Low charge overpotential of lithium-oxygen batteries with metallic Co encapsulated in single-layer graphene shell as the catalyst

Yunchuan Tu a,b,c,1, Haobo Li a,c,1, Dehui Deng a,b,*, Jianping Xiao a, Xiaoju Cui a,b,c, Ding Ding d, Mingshu Chen d, Xinhe Bao a,*,

a State Key Laboratory of Catalysis, iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China
b Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
c University of Chinese Academy of Sciences, Beijing 100039, China
d Coll Aerospace Materials 

1 These authors have contributed equally.

E-mail addresses: ddeng@dicp.ac.cn (D. Deng), xhbao@dicp.ac.cn (X. Bao).

1 These authors have contributed equally.

Article history:
Received 15 July 2016
Received in revised form 27 August 2016
Accepted 31 August 2016
Available online 1 September 2016

Keywords:
Charge overpotential
Electrocatalysis
Electron transfer
Lithium-oxygen batteries
Non-precious metals

Abstract

Rechargeable lithium-oxygen (Li–O2) battery has triggered tremendous attention as a promising candidate power source for portable electronics and light vehicles. Until now, a critical scientific challenge facing Li–O2 battery is the high charge overpotential due to the sluggish oxygen evolution reaction (OER) on the electrode, which results in low energy efficiency and poor cyclability. Here, we demonstrated that nitrogen-doped single layer graphene shell encapsulating non-precious metal Co can be used as a highly efficient catalyst for Li–O2 batteries. The catalyst showed significantly enhanced OER catalytic activity, with a charge overpotential of 0.58 V, which was remarkably lower compared with the corresponding N-free graphene encapsulating metal, metal oxide and metal-free carbon materials. DFT calculations revealed that the nitrogen dopants and enclosed metal clusters can synergistically modulate the electronic properties of the graphene surface, resulting in a dramatic reduction of the overpotentials. This study provides the possibility of the rational non-precious metal electrocatalysts designing for Li–O2 batteries.

© 2016 Published by Elsevier Ltd.

1. Introduction

The widespread pursuit of portable electronics and light vehicle demands advanced energy conversion and storage devices with high energy density. Because of the high theoretical gravimetric energy density (3505 Wh kg−1), aprotic Li–O2 batteries have received enormous attention as promising alternatives to conventional Li-ion batteries [1–3]. A typical aprotic Li–O2 battery is based on the reversible redox reaction: 2Li + + 2e− + O2 → Li2O2 (E0 = 2.96 V vs Li/Li+). During the discharge process, O2 is reduced (oxygen reduction reaction, ORR) and combined with Li+ ions to form insoluble and insulated Li2O2 products, which will sluggishly decompose and release O2 (oxygen evolution reaction, OER) in the following charge process [4,5]. Although a number of strategies have been devoted to reducing the severe hysteresis between charge and discharge, the commercial application of Li–O2 batteries has still been restricted by the large polarization of Li2O2 decomposition, which results in low round-trip efficiency, electrolyte degradation and poor cyclability [6,7].

To lower the high charge overpotential, a variety of catalytic materials with excellent activities have been proposed, including precious metals [8,9], transition-metal oxides [10,11], and carbonaceous materials [12–16]. Recent studies found that precious metals such as Ru [17] and the oxide RuO2 [18] can significantly decrease the charge overpotential. However, the widely commercial application of precious metals has been restricted because of their limited reserve and high cost. Due to the chemically tailorable surface, high specific surface area, high porosity, excellent conductivity and low cost, carbon-based materials have been considered as promising alternatives of oxygen electrodes for Li–O2 batteries. However, the charge overpotential of pristine carbon or graphene is higher than 1 V, leading to the formation of by-products (e.g. Li2CO3, LiOH) and the decomposition of electrolyte [19–21]. To achieve lower charge overpotential and avoid those side reactions, there has been many strategies to construct composite cathodes by loading 3d transition metals (TMs) and metal oxides, which act as the active sites, on graphene and other carbon materials [22–24]. Yet these exposed non-precious metal surfaces
readily suffer from oxidation and the activities decay quickly, and finally lead to a high charge overpotential.

In this work, we reported that a series of non-precious transition metal nanoparticles (NPs), including metallic Fe, Co and Ni, encapsulated within nitrogen-doped single layer graphene shells can be used as highly efficient oxygen electrode catalysts for Li–O2 batteries. The graphene shells can protect the metals from being oxidized in O2 atmosphere. Moreover, the electronic structure of graphene shell can be modulated by nitrogen dopants and encapsulated metal NPs, which can enhance both ORR and OER activity, thus resulting in lower discharge/charge overpotential in Li–O2 batteries. In particular, Co based electrode delivers high catalytic activity, with discharge and charge overpotentials of 0.14 and 0.58 V, respectively.

2. Experimental

2.1. Materials preparation

The catalysts M@NC (M=Fe, Co or Ni) were prepared according to our previous method [25]. In brief, 3.6 mmol metal-containing precursors, Fe(NO3)3·9H2O, Co(NO3)2·6H2O or Ni(NO3)2·6H2O were filled into the channels of 1.0 g SBA-15 by an impregnation method with methanol solution. After drying, the homogeneous mixture was then placed in a quartz tube and reduced at 700 °C in a tube furnace in 50 vol% H2/Ar atmosphere with a heating rate of 5 °C min⁻¹, followed by bubbling CH3CN with Ar for 20 min at 700 °C. After cooling to room temperature, the samples were treated in 4% HF aqueous solution for 8 h, followed by washing in distilled water and ethanol, and then drying at 80 °C for 12 h. The resulting samples were denoted as Fe@NC, Co@NC and Ni@NC, respectively according to the different types of the metal precursors. Co@C was prepared with the same procedure only using C2H2 instead of CH3CN as the carbon source. CoOx/NC was obtained via treating the Co@NC in 20 vol% O2/Ar at 300 °C for 1 h. The reference CNTs were purchased from Chengdu Organic Chemicals Co. Ltd. CAS, which were further treated by refluxing in concentrated HNO3 at 130 °C for 12 h. Graphene was prepared via ball milling graphite powder under Ar atmosphere at 450 rev/min for 20 h. The N-CNTs and N-graphene were obtained via treating the CNTs and graphene in NH3 atmosphere at 800 °C for 2 h.

2.2. Characterizations

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV diffractometer with Cu Kα radiation at a voltage of 40 kV and a current of 30 mA. The morphology and structure of the products were characterized using high resolution transmission electron microscopy (HRTEM; FEI Tecnai F20) at an accelerating voltage of 200 kV, and scanning electron microscopy (SEM; Hitachi S-4800) at 15 kV. Nitrogen adsorption-desorption measurements were tested on TriStar II 3020 V1.03. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was derived from the desorption branch using the Barret-Joyner-Halenda (BJH) method. Raman spectroscopy was conducted on a Jobin Yvon LabRAM HR 800 instrument with a 532 nm excitation laser at a power of around 0.8 mW. X-ray photoelectron spectroscopy (XPS) was carried out on a XPS1000 MK2 X-ray monochromator using Al Kα X-rays as the excitation source with a voltage of 15 kV. X-ray absorption near-edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) were measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF).

2.3. Electrochemical measurements

The oxygen electrode was prepared as follows. A mixture containing 90 wt% of the M@NC composite and 10 wt% of lithiated Nafion was well ultrasonic dispersion in isopropanol. Before coating this slurry onto Toray carbon paper (TGP-H-030), the carbon paper was punched into discs with a diameter of 14.0 mm. The as-prepared electrodes were vacuum dried at 80 °C for 12 h. The M@NC loading in each disc is around 0.5 mg/cm². Swagelok-type cells (MTI Corporation) were used to investigate the electrochemical performance. The cells were assembled inside a glovebox (H2O < 0.1 ppm, O2 < 0.1 ppm) using the M@NC as the cathode, a fresh Li metal (ϕ=15.6 mm) as the anode, and a glass fiber separator (Whatman, ϕ=19.0 mm). Before the test, all cells were stabilized for 3 h in oxygen atmosphere, the air electrode and separator were soaked in 250 μL 1 M LiClO4/DMSO electrolyte to ensure wetting. The cycling voltammetry measurements were conducted on an electrochemical workstation (PARSTAT MC) at a scan rate of 0.1 mV s⁻¹ between 2.4 and 4.3 V versus Li/Li⁺. Galvanostatic discharge/charge tests were carried out at room temperature on a LAND CT2001A battery-testing instrument. The current density and specific capacity were based on the total amount of catalyst (including M@NC and N-CNTs). All measurements were undertaken in 1 atm dry high-purity oxygen (99.999%) to avoid any negative effects of humidity and CO2.

2.4. Computational details

DFT calculations were performed using Vienna ab initio simulation packages (VASP) [26] with the projector-augmented wave (PAW) method [27]. All calculations were based on the same generalized gradient approximation method with the Perdew-Burke-Ernzerhof (PBE) [28] functional for the exchange-correlation term. The plane wave cutoff was set to 400 eV. The Brillouin zone was sampled by a 6 × 6 × 1 k-point grid for the charge density calculations and a 1 × 1 × 1 Monkhorst-Pack [29] k-point sampling for structural optimizations. The convergence of energy and forces were set to 1 × 10⁻⁵ eV and 0.05 eV Å⁻¹, respectively.

The model of metal encapsulated within single layer graphene was consisted of a (12.8 × 12.3 Å) Graphene supercell with a vacuum space of about ~20 Å, as well as a metal cluster with 11 metal atoms below the graphene layer. A Li6O6 cluster consists of 6 Li atoms and 6 O atoms was used to simulate the Li2O2 generated on the surface of the carbon layer.

3. Results and discussion

The N-doped graphene encapsulating 3d TMs (denoted as M@NC) were synthesized via a chemical vapor deposition (CVD) method in the channels of ordered mesoporous silica (SBA-15) (the Supporting information for details). High resolution transmission electron microscopy (HRTEM) images (Fig. 1a, S1 and S2) clearly illustrate that the M@NC are distributed on continuously interconnected skeleton of carbon nanotubes (CNTs). The diameter distribution of M@NC is around 6–10 nm, due to the confinement effect of SBA-15 channels during the preparation. Further HRTEM images reveal that the metal NPs are completely encapsulated within a single layer graphene shell (Fig. 1b). On the basis of the N2 adsorption-desorption isotherm measurements, the Brunauer-Emmett-Teller (BET) surface area of the Fe@NC, Co@NC and Ni@NC samples are 198, 103 and 97 m²/g, respectively (Fig. S3). The N content in these samples is around 2.0 wt% (the N content in Co@NC is 2.1 wt%) [25]. The X-ray diffractions (XRD) patterns (Fig. S4) and X-ray photoelectron spectroscopy (XPS) spectra (Fig. S5) corroborate that all Fe, Co, and Ni are of metallic
Fig. 1. The structural and electronic properties of Co@NC catalyst. (a, b) HRTEM images of Co@NC. The inset in (b) shows the (111) crystal plane of the Co particle. (c) The normalized Co K-edge XANES and (d) the corresponding $k^2$-weighted EXAFS spectra of Co@NC and CoOx/NC in comparison to Co foil and commercial Co$_3$O$_4$.

Fig. 2. Electrochemical tests of Li–O$_2$ batteries with M@NC catalysts. (a) Discharge/charge profiles of M@NC electrodes at first cycle at a current rate of 200 mA g$^{-1}$ with the fixed capacity of 2000 mA h g$^{-1}$. (b) The cycling voltammetry profiles of M@NC electrodes under 1 atm O$_2$ and Ar atmosphere at a scan rate of 0.1 mV s$^{-1}$ between 2.4 and 4.3 V. (c) Cycling stability and the terminal discharge voltage as a function of cycle number for the graphene, CNTs and Co@NC based Li–O$_2$ batteries.
state. X-ray absorption near-edge structure (XANES), which is sensitive to the chemical state of atoms, indicates that the near-edge structure of Co@NC is similar with the reference Co foil, suggesting the Co is in metallic state (Fig. 1c), which is consistent with the extended X-ray absorption fine structure (EXAFS) spectra analysis (Fig. 1d). These results indicate that uniform metallic Co nanoparticles have been completely encapsulated in single layer graphene shell.

The different types of M@NC samples were employed as cathode catalysts in Li–O2 batteries, in which a fresh Li metal plate was used as the anode and 1.0 M LiClO4 in dimethyl sulfoxide (DMSO) as the electrolyte. Firstly, the Toray carbon paper substrate alone was tested as a reference to determine its discharge capacity (Fig. S6). The capacity of the carbon paper electrode without catalyst was only 0.3 mA h cm\(^{-2}\) at most, which was 12 times lower than that of Co@NC cathode at the same current. We therefore concluded that the capacity contribution of the carbon paper was almost negligible. Fig. 2a shows the first cycle of galvanostatic discharge/charge profiles of the Li–O2 batteries with M@NC cathodes at a current density of 200 mA g\(^{-1}\) with the fixed capacity of 2000 mA h g\(^{-1}\). On discharging, Fe@NC displays higher discharge voltage plateau (2.82 V) than that of Ni@NC (2.78 V) and slightly higher than that of Co@NC (2.81 V). On charging, Co@NC shows an excellent OER catalytic activity with only 0.58 V charge overpotential, which is one of the most active non-precious metal catalysts for Li–O2 batteries in literatures (Table S3). Furthermore, as shown in the cyclic voltammetric (CV) curves (Fig. 2b), Co@NC presents a lower anodic onset potential during the oxidation process compared with Fe@NC and Ni@NC. These electrochemical evaluations prove that Co@NC exhibits outstanding electrocatalytic activities for both ORR and OER in Li–O2 batteries, giving rise to a voltage gap of 0.72 V. In addition, M@NC based electrodes exhibit two distinct charge plateaus with different overpotentials. In the contrast experiments, we found that the charge plateaus of Li–O2 batteries with carbon-based electrodes locate at 4.2–4.4 V (Fig. S7), such charge plateaus of carbon materials were also reported in previous publications [30,31]. Furthermore, M@NC based materials have two compositions (single layer graphene encapsulating 3d TMs and the interlaced N-CNTs), which have different active sites for Li2O2 decomposition, we speculate that the

![Fig. 3. Characterizations of Co@NC based electrodes at different reaction states. HRTEM images of Co@NC electrodes (a) after discharge and (b) after recharge. (c) The normalized Co K-edge XANES and (d) the corresponding \(k^2\)-weighted EXAFS spectra of Co@NC electrodes at different states in comparison to Co foil and commercial Co3O4. (e) Li 1s and (f) O 1s XPS spectra of the discharged and recharged electrodes with Co@NC as the catalyst. (g) XRD patterns of Co@NC electrodes at different states. (h, i) Raman spectra of Co@NC electrode at the discharged state.](image-url)
carbon regions (such as N-doped CNTs) without metal nanoparticles are responsible for the higher voltage plateau, and N-doped graphene shell encapsulating metal NPs for the lower voltage plateau [32]. More detailed discussion will be provided later combining with DFT calculations.

The cycling stability of Co@NC, graphene and CNTs electrodes were evaluated at a current density of 200 mA g\(^{-1}\) and a fixed capacity of 600 mA h g\(^{-1}\). As shown in Fig. 2c and S8, the terminal discharge voltage of graphite and CNTs electrodes decreased to 2 V at 23rd cycle and 67th cycle, respectively, whereas the cycling lifetime of Li\(_{2}\)O\(_2\) battery with Co@NC as the catalyst could reach 90 cycles with the terminal discharge voltage remaining about 2.7 V.

Morphologies of the discharge products on Co@NC electrodes were investigated by scanning electron microscope (SEM) and HRTEM. Compared to the pristine electrode, thin film-like products were deposited along the electrode structure (Fig. S9), which is consistent with the HRTEM analysis that thin layer discharge products were uniformly coating around the surface of the Co@NC structure during discharge (Fig. 3a).

After the subsequent recharge and 20th cycling recharge, the generated discharge products vanished and the graphene layer that encapsulating metal nanoparticles still remained integrity (Fig. 3b, S11). This is consistent with the XANES and EXAFS spectra (Fig. 3c and d), in which only the obvious Co–Co bond existed in the recharged electrode using Co@NC catalyst, no other bonds emerged, further confirming that cobalt nanoparticles maintained metallic state without oxidation.

To further confirm the reversibility of deposition products, we have determined the discharged and recharged oxygen electrodes with Co@NC cathode by XPS, XRD and Raman. As revealed in the Li 1s and O 1s XPS spectra (Fig. 3e and f), the main product after discharge was Li\(_2\)O\(_2\). After recharge, Li\(_2\)O\(_2\) was removed while some lithium carbonate species remained, which may be formed by the electrolyte decomposition. This result can be also confirmed by XPS analysis of Li and O (Fig. S12) on the Co@NC cathodes after 10th and 20th cycling. The diffraction pattern of Li\(_2\)O\(_2\) was formed in the XRD pattern of the discharged electrode, no other peaks of byproducts such as LiOH and Li\(_2\)CO\(_3\) were detected. After the following recharge process, these Li\(_2\)O\(_2\) peaks disappeared (Fig. 3g), indicating the complete decomposition of Li\(_2\)O\(_2\). The discharge species were further identified by Raman spectra (Fig. 3h and i), in which the peak (at around 780 cm\(^{-1}\)) of Li\(_2\)O\(_2\) could be observed. What is more, the signature peak of Li\(_2\)O\(_2\)-like component (at 1123 cm\(^{-1}\)) appeared, as well as the peak (at around 1505 cm\(^{-1}\)) which could ascribe to the strong interaction between graphite carbon surface and Li\(_2\)O\(_2\)-like component [33]. These results confirm that the electrode with Co@NC cathode leads to the favorable deposition of thin film Li\(_2\)O\(_2\) and superoxide species Li\(_2\)O\(_2\) during discharge.

Density functional theory (DFT) calculations were carried out to investigate the electrode reaction processes on the surface of the carbon layer. Two reaction mechanisms involving the following steps had been considered for the oxygen reaction process:

\[
\text{Li}^+ + O_2 + e^- \rightarrow \text{Li}_2\text{O}_2 \quad (O_2 \text{ electrode step 1}),
\]

\[
\text{Li}^+ + \text{Li}_2\text{O}_2 + e^- \rightarrow \text{Li}_3\text{O}_2 \quad (O_2 \text{ electrode step 2}).
\]

Here, we considered two reported mechanisms of discharge and charge processes. The M1 mechanism accounts for step 1 twice, followed by step 2 twice, which is believed to give smallest free energy variations for the Li\(_2\)O\(_2\) crystal surface [34]; while the M2 mechanism is a successively alternate process of step 1 and step 2, which has been used to investigate chemical reaction on oxygen electrode of Li\(_2\)O\(_2\) clusters on carbon layers [35,36]. The free energy diagram for the OER reactions (Li\(_4\)O\(_6\) → Li\(_2\)O\(_2\) + 4Li\(^+\) + 4e\(^-\) + 2O\(_2\)) along M1 and M2 on the surface of Co@NC substrate (Fig. 4a) and other materials (graphene, N-doped graphene, Co@C, Fe@NC, Ni@NC, see Fig. S13, Tables S1 and S2) have been calculated to determine the overpotentials of Li\(_2\)O\(_2\) batteries (see the Supporting information for details about the computational model). The standard free energy of Li\(_2\)O\(_2\) cluster is defined by: \(\Delta G^f = G(\text{Li}_2\text{O}_2) - G(\text{Li}_{4\text{at}}) - 3G(\text{O}_2\text{gas})\). The equilibrium potential \(U_0\) corresponds to \(-\Delta G^f/6e\). The overpotentials are used to evaluate the performance of the oxygen electrode reactions, defined by: \(\eta_{\text{charge}} = U_{\text{charge}} - U_0 = \max[\Delta G_i/e] - U_0\); \(\eta_{\text{discharge}} = U_{\text{discharge}} - U_0 = \min[\Delta G_i/e]\). Take the free energy plots of N-doped graphene (Fig. S13h) and Co@NC (Fig. 4a) with M2 as the example. For both of the two surfaces, the starting free energies at zero potential for Li\(^+\) and O\(_2\) are both 8.8 eV. The difference between them is the free energies of the superoxide intermediates in each step. Due to the more uniform energy gaps of each step of Co@NC, the free energies are uphill for all steps until the charge potential increasing to 2.51 V, while for N-doped graphene the charge potential reaches to 2.94 V. Therefore, the charge overpotential of Co@NC is significantly lower than that of N-doped graphene cathodes, the calculated overpotentials along M2 can explain well the present experimental observations.

From the calculated overpotentials shown in Fig. 4a and c, the nitrogen dopants and metal clusters can synergistically result in a dramatic reduction in the voltage gap between charge and discharge. Similar results were obtained from the experimental tests. As shown in Fig. 4b, Co@NC showed the lowest charge overpotential, while the charge plateaus of Co@C and N-doped graphene cathodes were as large as 4 V and 4.25 V, respectively. In the enlightenment of the previous work [38–40] and our present calculations (Fig. 4d), the electrons from encapsulated transition metals (such as Fe, Co, Ni) can enhance the charge density of the carbon layers. And with the N dopants, this enhancement of charge density will become much more apparent. To further compare the catalytic activity of such encapsulation construction, we oxidized the Co@NC to break the outer graphene layer. The obtained cobalt oxide anchored on N-CNTs (CoO\(_n\)/NC) showed the charge plateau as large as 4.2 V, demonstrating a lower OER activity than that of Co@NC.

DFT calculations were further carried out to investigate the electronic properties of different catalyst surfaces to understand the enhanced catalytic effect of the encapsulated Co clusters. As shown in Fig. 4e and f, both Co@NC and N-doped graphene can affect Li\(_2\)O\(_2\) by a similar extent, while for Li\(_2\)O\(_2\) clusters, the N-doped graphene surface have a relatively much weaker effect compared with that of Co@NC. Such effect of metal clusters in electronic modulation of the graphene layer is also reflected in Raman spectra. For the Co@NC discharge electrode, the C-LiO\(_2\) peak (around 1505 cm\(^{-1}\)) confirms this strong interaction between graphite carbon surface and Li\(_2\)O\(_2\)-like component. While for the N-doped graphene discharge electrode, such peak does not exist (Fig. S10), indicating that the interaction between electrons from N-doped graphene surface and Li\(_2\)O\(_2\)-like component is much weaker. In brief, enclosed metallic Co and nitrogen dopants can synergistically modulate the electronic properties on the graphene surface, thus changing the thermodynamic free energies of the intermediates of each reaction steps and affecting the potential difference between these steps, and ultimately resulting in a dramatic decrease in the voltage gap.

4. Conclusions

In conclusion, N-doped single layer graphene shell encapsulating non-precious metal Co catalyst is used as oxygen...
electrode catalyst for Li–O2 batteries. The catalyst shows superior catalytic activity, giving rise to a reduced hysteresis between discharge and charge overpotentials for highly efficient aprotic Li–O2 batteries. DFT calculations indicate that the nitrogen dopants and enclosed metal clusters can synergistically modulate the electronic properties of graphene surface, resulting in a dramatic decrease in the voltage gap. This study paves a new way towards rational design of excellent catalysts for the high efficiency oxygen electrodes in Li–O2 batteries.

Acknowledgements

We gratefully acknowledge the financial support from the Ministry of Science and Technology of China (Nos. 2016YFA0204100 and 2016YFA0200200), the National Natural Science Foundation of China (Nos. 21321002, 21573220 and 21303191), and the strategic Priority Research Program of the Chinese Academy of Sciences (No. XDA09030100). We thank staff at the BL14W1 beamline of Shanghai Synchrotron Radiation

Fig. 4. The catalytic process and mechanism on the oxygen electrode by combining the calculated and experimental results. (a) Calculated free energy diagram for the oxygen electrode reactions along M2 on the surface of N-doped graphene encapsulating Co NPs (Co@NC). Two formula units of Li2O2 are generated during discharge (red, left to right) and decomposed during charge (blue, right to left). The equilibrium potential (U0) is 1.93 V. The free energies are shown at different potentials, U = 0 is the open circuit potential, Udischarge = 1.86 V is the highest potential where discharge is still downhill in all steps, and Ucharge = 2.51 V is the lowest potential where charging is all downhill. Insets show the optimized configurations of intermediates on Co@NC. Light yellow sticks: C; blue balls: N; pink balls: Co; green balls: Li; red balls: O. (b) Discharge/charge profiles of the Li–O2 batteries with Co@NC, Co@C, CoOx/NC, graphene and N-graphene cathodes at a current rate of 200 mA g\(^{-1}\) with the fixed capacity of 2000 mA h g\(^{-1}\). (c) Calculated overpotentials (\(\eta_{\text{charge}}\) and \(\eta_{\text{discharge}}\)) and the voltage gaps compared to the experimental results of Li–O2 batteries based on different catalysts along M2. (d) The redistribution of electron densities of Co cluster covered by N-doped graphene. The differential charge density is defined as the difference of electron density with and without Co cluster. Optimized structure of Li6O6 (e) and Li5O6 (f) clusters on N-doped graphene (left) and Co@NC (right) with the electron density difference. Yellow and blue contours in the electron density difference represent the increased and decreased electron density, respectively. The isosurface level is set to be 0.0005 e/Bohr\(^{3}\) (e) and 0.0008 e/Bohr\(^{3}\) (f). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Facility (SSRF) for the assistance with EXAFS and XANES measurements. We also acknowledge the computational resources from Shanghai Supercomputer Center (SSC) and National Supercomputing Center in Shenzhen. We thank Tingting Cui, Junhao Yang and Qingfei Liu for help in HRTEM tests, and Prof. Quanfeng Dong, Prof. Hongzhong Zhang and Dr. Chaozhu Shu for fruitful discussions.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.08.066.

References


Yunchuan Tu received his B. S. degree in Applied Chemistry from Sichuan University in 2012. He is currently a Ph.D. candidate under the supervision of Prof. Xinhe Bao and Dehui Deng at Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS). His research is focused on novel non-precious metal catalysts for electrochemical energy conversion and storage, such as Li-air batteries and water electrolysis.

Dehui Deng received his B. S. in Light Industry Engineering and B. S. in National Economy Management from Sichuan University in 2007 and Ph.D. in Physical Chemistry from DICP, CAS in 2012. He subsequently joined State Key Laboratory of Catalysis, DICP as an Associate Professor. Since Jan. 2015, he served as an iChEM Research fellow at Xiamen University. He also served as a visiting scholar in Stanford University in 2015. His research interests include development of two-dimensional layered nanocatalysts and fundamental research in heterogeneous catalysis and electrocatalysis.

Jianping Xiao received his Ph.D. in computational physics at Bremen University in 2013. Then, he joined the group of Prof. Xinhe Bao at DICP as postdoctoral fellow. Since Nov. 2015, he become a postdoctoral researcher at SUNCAT center at Stanford University with design and synthesis of novel carbon-based catalysts for heterogeneous catalysis and electrocatalysis.

Xiaojun Cui received her Bachelor’s degree from Sichuan University in 2012. She is currently pursuing her Ph.D. under the supervision of Prof. Xinhe Bao and Dehui Deng in DICP, CAS. Her research mainly focuses on design and synthesis of novel carbon-based catalysts for heterogeneous catalysis and electrocatalysis.

Haobo Li received her B. S. in chemistry from Nankai University in 2012. Now she is a Ph.D. candidate in Prof. Xinhe Bao’s group at DICP, CAS. Her research is focused on theoretical study on confinement catalysis of two-dimensional atomic crystals.
Ding Ding received his B.S. in Chemistry from China Agriculture University in 2009. Now, he is a Ph.D. candidate in Prof. Mingshu Chen’s group at Xiamen University. His research interest mainly focused on model catalysis using surface science and in-situ spectroscopic study for catalytic mechanics.

Mingshu Chen received his undergraduate education at Chengdu University of Science and Technology (China) graduating in 1991 with a degree in Applied Chemistry. He earned a M.D. (Chemistry) in 1994 and a Ph.D. (Chemistry) in 1997 from Xiamen University (China), where he subsequently served as a research associate/lecturer. In 2002 he earned a Ph.D. in Engineering from Kyushu University (Japan) and shortly thereafter joined the research group of Dr. Wayne Goodman at Texas A&M University. In 2007, he moved back to Xiamen University as a full professor of Chemistry. His researches focus on surface chemistry, heterogeneous catalysis, and model catalysis study.

Xinhe Bao received his Ph.D. in Physical Chemistry from Fudan University in 1987. He held an Alexander von Humboldt Research Fellow position in Fritz-Haber Institute between 1989 and 1995, hosted by Prof. Gerhard Ertl. Following that, he joined DICP as a full Professor. He became a member of the CAS in 2009. His research interest is nano and interfacial catalysis, focusing on the fundamental understanding of heterogeneous catalysis, including development of new catalysts and novel catalytic processes related to energy conversion and storage.