Nitrogen-doped activated graphene/SWCNT hybrid for oxygen reduction reaction

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Abstract

Pt-free catalyst towards oxygen reduction reaction (ORR) that is highly active, stable, and low-cost is highly desirable for commercialization of fuel cells but still remains unresolved. Here, we report a hybrid material of nitrogen-doped activated graphene/carbon nanotubes via a simple self-assembly of graphene and carbon nanotubes followed by KOH activation and high temperature annealing in NH3 for an efficient metal-free catalyst for ORR. The single-walled carbon nanotubes are well intercalated into nanoporous graphene layers, which lead to a high surface area and electrical conductivity of the hybrid. The nitrogen doping provides more reactive sites for ORR and significantly enhances the reaction properties. The hybrid structure exhibits excellent catalytic behavior with a four-electron pathway in alkaline media and better stability than the commercial Pt/C catalyst. This study opens a new direction for developing low-cost and highly efficient carbon-based ORR electrocatalysts.

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1. Introduction

Energy is the most important issue in the 21st century. The depletion of fossil fuels and their effects on environmental pollution and global warming is ringing the alarm bell to human society [1,2]. Clean and renewable energy is certainly a solution for this energy crisis. The utilization of the renewable energy as well as the development of electrical vehicles urgently requires the high-capacity energy harvesting/storage systems (fuel cells, metal-air batteries, etc.) [3–5]. An electrocatalyst for the oxygen reduction reaction (ORR) is crucial in fuel cell devices [6].

Commercial Pt/C is the state-of-the-art electrocatalyst in fuel cell due to their low overpotential and high current density [7]. However, apart from the naturally limited resources and high cost, this noble metal catalyst suffers from the sluggish kinetics and poor stability [8–11]. These drawbacks have severely hindered the widespread applications of Pt/C. Numerous efforts have been done to search suitable alternatives for Pt-based catalysts such as nitrogen (N)-doped carbon nanotubes (CNTs) [12–16] and graphene [8,9,17–19], porous carbon [20–25], and nonprecious transition metal catalysts [26–30]. These alternative catalysts have relatively low cost and exhibited good electrocatalytic activity and long durability. However, their catalytic performances are still far from the requirements for practical fuel cell applications.

Accessible surface area and catalytically active sites are very crucial for ORR performance. The electrocatalysts with high surface area and mesoporosity could facilitate efficiently the adsorption of oxygen and accelerates the surface reaction, which enhances the ORR catalytic activity [5,9]. On the other hand, the ORR active sites induced by heteroatom doping play a critical role in the adsorption of oxygen molecules or peroxide anion and the first-step electron transfer (the rate determining step in ORR) [31]. In addition, high electrical conductivity of the catalysts could benefit the ORR electrocatalytic performance [32].

Recently, graphene/carbon nanotube hybrids have attracted much attention for energy-related applications due to their well-fined three dimension (3D) structure with high accessible surface area and electrical conductivity [33–39]. Several efforts have been devoted to synthesize the N-doped graphene/carbon nanotube hybrids as electrocatalysts for ORR [36,40]. The nitrogen impurities act as catalytically active sites that boost the ORR activity of the catalysts. However, either the electrocatalytic performance was still poor or the fabrication process was complex and non-scalable production. For examples, Chen and his co-workers reported a facile hydrothermal process at low temperature (180 °C) to
synthesize nitrogen-doped graphene/CNT nanocomposite as electrocatalyst for ORR [6]. The nanocomposite exhibited a close four-electron pathway with strong durability. However, the nanocomposite displayed a limited accessible surface area due to the random mixing of graphene and CNTs, and a low electrical conductivity due to the high oxygen content, leading to its mediocre electrochemical activity. By using chemical vapor deposition (CVD) approach, Tian and his co-workers synthesized a new N-doped graphene/single-walled carbon nanotube (SWCNT) hybrid as an efficient electrocatalyst for both ORR and oxygen evaluation reaction (OER) [3]. Nevertheless, the low nitrogen content (only 0.5 at.%) of the hybrid resulted in its low electron transfer number (3.22). In addition, the used CVD method is complex and hinders the scalable production of this material. In another work, Liu et al. reported N-doped CNTs and graphene nanohybrid prepared on FeNi catalyst by plasma-enhanced CVD in a mixture of N2, O2, and CH4 [40]. However, the resulted sample exhibited a far four-electron pathway for ORR; three-electron transfer in neutral medium and two-electron reductions in both alkaline and acidic solutions.

The design and synthesis of N-doped graphene/carbon nanotube-based catalysts with high accessible surface area, high electrical conductivity, high catalytic activity, and relevant N-doped active sites in low cost is desirable. We report here a simple and scalable mass production process to fabricate N-doped activated graphene/SWCNT (N-a-GS) hybrid as an efficient noble-metal-free electrocatalyst for ORR. It is worth mentioning that we choose SWCNTs because it displays better ORR activity due to its higher accessible surface area and lower defect density compared to MWNTs. The activated graphene/SWCNT (a-GS) was first prepared following our previous work by a simple self-assembly and KOH activation methods [33]. The static interaction between positively charged SWCNTs and negatively charged graphene oxides in the self-assemble process ensures the formation of well-defined 3D hybrid structure. The KOH activation resulted in the high accessible surface area of the hybrid. The N-doping of a-GS was done further by heat treatment under ammonia/argon ambient with controllable temperature (800–900 °C). Nitrogen was homogeneously doped into the highly porous structure. The resulted N-a-GS nanocomposite exhibits a high ORR catalytic performance with a close four-electron pathway, high positive onset potential, large peak current and strong durability. These results indicate that our material holds a promising potential as ORR electrocatalyst for energy conversion technologies.

2. Experimental

2.1. Fabrication of N-a-GS

The schematic illustration of the fabrication of N-a-GS samples is shown in Fig. 1. First, the a-GS sample was prepared following our previous work [33]. Briefly, graphene oxide (GO) was synthesized from graphite using the modified Hummer method [41]. The GO solution (1 mg/ml) was then prepared by dispersing the purified GO powder in water. The SWCNT (>95%, Time&Nano, China) solution was prepared by dispersing in water with cetyltrimethylammonium bromide (CTAB, >99%, SigmaAldrich) as surfactant. The GO solution was then mixed with the CTAB-SWCNT solution. After stirring for an hour, the mixture was freeze-dried for overnight. A KOH solution was added into the GO/CTAB-SWCNT powder with a mass ratio of KOH and GO/CTAB-SWCNT is 2:1. The mixture was then stirred for another hour and dried in a vacuum oven at 90 °C for 12 h. The resulting KOH/GO/CTAB-SWCNT powder was placed in a horizontal tube furnace (50 mm diameter). The temperature was increased to 300 °C for 30 min, then to 800 °C at a ramping rate of 5 °C/min, and held there for an hour under an argon gas flow of 500 sccm. After cooling, the powder was washed by 10% acetic acid and dionized water several times until a pH of 7 was reached, and dried in a vacuum oven at 120 °C for 12 h to get the a-GS powder. The nitrogen doping process was done by annealing the a-GS powder at high temperature in ammonia/argon gas ambient. We used two different annealing temperatures for the comparison. The samples prepared at 800 °C and 900 °C are marked as N-a-GS-800 and N-a-GS-900, respectively.

2.2. Characterization

The morphological studies were performed via field emission scanning electron microscopy (FESEM, JEOL JSM7000F, Japan). The X-ray diffraction patterns were collected using a Rigaku SmartLab X-ray diffractometer (Cu KR radiation, λ = 0.154 06 nm). Raman spectroscopy was performed using a micro–Raman system (Renishaw, RM1000-InVia, UK) with a laser wavelength of 532 nm. The specific surface area was measured via liquid nitrogen cryosorption (Micromeritics ASAP2020, USA) using the BET method. The micropore and mesopore size distributions were estimated via the HorvathKawazoe (HK) and BarrettJoyner-Halenda (BJH) methods, respectively. The samples were also characterized by X-ray photoelectron spectroscopy (XPS, ESCA 2000, VG Microtech, England).

2.3. Electrochemical measurements

Electrochemical measurements were conducted on Versatile Multichannel Potentiostat (Biologic Science Instruments). A three-electrode configuration with Pt coil counter electrode, Ag/AgCl reference electrode, and a working electrode of 3.0 mm diameter glassy carbon (GC) rotating disk electrode (RDE) was used. A RDE-3A (ALS Co., Ltd) was used for RDE measurements. Each catalyst ink was prepared by mixing 4 mg catalyst with 220 μl ethanol, 660 μl DI water and 80 μl 5 wt% Nafion solution, followed by sonication for a sonication at least 2 h. Then, 3 μl of the ink was dropped onto the glassy carbon and dried overnight at room temperature.

Commercial Pt/C (20 wt% Pt on Vulcan XC-72) electrode was prepared by the same procedure. Catalyst loading for all samples, including Pt/C, was 177 μg cm−2. 0.1 M KOH was saturated with N2 or O2 by bubbling nitrogen or oxygen for 30 min. All catalysts were activated by 20 cycles of cyclic voltammetry (CV) with a 50 mV s−1 scan rate from 0 to −1.0 V (vs. Ag/AgCl) in N2-saturated electrolyte before experiments. For CV measurements, the working electrode was cycled between 0 and −1.0 V at a scan rate of 10 mV s−1 with continuous N2 or O2 flow. For rotating disk electrode (RDE) measurements, the working electrode was rotated at 400–2025 rpm with a scan rate of 5 mV s−1 between 0.1 and −1.0 V with continuous O2 flow. The durability tests were conducted in O2-saturated electrolyte at −0.4 V with a rotation speed of 1600 rpm.

3. Results and discussion

The SEM images of the N-a-GS nanocomposite are shown in Fig. 2(a) and (b). The nanocomposite is a well-defined 3D porous structure which contains entangled SWCNTs and fragmented graphene flakes. XRD patterns were obtained to investigate the stacking of graphene and SWCNTs (Fig. 3(a)). The a-GS and N-doped graphene/SWCNT (N-GS) samples show a platform without typical (002) peak, indicating that SWCNTs were well intercalated into graphene layer, which prevented the graphene from restacking during self-assembly. Note that the N-GS sample was prepared by simply N doping of non-activated graphene/SWCNT nanocomposite. The very weak and broad peaks at 18.3° and 19° were observed in the N-a-GS-800 and N-a-GS-900 samples, respectively.
This appearance was due to the insignificant restacking of graphene layers during high temperature treatment.

Graphitic feature of all the samples was investigated by Raman spectra (Fig. 3(b)). The intensity ratio \( I_D/I_G \) of D band (\(-1350 \text{ cm}^{-1}\)) to G band (\(-1580 \text{ cm}^{-1}\)) is generally used to measure the disorder of graphitic carbon [7]. The higher \( I_D/I_G \) value, the more defects in carbon structure. The \( I_D/I_G \) values for N-GS, a-GS, N-a-GS-800 and N-a-GS-900 samples are 0.10, 0.14, 0.20 and 0.18, respectively. These small \( I_D/I_G \) values indicate that all of the samples possessed the high order of graphitic carbon, leading to the high electrical conductivity of the samples. The slight difference in \( I_D/I_G \) ratio of N-GS (0.10) and a-GS (0.14) reveals that N doping process produces fewer defects than KOH activation. The combination of N doping and KOH activation leads to a slight increase of the defects in N-a-GS-800 and N-a-GS-900 samples. The \( I_D/I_G \) ratio of N-a-GS-900 sample (0.18) was reduced from that of N-a-GS-800 sample (0.20) due to the graphitic reconstruction at higher annealing temperature.

To analyze the surface functionalities and doping level of N-a-GS-800, we conducted X-ray photoelectron spectroscopy (XPS) measurement. High resolution C1s spectra of the samples (Fig. 4(a)) show typical carbon species in nitrogen-doped carbons. The peak at
284.6 eV corresponds to the graphitic sp² carbon, taking the portion (55.5%). The peak at 285.6 eV reveals C–N peaks corresponding to the doping of nitrogen atoms. The other three peaks with binding energies of 286.8, 288.0, 289.3 eV with relatively small portion of 10.2%, 5.0%, 4.6% are attributed to C–OH, C=O, O=C=O bond, respectively [35]. High resolution XPS scans (Fig. 4(b)) show that the N1s spectrum can be deconvoluted into three N species centered at 398.4, 400.1 and 401.6 eV with relative portions of 56.9%, 28.7% and 14.4%, corresponding to pyridinic N, pyrrolic N and graphitic N, respectively [23]. The total nitrogen content in the sample was measured to be 2.3%.

Pore structure properties of the a-GS and N-a-GS-800 samples were investigated by the nitrogen adsorption/desorption isotherms at 77 K (Fig. 5). The isotherms are of type IV with the rapid increment at low $P/P_0$ region ($P/P_0 > 0.1$) and the hysteresis in the desorption branch, showing the existence of both micropores and mesopores in the samples (Fig. 5(a)) [7,42]. Table 1 provides the pore properties of the a-GS and N-a-GS-800 samples. The total BET surface area and micropore volume were slightly decreased after N doping, from 1373 m²/g of a-GS to 1191 m²/g of N-a-GS-800 and from 0.34 mL/g of a-GS to 0.30 mL/g of N-a-GS-800, respectively. This reduction is ascribed to the high temperature annealing (800 °C) for N doping process, which caused the insignificant restacking of graphene layers. This data is consistent with the appearance of the very weak and broad (002) peaks in the XRD patterns of the N-doped samples (Fig. 3(a)). The pore size
Fig. 5. (a) Nitrogen adsorption/desorption isotherm at 77 K and (b) Pore size distribution of the a-GS and N-a-GS-800 samples.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Total BET surface area (m²/g)</th>
<th>Micropore surface area (m²/g)</th>
<th>External surface area (m²/g)</th>
<th>Micropore volume (mL/g)</th>
<th>Mesopore volume (mL/g)</th>
<th>Total pore volume (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-GS</td>
<td>1373</td>
<td>835.6</td>
<td>537.4</td>
<td>0.34</td>
<td>0.44</td>
<td>0.78</td>
</tr>
<tr>
<td>N-a-GS-800</td>
<td>1191</td>
<td>718.8</td>
<td>472.2</td>
<td>0.30</td>
<td>0.44</td>
<td>0.74</td>
</tr>
</tbody>
</table>


distribution (Fig. 3(b)) shows the main micropores of ~0.6 nm in diameter and mesopores of ~2 nm in diameter in both a-GS and N-a-GS-800 samples. The appearance of another mesopores at ~4 nm in diameter in the N-a-GS-800 sample may be attributed to the ammonia activation during N doping process, which widens the pore size within the sample. It is worth noting that, the ammonia activation could improve the porosity and surface area of the N-doped sample. However, this improvement was depressed by the restacking of graphene layers during high temperature treatment.

To test the electrochemical performance of the catalysts for ORR, the samples were mounted on a rotating disk electrode (RDE) and measured in O₂-saturated 0.1 M KOH solution with a scanning rate of 5 mV s⁻¹. Fig. 6(a) shows the ORR polarization curves of a-GS, N-GS, N-a-GS-800, N-a-GS-900 and commercial Pt/C obtained at a rotation rate of 1600 rpm. N-a-GS-800 exhibits an onset potential of about 0.03 V (vs. Ag/AgCl) and a half-wave potential of ~0.19 V, much better than that of a-GS (~0.12 and ~0.39 V) and N-GS (~0.06 and ~0.21 V). Moreover, a-GS and N-GS show inferior limiting current densities. These results suggest the superiority of combining high surface area and nitrogen doping for the samples. N-a-GS-900 exhibits similar onset potential and limiting current density compared to that of N-a-GS-800 with a slightly more positive half-wave potential of ~0.16 V. This may result from its better crystallinity and conductivity after annealing at higher temperature. To compare the catalytic properties, we also conducted the measurement of commercial Pt/C. Both of N-a-GS-800 and N-a-GS-900 reveal similar onset and half-wave potential to Pt/C, which demonstrates the similar catalytic activity of our samples compared to that of Pt/C.

To gain an understanding of the electron transfer parameters, we performed the RDE experiment of N-a-GS-800 at different rotating speeds ranging from 400 to 2025 rpm (Fig. 6(b)), based on which the corresponding Koutecky-Levich (K-L) plots at different potentials were obtained. K-L equation relating the current density \( j \) to the rotation rate \( \omega \) of the electrode was used to calculate the electron transfer number \( n \).

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B \omega^{0.5}}
\]

where \( j_k \) is the kinetic current density and \( B \) is expressed by the following expression,

\[
B = 0.62nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2}
\]

Here \( F \) is the Faraday constant \((96,485 \text{ C mol}^{-1})\); \( D_{O_2} \) is the diffusion coefficient of O₂ in 0.1 M KOH \((1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})\); \( v \) is the kinematic viscosity of the electrolyte solution \((0.01 \text{ cm}^2 \text{ s}^{-1})\); \( C_{O_2} \) is the concentration of dissolved O₂ \((1.2 \times 10^{-6} \text{ mol cm}^{-3})\). The constant 0.62 is adopted when the rotation speed is expressed in rad s⁻¹ [30]. As shown in Fig. 6(c), the obtained electron transfer number of N-a-GS-800 is 3.97–4.08 ranging from ~0.4 to ~0.7 V, indicating that our sample catalyzes ORR through a four-electron pathway, corresponding to the complete reduction of oxygen into water. For comparison, the calculated \( n \) of different samples was plotted in Fig. 6(d). The electron transfer number of N-a-GS-800 is much higher than that of a-GS (2.64–3.35) and N-GS (3.45–3.61), slightly higher than that of N-a-GS-900 (3.78–3.96). The calculated \( n \) of Pt/C is nearly 4 throughout the potential range. All these results suggest that N-a-GS-800 shows the best ORR catalytic performance, which is close to commercial Pt/C. The onset potential, maximum current density, and electron transfer number could be the primary concern for ORR catalyst performance. Compared to previous works with heteroatom-doped carbon electrocatalysts listed in Table 2, our sample shows the most positive onset potential (0.03 V vs. Ag/AgCl), large electron transfer number (~4), and high current density (5.2 mA/cm²), which indicates the outstanding catalytic activity. The superior performance results from the advantages of both graphene and SWCNTs such as high conductivity and high surface area, which can be further improved by KOH activation. Due to their excellent structural properties and inherent heteroatom dopants, the material can serve as a good metal-free catalyst for ORR. Nevertheless, the ORR performance could be improved by introducing metal loading, for example, N-doped graphene loaded with Fe particles provides high current density...
Fig. 6. (a) RDE polarization curves of aGS, N-GS, N-aGS-800, N-aGS-900 and Pt/C at a rotation rate of 1600 rpm in O2-saturated 0.1 M KOH solution. (b) RDE polarization curves of N-aGS-800 at various rotation speeds. (c) The corresponding K-L plots of N-aGS-800 at different potentials. (d) Electron transfer number of the above five samples at different potentials. For all the RDE measurements, the loading of catalysts is 177 μg/cm²; scan rate: 5 mV/s.

Table 2

Electrochemical performance of different electrocatalysts for oxygen reduction reaction in alkaline media.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area [m²/g]</th>
<th>Loading [mg/cm²]</th>
<th>Onset potential [V vs. Ag/AgCl]</th>
<th>Half-wave potential [V vs. Ag/AgCl]</th>
<th>Current at –1 V at 1600 rpm [mA/cm²]</th>
<th>Electron transfer number</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-aGS-800 (Our work)</td>
<td>1191</td>
<td>0.18</td>
<td>0.03</td>
<td>–0.19</td>
<td>5.2</td>
<td>3.99</td>
</tr>
<tr>
<td>Pt/C (In our work)</td>
<td>–</td>
<td>0.18</td>
<td>0.05</td>
<td>–0.15</td>
<td>5.2</td>
<td>4</td>
</tr>
<tr>
<td>VA-NCNTs [12]</td>
<td>–</td>
<td>–</td>
<td>–0.08</td>
<td>–0.2</td>
<td>4.1</td>
<td>3.9</td>
</tr>
<tr>
<td>N-doped CNTs [16]</td>
<td>280</td>
<td>0.21</td>
<td>–0.11</td>
<td>–0.23</td>
<td>3.5</td>
<td>2.7</td>
</tr>
<tr>
<td>N-doped graphene [8]</td>
<td>508</td>
<td>0.05</td>
<td>–0.03</td>
<td>–0.4</td>
<td>3.8</td>
<td>3.82</td>
</tr>
<tr>
<td>N-doped graphene</td>
<td>1760</td>
<td>0.107</td>
<td>0</td>
<td>–0.17</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>N-doped graphene [18]</td>
<td>–</td>
<td>0.15</td>
<td>0.01</td>
<td>–0.16</td>
<td>4.4</td>
<td>3.7</td>
</tr>
<tr>
<td>N-RG-O [9]</td>
<td>350</td>
<td>1.0</td>
<td>–0.15</td>
<td>–0.3</td>
<td>5.6</td>
<td>3.35</td>
</tr>
<tr>
<td>3D-GN [43]</td>
<td>–</td>
<td>0.082</td>
<td>–0.04</td>
<td>–0.21</td>
<td>6.0</td>
<td>3.8</td>
</tr>
<tr>
<td>NGSH [3]</td>
<td>812.9</td>
<td>0.25</td>
<td>–0.01</td>
<td>–0.25</td>
<td>5.7</td>
<td>3.22</td>
</tr>
<tr>
<td>NG-NCNT [6]</td>
<td>–</td>
<td>0.05</td>
<td>–0.095</td>
<td>–0.285</td>
<td>3</td>
<td>3.7</td>
</tr>
<tr>
<td>B, N-doped CNFs [7]</td>
<td>306.3</td>
<td>0.32</td>
<td>–0.068</td>
<td>–0.213</td>
<td>4.3</td>
<td>3.43</td>
</tr>
<tr>
<td>NOMGAs [20]</td>
<td>510</td>
<td>0.026</td>
<td>–0.13</td>
<td>–0.35</td>
<td>6.1</td>
<td>3.89</td>
</tr>
<tr>
<td>NPMC [22]</td>
<td>1663</td>
<td>0.15</td>
<td>–0.04</td>
<td>–0.13</td>
<td>4.1</td>
<td>3.8</td>
</tr>
<tr>
<td>Micro/meso N-doped C [24]</td>
<td>1280</td>
<td>0.10</td>
<td>–0.03</td>
<td>–0.13</td>
<td>5.8</td>
<td>3.97</td>
</tr>
<tr>
<td>N-doped porous CS</td>
<td>1413</td>
<td>–</td>
<td>0.01</td>
<td>–0.16</td>
<td>4.8</td>
<td>3.99</td>
</tr>
<tr>
<td>N-doped porous C [44]</td>
<td>668</td>
<td>–</td>
<td>–0.12</td>
<td>–0.31</td>
<td>5.3</td>
<td>3</td>
</tr>
<tr>
<td>N, S, P-doped CNRs [45]</td>
<td>378</td>
<td>–</td>
<td>–0.05</td>
<td>–0.22</td>
<td>2.8</td>
<td>3.7</td>
</tr>
<tr>
<td>Fe3N/NGA [30]</td>
<td>116.9</td>
<td>0.05</td>
<td>0.00</td>
<td>–0.18</td>
<td>6.0</td>
<td>4</td>
</tr>
</tbody>
</table>

The bold in the Table 2 is used to highlight our results.

Notes:
- VA-NCNTs = vertically aligned nitrogen-containing CNTs, N-RG-O = N-doped reduced graphene oxide, 3D-GN = three-dimensional graphene networks, NGSH = N-doped graphene/SWCNT hybrid, NG-NCNT = N-doped graphene/carbon nanotube, CNFs = carbon nanofibers, NOMGAs = N-doped ordered mesoporous graphitic arrays, NPMC = N and P co-doped mesoporous carbon, C = carbon, CS = carbon sphere, CNRs = carbon nanorings, Fe3N/NGA = Iron nitride and N-Doped graphene aerogel.
and ideal electron transfer number [30]. This will be future work in our case as well.

Fig. 7(a) shows CV curves of N-a-GS-800 in O₂-saturated and N₂-saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹. A well-defined cathodic peak (reduction process) occurring at −0.17 V is observed in the O₂-saturated 0.1 M KOH solution. In contrast, no evident peaks are recorded in the same potential range in N₂-saturated KOH solution. The durability of N-a-GS-800 and Pt/C catalysts toward ORR was evaluated through chronoaamperometric measurements at −0.4 V with a rotation speed of 1600 rpm (Fig. 7(b)). After 20,000 s reaction, the commercial Pt/C catalyst suffers from 15.4% loss of the current density, whereas our sample only exhibits 10.7% decrease in current density. These results indicate a superior stability of N-a-GS-800 catalyst to commercial Pt/C catalyst in alkaline solution.

4. Conclusions

In summary, we have fabricated nitrogen-doped activated graphene/SWCNT hybrids through a simple self-assembly of graphene and SWCNTs, KOH activation and high temperature annealing in NH₃, and used the materials as efficient metal-free catalysts for oxygen reduction reaction. BET measurement revealed the high specific surface area of the sample, and XPS spectra demonstrated the successful nitrogen doping to the samples. Consequently, the hybrids showed similar catalytic activities but superior stability over commercial Pt/C. The calculated electron transfer number of nearly 4 indicated the efficient four-electron pathway of ORR. The excellent catalytic performance was ascribed to the structural superiority of good conductivity and improved surface area. In addition, the NH₃ annealing introduced heteroatom dopants to the hybrids, which increased the reaction sites for ORR and made the catalytic properties synergistically enhanced. Moreover, this carbon-based material could also potentially be used in other applications which require high surface area and high conductivity, such as hydrogen evolution reaction, supercapacitors, hydrogen storage and so on.

Acknowledgments

This work was supported by Institute for Basic Science (IBS-R011-D1) and in part by BK21-Plus through Ministry of Education, Korea.

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