Rational design of single atomic Co in CoN$_x$ moieties on graphene matrix as an ultra-highly efficient active site for oxygen reduction reaction

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The sharp increase in current energy consumption needs the development of fuel cells (FCs) as one of sustainable, renewable, efficient and eco-friendly electrochemical conversion systems of energy. The performance of electrocatalysts is crucially important for commercialization of FCs. Commercial Pt based catalysts are used due to their high catalytic activity. However, widespread commercialization is impossible because of the scarcity and poor durability of Pt based catalysts. We are on our quest to find a more stable and affordable alternative catalyst of Pt based catalysts. In particular, single-atom catalysts supported on

graphene are greatly attractive because of their unique characteristic and high catalytic activity. In this work, graphene is hydrothermally treated by sulfuric acid to introduce the ion-exchanging sites. Then, Co^{2+} ion-exchanging, 2-methylimidazole coordination and pyrolysis process are subsequently conducted to prepare highly-dispersed single-atom Co species catalyst with outstanding ORR activity and durability. This work presents a new direction for a rational design of single-atom catalyst on carbon matrix.

The efficient conversion of energy is one of the urgent problems because of the sharp increase in current energy consumption.[1] Electrochemical conversion of energy is one of the promising solutions for stable energy supply because it is sustainable, renewable, efficient and eco-friendly. In particular, fuel cells (FCs) have attracted the great interest as an environment-friendly and high-efficient power generation system without any inefficient combustion processes. FCs mainly consist of two electrochemical reactions: hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR).[2] Therefore, hydrogen is recognized as an eco-friendly and renewable energy source nowadays, and electrochemical hydrogen evolution reaction (HER) has also been developed as a hydrogen production process without consumption of fossil fuels unlike the conventional processes. Obviously the efficiency of these electrochemical reactions strongly depends on electrocatalysts.[3–5]

Pt based catalysts often show excellent electrocatalytic performances on these reactions; Pd-Pt bimetallic nanodendrites have high electrocatalytic activity,[6] and the alloys of Pt and early transition metals have high electrocatalytic activity for ORR.[7] They have been applied for fuel cell catalysts only for high-value added industries because of the scarcity, instability, and high cost of Pt. Large-scale commercialization requires abundant, stable and affordable catalysts with high efficiency comparable to the Pt based catalysts.[8–10]

For the realization of such electrocatalysts, graphene with π electrons exhibiting high electric conductivity like metals is anticipated to work as an excellent support due to their exceptional

chemical and physical properties such as high surface area (~2630 m^2 g^{-1}), exceptionally great thermal conductivity at room temperature (~5300 W m^{-1} K^{-1}) and ultrahigh electron mobility (200,000 cm^2 V^{-1} s^{-1}).[11–18] Graphene analogues doped with chalcogen or pnictogen show good electrocatalytic performance: N-doped graphene[19] and mesoporous graphene doped with sulfur and nitrogen.[20] But they are not as efficient as the Pt-based catalysts. To improve the electrocatalytic performance of the graphene analogues, we focus on the introduction of transition metals. In particular, nitrogen coordinated cobalt (CoN$_x$) species on the carbon matrix works as an efficient active site as electrocatalyst. Macrocyclic complex with CoN$_4$ moieties supported on carbon black exhibit high electrocatalytic activity for ORR and long-term stability[21,22]. The introduction of CoN$_x$ into graphene might be effective; in fact, cobalt and nitrogen-decorated graphene aerogel with unique hierarchical pores exhibits impressive electrocatalytic performance in an acid medium.[23] The electrocatalytic performance of the decorated graphene should arise from the high specific surface area. However, many studies reported that the metal aggregation during high-temperature pyrolysis processes probably decreases electrocatalytic activity.[24,25] Therefore, graphene with highly-dispersed CoN$_x$ species could be an ideal electrocatalyst if metal nanoparticles are prevented from aggregating during carbonization.[26]

 Highly-dispersed cobalt and nitrogen codoped carbon can be synthesized by using ion exchange resin anchoring Co^{2+} ion and 2-methylimidazole as ingredients, and the obtained catalyst shows excellent electrocatalytic performance for ORR.[27] Here, we propose a novel approach to synthesize highly-dispersed CoN$_x$ species on graphene as shown in **Figure 1**. After the treatment of sulfuric acid for the introduction of ion-exchanging sites, Co^{2+} ion and 2-methylimidazole were introduced to form highly-dispersed CoN$_x$ species on graphene. Moreover, we evaluate the electrocatalytic performance of the samples obtained from the new synthesis method as catalysts for ORR.

First, we hydrothermally treated graphene in sulfuric acid to introduce thiol groups as the ion-exchanging sites into graphene. The states of the S species in graphene before and after the hydrothermal treatment in sulfuric acid (G and GS) can be clarified by analyzing XPS spectra, which depend on oxidation number of the S atoms and on the atoms bonded to the S atoms (**Figure S1**). The first and second peaks (S1 and S2) at around 170.0 and 168.7 eV were detected for both the untreated and the treated graphene, and they are probably derived from oxidized sulfur ($-SO_n-$), where *n* is 2 and 3, respectively. These results suggest that the raw graphene originally contains oxidized sulfur as impurities and these S species remained after the treatment. The other two peaks detected at 164.2 and 163.0 eV (S3 and S4) only for GS are likely to be associated with the presence of thiol groups (S $2p_{3/2}$ at 163.0 eV, S $2p_{1/2}$ at 164.2 eV).[28–31] These results indicate that the hydrothermal treatment is effective for the introduction of thiol groups, which are expected to be good ligands for the Co^{2+} ions. In fact, the treated graphene has the ion exchange ability as confirmed by back titration. The increase of ion-exchanging sites in the hydrothermal treatment is estimated to be 0.3 mmol g^{-1}. This increase should be attributed to the generation of thiol groups.

Next, we introduced Co^{2+} ion into the obtained GS followed by the additioin of 2-methylimidazole (MeIm) that is expected to inhibit the aggregation of Co species and to introduce catalytic active sites (Co-N bond).[32,33] Nanoparticles (ca. 3.5~5.2 nm) can be observed in the TEM image of the sample after Co^{2+} ion-exchange and MeIm coordination (Co-MeIm/GS) as shown in **Figure S2**, indicating Co species with nitrogen coordination was successfully anchored on GS. Cobalt nanoparticles were not observed on the sample after Co^{2+} ion-exchange (Co-IE/GS), as showed in Figure S2. XRD patterns for all samples including G, GS, Co-IE/GS, and Co-MeIm/GS have only two peaks at 25.7 º and 43.4 º corresponding to the peaks of graphene as shown in Figure S2. Meanwhile, any peaks derived from Co species were not found even in Co-MeIm/GS, implying that Co/2-methylimidazole

complex could be anchored on the graphene without the formation of crystalline byproducts like ZIF-67.

We carbonized Co-MeIm/GS under N_2 atmosphere to covalently immobilize Co^{2+} ion and MeIm in GS (Co-N/GS). To confirm if MeIm inhibits the aggregation of Co species and works as a ligand of the active sites, we prepared GS doped with Co^{2+} ion without MeIm (Co/GS) for comparison. XRD petterns for both Co/GS and Co-N/GS show two broad peaks at 25.7 º and 43.3 º assigned to C(002) and C(100) of graphene. These results indicate that the structure of graphene does not change during the overall synthesis process. Meanwhile, no peaks derived from Co species are detected as displayed in **Figure S3**; the cobalt nanoparticles formed on Co/GS and Co-N/GS might be too small to be detected, or the amount of cobalt might be too small. In fact, the inductively coupled plasma (ICP) analysis idicates that the amount of Co species is 0.08 wt% as shown in **Table S1**. Cobalt nanoparticles can be found in the TEM image of Co/GS, whereas no nanoparticles can be found in the TEM image of Co-N/GS clearly as shown in **Figure S4**. These results imply that the Co^{2+} ion was successfully anchored by thiol group as the ion-exchanging sites, and that the aggregation of Co species is suppressed by the coordination of 2-methylimidazole during the carbonization process. STEM images for Co-N/GS indicate that isolated single-atom Co species exist as shown in **Figure 2**. The single-atom Co species on graphene is expected to work as an electrocatalyst.

We evaluated the electrocatalytic activity of the obtained carbon materials for ORR in alkaline medium as shown in **Figure 3**.[34–39] We found that Co-N/GS shows excellent onset potential and limiting current density compared to G, GS, and Co/GS and that the onset potential reach 0.89 V vs. RHE. ORR is likely to occur smoothly on Co-N/GS by comparing with the previously reported Co species supported on graphene[40–43]. We can say that the single-atom Co species with nitrogen coordination on Co-N/GS functions successfully. Moreover, we also found that Co-N/GS exhibits high current density at 0.65 V vs. RHE,

which is comparable to that of commercial Pt based catalysts (Pt/C 20 wt%) despite the amount of Co species on Co-N/GS as active sites was extremely small (0.08 wt%) as described above. We compared ORR catalytic activity of the Co-N/GS catalyst with previous Co/N co-doped graphene catalysts in alkaline media as shown in Table S2. Co-N/GS exhibits a comparable ORR catalytic activity with a more positive ORR onset potential and well-defined limiting current density, even though Co-N/GS has much lower cobalt content than other catalysts. These results suggest that the highly efficient catalytic activity of Co-N/GS is due to the highly-dispersed single-atom Co species, which have the maximized catalyst interface. Meanwhile, all the previously reported cobalt-based catalysts for ORR exhibit much poorer electrocatalytic activity in acid medium. The number of transferred electrons obtained during the ORR was followed by the current registered in the Pt ring during the experiments. G, GS and Co-GS show similar n profile during the whole potential range; however, sample Co-N/GS has a much higher selectivity towards water formation (from 2.6 to 3.4 at 0.5 V vs RHE in G and Co-N/GS, respectively). This fact points out the crucial role that single-atom Co species play in the ORR selectivity.

Next, we also measured the electrocatalytic activity of Co-N/GS for ORR in 0.1 M HClO$_4$ aqueous solution as one of the common acid media (**Figure S5**). Even Co-N/GS showed outstanding electrocatalytic peformance compared to G, GS and Co/GS, although the activity was not as good as the activity in alkaline solution. The high ORR activity in the acid medium might be attributed to single-atom Co species with nitrogen coordination, which would accelarate the rate-determining step of ORR: the proton and charge transfer to the OH species adsorbed on the catalysts.[44] Although commercial Pt based catalysts showed the best electrocatalyst activity in both alkaline and acid media, the durability and methanol tolerance of commercial Pt based catalysts is low[45].

We compare the durability and methanol tolerance of Co-N/GS with those of Pt/C. The durability was tested under steady state mass transport conditions in alkaline solution (0.65 V

vs. RHE and rotating speed for 1600 rpm). Methanol (1 M) was added after 7200 s continuous operation as methanol tolerance test. Whereas Co-N/GS showed high relative current density in alkaline medium (94 %), the relative current density of Pt/C 20 wt% decreased to 87 % as shown in **Figure S6**. Moreover, the relative current density of Pt/C 20 wt% significantly fell down after methanol injection. This is because platinum was poisoned by CO generated from methanol.[46] The dramatic decline of the current density was not found in Co-N/GS even after the addition of methanol. These results indicated that Co-N/GS has higher durability and methanol tolerance than Pt/C 20 wt%.

We can conclude that, the sequential treatments of sulfuric acid, Co^{2+} ion, and 2-methylimidazole are effective to prepare graphene with the ultra-low amount and single-atom Co species, working as a highly-durable electrocatalyst showing high efficiency comparable to Pt-based catalysts. The introduced ion-exchanging sites immobilize Co^{2+} ions to restrain their aggregation and to improve the electrocatalytic activities. The high durability of Co-N/GS is also a consequence of the covalent bonding between CoN_x species and graphene. This work provides a new synthesis route of highly-dispersed single-atom metal species with nitrogen coordination on carbon materials, which could reduce the usage of metal ions and improve the catalytic activity.

Experimental Section

Materials: 97 % sulfuric acid, $Co(NO_3)_2 \cdot 6H_2O$, 2-mehylimidazole (MeIm), 0.1 M NaOH, NaCl, Phenolphthalein and Methanol were purchased by Wako. Graphene nanoplatelets (extent of labeling: surface area 750 $m^2 g^{-1}$) was purchased by Aldrich. Potassium hydroxide (KOH) and Pt/C (20% loading) were purchased from Sigma-Aldrich. Perchloric acid (60%, $HClO_4$) were purchased from VWR-Chemicals Prolabo. All the electrochemical solution were prepared using ultrapure water (18 MΩ cm from an Elga Labwater Purelab system). The

gases N_2 (99.999%), O_2 (99.995 %) and H_2 (99.999%) were provided by Air Liquide and were used without any further purification or treatment.

Synthesis of sulfur group functionalized Graphene (GS): Graphene (1.5 g) was hydrothermally treated with sulfuric acid (30 mL) at 90 °C for 12 hours. And the processes of washing by the deionized water and drying were conducted sequentially. This sample is named as GS. The increase of ion-exchanging site number of GS was calculated using back titration procedure by measuring both G and GS. Deionized water (35 mL), NaCl (0.5 g), 1M NaOH (3 mL), and GS or G (0.2 g) were mixed and stirred for 24 hours. Subsequently, the solid was filtrated and supernatant liquid was mixed with few drops of phenolphthalein. And then the mixture was titrated with 0.1 M aqueous HCl until the color change from pink to transparency. The increase of ion-exchanging site number of GS was calculated from the difference of the titrated amount.

Synthesis of Co and N doped GS: GS (0.5 g) was stirred with $Co(NO_3)\cdot6H_2O$ (0.022 g) for 5 hours in deionized water (40 mL) at room temperature. Co^{2+} ion exchanged GS (Co-IE/GS) was washed with water and dried. Then, 0.25 g of Co-IE/GS was stirred with MeIm (0.0378 g) in Methanol (40 mL) for 5 hours at room temperature. MeIm coordinated Co-IE/GS (Co-MeIm/GS) was washed with methanol and dried. Finally, Co-MeIm/GS was carbonized at 800 °C for 3 hours with a ramp of 13 °C/min under an N_2 atmosphere in a tubular furnace. The sample is denoted as Co-N/GS. In order to investigate the effect of the MeIm, the carbonization of Co-IE/GS was also done under the similar condition. This sample is named as Co/GS.

Characterization: X-ray diffraction (XRD) patterns were obtained using a Philips X'Pert MDR diffractometer using Cu-Kα radiation. Transmission electron microscope (TEM) images were recorded on a Hitachi H-800. X-ray photoelectron spectroscopy (XPS) spectrum on Co 2p, S 2p and N 1s were obtained in a VG-Microtech Multilab 3000 spectrometer with an Al Kα radiation (1253.6 eV) as the energy source.

Electrochemical Measurements: Electrochemical activity tests towards ORR were carried out at 298 K in a three-electrode cell with 0.1M KOH and 0.1 M $HClO_4$ electrolytes using an Autolab PGSTAT302 (Metrohm, Netherlands) potentiostat, a graphite bar as counter electrode and Reversible Hydrogen Electrode (RHE) as reference electrode. A rotating ring-disk electrode (RRDE, Pine Research Instruments, USA) equipped with a glassy carbon (GC) disk (5.61 mm diameter) and an attached Pt ring was used as working electrode. The samples were dispersed in a solution of 20 vol% of isopropanol, 80 vol% of water and 0.02 vol% of Nafion@ to prepare a final dispersion of 1mg ml^{-1} of the prepared catalysts. And then, 100 µl (mass of electrode is 400 µg cm^{-2}) of the dispersion was pipetted on a GC electrode to obtain uniform catalysts layer for ORR study. The sample on the GC was dried by IR lamp for evaporation of the solvent. Cyclic Voltammetry (CV) and linear sweep voltammetry (LSV) from 1 to 0 V were carried out. The CV was performed in N_2 saturated atmosphere at 5 and 50 mV s^{-1}. The LSV was done in an O_2-saturated atmosphere for different rotation rates between 400 and 2025 rpm at 5 mV s^{-1}. The potential of the ring was kept at 1.5 V and the ring current by H_2O_2 oxidation was also measured during the LSV measurement. The electron transfer number (*n*) of ORR on the catalysts modified electrode was determined by the following equation.

$$n = (4 \times I_d)/(I_d + I_r/N)$$

where I_d is disk current, I_r is ring current, and *N* is the collection efficiency of the ring which was experimentally determined to be 0.37.

In order to study the stability performance and methanol poisoning test, chronoamperometric experiments were performed. The stability experiments of Co-N/GS and Pt/C 20 wt% were performed in 0.1 M KOH at a potential of 0.65 V and 1600 rpm for 7200s. After this time, methanol was added into the electrolyte to reach a concentration of 1 M methanol.

Supporting Information

References

[1]   L. Pérez-Lombard, J. Ortiz, C. Pout, *Energy Build.* **2008**, *40*, 394.

[2]   F. Jaouen, E. Proietti, M. Lefèvre, R. Chenitz, J. P. Dodelet, G. Wu, H. T. Chung, C. M. Johnston, P. Zelenay, *Energy Environ. Sci.* **2011**, *4*, 114.

[3]   Y. S. Li, T. S. Zhao, Z. X. Liang, *J. Power Sources* **2009**, *187*, 387.

[4]   J. S. Lee, S. T. Kim, R. Cao, N. S. Choi, M. Liu, K. T. Lee, J. Cho, *Adv. Energy Mater.* **2011**, *1*, 34.

[5]   I. Kruusenberg, L. Matisen, Q. Shah, A. M. Kannan, K. Tammeveski, *Int. J. Hydrogen Energy* **2012**, *37*, 4406.

[6]   F. H. B. Lima, J. Zhang, M. H. Shao, K. Sasaki, M. B. Vukmirovic, E. A. Ticianelli, R. R. Adzic, **2007**, 404.

[7]   J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J. K. Nørskov, *Nat. Chem.* **2009**, *1*, 552.

[8]   Y. Bing, H. Liu, L. Zhang, D. Ghosh, J. Zhang, *Chem. Soc. Rev.* **2010**, *39*, 2184.

[9]   D. S. Su, G. Sun, *Angew. Chemie - Int. Ed.* **2011**, *50*, 11570.

[10]   Y. Jiang, Y. Lu, X. Wang, Y. Bao, W. Chen, L. Niu, *Nanoscale* **2014**, *6*, 15066.

[11]   D. Higgins, P. Zamani, A. Yu, Z. Chen, *Energy Environ. Sci.* **2016**, *9*, 357.

[12]   M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, *110*, 132.

[13]   H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, *2*, 781.

[14]   C. Lee, X. Wei, J. W. Kysar, J. Hone, *Science* **2008**, *321*, 385.

[15]   Y. Shao, S. Zhang, M. H. Engelhard, G. Li, G. Shao, Y. Wang, J. Liu, I. A. Aksay, Y. Lin, *J. Mater. Chem.* **2010**, *20*, 7491.

[16]   M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, *Nano Lett.* **2008**, *8*, 3498.

[17]   K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H. L. Stormer, *Solid State Commun.* **2008**, *146*, 351.

[18]   A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, **2008**, DOI 10.1021/nl0731872.

[19]   H. Bin Yang, J. Miao, S.-F. Hung, J. Chen, H. B. Tao, X. Wang, L. Zhang, R. Chen, J. Gao, H. M. Chen, L. Dai, B. Liu, *Sci. Adv.* **2016**, *2*, e1501122.

[20]   J. Liang, Y. Jiao, M. Jaroniec, S. Z. Qiao, *Angew. Chemie - Int. Ed.* **2012**, *51*, 11496.

[21]   R. Liu, C. Von Malotki, L. Arnold, N. Koshino, H. Higashimura, M. Baumgarten, M. Klaus, **2011**, 10372.

[22]   M. Quernheim, H. Liang, Q. Su, M. Baumgarten, N. Koshino, H. Higashimura, K. Müllen, *Chem. - A Eur. J.* **2014**, *20*, 14178.

[23]   X. Fu, J. Choi, P. Zamani, G. Jiang, A. Hoque, F. M. Hassan, Z. Chen, **2016**, DOI 10.1021/acsami.5b12746.

[24]   H. Liu, M. Q. Wang, Z. Y. Chen, H. Chen, M. W. Xu, S. J. Bao, *Dalt. Trans.* **2017**, *46*, 15646.

[25]   Y. Chen, R. Gokhale, A. Serov, K. Artyushkova, P. Atanassov, *Nano Energy* **2017**, *38*, 201.

[26]   X. Yang, A. Wang, B. Qiao, J. U. N. Li, **2013**, *46*, DOI 10.1021/ar300361m.

[27]   Y. Zhu, K. Miyake, Y. Shu, A. Gabe, Y. Hirota, Y. Uchida, S. Tanaka, E. Morallón, D. Cazorla-Amorós, N. Nishiyama, *Catal. Sci. Technol.* **2019**, DOI 10.1039/C8CY02210K.

[28]   L. R. Arcot, M. Lundahl, O. J. Rojas, J. Laine, *Cellulose* **2014**, *21*, 4209.

[29]   D. G. Castner, K. Hinds, D. W. Grainger, *Langmuir* **2002**, *12*, 5083.

[30]   P. Gobbo, M. C. Biesinger, M. S. Workentin, *Chem. Commun.* **2013**, *49*, 2831.

[31]   P. F. Siril, N. R. Shiju, D. R. Brown, K. Wilson, *Appl. Catal. A Gen.* **2009**, *364*, 95.

[32]   M. Kim, D. H. Nam, H. Y. Park, C. Kwon, K. Eom, S. Yoo, J. Jang, H. J. Kim, E. Cho, H. Kwon, *J. Mater. Chem. A* **2015**, *3*, 14284.

[33]   J. Jin, X. Fu, Q. Liu, J. Zhang, *J. Mater. Chem. A* **2013**, *1*, 10538.

[34]   X. Tong, X. Xia, C. Guo, Y. Zhang, J. Tu, H. J. Fan, X. Y. Guo, *J. Mater. Chem. A* **2015**, *3*, 18372.

[35]   B. Y. Guan, L. Yu, X. W. Lou, *Energy Environ. Sci.* **2016**, *9*, 3092.

[36]   G. Tao, L. Zhang, L. Chen, X. Cui, Z. Hua, M. Wang, J. Wang, Y. Chen, J. Shi, *Carbon N. Y.* **2015**, *86*, 108.

[37]   X. Wang, J. Zhou, H. Fu, W. Li, X. Fan, G. Xin, J. Zheng, X. Li, *J. Mater. Chem. A* **2014**, *2*, 14064.

[38]   G. Panomsuwan, N. Saito, T. Ishizaki, *Electrochem. commun.* **2015**, *59*, 81.

[39]   J. Quílez-bermejo, C. Gonz, D. Cazorla-amor, **2017**, *119*, 62.

[40]   Q. Shao, J. Liu, Q. Wu, Q. Li, H. guo Wang, Y. Li, Q. Duan, *Nano-Micro Lett.* **2019**, *11*, DOI 10.1007/s40820-018-0231-3.

[41]   Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat. Mater.* **2011**, *10*, 780.

[42]   S. Mao, Z. Wen, T. Huang, Y. Hou, J. Chen, *Energy Environ. Sci.* **2014**, *7*, 609.

[43]   H. Wang, Y. Liang, Y. Li, H. Dai, *Angew. Chemie - Int. Ed.* **2011**, *50*, 10969.

[44]   Y. Han, Y. G. Wang, W. Chen, R. Xu, L. Zheng, J. Zhang, J. Luo, R. A. Shen, Y. Zhu, W. C. Cheong, C. Chen, Q. Peng, D. Wang, Y. Li, *J. Am. Chem. Soc.* **2017**, *139*, 17269.

[45]   A. Morozan, P. Jégou, B. Jousselme, S. Palacin, *Phys. Chem. Chem. Phys.* **2011**, *13*, 21600.

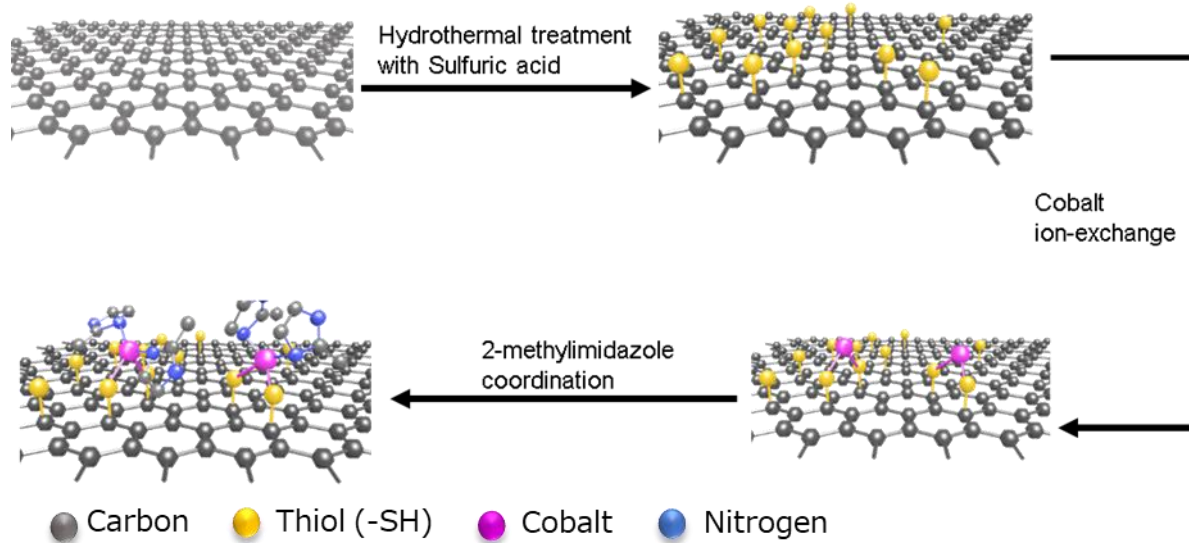[46]   E. Antolini, T. Lopes, E. R. Gonzalez, *J. Alloys Compd.* **2008**, *461*, 253.

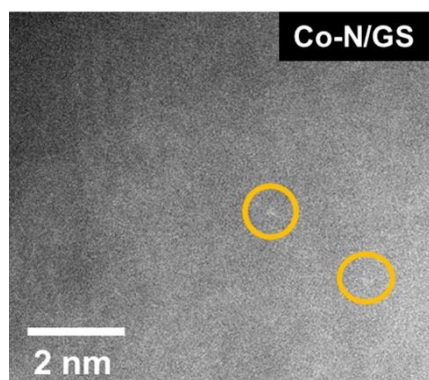**Figure 1.** Schematic diagram of synthesis process.

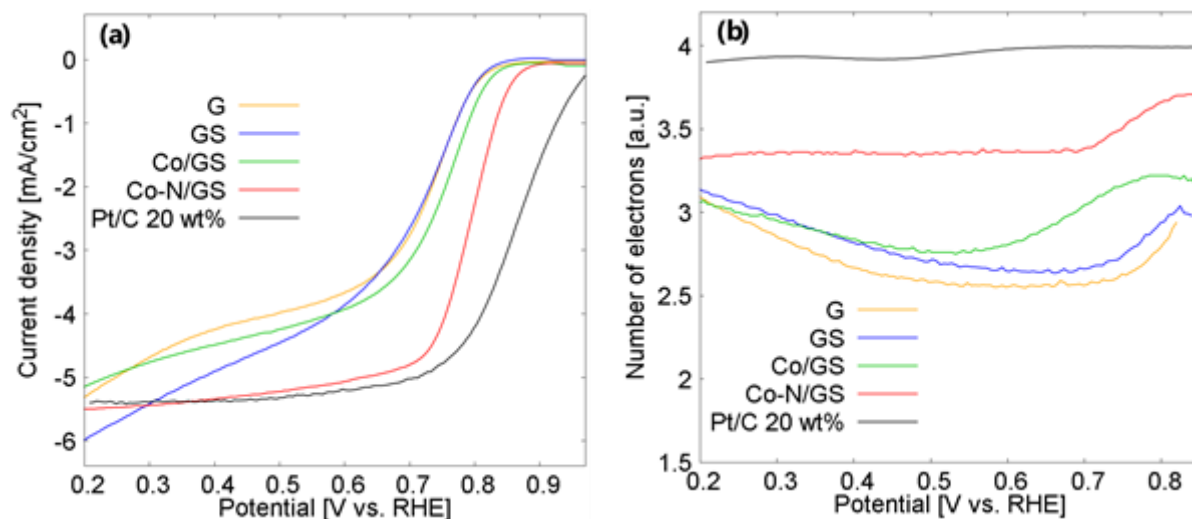**Figure 2.** STEM dark-field images of Co-N/GS.

Figure 3. (a) LSV curves of the G, GS, Co/GS, Co-N/GS and Pt/C 20 wt%, and (b) electron transfer number during ORR in O_2 saturated 0.1 M KOH at a scan rate of 5 mV s^{-1} and 1600 rpm.

15

Keyword ((graphene, single atom, ORR))

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ToC figure ((Please choose one size: 55 mm broad × 50 mm high **or** 110 mm broad × 20 mm high. Please do not use any other dimensions))
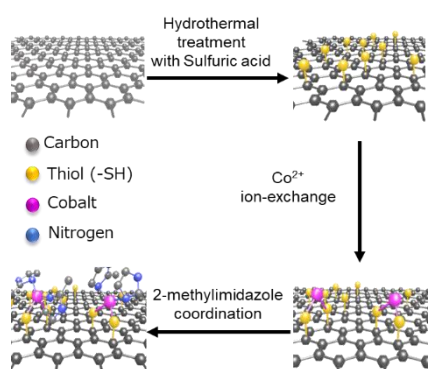
Supporting Information

Rational design of single atomic Co in CoN$_x$ moieties on graphene matrix as an ultra-highly efficient active site for oxygen reduction reaction

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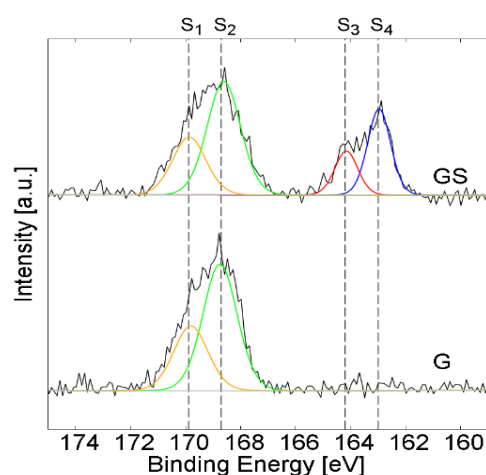
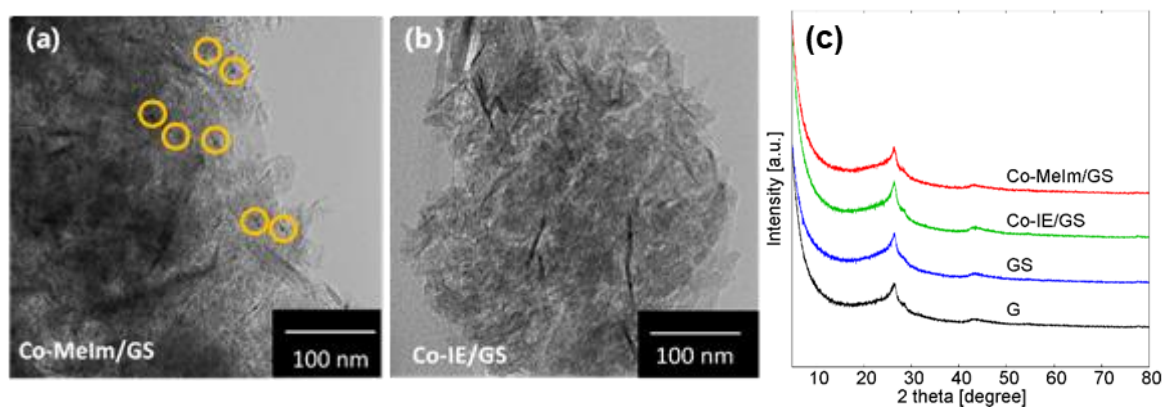**Figure S1**. XPS spectrum G and GS on S 2p.

Figure S2. TEM images of (a) Co-MeIm/GS, and (b) Co-IE/GS, and (c) XRD patterns of G, GS, Co-IE/GS, and Co-MeIm/GS.
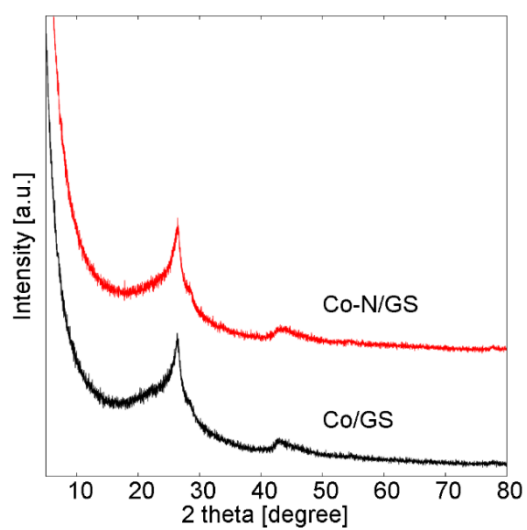
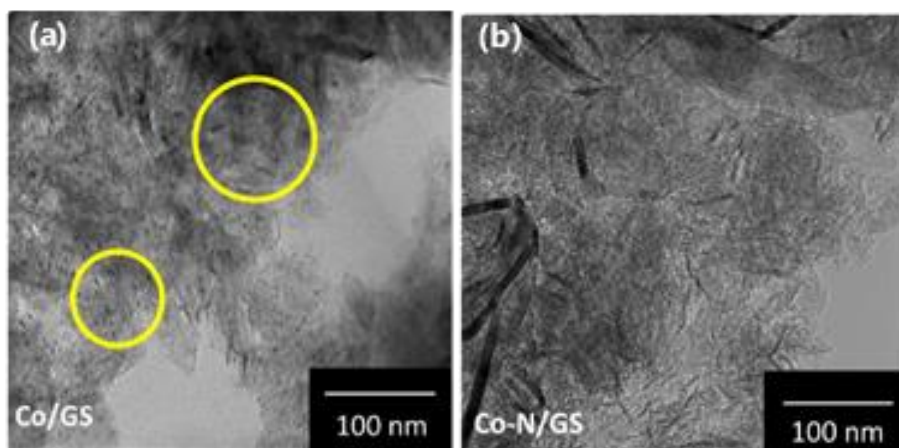**Figure S3.** XRD patterns of Co/GS, Co-N/GS.

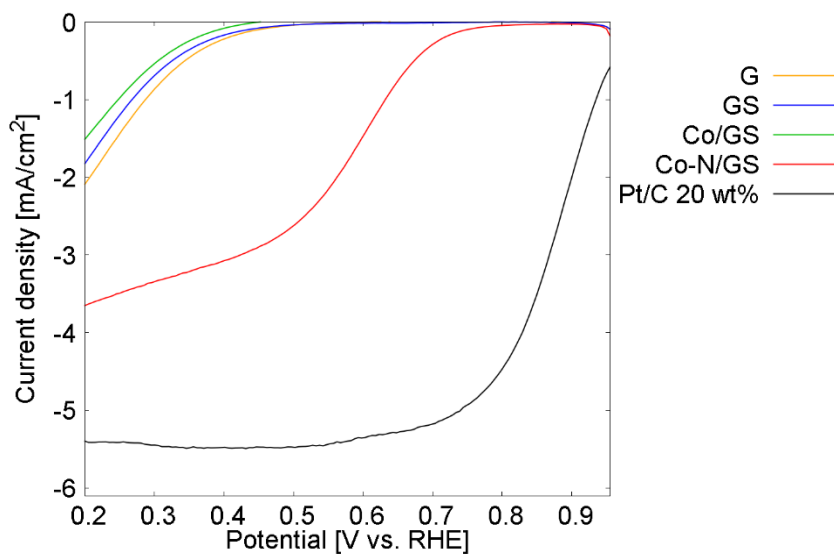**Figure S4.** TEM images of (a) Co/GS and (b) Co-N/GS.

Figure S5. LSV curves of the G GS, Co/GS, Co-N/GS and Pt/C 20 wt% in O_2 saturated 0.1 M $HClO_4$ at a scan rate of 5 mV s^{-1} and 1600 rpm.
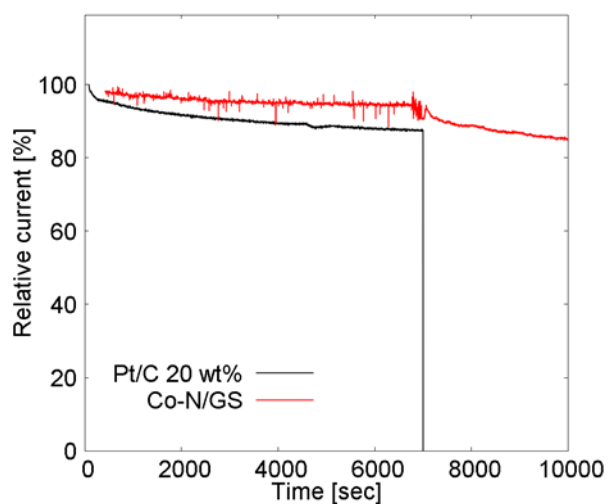

Figure S6. Relative current density versus Time for Pt/C 20 wt% and Co-N/GS at 0.65 V vs RHE in O_2 saturated 0.1 M KOH at a scan rate of 5 mV s^{-1} and 1600 rpm

Table S1. Composition of Co/GS and Co-N/GS obtained by inductively coupled plasma (ICP) analysis.

Sample	Co content [wt%]
Co/GS	0.08
Co-N/GS	0.08

Table S2. Summary of ORR activities in 0.1 M KOH for catalysts in this work and representative Co/N co-doped graphene catalysts in references.[1–5]

Catalysts	Cobalt Content	Onset Potential [V vs. RHE]	Half-wave Potential [V vs. RHE]	Limiting Current Density [mA cm^2]	Reference
Co-N/GS	0.08 wt%	0.89	0.79	-4.8	
Co^{II}A-rG-O	4.5 at%	0.88	0.81	-5.2	[1]
Co-NGA$_{600}$	~28 wt%	0.86	-	-4.5	[2]
Co/NG	40 wt%	0.89	0.82	-1.3	[3]
Co-N-graphene	2.6 wt%	0.87	0.80	-	[4]
Co-N-rGO	7.6 wt%	0.88	0.81	-4.2	[5]

[1]   J. Han, Y. J. Sa, Y. Shim, M. Choi, N. Park, S. H. Joo, S. Park, *Angew. Chemie - Int. Ed.* **2015**, *54*, 12622.

[2]   R. Liu, Y. Jin, P. Xu, X. Xing, Y. Yang, D. Wu, *J. Colloid Interface Sci.* **2016**, *464*, 83.

[3]   H. Ghanbarlou, S. Rowshanzamir, M. J. Parnian, F. Mehri, *Int. J. Hydrogen Energy* **2016**, *41*, 14665.

[4]   J. H. Yang, Y. Gao, W. Zhang, P. Tang, J. Tan, A. H. Lu, D. Ma, *J. Phys. Chem. C* **2013**, *117*, 3785.

[5]   L. F. Zhai, S. Y. Kong, H. Zhang, W. Tian, M. Sun, H. Sun, S. Wang, *Chem. Eng. Sci.* **2019**, 45.