-2}$ whereas the mass activity (MA) is 124 ± 17 , 55 ± 2 and $47 \pm 3 \text{ A gr}^{-1}$ for the samples with 10, 30 and 50 wt% Ir loading respectively, see Fig. 3. The SA of the sample with 10 wt% Ir loading is in the range of what is obtained for Ir NPs prepared in alkaline conditions ($120\text{--}140 \text{ } \mu\text{A cm}^{-2}$) whereas the MA of this same sample is about 4 times less than for NPs prepared in alkaline conditions (ca. 400 A gr^{-1}). The MA of 124 A gr^{-1} for the sample with 10 wt% Ir loading is slightly smaller than for Ir NPs obtained in EG without base [13] (ca. 180 A gr^{-1}). As the Ir loading increases to 30 and 50 wt% the SA and MA decreases. This suggests that the actual loading of Ir NPs on the support might be lower than expected (though the measure of the actual Ir loading remains a challenge [20,21] and/or a significant agglomeration of the NPs takes place). In attempts to obtain a higher loading of 70 wt% of Ir, the ECSA dropped to $24 \pm 3 \text{ m}^2 \text{ g}^{-1}$, the SA to $130 \pm 17 \text{ } \mu\text{A cm}^{-2}$ and the MA to $31 \pm 8 \text{ A gr}^{-1}$ which suggests agglomeration of the NPs on the support leading to a less efficient use the NPs surface. The decrease in MA as the loading increases is in contrast to a synthesis using alkaline conditions [15]. Overall, these results support and rationalise the use of alkaline conditions when using ethanol as solvent to develop highly active Ir NPs at high (>10 wt%) Ir loading as catalysts for the OER.

4. Conclusions

Surfactant-free colloidal Ir NPs ca. 2 nm in diameter are obtained in ethanol as solvent and reducing agent without the need for alkaline conditions. The activated NPs are readily active for the OER. It is however recommended to prefer a synthesis in alkaline conditions to achieve higher activity [15,16]. Combining different supports and low loading (<10 wt%) could lead to efficient catalysts for other electrochemical reactions where higher loadings are not required and for a range of other catalytic reactions.

CRediT authorship contribution statement

Francesco Bizzotto: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization, Writing – review & editing. **Matthias Arenz:** Conceptualization, Methodology, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing. **Jonathan Quinson:** Conceptualization, Methodology, Writing – original draft, Project

administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2021.131209>.

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