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Tailoring of Fe single-atoms on hollow carbon spheres for the oxygen reduction reaction

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Introduction. Single-atom catalysts (SACs) have emerged as one of the most promising alternatives to noble metal-based catalysts for highly efficient oxygen reduction reaction (ORR)[1]. A broad range of non-platinum group metal electrocatalysts has been developed, among which Fe−N−C nanostructures have been considered one of the most promising candidates. Most strategies for the synthesis of SACs need delicate procedures. Therefore, developing strategies to tailor atomically better dispersed Fe sites in N-doped carbon supports is highly desirable. Herein, we reported the design of hollow carbon spheres with highly stable Fe centres and enhanced catalytic activity in ORR.

Experimental/methodology. Carbon spheres (CSs) were synthesized by sol-gel polycondensation through Stöber's method, followed by thermal annealing and silica etching, according to a previously reported procedure [2]. The hollow CSs were then doped with nitrogen and Fe by adapting a procedure reported elsewhere [3]. The effect of metal loading was studied by varying the proportion of metal precursor during the synthesis. In addition, the role of each precursor during the synthesis of the optimized electrocatalyst was elucidated by preparing additional materials in the absence of specific precursors. All samples were physicochemically characterized using suitable techniques, including high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy-high angle annular dark field imaging (STEM-HAADF) in combination with energy-dispersive X-ray spectroscopy (EDX). The catalytic performance of the samples in ORR was assessed by electrochemical measurements using a three-electrode cell configuration in alkaline media.

Results and discussion. The performance of the Fe-N-doped hollow CSs in ORR seems to be governed by the quality of Fe species rather than the overall Fe load. Nitrogen seems to modulate the charge density nearby the active sites and limit the agglomeration of the metal precursor during the synthesis. Glucose enhances the metal-heteroatom coordination and subsequent dispersion of active sites on the carbon surface. The activity of the best-performing metal-free CSs (CS_7Fe-N) in ORR is still far from that obtained with the commercial noble metal-containing Pt/C. Nevertheless, it is thus noteworthy that CS_7Fe-N revealed superior stability (97%) than Pt/C (92%) in the same conditions. Therefore, the methodology herein reported opens a window of possibility for the development of highly stable ORR electrocatalysts based on single-atom Fe-N hollow CSs.

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