



Effectively incorporating iron, nitrogen, and sulfur functionalities on carbon surface for a superior electrocatalyst toward oxygen reduction reaction



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ABSTRACT

We demonstrate here a Fe, N, and S functionalized carbon (Fe/N/S-C) derived from an iron incorporated and *p*-toluenesulfonate doped polypyrrole precursor on a carbon support as an efficient catalyst for oxygen reduction reaction (ORR). Such a strategy could effectively suppress the formation of inferior activity metal species and less active oxidized type sulfur species. The as-synthesized Fe/N/S-C catalyst exhibited a highly catalytic activity for ORR which is comparable to the state-of-the-art commercial Pt/C catalyst at low overpotential range while have a better catalytic activity at the fuel cell operation potential range. In addition, this catalyst showed a higher durability and better tolerance to alcohol fuel than Pt/C catalyst.

1. Introduction

Fuel cell has been regarded as an ideal green energy supplier due to its attractive merits such as low pollutant emissions and high energy conversion efficiency. However, Pt based catalysts are still necessary to be utilized to catalyze the electrochemical reactions within fuel cells for the practical operation [1]. The high cost and the limited natural abundance of the platinum resource significantly hampered the wide commercialization application of fuel cells. Therefore, in the past decades, a great deal of effort has been continuously devoted to the research into low platinum loading or alternative non-noble metal catalysts for fuel cell catalytic reactions [2–4].

Although many metal oxides, carbides, and metal-free electrocatalysts have been confirmed effective for catalyzing ORR, the most active non-noble metal catalysts are identified to be the carbon based materials decorated with transition metal(s) such as Co and (or) Fe, and various heteroatoms (N, S, B, C, and/or P) on the surface. Among them, the catalysts containing Fe (or Co), N, and S have the best catalytic activity for ORR [5–8]. At the current stage, for the synthesis of metal-N or -S based electrocatalysts, the expensive N₄-metal-containing macrocycles are no longer necessary. And such electrocatalysts can be synthesized by pyrolyzing cheap mixed precursor consisted of metal(s), carbon, nitrogen and sulfur containing sources. However, these processes inevitably generate the inactive or less active metal species [6]. Therefore, in order to achieve desired stability and catalytic activity,

post-acid wash and pyrolysis to remove the unstable species are often necessary and critical, which cause an addition cost for the synthesis [9,10]. Herein, we synthesized a Fe/N/S-C catalyst by using a Fe, N, and S integrated polymer as the precursor which is a Fe incorporated and *p*-toluenesulfonate doped polypyrrole instead of a mixed precursor. The strategy is quite simple and no unstable metal species was detected in the final product. Also the as-synthesized catalyst exhibits good performance for ORR in the fuel cell operating potential range as well as excellent durability and alcohol fuel-tolerance in alkaline media.

2. Experimental

2.1. Chemicals

Pyrrrole monomer was purchased from Aladdin Industrial Corporation (Shanghai, China). Iron (III) *p*-toluenesulfonate hexahydrate (Fe (III) PTS) and Nafion solution (5 wt%) were purchased from Sigma-Aldrich. Black Pearl 2000 carbon (BP2000) was provided by Cabot Company. The reference Pt/C (20 wt%) was obtained from Johnson-Matthey.

2.2. Synthesis of Fe/N/S-C electrocatalyst

In brief, 0.25 g acid treated BP2000 carbon was ultrasonically dispersed in 95 mL ethanol. Then 5 mL solution containing 0.0175 mmol

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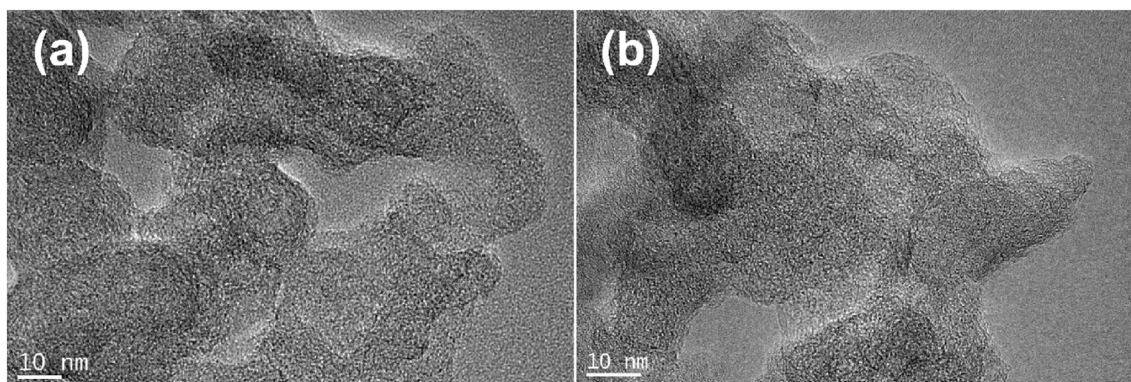


Fig. 1. HRTEM images of BP2000 carbon (a) and Fe/N/S-C catalyst (b).

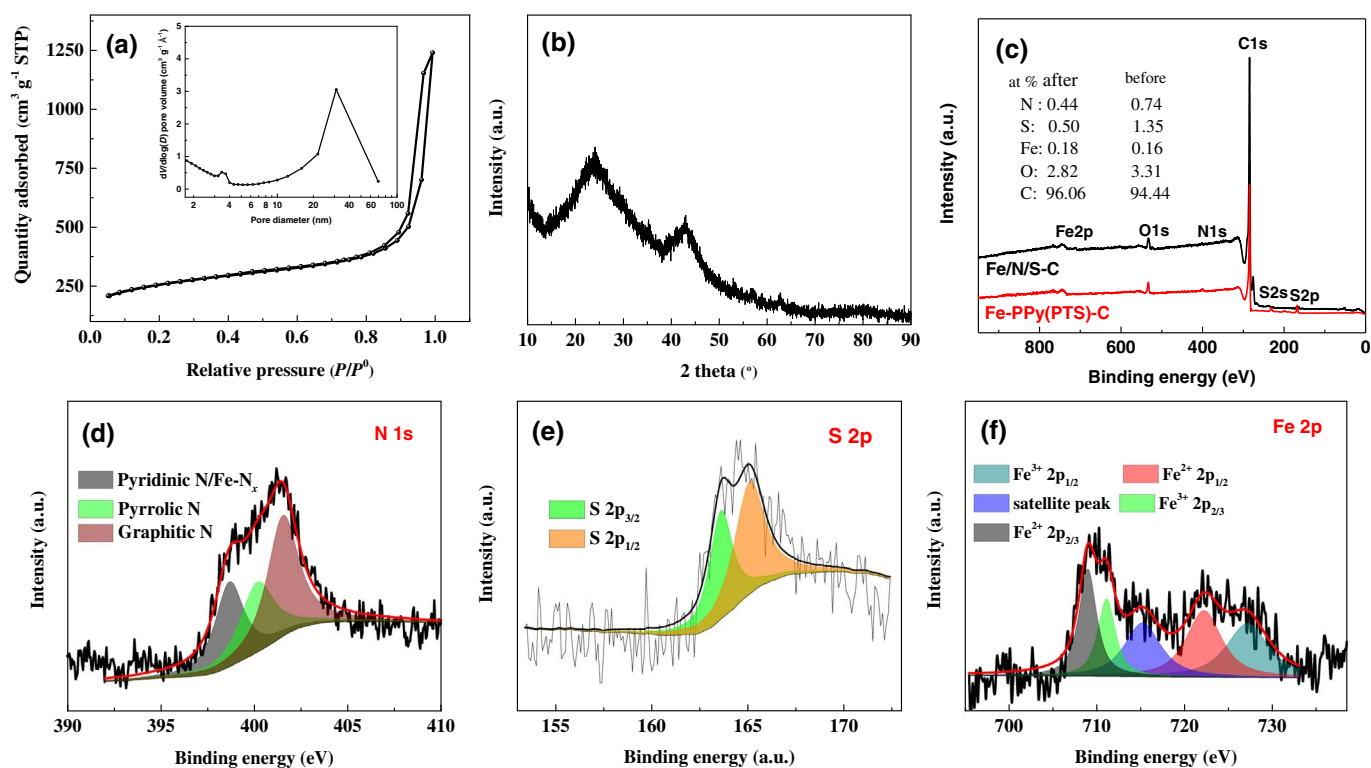


Fig. 2. (a) Nitrogen adsorption/desorption isotherm and the corresponding pore size distribution (inset), XRD pattern (b), XPS survey spectra for Fe/N/S-C and Fe-PPy (PTS)/C (c), and high resolution N 1s (d), S 2p (e), and Fe 2p (f) spectra of Fe/N/S-C catalyst.

Fe (III) PTS was added to the above suspension. After then, the mixture was cooled down to about 4 °C. To the suspension, 0.035 mmol freshly distilled and pre-cooled pyrrole monomer was added under vigorous stirring. The polymerization was maintained at 4 °C for 12 h. Then the temperature was increased to 80 °C and maintained for 8 h to facilitate the formation of a homogenous Fe-PPy (PTS)/C precursor. The solid powder was collected by centrifuge, washed with ethanol/H₂O, and vacuum dried at 100 °C for 12 h. Finally, the powder was pyrolyzed at 800 °C for 2 h in nitrogen atmosphere.

2.3. Characterization

The morphology investigation was studied by a TEM (JEM-2100F, JEOL Ltd., Japan). The specific Brunauer-Emmett-Teller (BET) surface areas and porosity were measured using a nitrogen sorption instrument (Micromeritics, ASAP2020). The crystalline property of materials was examined by XRD measurements using a Bruker D8 Advance X-ray diffractometer at 40 kV and 20 mA with a Cu K α radiation source. The surface elements of the sample were analyzed by an X-ray

photoelectron spectrometer (XPS, Kratos Axis Ultra DLD) with an Al K α excitation source.

The electrochemical experiments were carried out in a standard three-electrode cell using a CHI 760E bipotentiostat. A platinum wire and an Ag/AgCl electrode with saturated KCl and 10% KNO₃ liquid bridge were used as the counter electrode and the reference electrode respectively. To perform the electrochemical measurements, the catalyst ink was prepared by dispersing 5 mg electrocatalyst in a solution containing 950 μ L mixture solvents of Millipore water to isopropanol (volume ratio of 3:1) and 50 μ L Nafion solution (5 wt%). The solution was ultrasonicated for 60 min and formed a homogenous slurry. The ORR evaluations were conducted on a rotating disk electrode (RDE, 0.196 cm², Pine Research Instrumentation, USA) and a rotating glassy carbon disk with a platinum ring electrode (RRDE, 0.238 cm², Pine Research Instrumentation, USA). The catalyst loading contents were 0.25 mg cm⁻² for Fe/N/S-C electrode and 0.1 mg cm⁻² for Pt/C electrode, respectively.

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