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P23. NOBLE METAL-FREE HOLLOW CARBON SPHERES AS ELECTROCATALYSTS FOR THE OXYGEN REDUCTION REACTION

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Renewable energy sources are intermittent, *i.e.*, their output is dependent upon the weather. Therefore, renewable electricity supply and demand must be balanced, which poses the need for the development of new engineering solutions for energy storage and conversion. Electrochemistry plays a decisive role in this endeavor, offering the possibility of converting excess electrical energy into storable chemical energy to be used when needed. Briefly, the electrical surplus can be used to promote water electrolysis to yield H_2 and O_2 in an electrolyzer; which can then be converted back to electricity and water in a fuel cell. Among the electrochemical reactions involved in these processes, the oxygen reduction reaction (ORR) is the most unfavorable one due to the challenging electrochemical reaction of O_2 dissociation. Research efforts have thus been focused on the development of enhanced ORR electrocatalysts.

ORR electrocatalysts have been traditionally based on noble metals-containing nanoparticles supported on carbon black – mostly platinum (Pt) and its alloys [1]. However, these precious metals are expensive and unsustainable. Therefore, other options must be considered. Having this in mind, our group has been focused on the development of cost-effective, sustainable, highly active and stable electrocatalysts based on carbon materials (*e.g.*, hydrothermal carbons and carbon nanotubes) doped with transition metals (*e.g.*, iron and cobalt) and/or heteroatoms (*e.g.*, nitrogen) [2-4].

In the present study, hollow carbon spheres (CSs) were synthesized by sol-gel polycondensation of resorcinol with formaldehyde over silica nanoparticles previously obtained through the Stöber's method, followed by thermal annealing at 800 °C and silica etching with sodium hydroxide (10 mol L^{-1}) [5]. The particle size of the resulting CSs increased as the ethanol/water (E/W) volumetric ratio (2, 4.5 and 7) employed to obtain silica nanoparticles increased (Figure 1). The properties of the CSs were characterized by N_2 physisorption, elemental analysis, thermogravimetric analysis, scanning electron microscopy (SEM), X-ray diffraction and Fourier transform infrared spectroscopy. Moreover, the electrical conductivity was measured by the four-point probe method.

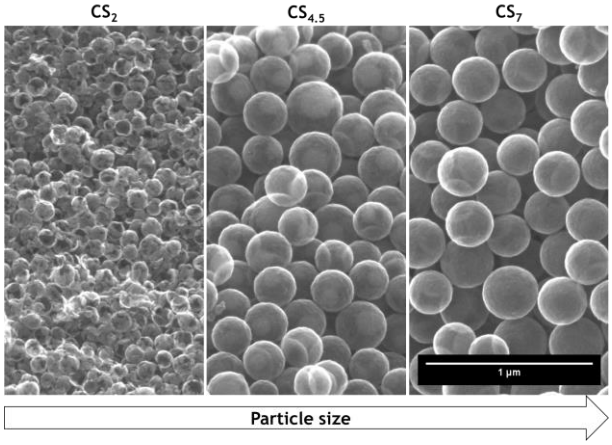

Figure 1. SEM micrographs of hollow carbon spheres (CSs).

Table 1. Onset potential (E_{onset}), half-wave potential ($E_{1/2}$), limiting current density (J_L), hydrogen peroxide (H_2O_2) formation and number of electrons exchanged (n_e) when employing the CSs in ORR

Material	E_{onset} (V)	$E_{1/2}$ (V)	J_L (mA cm^{-2})[a]	H_2O_2 (%)[b]	n_e[b]
CS_2	0.81	0.74	3.69	62	2.8
$CS_{4.5}$	0.80	0.73	3.78	45	3.1
CS_7	0.81	0.74	3.90	42	3.2
CS_7Fe-N	0.89	0.78	3.32	7	3.9
$CS_7Fe_{1/3}$-N	0.90	0.78	4.55	4	3.9
$CS_7Fe_{1/6}$-N	0.90	0.79	4.61	6	3.9
$CS_7Fe_{1/9}$-N	0.90	0.79	4.28	8	3.8

[a] Calculated at 0.15 V vs. RHE; [b] Calculated at 0.4 V vs. RHE.

The performance of the CSs in ORR was evaluated following the methodology previously described by Morais *et al.* [4]. As observed, the best performance was obtained with CS_7, *i.e.*, the CSs obtained upon employing an E/W volumetric ratio of 7 (Table 1), reason why this material was selected for functionalization with nitrogen and iron-containing actives using melamine and iron (III) nitrate as precursors. The resulting material was denoted as CS_7Fe-N. Additional materials were prepared with lower metal loadings, namely with 1/3, 1/6 and 1/9 of that initially considered. As observed, the functionalization of CS_7 is an effective strategy to enhance its electrocatalytic performance in ORR (Table 1). Moreover, chronoamperometry tests revealed stabilities of up to 99.6% (by applying a potential of 0.4 V vs. RHE for 10,000 s at 1600 rpm). Ongoing research efforts are thus focused on the optimization of the functionalization methodology.

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