Synthesis of M (Fe$_3$C, Co, Ni)-porous carbon frameworks as high-efficient ORR catalysts

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ABSTRACT

The rational construction of non-precious metals with carbonaceous material has attracted tremendous research attention with the aim to reduce the plethoric cost of platinum for catalyzing the oxygen reduction reaction (ORR). Herein, we synthesized a highly hierarchical nanostructure framework containing metal-carbon nanotubes anchored in metal embedded porous carbon spheres (M-CNTFs) and found it has similar ORR performance to that of commercial Pt-based electrocatalysts. Based on the unique hierarchical architecture, an effective platform was constructed to explore physic-chemical insights while providing guidance to search high-efficient ORR catalysts. Electrochemical measurements show that Co-CNTFs, Fe$_3$C-CNTFs, and Ni-CNTFs prefer to proceed through a 4e$^-$ pathway, 2e$^-$ and 4e$^-$ mixed pathways, and a 2e$^-$ pathway, respectively. Furthermore, Co-CNTFs were found to perform better than a commercial Pt-based electrocatalyst in ORR due to its lower overpotential, excellent methanol tolerance, and superior durability. In order to understand the effects of different transition metal centers on the electrocatalytic performance of M-CNTFs, corresponding calculations were performed based on the density functional theory (DFT). Results reveal that the metal active sites and hydrophilic property of the metal-carbon system play an important role in enhancing the electrocatalytic ability, which is significant for further research on (or synthesis of) excellent catalytic materials for ORR.

1. Introduction

Developing alternative catalytic materials with high-efficiency oxygen reduction reaction (ORR) activity is of great significance for next-generation energy conversion and storage technologies, including rechargeable metal-air batteries and fuel cells [1–5]. However, the state-of-the-art catalytic performance of Pt-based material still suffers enormously from limited supply, sluggish electron transfer kinetics, high cost, and poor durability [6–8]. To get past these bottlenecks, several studies have been reported to replace Pt-based catalysts with transition metals, metal oxides, carbides/nitrides, and nanocarbons for boosting ORR performance [9–13]. Yet, the catalytic efficiencies of those replacements are still inferior to commercially Pt-based catalysts owing to self-accumulation and intrinsically poor electrical conductivity [14]. Transition metal-based electrocatalysts have attracted considerable attention as a promising candidate due to their low cost, high chemical stability, exotic electronic structure, and high electrocatalytic properties, while conductive carbon materials have been commonly considered as a good supporter to enhance the structural stability and conductivity of catalysts [15,16]. Dodelet et. al. produced a microporous carbon supported iron-based catalyst, in which the catalytic efficiency is comparable to that of Pt-based cathode [17]. In addition, Kwon et al. reported an electrospun Co-CNF catalyst as an efficient catalyst for ORR [18]. However, efficient development and rational design strategy of desired high-performance electrocatalysts are still limited, and the origins behind their remarkable catalytic efficiency remain elusive.

Therefore, it is important to rationally design and construct active sites on carbon-supported transition metal-based ORR catalysts to obtain comparable or superior performance to that of noble metals [19]. A platform with similar hierarchical architecture is also a vital prerequisite to profoundly understanding the effects of different transition metals on catalytic performance. Recently, metal-organic coordination crystals, formed by metal ions and rigid organic molecules into a periodically porous architecture, have proven to be appealing precursors for the construction of carbon-supported metal hybrids and

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have attracted much attention for designing electrocatalysts [20–22]. Unfortunately, metal-organic coordination crystal-derived nanocomposites are mostly pyknotic, and possess limited catalytic active sites, which are unfavorable for electron or ion transport and catalytic activity [23]. This encouraged us to develop a more efficient approach for fabricating electrocatalysts with a hybrid architecture, which combines a hierarchical nanoarchitecture and robust framework to expose more catalytic active sites on the surface.

Herein, we controlled synthesized nanospheres of metal (iron, cobalt, and nickle)-glycerate coordination crystals through the assembly of metal ions and glycerinum, followed by oxidative self-polymerization of the organic ligands during hydrothermal treatment. The metal-glycerate coordination crystals were found to act as a self-template to directly anchor upright M-carbon nanotubes through porous M embedded carbon frameworks (M-CNTFs), in which 3D interconnected CNT networks served as a scaffold to expose catalytic active sites and a bridge for electron and ion transport. The hybridization of porous carbon with framework facilitated the fabrication of hierarchical nanoarchitectures, eventually generating abundant interconnected meso-/micropores without deteriorating the electron pathway. As expected, a faultless platform was constructed to investigate the effects of different active sites on catalytic performance, and experimental observation revealed that Co-CNTFs, Fe$_3$C-CNTFs, and Ni-CNTFs proceeded through a 4e$^-$ pathway, 2e$^-$ and 4e$^-$ pathways, and a 2e$^-$ pathway, respectively. Corresponding density functional theory (DFT) calculations were considered to provide a reasonable explanation for the chosen pathways. Based on the results, we propose a reasonable design that offers physic-chemical insight and a basis for exploration of novel catalysts as functional materials in potential ORR applications.

2. Result and discussion

The crystal structure and phase purity of the as-prepared M-CNTFs samples were first investigated by powder X-ray diffraction (XRD) (Fig. 1). Apart from the diffraction peak at about 26.2° assigned to the (002) plane of graphitic carbon, the rest diffraction peaks in Fig. 1a could be indexed to Fe$_3$C species (JCPDS 35-0772), suggesting the successful conversion of the Fe$_3$C-CNTFs from Fe-glycerate precursor after thermal treatment. Different from the Fe-glycerate precursor, the Co-glycerate and Ni-glycerate precursors converted to metallic cobalt and metallic nickel, respectively. As literatures reported, in the transition metals (iron, cobalt, nickel) and graphite carbon system, the evolution and behavior of their carbides under high temperature could be classified into two categories, nonstoichiometric carbides and stoichiometric carbides. In our work, nickel and cobalt form only nonstoichiometric carbides M$_x$C with graphite carbon, while iron form stoichiometric carbides. Because that the nonstoichiometric carbides have lower Curie temperature than metal itself, nonstoichiometric carbides (Ni$_x$C, Co$_x$C) further transferred to metallic cobalt and metallic nickel. However, Fe$_3$C still stable under high temperature. These differences certainly reflect the difference in the interactions between metal and carbon, which are related to the number of 3d-electrons in metals [24,25]. X-ray photoelectron spectroscopy (XPS) measurements (Fig. S1) were further confirm the formation of ferric carbides and the absence of metallic iron in Fe$_3$C-CNTFs, and the metallic cobalt and metallic nickel in Co-CNTFs and Ni-CNTFs, respectively. The morphology of these prepared M-CNTFs was characterized by field-emission scanning electron microscopy (FESEM). Fig. 1b, c, and d show the representative FESEM images of Fe$_3$C-CNTFs, Co-CNTFs, and Ni-CNTFs, respectively, which possess spherical morphology with uniform size, and abundant nanoparticles (bright dots) implemented on the surface of each sphere, providing a faultless platform to compare ORR activity.

The detailed morphology and microstructures of the synthesized metal-glycerate coordination crystal precursors and their corresponding M-CNTFs were further examined with FESEM and TEM. Fig. S2 present the representative images of the three different glycerate precursors, Fe-glycerate, Co-glycerate, and Ni-glycerate, respectively. It is clear that all precursors exhibit spherical morphology with smooth surfaces and average diameters of around 220, 300, and 330 nm, respectively. The size and spherical shape of the precursors were well retained after thermal treatment for 15 min (Fig. 2a, b, and c), while the surfaces of the particles became much rougher. Interestingly, many nanoparticles (black dots) were implemented on the surface of each sphere, and numerous nanoparticles with different sizes were homogenously embedded within the carbon framework (grey matrix), meanwhile, several short CNTs supporting the nanoparticles, and extruding from the surface of sphere, which created an interconnected bridge structure and sufficient pathways to facilitate mass transfer [26]. Zoom-in observations reveal that the Fe$_3$C (Fig. 2d), Co (Fig. 2e), and Ni (Fig. 2f) nanoparticles were clad together by a graphene shell. The HRTEM images of the dark core display clear inter-planar distances of 0.201 (Fig. 2g), 0.205 (Fig. 2h), and 0.203 (Fig. 2i) nm, which are in accordance with Fe$_3$C (301), Co (111), and Ni (111), respectively. Meanwhile, the clear distinct lattice fringes with a spacing of 0.34 nm in each image corresponds to the (002) plan of graphitic carbon, suggesting that such framework could play an important role in hosting stable ORR active sites *via* enhancing electronic conductivity and corrosion resistance of carbon [27].

Considering the importance of specific surface area and pore structure for ORR, N$_2$ adsorption/desorption isotherms were used to
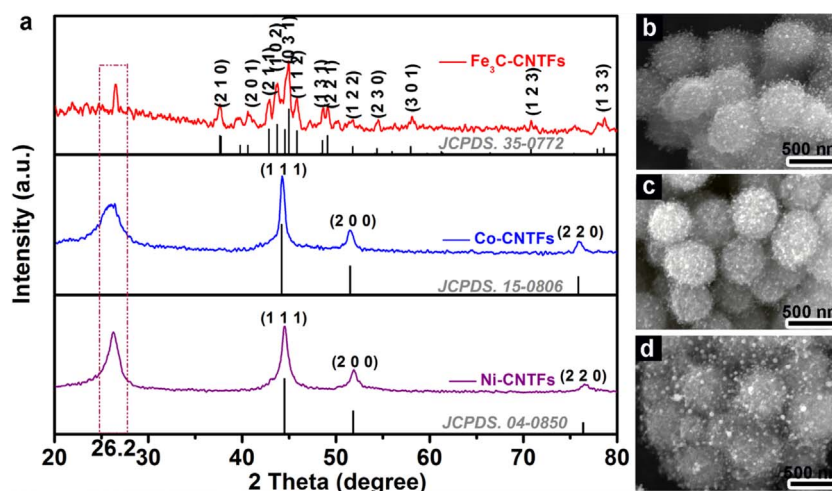

Fig. 1. a) Experimental and simulated XRD patterns and FESEM images of (b) Fe$_3$C-CNTFs, (c) Co-CNTFs, (d) and Ni-CNTFs obtained at 650 °C after 15 min of thermal treatment.