Hollow mesoporous Fe-N-C graphitic spheres with excellent activity and stability for electrocatalytic oxygen reduction

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Abstract: We describe a controllable strategy to preparing hollow mesoporous Fe-N-doped graphitic spheres *via* in-situ polymerization and functionalization. The optimized catalyst exhibits very superior ORR activity with a half-wave potential ($E_{1/2}$) of 0.886 V in 0.1 M KOH, 15 mV more positive than that of commercial Pt/C catalyst. In acidic solution, it also shows a competitive $4e^-$ ORR activity compared to Pt/C. The outstanding activity is contributed by the synergy of chemical functions (Fe-N species) and unique structures (hollow cores (~91 nm), open mesopores (~2.1 nm), and high graphitization), ensuring rapid mass-diffusion and electron-transfer kinetics and full accessibility of catalytic sites.

Keywords: Fe-N-C species, Electrocatalysis, Oxygen reduction reaction.

1. Introduction (11-point boldface)

Owing to its sluggish kinetics, the oxygen reduction reaction (ORR) occurring at the cathode has been one of the major limitations in widespread commercialization of metal-air batteries and low-temperature fuel cells. Pt and its alloys are the best ORR catalysts due to their high activity.[1] However, the resource scarcity, high-cost, poor durability and intolerance to methanol crossover of Pt-based catalysts restrict their large-scale applications.[2] Therefore, there is significant incentive to discover nonprecious materials with superior activity and durability to catalyze this reaction. Herein, we described an *in-situ* approach to the formation of hollow macroporous core-graphitic mesoporous shell Fe-N-doped carbon spheres (FeNCSs), serving as highly active and stable ORR electrocatalysts in both alkaline and acid solutions.[3-4] The doping of Fe could result in both the catalytic transformation of amorphous spheres into graphitic spheres with retained open mesopores and hollow cores, and the formation of functional Fe-N_x-coordinated configurations and carbon-encapsulated Fe/Fe_3C (Fe@C) NPs. The FeNCSs materials show excellent ORR performance in both alkaline and acidic electrolytes.

2. Experimental

Hollow polymer spheres (HPS), synthesized by soft-template self-assembly process, was treated in ammonia flow under NH_3 atmosphere to obtain NHCS-650. Fe-N-co-doped hollow mesoporous carbon spheres (FeNCSs) were prepared by co-pyrolysis of the mixture of NHCS-650 and $FeCl_3$ at different temperatures. The electrochemical performances for the catalysts were studied with an electrochemical workstation (Pine Instrument Co.). A conventional three-electrode system was employed using a Pt foil as the counter electrode, a saturated calomel electrode (SCE) as reference electrode and a rotating disk electrode (RDE) or a rotating ring-disk electrode (RRDE) coated with catalyst film as the working electrode. The alkaline and acid electrolytes were 0.1 M KOH and 0.5 M H_2SO_4 solution, respectively, for the electrochemical measurements. The measured potentials *vs*. SCE were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: $E_{RHE} = E_{SCE} + 0.0591 \times pH + E^*_{SCE}$, where E_{SCE} is the experimentally measured potential *vs*. SCE reference and E^*_{SCE} is equal to 0.2415 V at room temperature.

3. Results and discussion

The simultaneously acquired scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) images show that FeNCS-1000 comprises hollow spherical particles with average diameter of 135 nm and shell thickness of 22 nm. The simultaneously acquired energy dispersive spectroscopy (EDS) mapping shows uniform distribution of Fe element within the whole sample except for several Fe-based NPs in FeNCS-1000. Considering uniform N-doping, most Fe atoms could react with pyridinic N groups to form Fe-N$_x$ configurations before aggregating to produce Fe_3C/Fe NPs during the high-temperature treatment.

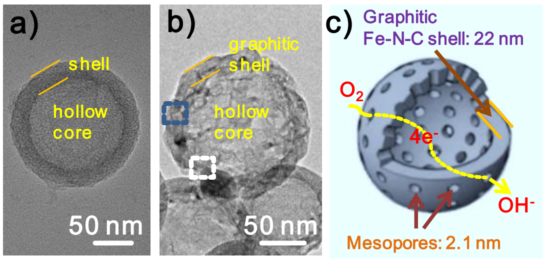

Figure 1. TEM images of (a) NHCS-650, and (b) FeNCS-1000. (c) A schematic illustration of FeNCS.

Transmission electron microscopy (TEM) images reveal that NHCS-650 is composed of hollow spheres (Figure 1a). After introducing Fe species, the resulting FeNCS-1000 has rough surfaces of hollow spheres (Figure 1b). The schematic illustration of FeNCSs is presented in Figure 1c. The XPS survey shows FeNCSs have a composition of C, N and O and total N content gradually decreases from 7.6 to 1.6% with increasing temperature from 800 to 1100 ^{o}C.

The ORR activity of FeNCSs was studied by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques in a conventional three-electrode system. Both CV and RDE measurements imply the optimum ORR performance obtained for FeNCS-1000 synthesized with 2 wt% Fe at 1000 ^{o}C.

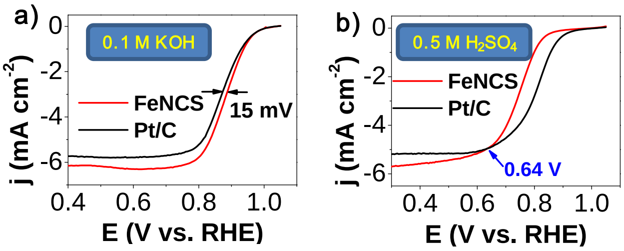

Figure 2. RDE voltammograms of FeNCS-1000 and commercial Pt/C in O_2-saturated (a) 0.1 M KOH or (b) 0.5 M H_2SO_4 solution. Rotating speed: 1600 rpm and scanning rate: 10 mV/s.

In O_2-saturted 0.1 M KOH solution (Figure 2a), FeNCS-1000 has significantly positively shifted half-wave potential ($E_{1/2}$) at 0.886 V (*vs*. RHE), which is 15 mV more positive than that of 20 wt% Pt/C catalyst (Johnson-Matthey). It implies that FeNCS-1000 with Fe-N$_x$ active moieties possesses better ORR activity than Pt/C. Based on the slopes of the Koutecky-Levich (K-L) plots, the number of transferred electrons (n = 4) for FeNCS-1000 is the same as that for Pt/C, corresponding to a highly efficient $4e^-$ ORR process. The FeNCSs also possess a competitive ORR activity in 0.5 M H_2SO_4. As shown in Figure 2b, FeNCS-1000 has an $E_{1/2}$ value (0.760 V), only 55 mV more negative than that of Pt/C. In terms of limiting current density, FeNCS-1000 exceeds Pt/C at 0.64 V, more positive than those for other Fe-N-doped materials with designed morphologies (e.g., capsules (0.15 V), mesoporous microspheres (0.38 V), and hollow spheres (0.59 V)). Very low peroxide yields (1.7~8.0%) give large n values of 3.84~3.97 over the tested potential range of 0.2~0.8 V for FeNCS-1000 in acidic solution. Moreover, FeNCS-1000 shows much better long-term stability and methanol intolerance than commercial Pt/C in both alkaline and acidic solution.

4. Conclusions

We have developed a facile procedure to prepare hollow macroporous core-graphitic mesoporous shell Fe-N-doped carbon spheres, showing much higher activity (more positive $E_{1/2}$ and larger limiting current density) and selectivity, better durability, and better tolerance to methanol crossover for ORR, compared to Pt/C ascribed to the synergistic combination of graphitic structures, hierarchical porosities, and Fe-N$_x$ active sites.

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