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Template-free synthesis of hierarchical peanut-like Co and N codoped porous carbon with highly efficient catalytic activity for oxygen reduction reaction

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ABSTRACT

Studies have shown that the performance of electrode materials greatly depends on their structures and compositions. Herein, unique hierarchical peanut-like Co and N codoped porous carbon (Co/N-PC) had been synthesized by using inexpensive melamine, formaldehyde and cobalt acetate as raw materials *via* a simple template-free hydrothermal reaction followed by heat treatment. The formation process of the peanut-like precursor was discussed in-depth, indicating that the morphological evolution with time followed a pathway of: solid microspheres → wrinkled and ultrathin shells wrapped microspheres → the peanut-like precursor formation. Furthermore, the unique structure combines the advantageous features of high surface area, sufficient active sites, easy access to medium and rapid mass transport. As a result, the peanut-like Co/N-PC showed high catalytic activity, superior methanol crossover resistance and excellent catalytic stability towards oxygen reduction reaction (ORR) in alkaline medium. Notably, the peanut-like Co/N-PC possessed a comparable ORR half-wave potential to commercial 20 wt% Pt/C catalyst. Therefore, it can be expected that the peanut-like Co/N-PC will be a promising alternative to commercial Pt/C catalyst for fuel cells.

1. Introduction

Peanut-like structure is a special class of core–shell structure with a distinctive core@void@shell configuration. The unique structure could lead to the increase in surface area to volume ratio and decrease in transport lengths for both mass and charge transport. Due to the special features, micro/nanomaterials with the peanut-like structure have displayed great potential for applications in various fields, such as fuel cells, lithium-ion batteries, photocatalysis and so forth [1–7]. However, many peanut-like materials are synthesized through soft or hard templating strategies [1,5,7], which are quite tedious and not very suitable for large-scale production. Additionally, the chemical compositions of the peanut-like materials are mainly metal nanoparticles (Pt and Pd) [1,2], metal oxides@inorginc materials (MnO@C, Fe_3O_4@N-C, Bi_2O_3@$BiVO_4$, α-Fe_2O_3@TiO_2, α-Fe_2O_3@ZnS and α-Fe_2O_3@SiO_2) [3–5,7] and perovskite nanoparticles ($SrSnO_3$) [6]. But to the best of our knowledge, peanut-like transition metal (Fe or Co) and N codoped carbon (M/N-C) materials, a class of non-precious metal catalysts for fuel cells, have not been reported so far. Therefore, the development of a simple, green and template-free method for the scalable synthesis of the peanut-like M/N-C materials is highly desirable.

M/N-C materials [8–14] are considered the practically most promising catalysts for oxygen reduction reaction (ORR) among various kinds of non-precious metal catalysts [8–21], owing to their relatively high catalytic activities, long-term catalytic stabilities and low costs. Studies have shown that the most desirable M/N-C catalysts should possess the favorable features towards ORR, such as high accessible surface area, sufficient active sites and rapid mass and charge transport. For this purpose, considerable attention has been paid to fabrication of the porous M/N-C catalysts with different morphologies, such as microporous or mesoporous nanoparticles [8–10], nanotubes [10,11], nanofibers [12], nano net-works [13] and hollowed-out octahedron [14]. However, the intrinsic problems, such as the complexity of synthesis [10,22] and improper building architecture are still associated with many reported M/N-C catalysts. Thus, we initiate a

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research effort to synthesize M/N-C catalysts with intricate architectures under simple reaction conditions.

Herein, we develop a novel template-free and scalable method to synthesize hierarchically structured peanut-like Co and N codoped porous carbon (Co/N-PC), which owns the above-mentioned remarkable features for ORR. In consequence, the resultant peanut-like Co/N-PC displays high catalytic performance for ORR. Especially, the peanut-like Co/N-PC possesses a competitive half-wave potential with commercial 20 wt% Pt/C catalyst. Additionally, the peanut-like Co/N-PC developed here could be easily fabricated on a large scale and shows great potential in alkaline fuel cells. Moreover, the present study provides an efficient method for the preparation of peanut-like M/N-C micro/nanomaterials.

2. Experimental Section

2.1. Materials

Commercial 20 wt% Pt/C catalyst was purchased from Alfa Aesar. $Co(CH_3COO)_2{\cdot}4H_2O$, melamine and formaldehyde were all purchased from Aladdin Chemistry Co. Ltd. Unless otherwise stated, all chemical reagents in this study were of analytical grade and were used as received without further purification. Double distilled water (DD water) was used throughout the experiments.

2.2. Synthesis of the peanut-like Co/N-PC

In a typical experimental procedure, 1.2 g melamine, 9.4 g formaldehyde solution (37%) and 1.246 g $Co(CH_3COO)_2{\cdot}4H_2O$ were added into 60 mL DD water with vigorous stirring at 60 °C for 10 min to form a clear pink solution. Then, the solution was heated to 90 °C and maintained for 10 min. Afterwards, the solution was transferred into a 100 mL Teflon-lined autoclave, followed by hydrothermal treatment at 160 °C for 10 h. Finally, the brown product was collected by filtration, washed repeatedly with distilled water and ethanol, and dried at 40 °C overnight. The dried product was heated in a quartz tube at 800 °C for 2 h with a heating rate of 3 °C min^{-1} under a high purity N_2 atmosphere. After the furnace was naturally cooled to room temperature, the peanut-like Co/N-PC was obtained. For comparison, the preparation of N-doped carbon (N-C) was also conducted under the same conditions described as the typical experiment in the absence of $Co(CH_3COO)_2{\cdot}4H_2O$.

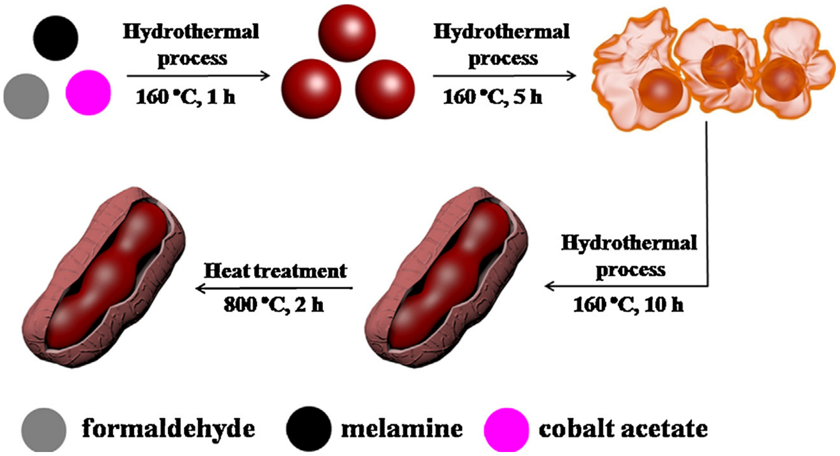
2.3. Characterization

Scanning electron microscopy (SEM) micrographs were acquired using a JSM-6390LV instrument (JEOL, Japan). Transmission electron microscopy (TEM) measurements were performed on a JEM-2100 electron microscope (Hitachi, Japan). The elemental mappings were obtained from a scanning transmission electron microscope (STEM) unit with a high-angle annular dark-field (HAADF) detector (HITACHI S-5500) operating at 30 kV. X-ray diffraction (XRD) patterns were carried out using a Bruker D8 ADVANCE (Bruker AXS, Germany) with a Cu Kα radiation source (λ = 0.15406 nm). Raman spectra were recorded using a RM2000 Microscopic Confocal Raman Spectrometer (Renishaw PLC, England) with an Ar laser at a wavelength of 514.5 nm. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Nitrogen adsorption/desorption isotherms were measured on an ASAP 2020 (Micromeritics, USA) at 77 K. Specific surface areas and pore size distributions were determined by the BET (Brunauer-Emmet-Teller) and BJH (Barrett-Joyner-Halenda) models, respectively.

2.4. Electrochemical measurements

The electrochemical measurements were evaluated on a CHI660D electrochemical workstation (Shanghai Chenhua Co., China) equipping with a model 616 electrode rotator (Princeton Applied Research) using a three-electrode electrochemical cell. The work electrode was prepared with the following procedure: 2 mg of the prepared catalyst or commercial Pt/C catalyst was added into 1 mL of ethanol and 40 μL of 5 wt% perfluorosulfonic acid, which was dispersed by ultrasonication for approximately 10 min to obtain a homogeneous suspension. Next, 18 μL of the dispersion was pipetted and spread on the glassy carbon rotating disk electrode (RDE, 4 mm in diameter), followed by drying under ambient conditions. The catalyst loading was 0.27 mg cm^{-2}. A Pt foil (1 cm^2) and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

The electrochemical experiments were carried out in O_2 saturated 0.1 M KOH electrolyte. The cyclic voltammograms were recorded with a scan rate of 50 mV s^{-1} in the potential range of –0.8 to 0.2 V *vs.* SCE. ORR steady-state polarization measurements were conducted at different rotating speeds from 400 to 3600 rpm at a scan rate of 10 mV s^{-1}.



Scheme 1. Schematic illustration of the formation process of the peanut-like Co/N-PC.