



Catalyst nanoarchitecturing *via* functionally implanted cobalt nanoparticles in nitrogen doped carbon host for aprotic lithium-oxygen batteries



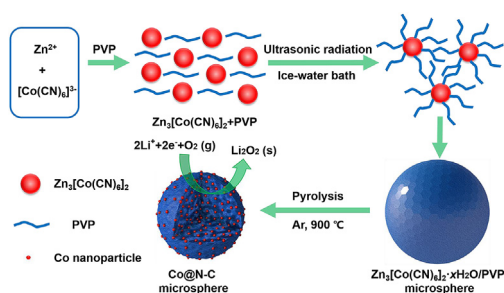
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HIGHLIGHTS

- Functionally cobalt nanoparticles are implanted in N-doped carbon host.
- The Co nanoparticles induce graphitic carbon form a porous network structure.
- The Co@N-C is employed as cathode material for Li-O₂ battery.
- The cathode shows improved discharge capacity and superior cycling stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Nonaqueous Li-O₂ batteries are of great interest because of their high theoretical energy density, and a stable porous cathode plays a vital role in electrochemical performance of Li-O₂ batteries. Herein, catalyst nanoarchitecturing *via* functionally implanted cobalt nanoparticles in N-doped carbon host is fabricated by an ultrasonic method combined with controlled calcination process and served as an effective electrocatalyst for Li-O₂ batteries. The synthesized catalyst holds a three-dimensional porous network structure, which could offer numerous active sites and provide the channels for mass transfer. When employed as an oxygen electrode, the Li-O₂ battery shows improved discharge capacity of 3862 mA h g⁻¹ at a current density of 0.1 mA cm⁻² and superior cycling stability up to 40 cycles with a limited capacity of 500 mA h g⁻¹, owing to the porous carbon substrate with highly graphitic and better catalytic activity of implanted Co nanoparticles. The N-doped carbon with a high degree of graphitization is obtained by a catalytic pyrolysis method and Co as main catalyst also give a good reference for future design of efficient catalysts for electrochemical application.

1. Introduction

Li-O₂ batteries have attracted considerable interest due to its ultrahigh theoretical energy density, low cost and environmental-friendly [1]. However, there still remain enormous challenging issues that must be addressed before the practical use of Li-O₂ batteries, one of the biggest hurdles is serious limitations in kinetics, which results in the

large overpotential, poor rate capability and cycling stability [2–4]. The electrochemical reactions in Li-O₂ batteries are closely related to the reversibility of lithium peroxide (Li₂O₂) formation and decomposition on the cathode [5–7]. As the main site that the complex reactions occurred during charge-discharge process, the electrochemical performances of Li-O₂ batteries strongly depend on their catalyst material, which determined the Li-ion transfer kinetics, electron conduction and

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the growth of discharged product [8]. Therefore, the rational design of bifunctional catalyst toward ORR and OER with high catalytic activity is urgently desirable for Li-O₂ batteries.

In recent years, transition metal based nitrogen-carbon composites especially based on earth-abundant elements such as Fe, Co and Ni, as representative of hybrid which consists of metal and carbon-based materials were regarded as effective catalysts for ORR [9–11], OER [12,13], and Li/Na-O₂ batteries [14–17] due to their high activity, low costs and durability. Metal based nitrogen-carbon catalysts contain both single metal or their compounds and N-doped carbon, and the samples are generally prepared by thermolysis of transition metals and ligated organic compounds containing nitrogen [18,19]. Generally, non-precious transition metals (e.g., Co, Ni, etc.) are always present superior catalytic activity especially toward OER compared with other compounds due to their good conductivity and promising catalytic activity [20,21]. However, there are still some challenges to optimize the catalytic activity of these catalysts by reasonable design due to the agglomeration effect of nanoscale particles as well as its poor chemical stabilities [22]. It inspires us that the highly active metal catalyst nanoparticles combine with a conductive porous structure may be a viable option. As far as we know, porous carbon-based materials have been as promising alternatives as electrocatalysts for Li-O₂ batteries due to its high specific surface area, good conductivity and low cost. Furthermore, heteroatoms especially N atoms has been introduced into carbon materials to further produce more active sites and enhance ORR activity due to improved adsorption of O₂ and decomposition of peroxide intermediate [23,24]. Tan et al. designed a biphasic nitrogen-doped cobalt@graphene, combined with a flexible stable porous electrode architecture, and the electrode exhibits much improved electrocatalytic properties for Li-O₂ battery [25]. There is also some work using nickel cobaltate nanoparticles on N-doped graphene or carbon fibers, and delivers excellent catalytic activities [26,27]. To achieve lower the overpotential and enhance the activity of catalysts, we design a porous cathode which combine the highly active non-precious metal with a conductive porous carbon-based materials as bifunctional catalysts for Li-O₂ batteries. It was generally believed that transition-metal-based N-doped carbon shows promising alternatives due to the high catalytic activity generated from metal-N_x structure and the synergistic effects of metal particles and N-doped carbon [20,23].

Herein, functionally cobalt nanoparticles implanted in N-doped carbon host was obtained through a simple ultrasonic method followed by controlled calcination process at Ar atmosphere. In the pyrolysis procedure, well-distributed Co nanoparticles which covered by graphitic carbon can be formed in the three-dimensional porous N-doped carbon network, labelled Co@N-C microspheres. The prepared material presents unique architectures with high bifunctional catalytic activity. When used in Li-O₂ batteries, the Co@N-C microspheres cathode showed lower overpotential together with better cycling stability than Super P. The outstanding electrochemical performance could attributed to the hierarchical porous structure of microsphere host as well as the synergistic effect of Co nanoparticles, Co-N_x coordination and nitrogen-doped carbon. This composite is promising nonprecious metal catalyst for Li-O₂ batteries.

2. Experimental

2.1. Preparation of Co@N-C microspheres

Co@N-C microspheres was prepared via a simple ultrasonic method followed by catalytic pyrolysis method according to the literature with little modification [28]. 1.32 g of Zn (ac)₂·2H₂O and 11.12 g of PVP (K30) were dissolved in 200 mL of distilled water, 1.33 g of K₃[Co(CN)₆] in 200 mL H₂O was added into the above solution dropwise under the magnetic stirring and ultrasonic radiation in an ice-water bath. Then the mixture was aged for 24 h, and the resulting white product was collected and washed with water several times. After

freeze-drying for 12 h, the Co@N-C was obtained by annealing the precursor at 900 °C for 6 h under Ar flow with a ramp rate of 5 °C min⁻¹, the product was cooled naturally after the heat treatment. The as-prepared samples were ground into powders before chemical and electrochemical characterization.

2.2. Materials characterization

Thermogravimetric analysis (TGA) was performed by using NETZCH STA449F3 from 30 to 1000 °C under N₂ flow with a heating rate of 10 °C min⁻¹. The X-ray diffraction pattern (XRD) was characterized by a Rigaku3014 equipped with Cu K α radiation. The morphology, particles sizes, and elemental analyses of the catalyst and the electrodes before and after discharge-charge were observed using Field-emission scanning electron microscopy (FESEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, Tecnai G2 20ST). Energy Dispersive X-ray spectroscopy (EDX) was performed to identify the elements distribution on the surface of the samples. Raman spectra were measured with a Jobin-Yvon LabRAM HR-800 Raman spectrometer. Meanwhile, nitrogen adsorption/desorption measurements were carried out on a Quantachrome instrument (Quabrorb SI-3MP) at 77 K, and the pore size distribution was measured by the adsorption branch of the isotherms based on the non-linear density functional theory (NLDFT). Additionally, the bond characteristics were determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB250xi).

2.3. Electrochemical measurements

The O₂ electrodes were prepared by mixing Co@N-C microspheres, polyvinylidene fluoride (PVDF) and Super P under the mass ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP) dispersant to form homogeneous slurry. The mixture was spread onto a Ni foam collector, and then drying at 60 °C for 12 h to remove residual solvent. The mass loading density of the catalysts was about 1 mg cm⁻². A Li foil was used as the reference electrode, a glass fiber separator (GF/D, Whatman) was separated from the cathode and reference electrode. And the organic electrolyte was contained a solution of 1 M lithium bis(trifluoromethane) sulfonimide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) and stored in a bottle containing 3 Å molecular sieves inside. The Li-O₂ batteries were assembled in an Ar-filled glove box (MIKROUNA-Universal 2440/750, H₂O < 1 ppm). The electrochemical tests were carried out using CR2032 coin cells, whose cathode side contained 17 machine-drilled holes with a diameter of 1.0 mm for oxygen access. The obtained coin-cells were transported to an oxygen chamber which including the cell holder, and purged with a flow O₂ for 1 h to avoid the negative effects from air humidity and CO₂. The batteries were rested at least 12 h before test. The galvanostatic discharge-charge tests were performed within a potential range of 2.2–4.5 V at various current densities in oxygen atmosphere under a LAND CT2001A testing system at room temperature. The specific capacity in this study were calculated from the total mass of the catalyst, PVDF and carbon black in the cathodes. The cyclic voltammetry (CV) was collected by an electrochemical measurement system (PARSTAT 2273) at a sweep rate of 0.2 mV s⁻¹ from 2.0 to 4.5 V.

3. Results and discussion

The strategy for the fabrication of the Co@N-C microspheres is illustrated in Scheme 1. First, the formation of uniform Zn₃[Co(CN)₆]₂·xH₂O/PVP nanoparticles was based on the reaction between the Zn²⁺ and [Co(CN)₆]³⁻, as well as Zn₃[Co(CN)₆]₂ crystal nuclei was capped by PVP. And then the nanoparticles aggregated together to form Zn₃[Co(CN)₆]₂·xH₂O/PVP microspheres under ultrasonic conditions [29]. The obtained precursor was calcined under a controlled carbonization treatment, and the thermal decomposition process of precursor

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