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Pony-size Cu nanoparticles confined in N-doped mesoporous carbon by chemical vapor deposition for efficient oxygen electroreduction

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The pony-size Cu nanoparticles confined in mesoporous C-N were directly synthesized by chemical vapor deposition (CVD) method using floating Cu atoms. The mesoporous C-N with high surface area not only stabilized the dispersed Cu nanoparticles but also improved the electrocatalytic activity of the Cu by changing the electronic structure of Cu. Combining the strong interaction between Cu nanoparticles and mesoporous C-N and the quantum size effect of Cu nanoparticles, the obtained Cu@C-N exhibited the catalytic activity superior to the reported Cu nanoparticles-based catalysts and commercial Pt/C-JM catalyst with a half-wave potential of 0.84 V for oxygen reduction reaction (ORR) in alkaline media. Additionally, it also showed remarkable catalytic stability and excellent methanol-tolerant property during the ORR process.

1. Introduction

The improvement for the ORR catalytic activity and durability of the non-noble metal electrocatalysts is crucially important for the widespread commercialization of the clean energy such as fuel cells and metal-air batteries [1–7]. Among the numerous electrocatalysts reported over the past decades, Fe(Co)-N/C catalytic materials showed superior activities for ORR in alkaline media [8–11]. On the other hand, Cu, due to its abundant reserves and low costs, has attracted much attention. The difference of the atomic mass between copper and platinum is very conspicuous, but copper is only one electron away from platinum in amount of the d electrons in the secondary outer shell of the atom. Cu-based materials have exhibited excellent electrocatalytic activities for various oxidation or reduction reactions, such as glucose oxidization [12], hydrogen peroxide reduction [12] and methanol oxidization [13]. In addition, the electronic structure of Cu can be modulated by the interaction with the catalyst carriers or ligands [14–16], the size effect of Cu nanoparticles [17–19] and the variation of oxidation-state [20,21], etc. These facts suggest that the Cu-based materials can be the promising ORR catalysts.

Recently, Cu-based materials are found with promising catalytic activity to catalyze ORR. For example, the Cu-N-codoped carbon materials with Cu-N$_x$ active sites (Cu-NC) obtained by pyrolyzing porphyrin metal organic frameworks revealed higher ORR activity, which had more positive onset potential and half-wave potential than commercial Pt/C catalyst [22]. However, other Cu-based materials such as Cu compounds, Cu complexes or Cu-based nanoparticles displayed low catalytic activities for ORR [14,23–26]. The onset potential for ORR over the encapsulated Cu nanoparticles with N-doped carbon shells (Cu@N-C) was 110 mV lower than commercial Pt/C catalyst [27]. The Cu$_{2-x}$S nanoplates supported on reduced graphene oxide exhibited onset potential of 0.90 V (vs. RHE) and half-wave potential of 0.82 V (vs. RHE). There are some gaps compared with those of commercial Pt/C [28]. Moreover, the onset potential and half-wave potential of TiO$_2$-grafted copper assembly deposited on multiwalled carbon nanotubes (CNTs@TiO$_2$–ZA–[Cu(phen^{NO2}) (BTC)]) were about 70 mV lower than those of commercial Pt/C catalyst [29]. Therefore, the design and fabrication of Cu-based electrocatalysts with high performance and durability for ORR are desirable to facilitate the commercial use of non-noble metal electrocatalysts in the clean energy.

Based on the above considerations, we directly synthesized the pony-size Cu nanoparticles confined in N-doped mesoporous carbon (Cu@C-N) by chemical vapor deposition (CVD) method. The prime feature of our work is the deposition of copper by subliming Cu atoms in the CVD process without additional reductant. The

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floating Cu atoms with flexible mobility can fully contact with the porous support materials with highly accessible surface. Furthermore, orderly mesoporous opening structure can prevent the aggregation of Cu nanoparticles. The metal-support interaction not only stabilizes the dispersed Cu nanoparticles but also enhances the catalytic performance of Cu. The obtained Cu@C-N exhibited impressive catalytic performance for ORR with a half-wave potential of 0.84 V, 10 mV higher than 20 wt % Pt/C-JM catalyst in alkaline media.

2. Experimental

2.1. Preparation of N-doped mesoporous carbon materials

The N-doped mesoporous carbon was prepared through a typical nanocasting procedure. In a typical synthesis, 800 mg glucose and 40 mg urea were dissolved in 30 mL deionized water, and then 200 mg of SBA-15 powders as templates were added. The mixture was stirred at room temperature in open air to evaporate the solvent. The resulting dry powders were heated to 900 °C at a heating rate of 2 °C $\min^{-1}$, and held at 900 °C for 4 h in a tube furnace under nitrogen atmosphere. The products were finally obtained by etching the silica templates with 10 wt % HF solution for 24 h at room temperature and named as mesoporous N-doped carbon (C-N).

2.2. Preparation of Cu@C-N

The C-N supported pony-size Cu nanoparticles were synthesized by CVD in a tube furnace using copper acetate as copper source and mesoporous C-N as the supports. In a typical preparation process, the high temperature resistant quartz glass plates ($SiO_2 > 99.999\%$) were cleaned successively in deionized water, anhydrous ethanol and acetone by ultrasound for 15 min in each kind of media before they were used. Then, a clean quartz plate was vertically immersed into saturated acetate copper solution for 24 h, followed by drying at 60 °C for 15 min in an oven. The resulting quartz plate with acetate copper was laid on the porcelain boat containing the as-synthesized mesoporous C-N powders on the bottom of it and then was covered with another porcelain boat to construct a small reactor. The whole reactor was heated to 1000 °C at a heating rate of 15 °C $\min^{-1}$ and calcined in argon atmosphere with a flow rate of 230 sccm at 1000 °C for 90 min. The resultant material was denoted as Cu@C-N. Furthermore, the pony-size Cu nanoparticles confined in mesoporous carbon without nitrogen (Cu@C) were also prepared using the same method.

2.3. Electrochemical measurement

A standard three-electrode cell connected to a CHI 760C electrochemical workstation was employed. Glass carbon rotating disk electrode (RDE, 5.0 mm) or rotating ring-disk electrode (RRDE, 5.6 mm) loaded with the catalysts is used as working electrode, an Ag/AgCl, KCl (3 M) electrode as the reference electrode and a Pt electrode as the counter electrode. For preparing the working electrodes, 10 mg catalysts were dispersed in 1.28 mL alcohol solution containing 30 μL Nafion (5 wt %) solution by sonication to form a homogeneous suspension. The obtained suspension of 15 μL was pipetted onto a polished glassy carbon electrode surface and dried at room temperature, leading to a mass loading of 0.47 mg cm^{-2}. Commercially available 20 wt% Pt/C catalyst purchased from Jonson Matthey Company (Pt/C-JM) was used to prepare Pt/C working electrode with a mass loading of 20 $\mu g_{Pt}\ cm^{-2}$ for comparison. The ORR catalytic activities of the as-prepared catalysts were investigated by cyclic voltammetry (CV), rotating disk electrode (RDE) and ring-rotated disk electrode (RRDE) techniques in 0.1 M KOH solution. The ORR current is obtained by deducting the current measured in N_2-saturated electrolyte from the current measured in the O_2-saturated electrolyte. All the reported potentials have been calibrated to the RHE potentials ($E_{RHE} = E_{Ag/AgCl} + 0.967$ V in 0.1 M KOH solution).

The HO_2^- percentage and the corresponding number of electron transferred during the ORR were determined by the following equations [30–32]:

$$\%HO_2^- = 200 \times \frac{I_R/N}{I_D + I_R/N} \qquad n = \frac{4I_D}{I_D + I_R/N}$$

where, I_R and I_D are the ring currents and disk currents, respectively. N is current collection efficiency of the Pt ring, which was determined to be 0.37 from the reduction of potassium ferricyanide ($K_3Fe[CN]_6$) [32] (Fig. S1).

Electrochemical impedance spectroscopy (EIS) experiments were performed in O_2-saturated 0.1 M KOH solution. The corresponding Nyquist diagram for the as-prepared catalysts was obtained in a frequency range of 10^5–10^{-2} Hz with the sinusoidal potential amplitude of ±10 mV.

2.4. Characterization

X-ray diffraction patterns (XRD) were obtained by a Bruker D8 Advance Powder X-ray diffractometer with Cu-Kα radiation source (40 kV, 40 mA). The low-angle XRD patterns were collected in the continuous scanning mode from $2\theta = 0.5°–5°$ with a scan rate of 1°/min, step size of 0.01° and dwell time (the time required for each step) of 0.6 s. The high-angle XRD pattern was carried out from $2\theta = 10°–80°$ with a scan rate of 5°/min, step size of 0.01° and dwell time of 0.12 s. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were recorded on a JEM-2010 transmission electron microscope using an accelerating voltage of 200 kV. The catalyst morphology was observed with a field-emission scanning electron microscope (FE-SEM, Hitachi ST-4800). The porous structure of the prepared materials was analyzed at 77 K on a Quadrasorb Evo surface area and porosity analyzer. Raman spectra were obtained on a GX-PT-1500 (150) instrument with laser excitation energy of 532 nm. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on the instrument of Thermo ESCALAB 250 by using Al-Kα radiation and C 1s (284.8 eV) was used as a reference to correct the binding energy. The metal content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II). By heating treatment of Cu@C-N (20 mg) at 550 °C for 3 h with a heating rate of 2 °C $\min^{-1}$ in air atmosphere, residual species CuO were obtained and then dissolved completely in hydrochloric acid solution. The weight percentage of Cu in Cu@C-N is 3.27 wt %.

3. Results and discussion

The Cu nanoparticles-based electrocatalysts were synthesized mainly by wet chemical reduction method with the reducing agent [14,23], solvothermal method [24,25] and thermal treatment method [26]. However, these methods are difficult to prevent the occurrence of agglomeration phenomenon and control the well dispersion of active Cu species on supports, which often affect the catalytic activity and stability of the catalyst. In this work, the mesoporous C-N-supported pony-size Cu nanoparticles (Cu@C-N) were prepared by CVD as shown in Fig. 1. In the preparation process, the copper acetate attached to quartz plate as the copper source directly decomposed into metallic copper and other volatile components such as CH_4, CO_2, etc. [33] at 240 °C. The resulted