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PAPER

Metal-free selenium doped carbon nanotube/graphene networks as a synergistically improved cathode catalyst for oxygen reduction reaction[†]

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The ongoing search for new non-precious-metal catalysts (NPMCs) with excellent electrocatalytic performance to replace Pt-based catalysts has been viewed as an important strategy to promote the development of fuel cells. Recent studies have proven that carbon materials doped with atoms which have a relatively small atomic size (*e.g.* N, B, P or S), have also shown pronounced catalytic activity. Herein, we demonstrate the successful fabrication of CNT/graphene doped with Se atoms, which has a relatively large atomic size, by a simple, economical, and scalable approach. The electrocatalytic performance of the resulting Se-doped CNT-graphene catalyst exhibits excellent catalytic activity, long-term stability, and a high methanol tolerance compared to commercial Pt/C catalysts. Our results confirmed that combining CNTs with graphene is an effective strategy to synergistically improve ORR activity. More importantly, it is also suggested that the development of graphite materials doped with Se or other heteroatoms of large size will open up a new route to obtain ideal NPMCs with realistic value for fuel cell applications.

Introduction

The high cost and scarcity of platinum catalysts as well as the sluggish oxygen reduction reaction (ORR) at the cathode have become the greatest stumbling blocks to the large-scale commercialization of fuel cells (FCs).¹ Intensive efforts have therefore been made to reduce or replace Pt-based catalysts in FCs.²⁻⁵ In particular, the ongoing search for new non-preciousmetal catalysts (NPMCs) with excellent electrocatalytic performance for ORR has been viewed as a long-term strategy to promote the development of FCs.6 Recently, various metal-free N-doped carbon materials (e.g. carbon nanotubes, graphene and ordered mesoporous graphitic arrays) have shown striking electrocatalytic performance for the ORR and become an important category of potential candidates for replacing Pt-based catalysts.7-11 Theoretical calculations and experimental observations have proved that tailoring of the surface electronic structure by the introduction of heteroatoms into sp²-hybridized carbon frameworks is expected to play a key role in the enhancement of catalytic activity for the ORR.12-14 Recently, P-doped graphite layers and B-doped carbon nanotubes (CNTs) have also been developed and shown to possess pronounced catalytic activity for ORR.15,16 Our recent efforts have revealed that sulfur or iodine doping also improves the electrocatalytic performance of graphene.17,18 These significant findings for several new

Nanomaterials and Chemistry Key Laboratory, Wenzhou University, Wenzhou, 325027 (P. R. China). E-mail: yang201079@126.com; smhuang@wzu.edu.cn; Fax: +86 577-8837-3064 † Electronic supplementary information (ESI) available. See DOI: heteroatom-doped graphite materials having pronounced catalytic activity strongly indicate that further development of heteroatom doped graphite materials may be an effective pathway to obtain ideal NPMCs with high activity and practical durability for ORRs.¹⁹⁻²¹ Furthermore it will be helpful to understand the mechanism of ORR activity enhancement induced by doping.

Selenium, as one of the chalcogen elements, often shows similar chemical properties to sulfur. For example, the electronegativity of selenium (2.55) is very close to that of sulfur (2.58), both selenophene (C_4H_4Se) and thiophene (C_4H_4S) are planar structures, and the bond length and bond angle of C–Se–C in C_4H_4Se are almost equal to those of C–S–C in C_4H_4S .²² On the other hand, selenium has a larger atomic size and higher polarizability than sulfur. These factors motivated our curiosity in exploring the use of selenium doped carbon materials as metal free catalysts for ORR after sulfur doping into graphene had been confirmed to improve electrocatalytic performance of the graphene.

Carbon nanomaterials, including one-dimensional (1D) CNTs and two-dimensional (2D) graphene, have been widely applied in electrochemical fields due to their superior electrical conductivity, large surface area, and high chemical stability.^{23–26} Recently, combining CNTs with graphene as electrode materials has exhibited very good synergistic effects in super-capacitor and Li-ion battery applications.^{27,28} The as-designed electrodes have several highlights, as follows: First, the long 1D CNTs can insert between the graphene sheets and increase the basal spacing as well as the electrolyte-accessible surface area in comparison with pure graphene. Second, CNTs can also bridge defects between

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graphenes to form a 3-D interpenetrating network structure, providing highly effective pathways for ion or electron conduction. Obviously, these advantages are also beneficial for promoting ORR. Considering the characteristics of Se and the advantages of CNT/graphene composite, to develop the new selenium-doped CNT/graphene composites for ORR may be of both scientific and practical significance.

Herein, we demonstrate the successful fabrication of seleniumdoped CNT/graphene composites (Se-CNT-graphene) by a facile thermal annealing process. The electrocatalytic performance of the resulting Se-CNT-graphene exhibits excellent catalytic activity, long-term stability, and a high methanol tolerance. Our results address a new type of NPMC with excellent electrocatalytic activity by a simple, economical, and scalable route, which not only enriches the study of metal-free ORR catalysts, but also provides useful information to clarify further the ORR mechanisms of carbon materials with heteroatom structures

Experimental

Synthesis of the Se-doped carbon materials

Graphene oxide (GO) and CNTs were purchased from a commercial corporation (Fig. S1[†]). CNTs were treated in a concentrated sulfuric acid-nitric acid mixture (3:1 v/v) and refluxed for 2 h at 100 °C. Se-Doped carbon materials were synthesized by directly annealing carbon materials and diphenyl diselenide (DDS) in argon. In a typical procedure, CNTs treated with acid (4 mg) and graphene oxide (4 mg) were firstly ultrasonically dispersed in ethanol for about 90 min, and subsequently DDS (4 mg) were added into the CNTs/graphene suspension under ultrasonic conditions. The resulting suspension was spread onto an evaporating dish and dried at 40 °C, forming a uniform solid mixture. The mixtures were placed into a quartz tube with an argon atmosphere and annealed at 900 °C. After that, the sample was cooled to room temperature under Ar ambient and collected from the quartz tube. As a control experiment, other carbon materials obtained under various conditions (such as the annealing temperature and the mass ratios of carbon materials and DDS) were synthesized in the same way. Their physical parameters, electrochemical properties, and corresponding experimental data are listed in Table 1. The contents and bonding configurations of selenium in these Se-doped carbon materials can be adjusted by varying the mass ratio of carbon materials and BDS as well as the annealing temperatures. The Sedoped CNTs (or Se-graphene) were also prepared by directly annealing CNTs (or graphene oxide) and DDS under the same conditions. For comparison, GO without any dopants was treated under the same conditions. The resulting materials are denoted CNTs-graphene-900, Se-CNTs-graphene-900, CNTs-900, Se-CNTs-900, graphene-900, Se-graphene-900 and so on (Scheme 1).

Electrode preparation

Glassy carbon (GC) electrodes (3 mm diameter, CH instrument Inc.) were polished with a 0.05 and 0.3 μ m alumina slurry (CH Instrument Inc.) and subsequently rinsed with ultrapure water and ethanol. The electrodes were then sonicated in ultrapure water, rinsed thoroughly with ultrapure water and dried under a gentle nitrogen stream. To prepare the working electrode, all of the carbon catalyst (1 mg) was ultrasonically dispersed in ethanol (1 mL) under the same process, 10 μ L of the resulting suspension was dropped onto the GC surface and dried at room temperature for 6 h, then 0.5% Nafion (10 μ L) was dropped onto the GC and dried at room temperature. For comparison, a commercially available Pt/C-modified GCE (40 wt% Pt supported on carbon black) was prepared in the same way.

Electrochemical measurements

The electrochemical measurements to evaluate ORR activity, including cyclic voltammograms (CV), rotating-disk electrode voltammograms and chronoamperometry, were performed using a computer-controlled potentiostat (CHI 760 C, CH Instrument) in a standard three-electrode system at room temperature in an O₂-saturated 0.1 M KOH solution. A carbon catalyst electrode was used as working electrode, a Pt wire as counter electrode, and an Ag/AgCl (3 M KCl filled) electrode as reference. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 0.01 Hz to 100 KHz, with 5 mV as the amplitude at a bias potential of 0.24 V vs. SCE.



Scheme 1 Schematic illustration of Se-CNTs-graphene preparation.

Table 1 Physical parameters, electrochemical properties and corresponding experimental data for various carbon materials

Samples	DDS : CNTs : GO	Se content (wt%)	Peak potential/V	Peak current density/mA cm ⁻²	Kinetic current density/mA cm ⁻²	Number of electron transfer, <i>n</i>
CNTs-900	0:4:0	0	-0.33	0.93	2.65	2.08
Se-CNTs-900	2:4:0	1.03	-0.32	1.76	6.06	3.68
Graphene-900	0:0:4	0	-0.32	0.92	2.63	2.15
Se-graphene-900	2:0:4	1.09	-0.30	1.62	6.13	3.65
CNTs-graphene-900	0:4:4	0	-0.30	1.41	5.92	3.31
Se-CNTs-graphene-900	4:4:4	1.05	-0.29	2.41	10.04	3.95

Characterizations of physical parameters

X-Ray photoelectron spectroscopy (XPS) measurements were carried out with an ultra-high vacuum setup, equipped with a monochromatic Al K α X-ray source and a high resolution Gammadata-Scienta SES 2002 analyzer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded with a JEOL-3010 instrument. The UV-vis spectra of these samples were recorded by a Shimadzu 2450 UV-vis spectrophotometer at room temperature.

Results and discussion

Fig. 1a and b present typical SEM and TEM images of Se-CNTgraphene-900. Interconnected CNT networks supported on the graphene and cross-link points between the CNTs and graphene are easily observable, and these are an important indication for highly effective ion or electron conduction. Elemental composition analysis from the EDX pattern shown in Fig. 1c confirmed the presence of elemental Se in Se-CNT-graphene-900. XPS measurements were carried out to determine the elemental compositions of the materials. From the XPS survey spectrum in Fig. 1d, it can be found that all of the Se-doped carbon materials



Fig. 1 (a) SEM, (b) TEM and (c) EDX of Se-CNTs-graphene-900, (d) XPS survey spectra of CNTs-900, Se-CNTs-900, graphene-900, Se-graphene-900, CNTs-graphene-900, Se-CNTs-graphene-900, (e) high-resolution Se_{3d} spectra of CNTs-900 + Se, Se-CNTs-900, graphene-900 + Se, Se-graphene-900, CNTs-graphene-900 + Se, Se-CNTs-graphene-900, and (f) UV-vis spectroscopy of Se-CNTs-900 and CNTs-900.

show a new Se_{3d} peak at *ca*. 55.5 eV compared with the carbon materials without any selenium dopant. The Se contents in Se-CNT-900, Se-graphene-900 and Se-CNT-graphene-900 are calculated to be 1.03, 1.09 and 1.05, respectively. To clarify further whether the Se signals in these Se-doped carbon materials arose from physical adsorption or from covalent bonds, highresolution XPS Se_{3d} spectra of the Se-doped carbon materials were compared with those of the mixtures of pure carbon materials and DDS (CNT-900 + Se, graphene-900 + Se, CNTgraphene-900 + Se). From Fig. 1e, it can be observed that the high-resolution Se_{3d} peak for Se-CNTs-900 has an evidently shifted binding energy (56.0 eV) from that of CNT-900 + Se (55.4 eV). Similar tendencies can also be seen for Se-graphene-900 and Se-CNT-graphene-900. These XPS results negated the possibility of physical adsorption of DDS molecules on the surface of the carbon materials. We speculated that the shift in Se_{3d} peaks of these Se-doped carbon materials may be attributed to a transformation of the DDS C-Se-Se-C bond into a C-Se-C bond in the Se-doped carbon material. Moreover, the results of UV-vis spectroscopy, shown in Fig. 1f, also provide information confirming the Se doping of carbon materials. Under similar conditions, the peak attributed to π - π * transitions of C-C bonds in the Se-CNT-900 red-shifted to 221 nm compared with 213 nm for CNT-900. This result indicates that the selenium doping altered the π electron system at the CNT surface. Previous reports have confirmed that n-type substitution doping generally increases the effective π conjugation system on graphene sheets, and induces a red shift of C-C bond π - π * transitions in graphitic material.^{29–31} We therefore speculate that the observed shift may be attributed to the formation of C-Se bonds at the edge of the carbon materials, and that the resulting selenophene-like structure may be the dominant environment of the Se atoms in the present Se-doped graphite materials. According to Dai's report, carbon atoms at defect sites or oxygen-containing groups in GO can react with NH₃ to form C-N bonds.³² Thus, we believe that formation of C-Se bonds in Se-doped carbon materials may have a similar mechanism. The observed XPS and UV-vis spectroscopy results suggested that Se atoms were successfully introduced into the graphene framework via covalent bonds.

To evaluate the electrocatalytic ORR activities of the samples, we carried out cyclic voltammetry (CV) measurements in 0.1 M KOH solution saturated with O2. Fig. 2 clearly shows ORR peaks in all samples. From Fig. 2a, a single cathodic reduction peak at -0.33 V can be observed for the CNTs-900 electrode in the O₂-saturated solution. After the introduction of Se atoms, the peak potential of the ORR for the Se-CNT-900 electrode shifted positively to -0.32 V. Its oxygen-reduction current density was measured to be 1.76 mA cm⁻² after correction for background current, obviously higher than that of the CNT-900 electrode $(0.93 \text{ mA cm}^{-2})$. These results clearly indicate that the ORR catalytic activity of Se-CNTs-900 is greater than that of CNTs-900. Compared with the graphene-900 electrode, the Se-graphene-900 electrode also showed a positive shift in ORR peak potential and a more pronounced increase in the ORR current density, as shown in Fig. 2b. A similar tendency was also observed for CNTs-graphene-900 and Se-CNTs-graphene-900 electrodes (Fig. 2c). These experimental results indicate that Se doping is very effective for ORR activity enhancement of



Fig. 2 Cyclic voltammograms for (a) CNTs-900 and Se-CNTs-900, (b) graphene-900 and Se-graphene-900, and (c) CNTs-graphene-900 and Se-CNTs-graphene-900, (d) LSV curves for various carbon materials and a Pt/C catalyst on a glass carbon rotating disk electrode saturated in O_2 at a rotation rate of 2500 rpm.

graphitic materials. To gain further insight into the ORR performance of these samples, linear sweep voltammetry (LSV) measurements were performed on a rotating-disk electrode (RDE) in O₂-saturated 0.1 M KOH at a rotation rate of 2500 rpm, and compared with those carried out on a commercial Pt/C catalyst (40 wt%). From Fig. 2d, it can be seen that all the Se-doped carbon materials (Se-CNT-900, Se-graphene-900, and Se-CNT-graphene-900) have more positive onset potentials and higher limiting current density than those of the corresponding undoped carbon materials (CNT-900, graphene-900, and CNT-graphene-900). This result further supports the above-described CV observations, and strongly indicates that the introduction of the C–Se bond in graphite materials plays a very key role in ORR catalytic activity enhancement.

By integrating the present cases with previously reported research on metal free ORR catalysts,7,13,14 we propose some possible explanations for the observed excellent ORR activity induced by Se doping: (i) From the observed XPS and UV-vis spectroscopy results, it is confirmed that Se atoms are successfully introduced into the graphene framework via covalent bonds in these Se-doped carbon materials. Furthermore, the electrochemical impedance spectroscopy (EIS) measurement results (in Fig. S2[†]) also show that all the Se-doped carbon materials (Se-CNTs-900, Se-graphene-900, and Se-CNTs-graphene-900) have a smaller value of interfacial charge-transfer resistance than those of the corresponding carbon materials without dopants (CNTs-900, graphene-900, and CNTs-graphene-900). From the XPS, UV-vis and EIS analysis, it is believed that increased electron transfer may be because introduction of Se is able to restore defects at the edge of carbon materials and induce formation of a π conjugation system, producing highly effective electron transfer, which should be one of the factors contributing to the significantly enhanced catalytic activity observed. (ii) Previous reports involving the origin of ORR activity

enhancement in N-, B-, or P-doped carbon materials have suggested that breaking of the electroneutrality of graphitic materials, owing to the difference in electroneutrality between carbon and dopant, is likely to be a promising factor for promoting ORR activity.7,16 In other words, carbon atoms or adjacent heteroatoms with δ + charge are the origin for ORR activity enhancement in metal-free carbon catalysts. In the present case, considering that selenium has a electroneutrality close to that of carbon and that the C-Se-C bonds are predominately at the edge and defect sites in the materials, it is believed that the change in atomic charge distribution for Se-doped carbon materials should be smaller than in N-, (B-, or P)-doped carbon materials, and that the contribution of the δ + charge on Se-doped graphite materials may not be a dominant factor for accelerating ORR. (iii) Some recent reports have suggested that introduction of functional groups or doping atoms will induce more strain in carbon materials.^{33,34} Considering that selenium has an evidently larger atomic size than carbon, introduction of Se atoms into carbon materials may cause higher strain at their edges, which may facilitate charge localization and associated chemisorption of oxygen. Furthermore, we also note that selenium has high polarizability and that lone selenium pairs can easily interact with molecules in the surrounding electrolyte compared with other heteroatoms such as N, P, or S. These advantages, derived from the relatively high atomic number of selenium, may be among the dominant reasons why the ORR activity of the present Se-doped carbon materials with a mere 1 wt% of Se was comparable to that of N-doped carbon materials with 4-8 wt% of N.^{7,9,35} In this sense, selenium doping of graphite materials for improving ORR activity may be more effective than doping with N, or B. Our observations also indicate that doping of graphite materials with large size atoms may be a promising strategy to obtain new metal free catalysts with high activity. Certainly, the mechanisms for various different dopants may be complicated, and are under investigation.

Combining graphene with CNTs will improve the microstructure of the composites, which usually benefit the reactant, ion, and electron transport resistance.^{26,27} From Fig. 2a-c, it is clear that Se-CNT-graphene-900 has the highest peak current density and most positive ORR peak potential of all of the samples. The EIS result shown in Fig. S2[†] revealed that the value of the interfacial charge-transfer resistance on Se-CNT-graphene-900 was much smaller than those of single Se-CNT-900 or Se-graphene-900. These results strongly prove our assumption that combining CNTs with graphene synergistically improves ORR catalytic activity due to the formation of an interpenetrating network structure between CNTs and graphene that highly effectively accelerates reactant, ion and electron transport. Thus, the development of CNT/graphene composites is expected be of significance for promoting the large-scale application of fuel cells. To our knowledge, although many investigations involving CNT/graphene composites for application in electrochemical fields such as super-capacitors or Li-ion batteries have been reported,26,27 research into Se-doped CNT/graphene composites as ORR catalysts in FCs is rare. Furthermore, it can also be observed from Fig. 2d that Se-CNT-graphene-900 has a slightly negative onset potential and an evidently high current density (at -0.9 V) compared with the Pt/C catalyst (40%). These results suggest that the ORR catalytic activity of Se-CNT-graphene-900 is comparable to that of commercial Pt/C catalysts. To further study ORRs with respect to these samples, we performed RDE measurements at various rotation speeds. For RDE, diffusion current density is dependent on the rotation rate, while the number of electron transfers (*n*) and kinetic-limiting current density (J_k) involved in the ORR can be calculated from the Koutecky–Levich equation (ESI S3, Fig. S3,† Table 1). The *n* for Se-CNT-graphene-900 was calculated to be 3.95 at -0.60 V, which indicated a four-electron-transfer reaction. The calculated J_k value was 10.04 mA cm⁻² at -0.40 V. The electrocatalytic activity of Se-CNT-graphene-900 is comparable to those of N-doped CNTs (or mesoporous graphitic arrays) in alkaline electrolyte.⁷⁻⁹ The above results further confirm that Se-CNT-graphene-900 is a promising metal-free NPMC with high catalytic activity for ORRs.

Possible crossover effects and stability of the catalyst materials are both important parameters for evaluation of their practical application in fuel cells. Therefore, chronoamperometric responses to methanol introduced into O₂-saturated electrolyte were measured for both Se-CNT-graphene-900 and commercial Pt/C catalyst. It can be seen from Fig. 3a that after the addition of 3 M methanol at 40 s, no noticeable change was observed in the ORR current at the Se-CNT-graphene-900 electrode. These results indicate that Se-CNT-graphene-900 exhibits high ORR selectivity, and has a good ability for avoiding crossover effects. The durabilities of the Se-CNT-graphene-900 and Pt/C catalysts were also compared by holding them at -0.30 V for 3 h in an O₂-saturated 0.1 M KOH solution. Fig. 3b shows that the resulting chronoamperometric response for Se-CNT-graphene-900 exhibited a very slow attenuation, and a high relative current of 92.1% still persisted after 3 h. In contrast, the Pt/C electrode exhibited a gradual decrease, with a current loss of approximately 78.5% after 3 h. These results confirm that Se-CNT-graphene-900 is a promising metal-free NPMC for use in methanol and alkaline fuel cells.

As a control experiment, the influences of the annealing temperature and the mass ratios of carbon materials and DDS on the electrocatalytic properties of the materials were further explored. Fig. S4† shows CV measurement curves for carbon materials obtained under various conditions. The data involving their physical parameters, electrochemical properties corresponding experimental environments are listed in Table S1.† All the experimental data confirm that the Se-CNT-graphene-900 obtained from a mass ratio of CNTs, GO and DDS of 4: 4: 4 at



Fig. 3 Chronoamperometric responses of Se-CNTs-graphene-900 and Pt/C-modified GC electrodes, (a) with 3 M methanol added at around 40 s, and (b) at -0.30 V in an O₂-saturated 0.1 M KOH solution.

900 $^{\circ}$ C exhibited the most outstanding ORR activity amongst all the carbon materials tested.

Conclusions

In summary, we have reported a new kind of metal-free Se-CNTgraphene catalyst fabricated through a simple, economical, and scalable approach, which boasts a greater electrocatalytic activity, long-term stability, and an excellent resistance to crossover effects for ORRs. It was confirmed that combining CNTs with graphene is an effective strategy to synergistically improve ORR activity. More importantly, our results also suggest that development of graphite materials doped with Se or other heteroatoms of large size will open up a new route to obtain ideal NPMCs with realistic value for fuel cell applications.

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