# Nitrogen-doped hierarchically porous carbon spheres as efficient metal-free electrocatalysts for an oxygen reduction reaction

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## HIGHLIGHTS

- N-doped hierarchically porous carbon spheres were prepared by nanocasting method.
- Methyl violet was used as carbon and nitrogen precursor with mesoporous silica as template.
- The catalyst exhibited high performance in ORR.
- The onset potential of the catalyst was very closer to that of Pt/C catalyst.

## GRAPHICAL ABSTRACT
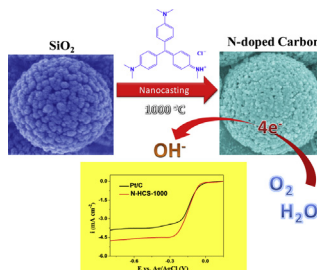
## ABSTRACT

Using hierarchically mesoporous silica spheres as a hard template and methyl violet as carbon and nitrogen source, nitrogen-doped hierarchically porous carbon spheres (N-HCS) are successfully prepared via a nanocasting method. The nitrogen-doped carbon spheres obtained after carbonization at 1000 °C (N-HCS-1000) exhibit a hierarchically micro-meso-macroporous structure with a relatively high surface area (BET) of 1413 m$^2$ g$^{-1}$ and a notably large pore volume of 2.96 cm$^3$ g$^{-1}$. In an oxygen reduction reaction (ORR) in alkaline media, the N-HCS-1000 material exhibits excellent activity with high current density, and its onset potential is notably close to that of the commercial Pt/C catalyst. The efficient catalytic activity of this catalyst could be attributed to the high electrical conductivity of the nitrogen-doped carbon matrix as well as the hierarchically porous framework. This catalyst also exhibits better methanol crossover resistance and higher stability than the commercial Pt/C catalyst.

## 1. Introduction

Development of catalytic materials for the oxygen reduction reaction (ORR) is the current technological bottleneck for fuel cells [1–3]. Pt and its alloys are the best-known ORR catalysts [4–6]; however, these catalysts exhibit sluggish kinetics for ORR at the cathodes of fuel cells and metal-air batteries. Moreover, the high cost, scarcity and weak durability of Pt-based catalysts hinder their further application. Consequently, tremendous efforts are aimed at developing non-precious metal [7–12] and metal-free [13–17] electrocatalysts to replace Pt-based catalysts. Heteroatom-doped carbon materials, particularly metal-free carbon-based catalysts, offer several noticeable advantages because they do not suffer crossover effects and exhibit long-term stability.

Nitrogen-doped porous carbon materials are known to act as excellent non-precious metal ORR catalysts in alkaline media. Recently, certain breakthroughs were attained by careful selection of suitable nitrogen and carbon precursors as well as optimization

of the preparation conditions, and several such catalysts have been reported, i.e., N-doped carbon nanotubes arrays [18], N-doped graphene film [19] and functionalized graphene oxide [20]. Porphyrin [10,21], ionic liquids [22,23] and metal-organic framework (MOF) or zeolitic imidazolate framework (ZIF) [24,25] have also been used as precursors to fabricate N-doped carbon materials. Nitrogen-doped porous carbons are also prepared by high temperature ammonia treatment [26,27] and by chemical vapour deposition (CVD) method [28]. However, some of the catalysts are expensive or tedious to prepare, thus rendering them less competitive.

It has been found that electrocatalytic activity can be limited by fewer surface catalytic sites. Porous structure of electrocatalysts with high surface area and large pore volume would be beneficial to mass transport of reactant and product in ORR. However, it would be difficult to enhance the porosity of the electrocatalysts by direct pyrolysis of the precursors and efforts to construct porous structure with high surface area usually adopt template approaches. Liu et al. prepared ordered mesoporous N-doped graphitic arrays by using ordered mesoporous silica (SBA-15) as hard template [29]. Mesoporous nitrogen and oxygen-doped carbons were synthesized by pyrolysis of polyaniline/SBA-15 composites via in-situ polymerization of polyaniline within the mesopores of SBA-15 [30]. Liang et al. prepared three-dimensionally ordered macroporous g-C$_3$N$_4$/C composites by using SiO$_2$ nanoparticles as hard template [31]. It would be desirable if the electrocatalysts possess both mesoporous and macroporous texture, and up to now facile preparation of hierarchically porous N-doped carbon materials remains still a challenge.

Recently, we reported the synthesis of hierarchically mesoporous silica spheres, possessing well-ordered mesoporous structure as well as interconnected macroporosity [32]. Herein, by using this hierarchically mesoporous silica spheres as a hard template and methyl violet (a commonly used dye) as both nitrogen and carbon precursor, N-doped hierarchically micro-meso-macroporous carbon spheres (N-HCS-1000) are facilely fabricated. The N-HCS-1000 exhibits high surface area, large pore volume and high electrical conductivity. When used as metal-free ORR electrocatalysts in alkaline media, N-HCS exhibits high catalytic activity, better methanol tolerance and higher stability than those of the commercial Pt/C catalyst.

## 2. Experimental

### 2.1. Chemicals and materials

All reagents were of analytical grade and used without further purification. Methyl violet was from Alading Chemical (China). Tetraethoxysilane (TEOS), ammonia (NH$_3$·H$_2$O), n-butanol, and hexadecyl trimethyl ammonium bromide (CTAB) were obtained from Tianjin Guangfu Chemical Co. Poly (acrylic acid) (PAA) (average molecular weight = 240,000, 25 wt % solution in water), commercially available triblock copolymer (EO$_{20}$PO$_{70}$EO$_{20}$ MW = 5800) (Pluronic P123) were from Aldrich, and Pt/C (20% by wt., Pt nanoparticles on a Vulcan XC-72 carbon support) catalyst were purchased from Alfa Aesar (WardHill, MA, USA). Nafion solution (5% in a mixture of lower aliphatic alcohols and water) was purchased from Sigma Aldrich.

### 2.2. Syntheses of different mesoporous silica templates

Hierarchically mesoporous silica spheres (HMS) were synthesized following our previously reported method [32]. In a typical synthesis, 0.55 g of CTAB was completely dissolved in 25.0 mL of distilled water under stirring, and 3.0 g PAA (25% solution) was added under vigorous stirring at 20 °C. Next, 2.0 g ammonia (25%) was added to the above solution under vigorous stirring. After 20 min of stirring, 2.08 g of tetraethoxysilane (TEOS) was added to the solution under continued stirring for 15 min, and the mixture was transferred into an autoclave. After placement in an oven at 100 °C for 48 h, the white final product was centrifuged, washed with distilled water, and dried at 60 °C. The organic templates were removed by calcination at 550 °C for 6 h.

Mesoporous silica SBA-15 was synthesized following the previously described method [33]. In a typical synthesis, 1.6 g of P123 and 2.2 g of KCl were dissolved into 60 g of 2 M HCl at 40 °C, and 4.2 g of TEOS was added under vigorous stirring. After stirring for 8 min, the mixture was held under static conditions at the same temperature for 24 h, and the mixture was subsequently transferred into the autoclave and heated at 100 °C for another 24 h. The solid products were filtered, washed and dried at 80 °C. The resulting powders were calcined at 550 °C for 6 h to obtain mesoporous silica materials.

KIT-6 (mesoporous silica with 3-D cubic la3d meso-structure) was prepared according to literature [34]. In the typical synthesis, 6.0 g of P123 was dissolved in 217 g of distilled water and 11.8 g of concentrated HCl (36%). To this solution, 6.0 g of n-butanol was added under stirring at 35 °C. After 1 h of stirring, 12.9 g of TEOS was added at 35 °C, and the mixture was held under stirring for 24 h at 35 °C and was subsequently heated for 24 h at 100 °C under static conditions in the autoclave. The solid powder was filtered, washed and dried at 100 °C. The template was removed by calcination at 550 °C for 6 h.

### 2.3. Synthesis of N-doped mesoporous carbon materials

An amount of 1.0 g of methyl violet (MV) was mixed with 1.0 g of HMS in 7 mL of ethanol at 40 °C under stirring in a 50-mL beaker. After evaporation of ethanol, the obtained MV/HMS composite was dried at 60 °C for 12 h and subsequently carbonized in high-purity nitrogen gas with the flow rate of 15 mL min$^{-1}$ at 600, 750, 900 and 1000 °C for 2 h, respectively. After removal of silica by HF (20 wt. %) etching, N-HCS were obtained. For comparison, we also prepared hierarchically porous carbon spheres without nitrogen doping using rosolic acid as the carbon precursor (denoted as HCS-1000). When SBA-15 and KIT-6 were used as the mesoporous silica templates, respectively, the same procedure was followed.

### 2.4. Characterization

Field-emission scanning electron microscopy (FESEM; JEOL, JSM-7500F, 8 kV) was used to analyse the morphology of the samples. Transmission electron microscopy (TEM) was performed on a Philips Tecnai F20 microscope at 200 kV. All samples subjected to TEM measurements were ultrasonically dispersed in ethanol and dropped on copper grids. The XPS spectra were obtained with a Kratos Axis Ultra DLD spectrometer. Nitrogen adsorption and desorption isotherms were measured on a BELSORP-mini II sorption analyser at 77K.

### 2.5. Electrochemical measurements

Electrochemical experiments were conducted at 20 °C on a CHI660D electrochemical workstation. The catalytic measurements of different catalysts were conducted at a scan rate of 5 mV s$^{-1}$. A conventional three-electrode system, including a glassy carbon rotating disk electrode (RDE) coated with catalysts, a platinum wire auxiliary electrode, and a KCl-saturated Ag/AgCl reference electrode (with a nominal potential of 0.197 V versus that of a reversible hydrogen electrode). For electrode preparation, 2 mg of sample was