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Electrocatalytic property of nitrogen-doped graphite-supported CeO$_2$-CoO$_x$

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Abstract

Ceria has been widely used as a catalyst in photocatalysis, automobile exhaust purification, and organic degradation. However, ceria has poor intrinsic catalytic performance and usually requires modifications. In this study, N-doped graphite was used as a substrate, and then CeO$_2$-CoO$_x$ was attached to N-doped graphite. Afterward, the effects of the recombination with N-doped graphite and those of Co doping on the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) catalytic ability of CeO$_2$ were studied. The experimental results showed that the electrocatalytic performance of CeO$_2$-CoO$_x$/N-rGO is higher than that of pure CeO$_2$ and CeO$_2$/N-rGO. After the N-doped graphite recombination, the number of transferred electrons increased at high potential, which fully illustrates that graphite can effectively reduce the overpotential of ORR. The 0.56 eV shift of the Cs in CeO$_2$-CoO$_x$/N-rGO to high binding energy revealed that CeO$_2$-CoO$_x$ and N-rGO were combined with each other through covalent bonds. In addition, the increased pyridine nitrogen of N-rGO after the recombination improved the electrocatalytic performance of CeO$_2$-CoO$_x$/N-rGO. Overall, the catalytic ability of CeO$_2$ was greatly improved, and the modified CeO$_2$-CoO$_x$/N-rGO composite showed better catalytic performance for the ORR and OER compared with Pt/C and RuO$_2$.

1. Introduction

As a catalyst, ceria has been widely used in the fields of photocatalysis, automobile exhaust purification, and organic matter degradation. In recent years, the application of ceria in the field of medium and high-temperature electrocatalysis has become a research hot spot. However, ceria has poor intrinsic catalytic performance, and its catalytic effect on the ORR and OER is not strong. Therefore, it is usually necessary to improve its electrocatalytic activity by doping other elements or by compounding it with other materials.

Doping with transition-metal or rare-earth elements can increase the content of ceria oxygen vacancies and improve their electronic conductivity. A lot of application research has been carried out on ceria doped with such elements in the fields of fuel cells [1, 2], CO catalysis [3, 4], photocatalysis [5, 6] etc and it was found that doping with some other elements can indeed change the catalytic properties of oxide materials. We have also studied the electrocatalysis activity of cobalt-doped ceria in detail [7]. However, we found that the ceria doped with different elements alone has a limited effect on the increase in the catalytic ability of the ORR.

It is a common method to improve the ORR and OER catalytic performance by loading metal oxides (or sulfides, etc) on the surface of carbon materials. Dou et al [8] synthesized reduced graphite oxide loaded with Co$_9$S$_8$ nanoparticles using the hydrothermal method. Then, they etched it by NH$_3$ plasma to obtain N-doped redox graphite nanomaterials (N-Co$_9$S$_8$/G) loaded with N-doped Co$_9$S$_8$ nanoparticles, where the reduced graphite oxide loaded with Co$_9$S$_8$ nanoparticles was calcined under NH$_3$ for several hours (NA-Co$_9$S$_8$/G). After electrochemical tests, the ORR catalytic performance of the former had been significantly improved compared...
with that of the latter, and the catalytic performance of both materials was found to be stronger than that of the N-doped Co₉S₈ nanoparticles. The authors attribute this result to two reasons: the graphite decreased the overpotential, and the surface defects of the material increased after the NH₃ etching. Hao et al [9] synthesized a composite material (Ni₉Co₉O₄/Co-NG) with N-doped graphite as a substrate. Then, Ni₉Co₉O₄ and Co nanoparticles were loaded on it using the MOF method. In the same way, N-doped carbon (Ni₉Co₉O₄/Co-NG) coated with Ni₉Co₉O₄ and Co nanoparticles were synthesized. Through electrochemical tests, it was found that the former method had better catalytic performance concerning the ORR and OER compared with the latter method. Also, the electrochemical catalytic behavior (ORR and OER) of the former method was comparable to that of commercial catalysts (Pt/C and IrO₂/C). The authors found that graphite can improve the electrochemical active area and charge transfer efficiency. In addition, the composites of functional and carbon materials, such as N-doped graphite and carbon nano-tube, were widely used in the catalytic performance research of lithium ion batteries, zinc-air batteries and other fields, leading to significant progress [10–13].

In this study, due to the excellent performance of the composite materials of ceria and graphite, we chose graphite as a substrate. CeO₂–CoOₓ was loaded on N-doped graphite, combined with the effect of cobalt doping on the catalytic ability of ceria and the double effects of the increasing conductivity and decreasing ORR overpotential by N-doped graphite. The obtained experimental results have proven that the catalytic ability of CeO₂ for the ORR and OER has been greatly improved. Moreover, the preparation method was simple and fast, and it was easy to implement.

2. Experimental

The used chemical reagents in the experiment mainly included cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, AR, 99.0%), cobalt nitrate hexahydrate (Co(NO₃)₃·6H₂O, AR, 99.0%), hydrogen peroxide (H₂O₂, 30wt %), ammonia (NH₃·H₂O, 25 ~ 28 wt%), and acetylene black (battery grade), and they were purchased from Sinopharm Chemical Group Co., Ltd. In addition, anhydrous ethanol (CH₃CH₂OH, AR, 99.9%, Jiangsu Qiangsheng Functional Chemical Co., Ltd), NaOH solution (5 wt%, Dupont D520, Alfa Essa (China) Chemical Co., Ltd), Pt/C catalyst (Pt 20 wt%, Alfa Essa (China) Chemical Co., Ltd), and RuO₂ catalyst (99.9 wt%, Alfa Essa (China) Chemical Co., Ltd) were used.

According to our previous research results [7], the cerium nitrate to graphene oxide (GO) mass ratio was chosen as 2:5. First, 20 mg of cerium nitrate were dissolved in 20 ml ultrapure water, and 50 mg of GO were added to 50 ml ultrapure water. After ultrasonication for 1 h, hydrogen peroxide was added dropwise with stirring until pH = 7. After stirring for 5 min, the prepared nitrate solution was added dropwise. After centrifugal washing, the mixture was placed in a 120 °C oven, and it was then taken out after 24 h. The sample was labeled as CeO₂/N-rGO (N-rGO-nitrogen-doped redox graphene). The preparation methods of the solution containing only cerium nitrate and that of the colloid containing only 50 mg of GO were the same as in the above operation, and they were labeled as CeO₂ and N-rGO, respectively.

After dropping the cerium nitrate solution and the colloid of GO according to the above mass ratio, stirring was continued for 12 h. Finally, 10 vol. % hydrogen peroxide solution was slowly added dropwise until pH > 9. After stirring for 24 h, the suspension was placed in a hydrothermal reaction lining and kept at 150 °C for 3 h. After the reactor was cooled to room temperature, the black suspension was taken out, and the precipitate after the high-speed centrifugation was washed several times with deionized water and ultrapure water. Finally, the sample was frozen and transferred to a lyophilizer for freeze-drying until the water was sublimated to obtain a dry black sample powder.

The sample with the best load through the conducted electrochemical performance test was selected. Then, at this loading amount, a mixed ion solution of cerium nitrate and cobalt nitrate was prepared in a molar ratio of Co²⁺: Ce³⁺ = 1: 4, and N-doped graphene loaded with cobalt-doped cerium oxide nanoparticles was prepared using the same method again. The sample was labeled as CeO₂–CoOₓ/N-rGO.

Scanning Electron Microscope (SEM) (SU8010, Hitachi, Ltd) was used to observe the microscopic morphology of the graphite load and to detect the content of each element, and X-ray Photoelectron Spectroscopy (XPS) (ESCALAB 250XI, Thermo Scientific, USA) was used to analyze the surface elements. The rotating disk electrode method was used to detect the difference in the ORR and OER catalytic performance, and a High Resolution Transmission Microscope (HRTEM) (Tecnai G220, US FEI) was used to observe the internal morphology and crystal structure.
3. Results and discussion

3.1. Microstructure and element analysis

The experimental results showed that when the mass of the cerium nitrate and GO was relatively low, the graphene surface was smooth. However, when the mass ratio increased, the graphene surface became roughened (due to the cerium oxide particles adsorption), see figure 1(a). Similarly, the graphene loaded with cobalt-doped cerium oxide became roughened (figure 1(b)). Through the conducted EDS spectrum analysis (see tables 1 and 2, the corresponding selection is shown in figure 1(b)), it can be seen that the relative content ratio of cobalt and cerium in the sample was basically consistent with the added amount of raw materials.

Further, the HRTEM analyses of CeO$_2$/N-rGO and CeO$_2$-CoO$_x$/N-rGO are shown in figures 1(c) and (d). It can be observed that the lattice spacing of the adsorbate on the graphite surface has two characteristic ranges: 0.314 $\sim$ 0.316 nm and $\sim$0.196 nm, which correspond to the (111) crystal plane ($\sim$0.312 nm) and cerium oxide (220) crystal plane ($\sim$0.192 nm)$^{[14]}$. This result indicates that the adsorbed cerium oxide on the graphene surface has a certain preferred orientation.

3.2. Thermogravimetric analysis and discussion

The supported amount of ceria can be quantitatively studied through the thermogravimetric mass change of the loaded graphite under oxidizing atmosphere. According to the thermogravimetric loss mass of the two materials

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Table 1. EDS element analysis results of the selected area 1.

| Element | Weight% | Atom% | Net strength | Error% |
|---------|---------|-------|--------------|--------|
| C K     | 40.81   | 62.22 | 95.51        | 7.37   |
| N K     | 7.22    | 9.44  | 4.23         | 24.63  |
| O K     | 20.62   | 23.6  | 37.61        | 12.7   |
| Ce L    | 27.79   | 3.63  | 30.04        | 14.43  |
| Co K    | 3.56    | 1.1   | 3.99         | 41.41  |

Figure 1. (a) SEM patterns of CeO$_2$/N-rGO; (b) SEM patterns of CeO$_2$-CoO$_x$/N-rGO for the Energy Dispersive Spectrometer (EDS) element analysis; (c) HRTEM images of CeO$_2$/N-rGO; (d) HRTEM images of CeO$_2$-CoO$_x$/N-rGO.
in figure 2, it can be seen that the load of the two materials is basically the same, close to 45%. Combined with the cerium nitrate hexahydrate amount of the initial input, it was found that the mass of GO was reduced by 22% through the hydrothermal reaction. In addition, a mass loss of 100 °C was caused mainly by the bound water desorption. With the increase in temperature, the N-rGO began to thermally decompose at around 230 °C. At around 340 °C, both endothermic peaks appeared, and the weight loss rate was extremely high. In addition, CeO$_2$-CoO$_x$/N-rGO had one more endothermic peak than CeO$_2$/N-rGO, and the reason might be that cobalt-doped ceria is unstable at higher temperatures, causing cobalt to precipitate out in the form of oxide.

3.3. Co-doping effect on the electrocatalytic performance

According to previous research, we aimed to further improve the electrocatalytic performance by doping Co after determining the CeO$_2$ content. By comparing the polarization curves of different loads, as shown in figure 3, it was found that CeO$_2$-CoO$_x$/N-rGO has the strongest catalytic ability for the ORR and OER through doping Co. Although there was still a gap of 87 mV between its half-wave potential and the half-wave potential of Pt/C, it was greatly reduced relative to CeO$_2$. In addition, it can be seen from figure 3(b) that the catalytic effect

| Table 2. EDS element analysis results of the selected area 2. |
|-----------------|-------|-------|--------|-------|
| Element         | Weight% | Atom% | Net strength | Error% |
| C K             | 36.96   | 66.1  | 50.32         | 8.62   |
| N K             | 4.36    | 6.69  | 1.7           | 39.66  |
| O K             | 14.09   | 18.92 | 17.71         | 14.69  |
| Ce L            | 37.73   | 5.78  | 26.04         | 14.66  |
| Co K            | 6.86    | 2.5   | 4.86          | 30.8   |

Figure 3. (a) ORR polarization curves of different samples; (b) OER polarization curves of different samples.

Figure 2. (a) Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) curves of CeO$_2$/N-rGO; (b) TGA and DSC curves of CeO$_2$-CoO$_x$/N-rGO.
of CeO$_2$-CoO$_x$/N-rGO on the OER was slightly better than that of the commercial RuO$_2$. Overall, it was found that a small amount of Co doping can enhance the electrocatalytic activity of the tested composite. One of the reason for the performance improvement is that Co element has a good catalytic effect. When doped into cerium oxide, Co is most likely to be the active site for the reaction, which can accelerate the formation of metal peroxide hydrogen bonds \cite{15}.

3.4. Transfer electron number analysis of the ORR

According to figure 4, the electron transfer path is the $4e^-$ transfer path through loading. Also, the calculated number of transferred electrons using the K-L curve method in figure 4(b) shows that the number of transferred electrons of CeO$_2$ at high potential increased after loading graphite, which also fully shows that graphite can effectively reduce the overpotential of ORR.

3.5. Catalytic stability analysis

By comparing the chronopotentiometric curves of different loads (figure 5(a)), it was found that the ORR stability of CeO$_2$ was better than that of CeO$_2$/N-rGO and that the ORR stability of both of CeO$_2$ and CeO$_2$/N-rGO was better than that of CeO$_2$-CoO$_x$/N-rGO. In addition, it was found in figure 5(a) that the OER stability of CeO$_2$ was significantly better than that of CeO$_2$/N-rGO-3, but their OER catalytic performances are similar. This may be due to the fact that graphite was oxidized at a high potential for a long time, as when measuring the chronoamperometric curve of CeO$_2$-CoO$_x$/N-rGO, it was found that the current significantly decreased after a prolonged time, and this phenomenon did not exist at low potential. Another possible reason is that the adsorbed O$_2$ on the graphite surface could not be discharged on time, resulting in poor catalyst performance. As for the ORR catalytic stability, figure 5(a) reflects that CeO$_2$-CoO$_x$/N-rGO performed better.
than the commercial Pt/C catalysts. As for the OER catalytic stability, figure 5(b) reflects that CeO2-CoOx/N-rGO performed best among all the supporting materials in the comparison and that it was far stronger than the commercial Pt/C and RuO2 catalysts. The reason should be the cobalt doping and graphite recombination synergistic effects.

3.6. XPS analysis before and after modification

Figure 6 shows the results of the XPS scanning peak separation of each element before and after the CeO2 modification. Figure 6(a) shows that the C1s peak was significantly enhanced and that the Ce3d peak was significantly weakened after loading graphite. Since the Co-doping amount was small and the XPS full-spectrum baseline noise of CeO2-CoOx was relatively large, the Co2p peak in figure 6(a) is not obvious, and figure 6(c) only shows a partially enlarged view. According to the peak splitting results and related literature [16–19], Co was
dominated by the low valence (+2 valence), and there was also a small amount of trivalent Co^{3+}. Co^{2+} positively promoted the ORR process, while Co^{3+} could provide an active site for the OER process. By comparing the polarization curves of the two samples (CeO_2-N-rGO and CeO_2-CoO_x/N-rGO) before and after the Co doping, it was found that Co^{2+}/Ce^{3+} synergistically enhances the ORR and OER electrocatalytic activity. This result is consistent with that of previous studies [7].

To further study the effect of compounding other materials on the internal structure of ceria, the obtained results after fitting the XPS peaks were tabulated, as shown in Table 3. According to literature [20–23], two reactions occurred in Figure 6(b): Ce^{4+} = u'' + u' + u + ν'' + ν' + ν and Ce^{3+} = u' + ν'. The peak position of Ce moved toward the high binding energy direction with compounding and doping, indicating that the CeO_2 and N-rGO were bonded with the covalent, which is consistent with related literature [24, 25]. In addition, from the calculations, it was found that the ratio of Ce^{3+}/(Ce^{4+} + Ce^{3+}) in CeO_2-CoO_x/N-rGO is higher than the corresponding value of pure CeO_2, which may also be the reason why the electrocatalytic ability was greatly enhanced after compounding.

In Figure 6(d), O_1, O_2, and O_3 represent the lattice oxygen, O^{2−}/O^−, adsorbed-OH and O_2, respectively, and C_1 represents the molecular water on the surface, carbonaceous substances, or oxygen-containing groups on the carbon surface, etc. [26–28]. From Table 3, it can be seen that the lattice oxygen content of ceria decreases after compounding and that the active oxygen species content increases. These changes are beneficial to the catalytic performance improvement. Also, the content of O_3 in Table 3 was significantly increased after compounding and doping, which might be because of any adsorbed water molecules or carbonates on the surface of pure CeO_2.

Figure 6(e) shows the XPS peak graph of the N element in N-rGO and CeO_2-CoO_x/N-rGO. The comparison shows that the peak graph of N in CeO_2-CoO_x/N-rGO is very similar to the related literature reports [29]. Through the area method integral calculation, the pyridine nitrogen, pyrrole nitrogen, and graphitized nitrogen contents were 39.7%, 32.2%, and 28.0%, respectively. However, the graphitized nitrogen content in N-rGO was very small, while that of pyridine nitrogen and pyrrole nitrogen was 76.1% and 23.9%, respectively. This indicates that the Ce and Co are more likely to combine with pyrrole nitrogen in CeO_2-CoO_x/N-rGO and that N-rGO is more likely to form graphitized nitrogen after loading. Among the three types of nitrogen, pyridine nitrogen is the main active site in the ORR process, so the increase in pyridine nitrogen content in CeO_2-CoO_x/N-rGO is also one of the reasons for the increase in the electrocatalytic activity [30]. Figure 6(f) shows the Cls XPS peak fitting graph [31, 32].

Compared with N-rGO, the Cls of the CeO_2-CoO_x/N-rGO shifts in the high binding energy direction, about 0.56 eV. This means that the electrons move away from the C atoms and approach the N-doped atoms through CeO_2–CoO_x recombination [33, 34], which further proves that CeO_2–CoO_x is bonded through the covalent bond between N and N-rGO.

### 4. Conclusions

In this study, we investigated the effects of the electrocatalytic performance of ceria nanoparticles through N-doping graphite and Co doping. The catalytic activity, relative content of oxygen-active species, crystal structure, and other characteristics of the material were characterized using an electrochemical workstation, a photoelectron spectrometer, a transmission electron microscope, a laser confocal Raman, and other devices. The experimental analysis results are as follows:

1. The experiment successfully prepared CeO_2/N-rGO, where the mass ratio of cerium nitrate to GO was chosen as 2:5 (cobalt-doped ceria-graphite composite catalyst with loading nano-sized particles).

2. The electrocatalytic performance of CeO_2-CoO_x/N-rGO is higher than that of pure CeO_2 and CeO_2/N-rGO, the catalytic stability of CeO_2-CoO_x/N-rGO is much better than that of Pt/C, and the catalytic performance of OER is better than that of commercial RuO_2.

3. The displacement of Cls in CeO_2-CoO_x/N-rGO to the high binding energy direction was 0.56 eV, which indicates that the two are mainly bonded by covalent bonds. Through compounding and doping, the...
relative oxygen vacancies content increases, which facilitates the rapid progress of electrocatalytic reactions. In addition, the relative content of the pyridine nitrogen of N-rGO increases with compounding, which also improves the electrocatalytic performance of CeO₂–CoOₓ/N-rGO.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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References

[1] Uthayakumar A et al 2016 Interfacial effect of the oxygen-ion distribution on the conduction mechanism in strontium-added Ce₅₋ₓSmₓOₓ₋₁₋ₓ/Na₂CO₃ nanocomposite J. Phys. Chem. C 120 25068–77
[2] Shimada H, Yamaguchi T, Suzuki T, Sumi H, Hamamoto K and Fujishiro Y 2016 High power density cell using nanostructured Sr-doped SmCoO₃ and Sm-doped CeO₂ composite powder synthesized by spray pyrolysis J. Power Sources 302 508–14
[3] Voskanyan A A, Chan K and Li C V 2016 Colloidal solution combustion synthesis: toward mass production of a crystalline uniform mesoporous CeO₂ catalyst with tunable porosity Chem. Mater. 28 2768–75
[4] Wang X et al 2017 The synergy between atomically dispersed Pd and cerium oxide for enhanced catalytic properties Nanoscale. 9 6645–9
[5] Huang Y C et al 2016 Bifunctional catalytic material: an ultrastable and high-performance surface defect CeO₂ nanosheets for formalddehyde thermal oxidation and photocatalytic oxidation Appl Catal B 181 779–87
[6] Xie S, Wang Z L, Cheng F L, Zhang P, Mai W J and Tong Y X 2017 Ceria and ceria-based nanostructured materials for photoenergy applications Nano Energy. 34 313–37
[7] Yang Z B, Yue T L, Yu X N and Wu M M 2018 J. Inorg. Mater. 33 845–53
[8] Dou S, Tao L, Huo J, Wang S and Dai L 2016 Etched and doped CoₓSn₀.₅ₓ/graphene hybrid for oxygen electrocatalysis Energy Environ. Sci. 9 1320–6
[9] Hao Y C, Xu Y Q, Liu J F and Sun X M 2017 Nickel–cobalt oxides supported on Co₀/N-doped graphene as an excellent bifunctional oxygen catalyst J. Mater. Chem. A 5 5594–600
[10] Xie J, Cao G S and Zhao X B 2005 CoSnₓ–graphite composite anode material for lithium ion batteries Rare Met. 24 42
[11] Chen Z Y et al 2018 N-doped defective carbon with trace Co for efficient rechargeable liquid electrolyte-/all-solid-state Zn-air batteries Sci. Bull. 63 548–55
[12] Liu J et al 2019 J. Mater. Chem. A 7 12451–6
[13] Wang Q C et al 2019 Chem. Commun. 55 14801–4
[14] Cwede T, Mahadevaiah N, Singh S and Friedrich H B 2016 Effect of Cu additives on the performance of a cobalt substituted ceria (CeₓCo₁₋ₓO₂)₁₋ₓ catalyst in total and preferential CO oxidation Appl Catal B 182 1–14
[15] Fan K et al 2018 Direct observation of structural evolution of metal chalcogenide in electrolytic water oxidation ACS NANO 12 12369–79
[16] Dou S et al 2017 Atomic-scale Co₃O₄ species in metal–organic frameworks for oxygen evolution reaction Adv. Funct. Mater. 27 1702546
[17] Gao K et al 2019 Efficient metal–free electrocatalysts from n-doped carbon nanomaterials: mono-doping and Co-doping Adv. Mater. 31 1805121
[18] He Y et al 2017 Ultrathin CeO₂ nanofilm as an efficient bifunctional catalyst for oxygen evolution and reduction reaction in rechargeable zinc-air batteries Nanoscale. 9 8623–30
[19] Zhuang L Z et al 2017 Ultrathin iron–cobalt oxide nanosheets with abundant surface functionalities for the oxygen evolution reaction Adv. Mater. 29 1606793
[20] Feng J X, Ye S H, Xu H, Tong Y X and Li G R 2016 Design and synthesis of FeOOH/CeO₂ heterolayered nanotube electrocatalysts for the oxygen evolution reaction Adv. Mater. 28 4698–703
[21] Deng W, Dai Q G, Lao Y J, Shi B B and Wang X Y 2016 Low temperature catalytic combustion of 1,2-dichlorobenzene over CeO₂–TiO₂ mixed oxide catalysts Appl Catal B 181 848–61
[22] Zang C J, Zhang X S, Hu Y Y and Chen F 2017 The role of exposed facets in the Fenton-like reactivity of CeO₂ nanocrystal to the Orange II Appl Catal B 216 106–13
[23] Béche E, Charvin P, Perarnau D, Abarandes S and Flamant G 2008 Ce 3d XPS investigation of cerium oxides and mixed cerium oxide (CeₓTi₁₋ₓO₂) Surf. Interface Anal. 40 264–7
[24] Srivastava M, Das A K, Khanra P, Uddin M E, Kim N H and Lee J H 2013 Characterizations of in situ grown ceria nanoparticles on reduced graphene oxide as a catalyst for the electrooxidation of hydrazine J. Mater. Chem. A 1 9792–801
[25] Huang K et al 2014 One-step synthesis of reduced graphene oxide–CeO₂ nanocubes composites with enhanced photocatalytic activity Mater. Lett. 124 223–6
[26] Liang F L, Yu Y, Zhou W, Xu Y Y and Zhu Z H 2015 Highly defective CeO₂ as a promoter for efficient and stable water oxidation J. Mater. Chem. A 3 634–40
[27] Li L et al 2017 Ultra-low loading of copper modified TiO2/CoO2 catalysts for low-temperature selective catalytic reduction of NO by NH3 Appl Catal B 207 366–75
[28] Chen J et al 2015 Chem. Commun. 51 10123–6
[29] Jiang Y X et al 2016 In-situ growth of CeO2 nanoparticles on N-doped reduced graphene oxide for anchoring Li2O2 formation in lithium-oxygen batteries Electrochim. Acta 210 712–9
[30] Cui X Y et al 2016 Pyridinic-nitrogen-dominated graphene aerogels with Fe-N-C coordination for highly efficient oxygen reduction reaction Adv. Funct. Mater. 26 5708–17
[31] Cong H P, Wang P, Gong M and Yu S H 2014 Facile synthesis of mesoporous nitrogen-doped graphene: an efficient methanol–tolerant cathodic catalyst for oxygen reduction reaction Nano Energy. 3 55–63
[32] Niu Y L, Huang X Q, Wu X S, Zhao L, Hu W H and Ming Li C 2017 One-pot synthesis of Co/N-doped mesoporous graphene with embedded Co3O4 nanoparticles for efficient oxygen reduction reaction Nanoscale. 9 10233–9
[33] Choi C H, Park S H and Woo S I 2012 Binary and ternary doping of nitrogen, boron, and phosphorus into carbon for enhancing electrochemical oxygen reduction activity ACS Nano. 6 7084–91
[34] Maldonado S, Morin S and Stevenson K J 2006 Structure, composition, and chemical reactivity of carbon nanotubes by selective nitrogen doping Carbon 44 1429–37