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# Facile synthesis of cobalt and nitrogen co-doped graphene networks from polyaniline for oxygen reduction reaction in acidic solutions<sup>†</sup>

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Direct pyrolysis of a mixture comprising polyaniline nanofibers and cobalt(II) nitrate is found to be a simple and scalable approach to the synthesis of Co and N co-doped graphene networks for oxygen reduction reaction in acidic solutions with high catalytic activity and excellent durability.

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Three-dimensional (3D) graphene with interconnected porous structures can show high specific surface area, excellent conductivity, low mass density, elegant flexibility and good mechanical strength, due to the combination of 3D porous structures and intrinsic properties of graphene.<sup>1</sup> Various 3D graphene materials have been extensively prepared and investigated for various applications including supercapacitors, microbial fuel cells, lithium-ion batteries, electrocatalysis, solar cells, environmental protection, and chemical sensors, with better functions than 2D graphene sheets.<sup>2</sup> 3D graphene materials derived from graphene oxide and reduced graphene oxide have been prepared via controlled self-assembly and template-directed deposition.3 However, graphene oxide products are generally prepared by conventional and improved Hummers methods that involve complicated procedures, making the whole synthesis procedure for 3D graphene timeconsuming. Highly conductive 3D graphene can be prepared on porous substrates (e.g., Ni foam) by chemical vapor deposition from molecular carbon precursors (e.g., CH<sub>4</sub>).<sup>4</sup> However, special porous metal substrates are strongly needed, which may increase the cost of 3D graphene products. Therefore, it is interesting and important to develop a simple and scalable approach for 3D graphene preparation.

Electrochemical energy conversion devices, ranging from fuel cells to metal-air batteries, require effective catalysts for

oxygen reduction reaction (ORR).5 Pt and its alloy nanoparticles have been extensively used as effective catalysts for ORR, but their high cost, limited supply, and weak durability severely hinder their applicability to broad commercialization. Great research efforts have therefore been focused on the development of non-precious metal catalysts with ORR activity comparable to that of Pt-based catalysts but much lower cost.6 Although many materials can show high catalytic activities in alkaline media,7 few non-precious metal catalysts can show high ORR activities in acidic solutions. M-N-C (M = Co and/or Fe) catalysts are only one of several successful examples in acidic solutions.8 M-N-C catalysts are a class of carbonaceous materials doped with nitrogen functionalities possibly coordinated by metallic species, which can be simply prepared via pyrolysis of precursors comprising nitrogen, carbon and metal salts. Despite the great progress, the ORR activities of M-N-C catalysts are still less competitive than those of Pt-based catalysts. To further improve the ORR activity, synthesis of a novel M-N-C catalyst with high specific surface area, abundant pore structure, and high electrical conductivity, is still of great interest and importance.

In our design concept, Co and N co-doped 3D graphene can integrate the advantages of 3D graphene with M–N–C catalysts, and thus are expected to serve as a highly active catalyst for ORR. In this work, novel Co and N co-doped graphene networks (Co–N-GNWs) were facilely prepared by simple pyrolysis of a mixture comprising polyaniline nanofibers and cobalt(II) nitrate. The as-prepared Co–N-GNWs with an interconnected porous structure showed high specific surface area, high crystallization degree, and Co and N co-doping, all of which are beneficial to the improvement of ORR activity. As a result, the Co–N-GNWs showed comparable catalytic activity for four-electron ORR in acidic solutions but superior stability and methanol tolerance to a commercial Pt/C catalyst.

The synthesis procedure of Co–N-GNWs is shown in Scheme S1 in the ESI.† In brief, the pre-synthesized polyaniline nanofibers (Fig. S1 in the ESI†) were mixed with a cobalt( $\pi$ ) nitrate powder in a weight ratio of 1 : 1 by a dry method using a mortar

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and pestle. The mixture was subjected to heat treatment at 200 °C for 2 h and then at 900 °C for 5 h under a N<sub>2</sub> atmosphere, at a heating rate of 10 °C min<sup>-1</sup>. After cooling to room temperature, the resulting sample was etched in excessive 3 M HCl aqueous solution. Finally, the pre-leached catalyst underwent a second heat treatment at 900 °C for 2 h under a N<sub>2</sub> atmosphere.

The morphology of the as-prepared Co–N-GNWs was characterized by scanning electron microscopy (SEM). As shown in Fig. 1a–c, the Co–N-GNWs show an interconnected macroporous structure with pore sizes ranging from 200 to 400 nm. The network structure was further confirmed by transmission electron microscopy (TEM). As shown in Fig. 1d–f, the Co–N-GNWs are obviously composed of 2D graphene nanosheets. The thickness of the few-layer graphene wall is ~3 nm, which was confirmed by the high-resolution TEM (HR-TEM). Some small carbon-coated metal nanoparticles also formed during the synthesis process; so some mesopores with pore sizes smaller than 30 nm can also be observed after acid leaching (Fig. S2 in the ESI $\dagger$ ). The lattice fringes clearly show an interplanar spacing of 0.33 nm, which is consistent with the (002) lattice spacing of graphite.

To understand the formation mechanism of graphene networks, the mixture of polyaniline nanofibers and cobalt(II) nitrate was heated to different temperatures. Fig. 2a shows an X-ray diffraction (XRD) pattern of the mixture after being heated to 200 °C, which clearly indicates that some crystallized CoO (JCPDS 89-7099) nanoparticles exist. Some diffraction peaks at 36.5°, 42.4°, 61.5°, 73.7° and 77.5° are observed, in good agreement with (111), (200), (220), (311) and (222) planes of the cubic CoO. Although some diffraction peaks of Co3O4 are overlapped with those of CoO, small diffraction peaks at 18.8°,  $31.3^{\circ}$ ,  $59.4^{\circ}$  and  $65.2^{\circ}$  are still observed, indicating that some Co<sub>3</sub>O<sub>4</sub> (JCPDS 64-0437) also exists at 200 °C. The TEM image (Fig. 2b) clearly indicates that small CoO nanoparticles are embedded in a polyaniline matrix. The HRTEM image (Fig. 2c) indicates that the lattice spacing is 0.205 nm, consistent with the (200) lattice spacing of the cubic CoO. As is well known,  $cobalt(\pi)$  nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) has a lower melting point (55 °C) than other cobalt( $\pi$ ) salts. The melted cobalt( $\pi$ ) nitrate can penetrate into polyaniline nanofibers. As shown in Fig. 2b, the one dimensional structure of polyaniline was completely



Fig. 1 SEM (a-c) and TEM (d-f) images of Co-N-GNWs.



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Fig. 2 XRD patterns (a and d) and TEM images (b, c, e, and f) of a mixture of polyaniline nanofibers and cobalt(II) nitrate after being heated to 200 (a–c) and 900 °C (d–f). Note here that these samples were prepared only by heat treatment without acid leaching.

destroyed after cobalt salt penetration; so no well-defined nanowire structure is observed. The decomposition of cobalt(II) nitrate can be explained as follows:

$$2\text{Co}(\text{NO}_3)_2 \rightarrow 2\text{CoO} + 4\text{NO}_2\uparrow + \text{O}_2\uparrow \tag{1}$$

$$5\text{Co}(\text{NO}_3)_2 \rightarrow 2\text{Co}_3\text{O}_4 + 12\text{NO}_2\uparrow + 2\text{O}_2\uparrow$$
(2)

*i.e.*  $Co(NO_3)_2$  is converted to CoO and  $Co_3O_4$ . After pyrolysis under a  $N_2$  atmosphere, polyaniline is converted to amorphous carbon, which can react with CoO according to the following reaction:

$$CoO + C \rightarrow Co + CO \uparrow$$
 (3)

The thermodynamic feasibility of formation of Co via the reduction of CoO by carbon can be examined using Ellingham diagrams. Kannan has reported that the thermodynamic reduction temperature for CoO is ca. 505 °C by using Ellingham diagrams.9 The heat treatment temperature in our experiment (900 °C) is higher than the thermodynamic reduction temperature for CoO; so the reduction of CoO is feasible. The formation of Co is also confirmed by XRD. Fig. 2d shows an XRD pattern of the mixture of polyaniline nanofibers and cobalt(II) nitrate after being heated to 900 °C, which indicates that some well crystallized Co (JCPDS 15-0806) nanoparticles also exist besides CoO and Co<sub>3</sub>O<sub>4</sub>. Three sharp diffraction peaks at 44.2°,  $51.5^{\circ}$ , and  $75.9^{\circ}$  are observed, in good agreement with (111), (200), and (220) planes of the cubic Co. The average size of Co nanoparticles calculated through Scherrer's equation by analyzing the XRD diffraction peaks is ca. 30 nm. The diffraction peaks in Fig. 2d for various Co species are much sharper than those in Fig. 2a, indicating that cobalt oxides undergo aggregation at high temperatures. As shown in Fig. 2e, carbon coated cobalt-based aggregates are observed. As shown in Fig. 2f, the lattice spacing of 0.205 nm is consistent with the (220) lattice spacing of  $Co_3O_4$ , and the lattice spacing of 0.177 nm is consistent with the (200) lattice spacing of cubic Co.

Co can serve as a catalyst for graphitization at low temperatures;<sup>10</sup> so graphitic carbon shells are coated on cobalt-based aggregates (Fig. 2f). After removing cobalt-based aggregates by acid leaching, open and interconnected carbon shells, *i.e.* graphene networks, were obtained. Note that the second heat treatment is not strongly needed for the formation of graphene networks, but is favorable for improving the catalytic activity toward ORR.<sup>8a</sup> As shown in Fig. S3 in the ESI,† graphene networks with an interconnected macroporous structure are still observed in the absence of the second pyrolysis.

From the above discussion, we can conclude that  $cobalt(\pi)$  nitrate underwent melting, decomposition, and partial reduction in the formation process of graphene networks. Thus  $cobalt(\pi)$  nitrate plays very important roles in the synthesis of graphene networks. As shown in Fig. S4 in the ESI,† only nitrogen-doped carbon nanowires (N-CNWs) can be obtained in the absence of  $cobalt(\pi)$  nitrate. The weight ratio of polyaniline nanofibers and  $cobalt(\pi)$  nitrate is also important for controlled synthesis of Co–N-GNWs. When the weight ratio of polyaniline nanofibers to  $cobalt(\pi)$  nitrate is 2:1, only carbon networks without a well-defined nanosheet structure are observed (Fig. S5a in the ESI†). When the weight ratio of polyaniline nanofibers to  $cobalt(\pi)$  nitrate is 1:2, only graphene nanosheets without an interconnected macroporous structure are observed (Fig. S5b in the ESI†).

The Co–N-GNWs were further studied by XRD and Raman spectroscopy. A strong and sharp diffraction peak observed at 26.1° (Fig. 3a) is attributed to the (002) plane of the hexagonal graphite structure, indicating a high crystallization degree for Co–N-GNWs. In contrast, the N-CNWs synthesized in the absence of cobalt(II) nitrate shows no obvious diffraction peak in the XRD pattern. Three peaks at 1347 (D-band), 1572 (G band), and 2695 cm<sup>-1</sup> (2D band) can be observed in the Raman spectrum for Co–N-GNWs (Fig. S6 in the ESI†). The intensity



Fig. 3 (a) XRD patterns of Co–N-GNWs and N-CNWs prepared at a carbonization temperature of 900 °C. (b) Nitrogen adsorption/ desorption isotherms and pore distribution (inset) of Co–N-GNWs and N-CNWs. (c) XPS survey spectrum and Co 2p peak (inset) of Co–N-GNWs. (d) High resolution XPS spectrum of N 1s.

ratio of D-band to G-band  $(I_D/I_G)$  is generally used to evaluate the crystallization degree of carbon materials. The values of  $I_D/I_G$  for Co–N-GNWs and N-CNWs are 0.46 and 1.18, respectively. The low  $I_D/I_G$  ratio also indicates a higher graphitization degree of Co–N-GNWs than that of N-CNWs.

Fig. 3b shows nitrogen adsorption-desorption isotherms and pore size distribution of Co-N-GNWs and N-CNWs. The Co-N-GNWs shows a high Brunauer-Emmett-Teller (BET) surface area of 401 m<sup>2</sup> g<sup>-1</sup>. A distinct hysteresis loop is observed at high relative pressures  $(P/P_0 > 0.43)$  for Co-N-GNWs, indicating the presence of a mesoporous structure in Co-N-GNWs. The pore size distribution of Co-N-GNWs (inset of Fig. 3b) calculated from absorption data using the Barrett-Joyner-Halenda (BJH) model shows that abundant mesopores exist in the range of 3-30 nm. The N-CNWs show a BET surface area of 696 m<sup>2</sup> g<sup>-1</sup>. An obvious N<sub>2</sub> adsorption at low relative pressures  $(P/P_0 < 0.1)$  but no hysteresis loop at high relative pressures can be observed for N-CNWs, indicating the presence of abundant micropores but few mesopores in N-CNWs. The pore size distribution (inset of Fig. 3b) also shows that Co-N-GNWs have more abundant mesopores than N-CNWs.

The involvement of both N and Co in Co-N-GNWs was verified by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3c, XPS data reveal that the N content in Co-N-GNWs is as high as 4.13 at%, which is a little lower than that in N-CNWs (4.57 at%, Fig. S7a in the ESI<sup>†</sup>). Fig. 3d shows high resolution XPS spectra of N 1s for Co-N-GNWs. The N 1s peaks can be fitted by four component peaks, namely, pyridinic N (398.6 eV) bonded to two C atoms in six-membered rings at the edge of carbon matrix, pyrrolic N bonded to two C atoms in fivemembered rings at the edge of carbon matrix (399.8 eV), graphitic N (401.2 eV) bonded to three C atoms in central or valley position of carbon matrix, and oxidative N species (403 eV). The peak deconvolution analysis shows that the percentages of pyridinic N, pyrrolic N, graphitic N, and oxidative N in Co-N-GNWs are 22.7%, 15.8%, 52.4%, and 9.1%, respectively. The percentages of pyridinic N, pyrrolic N, graphitic N, and oxidative N in N-CNWs are 28.1%, 21.0%, 36.7%, and 14.2%, respectively (Fig. S7b in the ESI<sup>†</sup>). Obviously, the percentage of graphitic N in Co-N-GNWs (52.4%) is higher than that in N-CNWs (36.7%). Because cobalt incorporation can result in higher graphitization,10 other N components tend to be transformed to graphitic N.11 Pyridinic and pyrrolic nitrogens might coordinate with a metal to form  $M-N_x$  (M = Fe or Co) moieties, which serve as active sites of M-N-C catalysts for ORR in acidic solutions.<sup>8d,8e</sup> XPS analysis (inset of Fig. 3c) also reveals the presence of a trace amount of Co species (0.17 at%) in Co-N-GNWs. Two sets of peaks are observed in the cobalt region for Co–N-GNWs, with binding energies of  $\sim$ 780 and  $\sim$ 795 eV, corresponding to  $2p_{3/2}$  and  $2p_{1/2}$ .

As shown in Fig. S8 in the ESI,† fitting of the C 1s spectrum can be resolved into three individual component peaks at binding energies of 284.7, 287.1 and 289.5 eV, representing graphitic carbon, carbonyl group and carboxyl group, respectively. XPS results reveal that the atom ratio between C and O in Co–N-GNWs is  $\sim$ 32 : 1, while the atom ratio between C and O in N-CNWs  $\sim$ 11 : 1 (Fig. S7a in the ESI†), indicating that heat

treatment in the presence of cobalt(II) nitrate can result in higher graphitization and lower O content.

The Co-N-GNWs with unique structure and composition are expected to have high ORR activity. The Co-N-GNWs were tested as a catalyst for ORR, and cobalt-free N-CWs and Pt/C were used as reference catalysts. The ORR measurements of Co-N-GNWs and N-CNWs were performed in an O2-saturated 0.5 M H2SO4 aqueous solution at room temperature by using a rotating disk electrode (RDE). As is well known, the ORR activity of Pt/C measured in a non-adsorbing electrolyte (HClO<sub>4</sub>) is much higher than that in an adsorbing electrolyte  $(H_2SO_4)$ ; so the ORR measurement of Pt/C was performed in an O2-saturated 0.1 M HClO<sub>4</sub> aqueous solution. A characteristic set of polarization curves for ORR on Co-N-GNWs, N-CNWs and Pt/C catalyst modified RDEs are displayed in Fig. 4a. The RDE polarization curves show that the Co-N-GNW catalyst has an onset potential of 0.95 V, which is much more positive than that of the cobaltfree N-CNW catalyst (0.77 V). In addition, the diffusion-limiting current of the Co-N-GNW catalyst is much higher than that of the N-CNW catalyst. These results indicate that the Co-N-GNW catalyst exhibits ORR activity superior to that of the N-CNW catalyst. The half-wave potential  $(E_{1/2})$  of the Co–N-GNW catalyst is 0.81 V, which is only a 30 mV negative shift compared with a commercial Pt/C catalyst (0.84 V). Fig. 4b shows the corresponding Tafel plots of Co-N-GNW and Pt/C catalysts. A similar slope was observed for Co-N-GNWs (63 mV dec<sup>-1</sup>) and Pt/C  $(67 \text{ mV dec}^{-1})$ , suggesting a similar reaction mechanism of ORR on the catalyst surface where the rate-determining step at both catalysts was likely the first electron reduction of oxygen. The kinetic mass activity  $(j_m)$  of the Co-N-GNW catalyst at 0.80 V calculated through the Koutecky–Levich equation is  $13.2 \text{ Ag}^{-1}$ , which is higher than the values of polyaniline-based Fe-N-C catalyst (~6.7 A g<sup>-1</sup>),<sup>8a</sup> VB12-based mesoporous Fe-N-C (5.0 A g<sup>-1</sup>),<sup>8b</sup> and phenylenediamine-based Fe-N-C (11.5 A g<sup>-1</sup>),<sup>8c</sup> highlighting the high ORR activity of our Co-N-GNW catalyst. Note that a second heat treatment is strongly needed for the improvement of ORR activity. As shown in Fig. S9 in the ESI,† the half-wave potential of the catalyst prepared without a second pyrolysis is ~120 mV negative shift compared with that of the catalyst prepared with a second pyrolysis, consistent with previous report.7a The catalytic activities of the samples with different weight ratios of polyaniline nanofibers to cobalt nitrate were tested. Co-N-GNWs with a well-defined interconnected



Fig. 4 (a) ORR polarization curves for Co–N-GNWs, N-CNWs and Pt/C catalysts recorded at room temperature at a sweep rate of 10 mV s<sup>-1</sup> and a rotation rate of 900 rpm. (b) Corresponding Tafel plots of Co–N-GNWs and Pt/C catalysts.

graphene-like network structure can be prepared only when the weight ratio of polyaniline nanofibers to cobalt nitrate is 1 : 1 (Fig. 1 and S5 in the ESI†). As shown in Fig. S10 in the ESI,† the Co–N-GNWs show the highest catalytic activity, highlighting the advantage of the well-defined interconnected graphene-like network structure of Co–N-GNWs. The well-defined interconnected graphene-like network structure of Co–N-GNWs can not only increase electrochemically accessible active sites but also facilitate electron/mass transfer, resulting in enhanced catalytic activity.

To investigate the active sites of Co–N-GNWs, X-ray absorption fine structure (XAFS) spectroscopy measurement for Co–N-GNWs was carried out. Fig. S11 in the ESI† shows the XAFS spectrum of Co–N-GNWs. The bonding environment of the Co atoms is investigated by Fourier transforms of k2-weighted Co *K*-edge extended XAFS (EXAFS). The quantified fitting result shows that Co–N bonding is found and its coordination number was estimated to be ~4.6. These results confirm the formation of Co complexes. In fact, the formation of metal–nitrogen complexes during heating treatments has also been reported elsewhere.<sup>8d,8e</sup> Therefore, the high ORR activity of Co-NGNWs is mainly attributed to the involvement of ORR-active Co–N complex in Co–N-GNWs.

To investigate the ORR catalytic pathway, rotating ring-disk electrode (RRDE) measurements were carried out to monitor the formation of  $H_2O_2$  in the ORR. As shown in Fig. S12 in the ESI,<sup>†</sup> the H<sub>2</sub>O<sub>2</sub> yield measured for the Co-N-GNW catalyst is below 2%, and the corresponding electron transfer number (n)is above 3.96 over the potential range from 0.1 to 0.9 V, indicating virtually complete reduction of O2 to H2O in a fourelectron process. In contrast, the N-CNW catalyst produced 13.1-21.8% H<sub>2</sub>O<sub>2</sub> and the value of electron transfer number is 3.56-3.74 over the potential range from 0.10 to 0.60 V. Fig. S13 in the ESI† shows polarization curves for a Co-N-GNW catalyst at different rotation rates. The limiting currents of the Co-N-GNW catalyst increased with increasing rotation speed (from 400 to 2025 rpm). The corresponding Koutecky-Levich plots within the potential range from 0.40 to 0.70 V exhibit good linearity with a rather consistent slope, suggesting first-order reaction kinetics for ORR with respect to oxygen concentration in the solution. The slopes of their linear fit lines are used to calculate the electron transfer number on the basis of the Koutecky-Levich equation. The Co-N-GNW catalyst exhibits the electron transfer number of 3.95-3.96 depending on the potentials, well consistent with the result obtained from RRDE measurements.

Various catalysts were subjected to testing the possible crossover in the presence of 1 M methanol. Fig. S14 in the ESI<sup>†</sup> compares the effect of methanol on the ORR over various catalysts. The ORR on a Pt/C catalyst is seriously restrained in the presence of methanol due to the occurrence of methanol oxidation reaction on Pt. In contrast, the ORR onset potential and current density for Co–N-GNW and N-CNW catalysts remain almost unchanged in the presence of methanol. These results suggest that the Co–N-GNWs and N-CNWs catalysts are methanol tolerant and can selectively perform the ORR in the presence of methanol. The durability of various catalysts toward ORR was evaluated by the accelerated durability tests, which were carried out at room temperature in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions by applying cyclic potential sweeps between 0.6 and 1.1 V at 50 mV s<sup>-1</sup> for 3000 cycles. As shown in Fig. S15 in the ESI,† the Co-N-GNW and N-CNW catalysts showed a negative shift of the half-wave potential by 2 and 5 mV, respectively. In contrast, the Pt/C catalyst showed a negative shift of the halfwave potential by 25 mV. The durability of Co-N-GNW and Pt/C catalysts toward ORR was also evaluated through chronoamperometric measurements at 0.70 V in an O2-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. As shown in Fig. S16 in the ESI,† the Co-N-GNW catalyst lost only ~13% of its initial activity after 10 000 s continuous operation, whereas Pt/C lost nearly  $\sim$ 32% of its initial activity. These results indicate a much better stability of the Co-N-GNW catalyst than the Pt/C catalyst in acidic solutions.

In conclusion, Co–N-GNWs were facilely synthesized from a mixture comprising polyaniline nanofibers and cobalt(II) nitrate *via* simple pyrolysis and acid leaching. The Co–N-GNWs showed many attractive features including interconnected network structure, high specific surface area, high crystallization degree, and Co and N co-doping. More importantly, the Co–N-GNWs showed comparable catalytic activity but superior stability and methanol tolerance to a commercial Pt/C catalyst for four-electron ORR in 0.5 M  $H_2SO_4$  aqueous solutions. This work not only provides a simple and scalable approach to direct synthesis of 3D graphene from polymers, but also demonstrates a promising non-precious metal catalyst for fuel cell applications.

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