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One-step synthesis of cobalt and nitrogen co-doped carbon nanotubes and their catalytic activity for oxygen reduction reaction

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In this paper, cobalt and nitrogen co-doped carbon nanotubes were successfully synthesized by a simple thermal treatment method with dicyandiamide and cobalt (II) chloride hexahydrate. The as-synthesized nanostructures presented excellent catalytic activity and stability toward oxygen reduction reaction in alkaline solution. Especially, when the molar ratio between dicyandiamide and cobalt (II) chloride hexahydrate was 22:1, the catalyst showed close onset potential, half-wave potentials and limiting current density comparing to the commercial platinum/carbon catalyst, which might be attributable to the formation of pyridinic and quaternary nitrogen functional groups as well as the incorporation of cobalt during the thermal treatment. Moreover, the as-synthesized catalyst exhibited good tolerance to methanol crossover effect.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered to be promising energy converting devices due to their environmental friendliness and high conversion efficiency.¹⁻³ Unfortunately, the intrinsically sluggish kinetics of oxygen reduction reaction (ORR) at the cathode obstructs the commercialization of PEMFCs.^{4,5} Thus, researches are focused on developing the advanced electrocatalysts for ORR to accelerate the reaction kinetics. Traditionally, platinum (Pt) nanoparticles (NPs) supported on carbonaceous materials with high surface area are considered to be the most efficient catalysts for ORR due to their high activity and stability.⁶⁻⁸ However, the high cost and scarcity of Pt limits their widespread application on PEMFCs. Therefore, the priority in the development and industrialization of PEMFCs is to investigate the efficient and affordable catalyst materials.

It is crucial to replace Pt-based catalysts by other low cost materials, such as transition metal oxides, transition metal nitride, doped carbon materials, conductive polymers, etc.⁹⁻¹⁶ Among them, cobalt (Co) and nitrogen (N) co-doped carbon materials have obtained increasing attention owing to their promising catalytic activity and stability toward ORR, along with utilization of abundant and inexpensive precursors.^{2, 17-19} Although the catalytic mechanism is still under debate,^{2, 20} the catalytic properties strongly depend on the precursors, support morphology, synthesis condition. Normally, Co and N co-doped materials are synthesized by thermal treatment at high

temperature in inert environment (nitrogen or argon). Upon pyrolysis, the ORR active sites are formed.²¹⁻²³ However, most reported works use complex synthesis procedures which include more than one step pyrolysis to get the co-doped materials which are active to ORR.^{10, 17-19, 24}

In this work, we proposed a one-step pyrolysis method to synthesize Co and N co-doped carbon nanotubes (Co-N-CNTs) using dicyandiamide and cobalt chloride as precursors.^{25, 26} The as-prepared Co-N-CNTs catalyst exhibited excellent electroactivity and stability toward ORR in alkaline solution, which was attributed to the special structure, the addition of Co, as well as the formation of nitrogen functional groups in the carbon materials.

Experimental

Chemicals and reagents

Dicyandiamide (C₂H₄N₄, 99%), commercial platinum/carbon (Pt/C) 20 wt. % (Pt loading: 20 wt. %, Pt on carbon black) were purchased from Alfa Aesar. Nafion perfluorinated resin solution (5 wt. % in mixture of lower aliphatic alcohols and water, contains 45% water) was obtained from Sigma-Aldrich. Potassium hydroxide (KOH, reagent grade) was bought from Amresco. Cobalt (II) chloride hexahydrate (CoCl₂•6H₂O) was purchased from Acros Organics.

Characterization

FEI Sirion field emission scanning electron microscope (FESEM) was used for imaging. Transmission electron microscopy (TEM) images were obtained by Philips CM200 UT (Field Emission Instruments, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS-165 multi-technique electron spectrometer system with a base pressure of 1×10^{-9} Torr. The spectra of the surfaces were obtained with an AXIS-165 manufactured by Kratos Analytical Inc. (Spring Valley, NY, USA) using a monochromatic X-ray radiation of 1487 eV (AlK α). The spectrometer was calibrated against both the Au 4f_{7/2} peak at 84.0 eV and the Ag 3d_{5/2} peak at 368.3 eV. Static charging when present was corrected with a neutralizer (flood gun) by placing the carbon peak (C 1s) at about 285 eV. X-ray diffraction (XRD) characterization was carried out by Rigaku Miniflex 600. The tube was operated at 40 kV accelerating voltage and 15 mA current.

Electrochemical experiments

The Co-N-CNTs-1, Co-N-CNTs-2 and commercial Pt/C catalysts (2 mg/mL) were obtained by mixing the powders into nafion solution which contains 2 mL 2-propanol, 8 mL deionized water and 0.05 mL nafion. The mixture was then ultrasonicated for several minutes to get homogeneous catalyst ink. 10 μ L of the catalysts were dropped onto the polished and cleaned glassy carbon electrode (GCE, 5 mm in diameter) surface and dried at 60 $^{\circ}$ C to obtain the working electrodes.

The electrochemical properties were characterized using an electrochemical workstation (CHI 630E) with a three-electrode system. Pt wire and Ag/AgCl electrode filled with saturated KCl aqueous solution were used as the counter electrode and reference electrode, respectively. The number of electrons transferred in ORR can be obtained according to the corresponding Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) at various electrode potentials which were analysed using Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

Here J is the measured current density, J_L is the diffusion-limiting current density, J_K is the kinetic current density, ω is the electrode rotating speed in rad/s, n is the overall electron-transfer number in oxygen reduction, F is the Faraday constant ($F=96485$ C/mol), C_0 is the bulk concentration of O₂, D_0 is the diffusion coefficient, ν is the kinetic viscosity of the electrolyte, and k is the electron-transfer constant. By using the values $C_0=1.2 \times 10^{-3}$ mol/L, $D_0=1.9 \times 10^{-5}$ cm²/s, $\nu=0.01$, the number of transferred electrons can be calculated based on equation (1) through (3).

Results and discussion

Synthesis of Co-N-CNTs catalysts

Co-N-CNTs were synthesized by a simple thermal treatment method. Briefly, 3 g C₂H₄N₄ was mixed with 0.385 g CoCl₂·6H₂O thoroughly, followed by thermal treatment at 900

$^{\circ}$ C in a tube furnace under nitrogen atmosphere for 0.5 hour. The heating and cooling rate was 3 $^{\circ}$ C/min. The molar ratio of C₂H₄N₄ to CoCl₂·6H₂O is 22:1. The product was denoted as Co-N-CNTs-1. Co-N-CNTs-2 was synthesized with the same method, where the molar ratio of C₂H₄N₄ to CoCl₂·6H₂O is 44:1.

Characterization of Co-N-CNTs

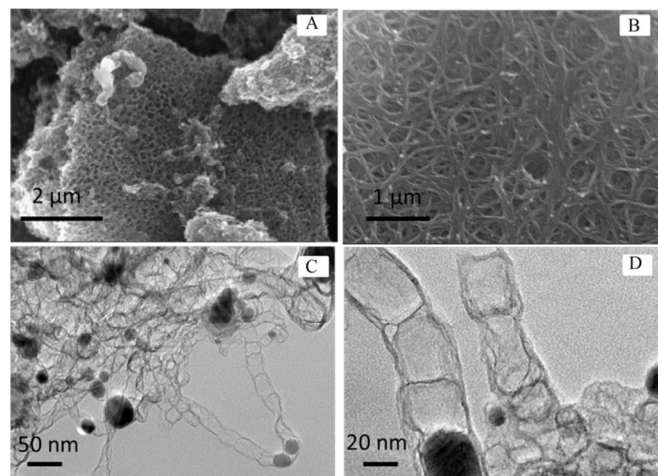


Fig. 1 SEM (A and B) and TEM (C and D) images of Co-N-CNTs-1.

The morphology and structure of the synthesized product was first studied by scanning electron microscope (SEM) and transmission electron microscopy (TEM). Fig. 1A and B show the morphology of Co-N-CNTs-1. It reveals that the CNTs cross-link with each other, forming interwoven networks. The SEM image with high magnification (Fig. 1B) shows that few white dots disperse among the CNTs, indicating the incorporation of Co by thermal treatment. The nanotubular structures were further confirmed by TEM image as shown in Fig. 1C and D. The diameter of the CNTs is about 25 nm with Co nanoparticles encapsulated in the CNTs. This confirms the CNTs, catalyzed by Co,²⁷ were successfully synthesized.

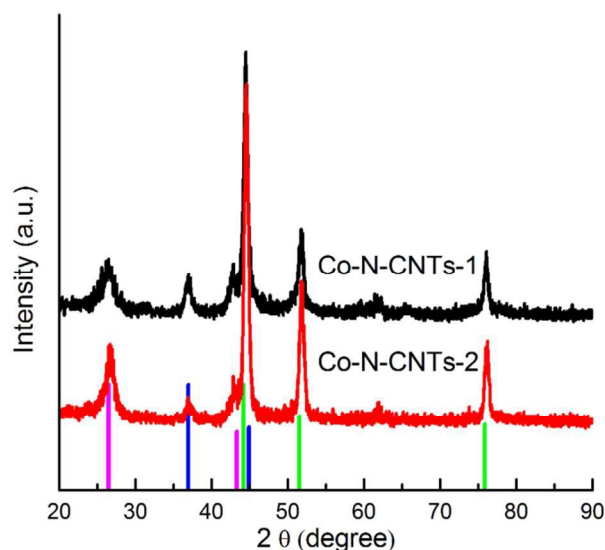


Fig. 2 XRD patterns of Co-N-CNTs-1 and Co-N-CNTs-2. JADE database peak positions for graphite (pink), Co (green), and Co₃O₄ (blue) are marked.

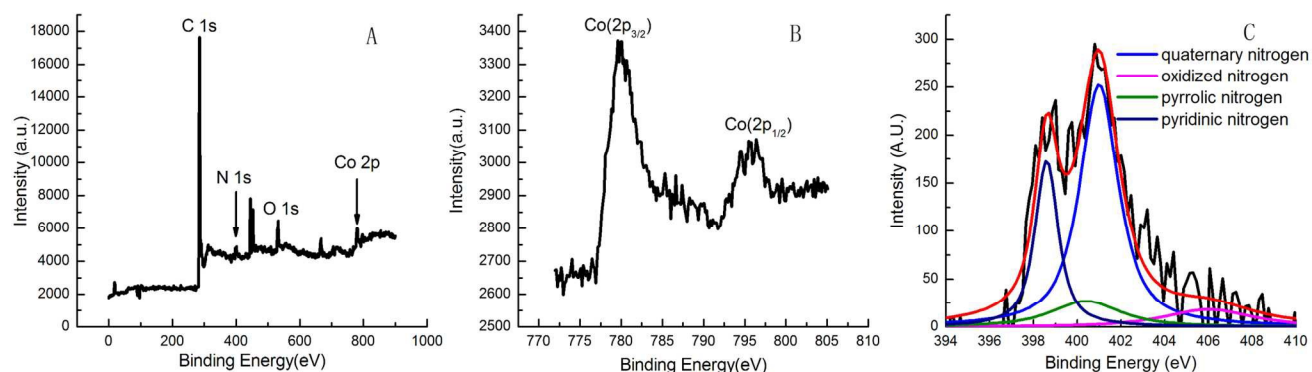


Fig. 3 XPS (A), Co 2p (B) and N 1s (C) spectra of Co-N-CNTs-1.

X-ray diffraction (XRD) patterns of Co-N-CNTs-1 and Co-N-CNTs-2 are shown in Fig. 2. The patterns reveal the presence of graphite ($2\theta=26.6^\circ$, 43.4°), Co ($2\theta=44.5^\circ$, 51.6° , 76°) and Co_3O_4 ($2\theta=36.9^\circ$, 44.9°). The graphite peaks are in agreement with the structure properties of CNTs which further confirm the formation of CNTs. The XRD patterns also indicate that the formats of Co element in the product are Co and Co_3O_4 . The surface composition of Co-N-CNTs-1 and Co-N-CNTs-2 were further characterized by X-ray photoelectron spectroscopy (XPS) as shown in Fig. 3 and Fig. S1. In Fig. 3A, the XPS spectrum reveals the presence of Co, C and N in Co-N-CNTs-1, indicating the successful incorporation of Co and N. The quantification result shows that the atomic concentrations of Co and N are 1.22% and 3.9%, respectively. Fig. 3B shows two peaks at binding energy of 779.74 eV and 795.63 eV, which correspond to Co $2p_{3/2}$ and Co $2p_{1/2}$. The complex N 1s spectrum was further deconvoluted into four peaks at 398.6 eV, 400.4 eV, 401 eV and 406 eV, corresponding to pyridinic nitrogen, pyrrolic nitrogen, quaternary nitrogen and oxidized nitrogen, respectively.²⁸ Compared with Co-N-CNTs-1, the XPS quantification result of Co-N-CNTs-2 shows a lower atomic concentration of Co (0.86%) due to the lower ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ used in synthesis process. The concentration of N in Co-N-CNTs-2 (3.3 at%) is a little bit lower than that in Co-N-CNTs-1 (3.9 at%).

Electrocatalytic activities of Co-N-CNTs toward ORR

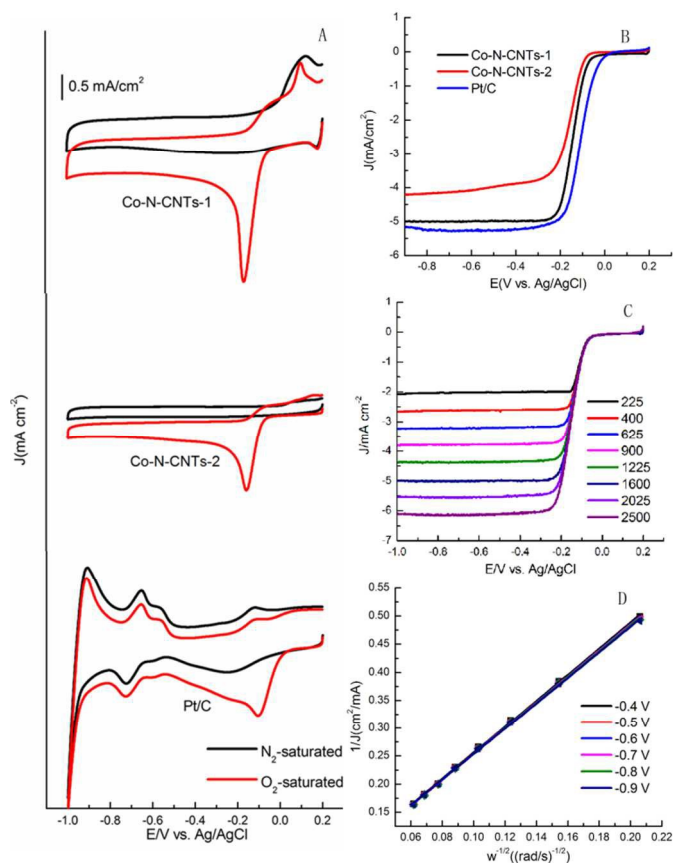


Fig. 4 (A) CV curves of Co-N-CNTs-1, Co-N-CNTs-2, and commercial Pt/C catalysts in N_2 and O_2 -saturated 0.1 M KOH solution with a scan rate of 50 mV/s. (B) LSV curves of Co-N-CNTs-1, Co-N-CNTs-2 compared with commercial Pt/C with a scan rate of 10 mV/s at a rotation rate of 1600 rpm. (C) LSV curves of Co-N-CNTs-1 at different rotation rate. (D) Koutecky-Levich (K-L) plots of Co-N-CNTs-1 at different potentials.

The electrocatalytic activities toward ORR of Co-N-CNTs were studied by cyclic voltammetry (CV) in N_2 and O_2 -saturated 0.1 M KOH solution from -1.0 V to 1.2 V vs. Ag/AgCl with 50 mV/s scanning rate. Co-N-CNTs-1, Co-N-CNTs-2 and commercial platinum/carbon (Pt/C) catalysts display featureless curves in N_2 -saturated solution as shown in Fig. 4A. On the contrary, the CV curves present a well-defined ORR peak in O_2 -saturated solution for all samples, which demonstrates the good electrocatalytic activity of Co-N-CNTs catalysts toward

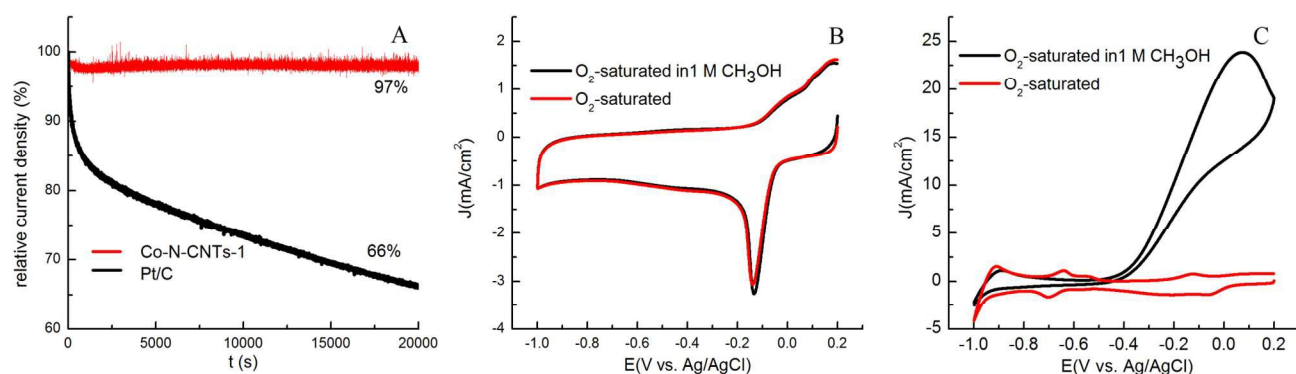


Fig. 5 (A) Chronoamperometric responses of Co-N-CNTs-1 and commercial Pt/C. CV curves of Co-N-CNTs-1 (B) and commercial Pt/C (C) catalysts in O₂-saturated 0.1 M KOH solution before and after the addition of CH₃OH.

ORR. To further investigate the kinetics of ORR catalysed by Co-N-CNTs, the linear sweep voltammetry (LSV) was carried out on a rotating disk electrode (RDE) in O₂-saturated 0.1 M KOH solution at different rotation rate from 225 rpm to 2500 rpm. The electrocatalytic activities of Co-N-CNTs-1 and Co-N-CNTs-2 were compared with commercial Pt/C under the same condition at a rotation rate of 1600 rpm. As shown in Fig. 4B, the onset potential of Co-N-CNTs-1 and Co-N-CNTs-2 are -0.138 V and -0.156 V, respectively, which are very close to that of commercial Pt/C (-0.11 V). The similar trend is observed on the half-wave potential as well. Moreover, the limiting current density of Co-N-CNTs-1 (~5 mA/cm²) is very close to that of commercial Pt/C catalyst, which is much larger than that of Co-N-CNTs-2 (~4.2 mA/cm²). These confirm the good electrocatalytic activity of Co-N-CNTs toward ORR because of the Co and N functionalization.¹⁶ It is generally accepted that the formation of nitrogen functional groups, such as pyridinic nitrogen and quaternary nitrogen, contributes to the good catalytic activity toward ORR. These two kinds of nitrogen could provide active sites for ORR. That is, the π electrons in C will be activated by neighbor N atoms. Therefore, O₂ is reduced on the positively charged C atoms.²⁹ On the other hand, it is demonstrated that the incorporation of Co has an important effect on the activity of catalysts.¹⁷ Studies have revealed that a charge transfer exists across the carbon-metal interface due to the carbon-metal spacing and Fermi level difference between carbon material and metal. This kind of charge transfer might contribute to the enhanced catalytic activities.³⁰ Certain works have demonstrated that a series of composites exhibited good catalytic activity for ORR in alkaline or acid media, such as graphene-Co₃O₄,³¹ graphene-Fe₃O₄.³² Unlike the acid solution, where cobalt oxides are inactive for ORR,³³ the active cobalt hydroxide was formed in alkaline solution. This is confirmed by the presence of an obvious pair of redox peak in Co-N-CNTs-1 around 0.1-0.2 V, which is reported to be active for ORR.^{34, 35} Therefore, the better performance of Co-N-CNTs-1 compared to Co-N-CNTs-2 might be attributed to the higher concentration of N and Co species in Co-N-CNTs-1. In addition, Co-N-CNTs catalysts with other ratios between C₂H₄N₄ and CoCl₂·6H₂O were also synthesized and compared with each other, as shown in Fig. S2. Among the four catalysts, Co-N-CNTs-1 presents the best catalytic activity toward ORR. This indicates that the catalytic performance of as-prepared Co-N-CNTs becomes better with larger amount of C₂H₄N₄ in a certain range. When the amount of C₂H₄N₄ keeps increasing, lower activity presents.

The LSV curves of Co-N-CNTs-1 and Co-N-CNTs-2 at different rotation rate are shown in Fig. 4C and S3A. The limiting current density increases with the increasing rotation rate due to the fast oxygen flux on the electrode surface. The specific parameters of ORR can be obtained by Koutecky-Levich (K-L) equation. The corresponding K-L plot in Fig. 4D and S3B show good linearity between J^{-1} and $\omega^{-1/2}$, indicating the first-order reaction kinetics with respect to the concentration of dissolved oxygen.³⁶ The number of transferred electrons is about 4 for the as-prepared catalysts, reflecting the four-electron reaction pathway on the electrode surface. These facts further demonstrate the excellent electrocatalytic activity of Co-N-CNTs catalysts toward ORR.

Additionally, the stability of the Co-N-CNTs-1 and commercial Pt/C catalysts were evaluated by chronoamperometry at -0.3 V vs. Ag/AgCl in O₂-saturated 0.1 M KOH solution at a rotation rate of 200 rpm. As shown in Fig. 5A, the current density of Co-N-CNTs-1 catalyst almost kept same during the test. In contrast, only about 66% initial current density was remained for commercial Pt/C catalyst. This reflects the better stability of Co-N-CNTs-1 catalyst toward ORR in alkaline media.

Another important factor to evaluate the performance of electrocatalysts is the selectivity for the electrode reaction. In fuel cells, the small-molecule fuels, such as methanol, could penetrate through the polymer electrolyte membrane from anode to cathode easily, which will decrease the efficiency of the whole cell.³⁷ In order to test the selectivity of the as-synthesized catalyst in this work, the methanol crossover tests were carried out on Co-N-CNTs-1 and commercial Pt/C catalysts as shown in Fig. 5B and 5C. Co-N-CNTs-1 showed a consistent ORR curve when methanol was added into the KOH solution, indicating a good selectivity toward electrode reaction. For the Pt/C catalyst, a typical methanol oxidation peak showed up after the addition of methanol. The good tolerance to methanol crossover effect of Co-N-CNTs-1 further confirms the good electroactivity toward ORR.

Conclusions

In conclusion, Co-N-CNTs catalysts were synthesized by a simple thermal treatment method. The CNTs was cross-linked with each other with Co incorporated. The as-synthesized catalysts presented excellent catalytic activity and stability toward ORR through a four-electron reduction pathway in alkaline solution. In particular, the Co-N-CNTs-1 showed close onset potential, half-wave potentials and limiting current density to that of commercial Pt/C catalyst. Moreover, the Co-

N-CNTs-1 catalyst also exhibited the tolerance to methanol crossover effect. The simply synthesized Co-N-CNTs catalysts possess promising application in fuel cells.

Acknowledgements

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Notes and references

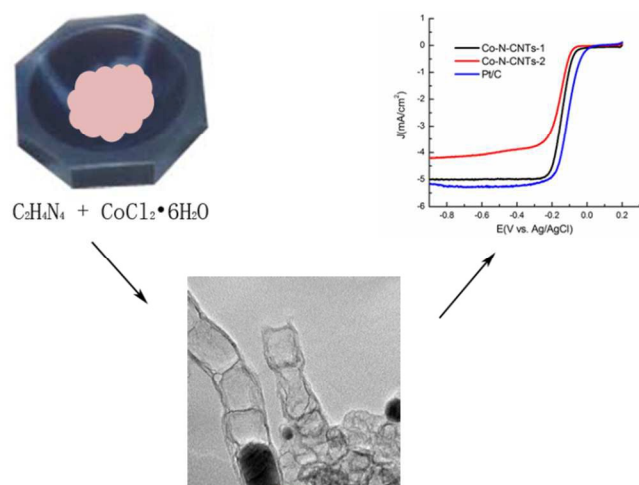
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Electronic Supplementary Information (ESI) available: [XPS spectra, LSV curves and K-L plot of Co-N-CNTs-2]. See DOI: 10.1039/b000000x/

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