Porous yolk–shell microspheres as N–doped carbon matrix for motivating the oxygen reduction activity of oxygen evolution oriented materials

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Received 6 April 2017, revised 29 May 2017
Accepted for publication 7 June 2017
Published 16 August 2017

Abstract

It is highly challenging to explore high–performance bi-functional oxygen electrode catalysts for their practical application in next-generation energy storage and conversion devices. In this work, we synthesize hierarchical N–doped carbon microspheres with porous yolk–shell structure (NCYS) as a metal-free electrocatalyst toward efficient oxygen reduction through a template-free route. The enhanced oxygen reduction performances in both alkaline and acid media profit well from the porous yolk–shell structure as well as abundant nitrogen functional groups. Furthermore, such yolk–shell microspheres can be used as precursor materials to motivate the oxygen reduction activity of oxygen evolution oriented materials to obtain a desirable bi-functional electrocatalyst. To verify its practical utility, Zn–air battery tests are conducted and exhibit satisfactory performance, indicating that this constructed concept for preparation of bi-functional catalyst will afford a promising strategy for exploring novel metal–air battery electrocatalysts.

Supplementary material for this article is available online

Keywords: oxygen reduction reaction, oxygen evolution reaction, bi-functionality

(Some figures may appear in colour only in the online journal)

1. Introduction

The practical application of next-generation energy storage and conversion devices calls for the development of high-performance bi-functional oxygen electrode catalyst. One constructed concept includes combining oxygen reduction oriented materials with oxygen evolution oriented materials. Although Pt and Pt-based materials exhibit relatively high activity toward oxygen reduction reaction (ORR), their large-scale applications are significantly hindered due to their high cost and poor durability [1–5]. To get past these bottlenecks,
great efforts have been made to explore efficient, durable and inexpensive metal-free catalysts as alternatives for boosting ORR. Compared to Pt-based catalysts, metal-free catalysts possess notable advantages, such as low cost, rich resources and comparable electrocatalytic activity.

Recently, nitrogen-doped carbons such as carbon nanotubes (CNTs) [6, 7], graphene [8, 9] and mesoporous carbons [10–12], have attracted significant attention as a kind of efficient metal-free electrocatalyst, because the electron donation from nitrogen to adjacent carbon resulted in disordered carbon nanostructures and higher surface polarity, which were significant for ORR activity [6, 8, 13–15]. More specifically, the enhanced electrocatalytic property can be ascribed to the net positive charge on carbon atoms derived from the higher electronegativity of nitrogen dopants [6]. The charge redistribution induced from nitrogen doping changes the chemisorption mode of O2 so as to effectively weaken the O–O bonding. In addition, the positively charged carbon atoms also make it easy to obtain electrons from the anode, thus accelerating the ORR process [6, 7, 16]. However, whether the active sites attributed to the nitrogen dopant could efficiently play a role in the oxygen reduction largely depended on the construction features.

Materials with core–shell structure are interesting systems for enhancing utilization of active sites. Yolk–shell structure, a special extension of core–shell systems, demonstrated a distinctive core@void@shell configuration with a solid core, an interspace between core and shell, and a (in most cases) porous shell [17, 18]. The distinct structural characteristic made them promising candidates for highly active catalysts: (i) high specific areas with plentiful active sites for ORR process offered by their nanocrystal subunits; (ii) electrochemical kinetics enhanced by the short diffusion lengths; and (iii) catalytic stabilities benefited by structural integrity [17, 19]. Two essential routes were used to fabricate yolk–shell structures: a bottom–up route in an inside to outside order [20–24]; a top–down route, also called pre-shell post-core approach [25–27]. Basically, yolk–shell particles have mostly been produced through templating methods with core–shell materials as building blocks [28, 29] which confined their scalability and compatibility with practical manufacturing processes.

Herein, hierarchical N–doped carbon microspheres with porous yolk–shell structure (NCYS) as an efficient metal-free electrocatalyst were firstly synthesized through a template–free route. The resultant material exhibited superior oxygen reduction activity as well as stability in both alkaline and acidic conditions. The excellent activity can be attributed to the porous yolk–shell structure and abundant nitrogen functional groups. Furthermore, NCYS can be used as a precursor material to combine with oxygen evolution oriented materials to obtain a desirable bi-functional electrocatalyst. Co3O4 nanoparticles, a material with high oxygen evolution reaction (OER) but low ORR activity by itself, were served as an instance and controlled nucleated on the carbon matrix of NCYS (Co3O4@NCYS). As a bi-functional catalyst, the Co3O4@NCYS exhibited high activity with a lower over-voltage between ORR and OER compared to other hybrid materials consisting of Co3O4 and carbon materials. It is worth noting that Co3O4@NCYS was also applied for a Zn-air battery and exhibited satisfactory performance. This constructed concept afforded a promising strategy for developing a low cost but highly efficient bi-functional catalyst to be applied in novel metal–air batteries.

2. Experimental section

2.1. Synthesis of NCYS, Co3O4 and Co3O4@NCYS

The preparation of the NCYS catalyst involved two steps: (1) fabrication of polypyrrole (PPy) spheres according to a reported method [30, 50] (2) pyrolysis of the prepared materials at a temperature of 900 °C for 2 h under flowing Ar (200 sccm) atmosphere. For synthesis of Co3O4@NCYS, 1.2 ml of 0.2 M Co(Ac)2 aqueous solution was added to 24 ml of 4 mg ml−1 NCYS anhydrous ethanol suspension liquid, then 1.2 ml of deionized water was pipetted into the mixture at RT. After that, the reaction was maintained at 80 °C by oil bath with magnetic stirring for 10 h. Next, the product derived from the first step underwent a hydrothermal reaction in a 40 ml autoclave at 150 °C for 3 h. With centrifugation and washing by ethanol and water, the resulting Co3O4@NCYS material was finally acquired. A free Co3O4 nanoparticle was made with the same method as making Co3O4@NCYS without the addition of any NCYS [51].

2.2. Physical characterization

SEM (SU8010, Japan) and FETEM (FEI Tecnai G2 F20 S-TWIN TMP, Hongkong) were used to observe the morphology of these samples. The crystal structure of the samples was examined with XRD performed on a Rigaku D/ max-2000PC diffractometer with Cu KR radiation. Element binding analysis was conducted by XPS (VG ESCALAB MKII). The specific surface area and pore size distributions were measured by nitrogen sorption measurements at 77 K (Quantachrome, QuadaSorb SI) calculated by Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) method, respectively.

2.3. Electrochemical measurements

Electrochemical measurements were performed using a Pine conventional three-electrode electrochemical system (Pine Instrument Company, USA) with Ag/AgCl (4 M KCl) as the reference electrode and platinum wire as the counter electrode. A rotating disk electrode (RDE) with a catalyst-coated glassy carbon disk (diameter of 5.0 mm, geometric surface area of 0.196 cm2) served as the working electrode for evaluating ORR and OER activity. The catalyst ink was prepared by mixing 8 mg catalysts with 350 ul ethanol and 95 ul Nafion solution (5 wt%) by ultrasonic vibration for 1 h. 7 ul of catalyst ink was then pipetted onto a glass carbon surface, resulting in a loading of 0.64 mg cm−2. Catalytic activity of Pt/C powders (20 wt%, Johnson Matthey) was also investigated with a catalyst loading of 0.15 mg cm−2 for
Aqueous 0.1 M KOH electrolyte was saturated with N\textsubscript{2}/O\textsubscript{2} by bubbling N\textsubscript{2}/O\textsubscript{2} for 30 min. The CV tests were performed with a 50 mV s\textsuperscript{-1} scanning rate and RDE tests were conducted in O\textsubscript{2}-saturated electrolyte at 400, 625, 900, 1225, 1600, 2025, 2500 rpm with a sweeping speed of 10 mV s\textsuperscript{-1}. Electron transfer numbers were calculated by Levich equations:

\[ \frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{(B\omega^{1/2})} \]  
\[ B = 0.62 n F \frac{C_0(D_0)^{2/3} \nu^{-1/6}}{\pi^{1/2}} \]  

In these equations, \( j \), \( j_L \) and \( j_k \) are the measured current density, the diffusion-limiting current density and kinetic current density; \( \omega \) is the speed of the rotation disk \( (\omega = 2\pi N, N \text{ is the linear rotation speed}) \); \( n \) represents the electron transfer number gained by per O\textsubscript{2} molecule; \( F \) is the Faraday constant \( (96.485 \text{ C mol}^{-1}) \); \( D_0 \) is the diffusion coefficient of O\textsubscript{2} in 0.1 M KOH electrolyte \( (1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \); \( C_0 \) is the bulk concentration of O\textsubscript{2} dissolved in the electrolyte \( (1.2 \times 10^{-6} \text{ mol cm}^{-3}) \); \( \nu \) is the kinetic viscosity of the solution \( (0.01 \text{ cm}^2 \text{ s}^{-1}) \). To examine the performance of electrocatalytic OER, LSVs of the catalysts were conducted with a sweep rate of 10 mV s\textsuperscript{-1} at a rotating rate of 1600 rpm. For the button Zn-air battery test, the as-prepared catalyst ink was uniformly coated onto carbon paper for preparing the air electrode with mass loading of 1 mg cm\textsuperscript{-2}. A Zn plate was used as the anode and the electrolyte was 6 M KOH aqueous solution with 0.2 M zinc acetate. The galvanostatic discharge—charge cycling (5 min discharge and then 5 min charge and that cycle repeated) was carried out with a LAND testing system. The green LEDs were commercially available.

3. Results and discussion
3.1. Microstructures and characterization of the NCYS catalyst
To clearly illustrate the oxygen reduction process of NCYS in alkaline and acidic solution, a distinct schematic (figure 1(a)) was presented which vividly demonstrated the NCYS with unique yolk—shell structure. The preparation of the NCYS catalyst involved fabrication of polypyrrole (PPy) spheres and the following carbonization. The morphology of PPy spheres is shown in supplementary figure S1 available online at stacks.iop.org/NANO/28/365403/mmedia. Since PPy was obtained by layer-by-layer polymerization of pyrrole monomer, the yolk—shell structure can already be seen in PPy spheres (supplementary figure S1(b)). Then, the yolk—shell structure experienced further shrinkage during carbonization and became more evident. Figure 1(b) displayed the representative scanning electron microscopy (SEM) image of as-synthesized NCYS to gain the real morphology. Well-dispersed microspheres with uniform size of about 800 nm were obtained, and a yolk—shell structure can be clearly seen from the image of a cracked microsphere with exposed cores inside (with an average scale of 500 nm). Well-defined yolk—shell structure is also indicated in the transmission electron microscopy (TEM) image in figure 1(c), and the image enlarged from the yolk—shell sphere exhibited shells with a thickness of about 50 nm. It is worth mentioning that the carbon shell framework was porous with a pore size of ~20 nm, which provided sufficient pathways to facilitate mass transfer. The yolk—shell structure and chemical composition were further revealed by the dark-field scanning transmission electron microscopy (HAADF—STEM) elemental mapping images of C, N, shown in figures 1(d)—(f). These two elements were well uniformly dispersed on the cores and shells of the NCYS.

To elucidate the element bonding configurations and active sites derived from N species, x-ray photoelectron spectroscopy (XPS) measurement was conducted. As shown in figure 2(a), it was evident that the peaks of Cl\textsubscript{1s}, N\textsubscript{1s}, O\textsubscript{1s} all existed in the survey region of 200—800 eV. The high-resolution C 1s spectrum (figure 2(b)) revealed the presence of sp\textsuperscript{3} C (284.7 eV), C—N (285.2 eV), C—O/C=N (286.3 eV) and C=:O (289.2 eV) [16, 30, 31]. Further, the complex N\textsubscript{1s} spectra in figure 2(c) shows four deconvolved contributions.
assigned to the pyridinic N (398.7 eV), pyrrolic N (400 eV), graphitic N (401.2 eV), and oxidized N (403.8 eV) [32, 33], consistent with the presence of the C–N–C peak in the C1s spectrum. The content of doped nitrogen in the NCYS was measured to be ∼3.24 at.% and all of these N species were believed to be beneficial to the generation of catalytic effective sites except that the contribution of oxidized N was uncertain [33, 34]. Therefore, a synergetic catalytic effect may be generated by the active structures and thus further enhance the ORR activity.

The surface area and pore volume of NCYS were obtained through N2 adsorption/desorption measurement. The BET surface area was 300.3 m2 g−1, which provided a high density of active sites for redox reactions and the BJH pore volume was 0.19 cm3 g−1 which favored the mass transfer. The isotherm curve in figure 2(d) was type IV isotherms with an obvious hysteresis loop at a relative pressure P/P0 range of 0.4 to 1, indicating the presence of mesopores and micropores within NCYS [18]. Additionally, the pore-size distribution of NCYS was centered at 2.1 nm. The high surface area and nanoporous size would be positive for the ORR due to the facilitated O2 diffusion and largely exposed catalytic active sites benefited from its high electrode–electrolyte contact area.

3.2. Catalytic oxygen reduction activity in alkaline and acidic electrolyte, respectively

The electrocatalytic activity of NCYS was evaluated in 0.1 M KOH alkaline aqueous solution saturated with oxygen by linear sweep voltammetry (LSV) polarization curves. For comparison, under the same conditions, state-of-the-art Pt/C (20% Pt) catalyst was also tested. NCYS catalyst exhibited a more positive onset potential (Eonset) of 0.93 V and half–wave potential (E1/2) of 0.81 V versus RHE along with a larger diffusion–limited current density of 5.3 mA cm−2 (at a rotating speed of 1600 rpm), showing better ORR activity than Pt/C catalyst (figure 3(a)). As shown in figure 3(b), the Tafel slope of NCYS was close to that of Pt/C, suggesting once again the high catalytic activity for ORR [35]. This desirable catalytic activity offered by NCYS can be ascribed to the synergetic effect of yolk–shell structure and abundant nitrogen functional groups, which not only ensured large exposure extent of active sites but also enhanced intrinsic activity of each active site. Long-term durability was a significant issue for metal–air batteries or fuel cells. As shown in figure 3(c), the current retention of NCYS exhibited a slow decay, and a high current retention of 90% was maintained after continuous operation for 60 000 s. On the other hand, Pt/C catalyst showed 20% current loss in current density. It was known that the surface oxidation, particle agglomeration, migration and even detachment from carbon supports of Pt metal accounted for the degradation of Pt/C during the durability tests [36, 37]. In addition, methanol-tolerant ability
was another major concern for electrochemical catalysts to avoid possible fuel-crossover effects. In Figure 3(d). Upon addition of 1 M methanol, an instantaneous current drop appeared suddenly for Pt/C because of the methanol oxidation reaction, suggesting its sensitivity to fuel crossover. In contrast, no obvious current change was observed on the NCYS catalyst, reflecting its great tolerance to methanol crossover effect and implying good catalytic selectivity [38].

Electron transfer number gained by per dioxygen molecule of NCYS can be obtained by using the Koutechy–Levich (K–L) equation. The K–L plots of NCYS manifested good linearity with a similar slope over the entire potential range (0.20–0.60 V). As a result, the \( n \) of NCYS was about 4.0, close to that of Pt/C, implying a four-electron reduction of dioxygen to \( \text{OH}^- \) (supplementary figure S2). This satisfactory value can be attributed to the nitrogen doping. Usually carbon shows a 2e\(^-\) pathway. As long as nitrogen was doped, the higher electronegativity of nitrogen dopants could result in the net positive charge on carbon atoms. The charge redistribution induced from nitrogen doping changed the chemisorption mode of \( \text{O}_2 \) so as to effectively weaken the O–O bonding. In addition, the positively charged carbon atoms also made it easy to obtain electrons from the anode, thus accelerating the ORR process. At the same time, the large exposure extent of active sites derived from the yolk–shell structure also contributed to the 4e\(^-\) pathway.

Electrocatalytic performances of NCYS and Pt/C in 0.5 M \( \text{H}_2\text{SO}_4 \) electrolyte were also evaluated at room temperature. Interestingly, our NCYS catalyst was also active and durable for ORR when tested in acidic solution. The ORR polarization curve (figure 4(a)) exhibited \( E_{\text{onset}} \) of 0.86 V and \( E_{1/2} \) of 0.70 V, comparable to commercial Pt/C and even superior to many state-of-art catalyst materials recently reported in top publications [7, 39–43]. Kinetic currents derived from the mass transport corrected ORR currents (figure 4(b)) showed a little lower Tafel slope than that of the commercial Pt/C catalyst, indicating a similar electrochemical reaction rate between the catalysts. Surprisingly, the current of NCYS only showed a loss of 20% due to the integrity of the yolk–shell structure while Pt/C showed a huge loss of 78% after 50 000 s operation (figure 4(c)). Further, the NCYS catalyst also revealed a great tolerance to methanol crossover effect in 0.5 M \( \text{H}_2\text{SO}_4 \) (figure 4(d)). In addition, the K–L plots (supplementary figure S3) exhibited a great linearity and parallelism within the voltage range of 0.3 to 0.5 V, indicating the values of electron transfer number were similar around 4.0 for ORR at different potentials in acidic media.

### 3.3. NCYS acted as an N-doped carbon matrix for motivating the oxygen reduction activity of oxygen evolution oriented materials

As a catalyst with great ORR properties, NCYS as a kind of carbon support could be integrated with some OER-activated materials to synthesize bi-functional electrocatalysts. For instance, \( \text{Co}_3\text{O}_4 \) nanocrystals, reported with low ORR activity.
but good OER performance, were homogeneously nucleated on NCYSs (supplementary figures S4(b)–(d)). X-ray diffraction (XRD) and XPS analyses (supplementary figure S5) both confirmed the existence of Co$_3$O$_4$ in this composite. For comparison, bare Co$_3$O$_4$ was also prepared and tested (supplementary figures S4(a) and S5(a)).

The electrocatalytic activities for ORR of the as-synthesized Co$_3$O$_4$@NCYS catalysts were first investigated by cyclic voltammetry (CV) method. As can be seen in supplementary figure S6, NCYS showed its cathodic peak at around 0.75 V, again confirming its superior ORR activity. Although the peak potential for bare Co$_3$O$_4$ was only 0.44 V, its ORR performance experienced a pronounced improvement after the combination with the carbon matrix of NCYS and Co$_3$O$_4$@NCYS exhibited a well-defined cathodic peak at much more positive potential of 0.64 V. In LSV tests (supplementary figure S7), bare Co$_3$O$_4$ also exhibited undesirable performance whether in terms of onset potential ($E_{\text{onset}}$ = 0.62 V), half-wave potential ($E_{1/2}$ = 0.52 V) or limiting current (1.85 mA cm$^{-2}$). As expected, the combination between Co$_3$O$_4$ and NCYS did boost the electrocatalytic activity with $E_{\text{onset}}$ of 0.89 V, $E_{1/2}$ of 0.76, and limiting current of 5.39 mA cm$^{-2}$, suggesting that the carbon support NCYS played a critical role in the enhancement of the electrocatalytic activities for ORR. It is worth noting that compared to NCYS, Co$_3$O$_4$@NCYS only lost 50 mV of half-wave potential. As a bi-functional electrocatalyst, this degree of loss can be fully compensated by the greatly enhanced OER activity since Co$_3$O$_4$ could efficiently play a role in the OER process. Additionally, the ORR durability comparison of Co$_3$O$_4$@NCYS was also measured compared with commercial Pt/C, revealing good stability (supplementary figure S9(a)).

To assess the bifunctionality of the Co$_3$O$_4$@NCYS nanocomposites catalyst, the catalytic activity for OER was also investigated, compared with commercial Pt/C, bare Co$_3$O$_4$ and NCYS, in order to confirm the synergistic function of Co$_3$O$_4$ and NCYS for improving the bi-functional electrocatalytic activity. The overvoltage between ORR and OER was a quite critical parameter when evaluating the bi-functional electrocatalytic performance. The ORR activity of the catalysts was compared at the half-wave potential and the OER activities were computed as the potential at a current density of 10 mA cm$^{-2}$ [35, 44–46]. As expected, the Co$_3$O$_4$@NCYS showed the lowest overvoltage of only 0.87 V compared to that of NCYS (0.93 V), commercial Pt/C (1.11 V) and Co$_3$O$_4$ (1.12 V) (figure 5(a)). The N-doped carbon microspheres with porous yolk–shell structure indeed significantly improved the ORR catalytic activity of Co$_3$O$_4$ nanocrystals, resulting in a superior bi-functional catalyst. The chronopotentiometric measurements showed no loss in activity after 60 000 s operation, indicating that Co$_3$O$_4$@NCYS was able to sustain a stable performance over a long period of time (supplementary figure S9(b)).

To further display the potential of the bi-functional performance of a Co$_3$O$_4$@NCYS cathode catalyst under real battery operation conditions, we explored the possibility of using a Co$_3$O$_4$@NCYS catalyst in rechargeable Zn–air...
battery applications [35, 47]. For two-electrode primary Zn–air battery, its open-circuit potential (OCP) was determined to be as high as 1.39 V (figure 5(b)), suggesting a good catalytic performance of Co₃O₄@NCYS, even in this cell configuration [35]. As shown in the inset of figure 5(b), two Zn–air button batteries were connected in series based on the Co₃O₄@NCYS air–cathode, leading to a stable OCP of 2.8 V, and were used to illuminate a green light-emitting diode (LED) screen, fully demonstrating its potential for practical application. In addition, when cycled at the constant current rate of 5 mA cm⁻², the Zn–air battery reached an initial charge potential of 1.94 V and discharge voltage of 1.14 V, thus obtaining a small potential gap of 0.80 V (figure 5(c)). After long-term charge–discharge cycling, negligible potential drop was observed and the final values were 1.96 and 1.10 V, respectively, with a small potential gap loss of 0.06 V [48, 49]. The superior performance of the Co₃O₄@NCYS electrocatalyst, especially its satisfactory cycling durability, was mainly attributed to the unique composite architecture which not only provided high specific areas with plentiful active sites for oxygen reactions due to their nanocrystal subunits but also ensured desirable catalytic stabilities due to structural integrity.

4. Conclusion

In conclusion, as an alternative to platinum catalysts, a metal-free catalyst with active sites attributed to nitrogen doping and unique porous yolk–shell structure was reported, which exhibited outstanding ORR activity in both alkaline and acidic conditions. More importantly, the NCYS as a kind of carbon support could be integrated with some OER-activated materials to synthesize bi-functional electrocatalysts, which exhibited superior performance with a lower overvoltage between ORR and OER. Such bi-functional electrocatalysts can also be applied in Zn–air battery tests and exhibited satisfactory performance, further confirming that this kind of constructed concept could pave a new way for developing a low cost but highly efficient bi-functional catalyst to be applied in novel metal–air batteries.

Acknowledgments

The staff members were acknowledged for their support in measurements and data reduction. Also, this work was supported by the ‘Thousand Talents Program’, the Natural Science Foundation of Jiangsu Province of China (no. BK20140315), the National Natural Science Foundation of China (no. 51402202), the National Basic Research Program of China (no. 2015CB358600), Jiangsu Shuangchuang Plan,
and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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