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Single atomic Co coordinated with N in microporous carbon for oxygen reduction reaction obtained from Co/2-methylimidazole anchored to Y zeolite as a template --Manuscript Draft--

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Abstract:	Zeolite templated carbons (ZTCs) composed of curved and single-layer graphene frameworks have uniform micropores (ca. 1.2 nm) and high surface areas (~4000 m ² g ⁻¹). Due to their outstanding properties originating from the porous structures, ZTCs have been utilized in many applications. In this work, we synthesized Co/N doped ZTC (Co/N-ZTC) by complexing Co ion with 2-methylimidazole in Y zeolite to expand the further utilization of ZTCs. The obtained Co/N-ZTC has a high surface area (ca. 2000 m ² g ⁻¹) and single atomic Co species in CoN _x moieties, which actually contributes to its excellent catalytic performance on oxygen reduction reaction. This synthetic concept is beneficial to fabricate single atomic transition metals coordinated with heteroatoms in ZTCs, which contributes to the progress of material design of single atomic catalysts supported porous materials.
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16th February, 2020

Dear the Editor of *Materials Today Nano* and Referees,

Uploaded please find our manuscript entitled “Single atomic Co coordinated with N in microporous carbon for oxygen reduction reaction obtained from Co/2-methylimidazole anchored to Y zeolite as a template” for consideration of publication as *Research Paper* in *Materials Today Nano*.

In this paper, we first report the synthesized zeolite templated carbon with single atomic Co species incorporated as CoN_x moieties (Co/N-ZTC) by complexing Co species with 2-methylimidazole in Y zeolite as a template. Co/N-ZTC shows excellent catalytic performance on oxygen reduction reaction, which is probably attributed to the high microporosity and the single atomic Co in CoN_x moieties. Our synthetic concept can be applied to a variety of zeolite templated carbons (ZTCs) with other transition metals and heteroatoms. Thus, this work provides a new direction for the materials design of single atomic metal coordinated with heteroatoms in uniform micropores of ZTCs and expands the further utilization of ZTCs.

We believe that this work can contribute to the progress of materials design of single atomic catalysts supported porous materials in nanometer scale. We feel this work is of great interest to warrant publication as *Research Paper* in *Materials Today Nano*.

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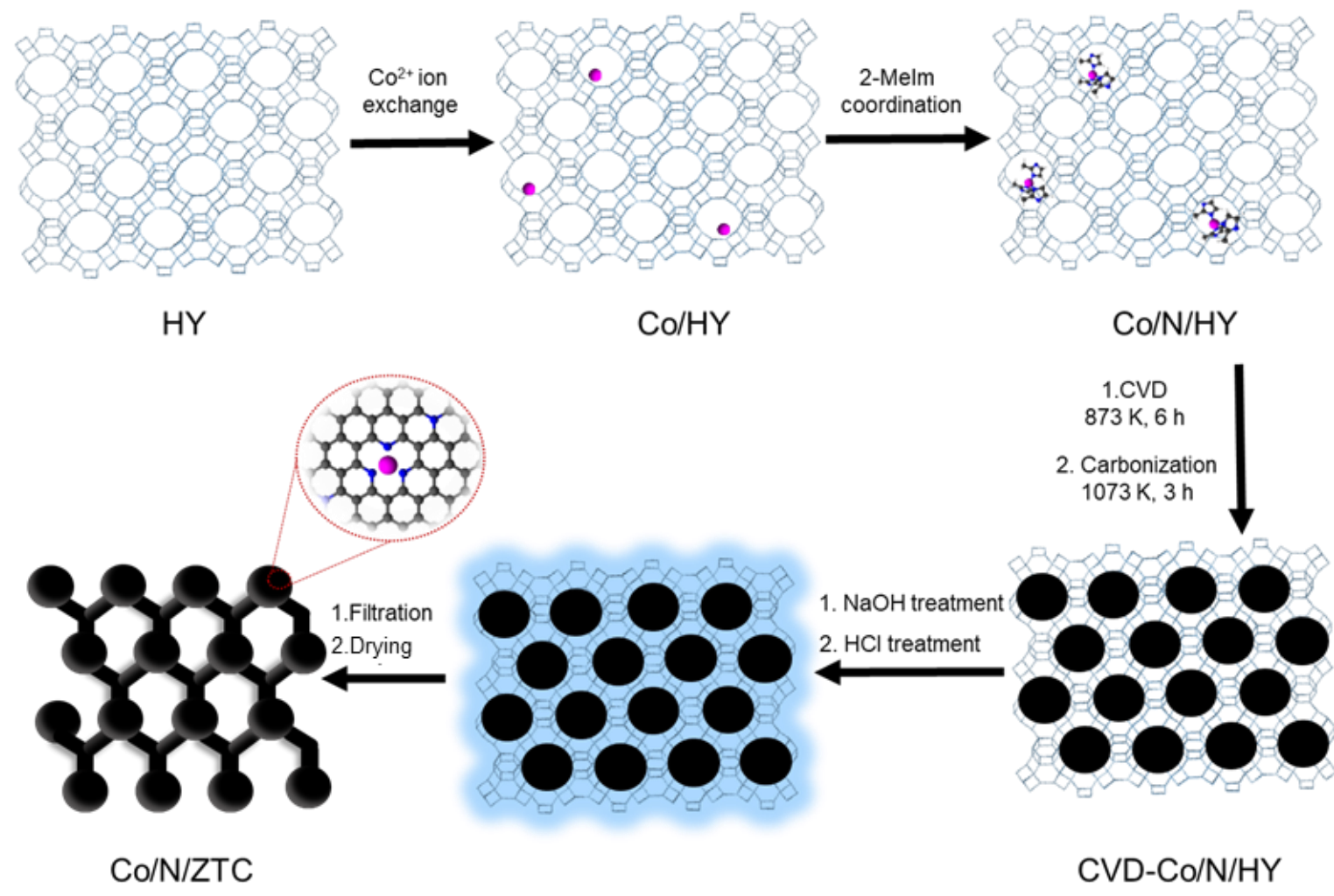
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Single atomic Co coordinated with N in microporous carbon for oxygen reduction reaction obtained from Co/2-methylimidazole anchored to Y zeolite as a template

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Abstract

Zeolite templated carbons (ZTCs) composed of curved and single-layer graphene frameworks have uniform micropores (ca. 1.2 nm) and high surface areas ($\sim 4000 \text{ m}^2 \text{ g}^{-1}$). Due to their outstanding properties originating from the porous structures, ZTCs have been utilized in many applications. In this work, we synthesized Co/N doped ZTC (Co/N-ZTC) by complexing Co ion with 2-methylimidazole in Y zeolite to expand the further utilization of ZTCs. The obtained Co/N-ZTC has a high surface area (ca. $2000 \text{ m}^2 \text{ g}^{-1}$) and single atomic Co species in CoN_x moieties, which actually contributes to its excellent catalytic performance on oxygen reduction reaction. This synthetic concept is beneficial to fabricate single atomic transition metals coordinated with heteroatoms in ZTCs, which contributes to the progress of material design of single atomic catalysts supported porous materials.

1. Introduction

Carbon materials, with controllable nanostructures, high surface area, well developed porosity, and excellent electrical conductivity, [1-9] have been proved to be promising components in energy-related applications: gas storage/separation, water purification, and energy conversion/storage. [10-21] Although CO_2 activation is one of the most common

methods to improve the porosity and surface area of carbon materials, it is uncontrollable and not much effective. Recently, zeolite-templated carbons (ZTCs) have been widely investigated as three-dimensional carbon materials with highly ordered channels; the structures of zeolites transferred by nanocasting the ingredients into sacrificial template-zeolites. [22-24] Some ZTCs exhibit uniform micropores (c.a. 1.2 nm) and large surface areas ($\sim 4000 \text{ m}^2 \text{ g}^{-1}$), [25] which are beneficial especially for the applications in catalytic processes because they improve the accessibility of reactants to the active centers. [26, 27]

Besides, currently intensive research efforts to extend the versatility of ZTCs doped with heteroatoms [28-31] and/or metal nanoparticles [32-34]. Kwon *et al.* reported that a nitrogen-doped ZTC (N-ZTC) containing 4 wt% nitrogen atoms can be synthesized using acetonitrile as the nitrogen containing carbon source. The N-ZTC showed superior performance for oxygen reduction reaction (ORR) [30]. Choi *et al.* presented that an atomically dispersed platinum catalyst can be synthesized by wet-impregnation of H_2PtCl_6 on a sulfur-doped ZTC, which is effective to produce H_2O_2 , which is an important fine chemical. [34] The outstanding catalytic performance of ZTCs doped with heteroatoms and/or metal nanoparticles comparing to conventional materials is likely to originate from their highly developed porosity and good mass transport property.

Meanwhile, transition metal and heteroatom co-doped carbon materials (TM/Het-C) are regarded as one kind of the most promising candidates of electrocatalysts for ORR in alkaline conditions, which can substitute platinum on carbon (Pt/C) due to the relatively low cost and superior performance. [35-38] Zhao et al. synthesized a Fe/N-C electrocatalyst with high performance for ORR by pyrolyzing an iron and zinc-doped zeolitic imidazolate framework. [39] In general, when there is a high density of metal ions in the precursor, the aggregation of metal atoms occurs under high temperature pyrolysis. Commercial applications for fuel cells demand a novel synthesis method for the inhibition of the aggregation of metal atoms in the preparation of TM/Het-ZTC with large surface area for exposing the active sites and promoting the transport of reactants.

In our recent work, Co/N-C with highly dispersed Co species was synthesized by using a commercial ion exchange resin Amberlyst 15, as a support for Co/2-methylimidazole complex. [40] In this method, 2-methylimidazole works as a N source for CoN_x complexes directly formed after carbonization as active sites, and it efficiently suppresses the aggregation of Co atoms. In the present work, we propose a new method to synthesize Co/N-ZTC catalysts with high surface areas and highly dispersed CoN_x species; Co/2-methylimidazole complex is introduced into Y zeolite with 12-membered ring as the sources of Co and N and removal of Y zeolite after carbonization as shown in Fig. 1.

Moreover, we actually investigated ORR catalytic performance of the obtained Co/N-ZTC.

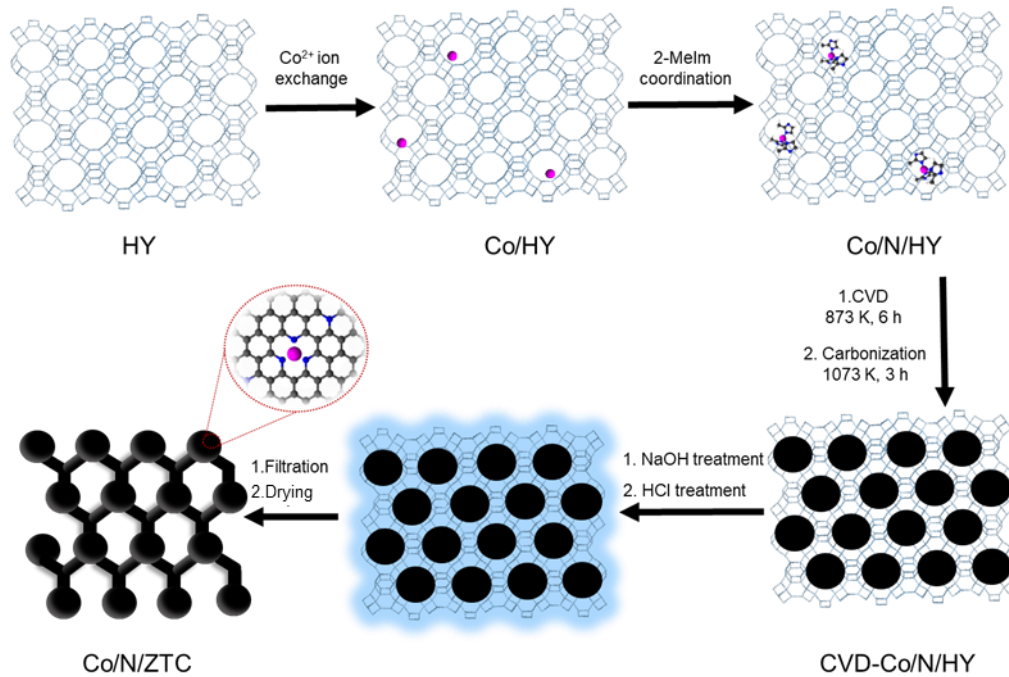


Fig. 1 The Schematic procedure of synthesis method of Co/N-ZTCs.

2. Experimental

2.1 Preparation of Co/N/HY

In a typical synthesis of Co/2-methylimidazole anchored to Y zeolite (Co/N/HY), the 2 g proton type Y (HY) zeolite ($1.0 \text{ Al}_2\text{O}_3 \cdot 5.5 \text{ SiO}_2$, Tosoh corporation, Japan) was added into the 3.0 mM cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) aqueous solution at room temperature (300 K) for 24 h to perform the ion exchange. After filtration and drying, 1 g of the obtained precursor (Co/HY) was added into 47.2 mM of 2-methylimidazole (2-MeIm) methanol

solution (150 ml). The resulting material (Co/N/HY) was washed with methanol to remove excess 2-MeIm and dried for several hours. We also prepared the sodium type Y (NaY) zeolite by sodium ion exchange of HY zeolite.

2.2 Preparation of ORR electrocatalysts

The three quartz boats with 0.5 g of the the obtained HY, Co/HY and Co/N/HY was placed in a flow-through tube furnace, respectively. The furnace was heated to 873 K under a nitrogen flow and then maintained the target temperature for 6 h under a flow of nitrogen saturated with methanol at room temperature, followed by further heat treatment in a nitrogen atmosphere at 1073 K for 3 h. After cooling down to room temperature under nitrogen atmosphere, the resulting carbon/zeolite composites are named as CVD-HY, CVD-Co/HY, CVD-Co/N/HY, respectively. As a control experiment, the CVD and carbonization processes were carried out for NaY zeolite. To remove Y zeolite templates, the CVD samples were immersed in 2 M NaOH aqueous solution at 353 K for 8 h. After washing with distilled water and drying, obtained samples were immersed in 0.1 M HCl aqueous solution at room temperature. The acid treatment was performed overnight, followed by washing with distilled water several times and drying at 363 K in the oven. The obtained samples were labelled as HY-ZTC, Co-ZTC, Co/N-ZTC.

2.3 Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on the PANalytical X'Pert PRO X-ray diffractometer with Cu-K α radiation. Scanning Electron Microscope (SEM) images were recorded on JEOL JCM-6000PLUS. Transmission electron microscopy (TEM) and high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were recorded on Hitachi H800 (Hitachi) and JEM-ARM200F (JEOL), respectively. The porosity of the obtained samples was evaluated by N₂ adsorption and desorption measurements at 77 K using the BELSORPmax (MicrotracBEL). The specific surface area determination, pore size analysis was performed by Brunauer–Emmett–Teller (BET) method and Density Functional Theory (DFT) method using slit shaped pores, respectively. The energy dispersive X-ray spectroscopy (EDX) for the determination of Si and Al species derived from zeolites was performed on JEOL JCM-6000PLUS. We measured Co content by using Inductively Coupled Plasma (ICP) measurements. The X-ray absorption fine structure (XAFS) measurement was performed at BL-3 of the Ritsumeikan Synchrotron Radiation Center (Japan) using a Si(220) double crystal monochromator. The Co K edge XAFS spectra were measured in fluorescence yield mode using a three-element Ge solid state detector.

2.4 Electrochemical measurements

The electrochemical measurements were carried out on a VersaSTAT 3 Potentiostat. Electrochemical characterization of the synthesized catalysts was performed in a rotating ring-disk electrode as the working electrode; a Pt coil electrode is the counter electrode and an Hg/Hg₂Cl₂ electrode acts as the reference electrode. The potentials were normalized to the reversible hydrogen electrode (RHE) referred to the Nernst equation:

$$E_{RHE} = E_{Hg/Hg_2Cl_2} + 1.0083$$

The electrocatalysts (8.8 mg) were dispersed ultrasonically in a 1 ml solvent with 0.1 ml Nafion, 0.1 ml isopropanol and 0.8 ml deionized water. The electrocatalytic activity of the catalyst was measured in an O₂ saturated 0.1 M KOH aqueous solution as the electrolyte. Accelerated durability testing (ADT) was conducted by cycling the electrode potential 10000 times between 0.6 V and 1.0 V vs RHE under oxygen saturation. The linear sweep voltammetry (LSV) tests were measured at a sweep rate of 10 mV·s⁻¹ under different rotating rates (1200, 1600, 2000 and 2400 rpm). The electron transfer number (*n*) per an oxygen molecule at different potentials during the oxygen reduction reaction (ORR) was calculated from the Koutecky-Levich (K-L) equation:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{nFkC_0} + \frac{1}{0.62nFC_0D_0^{\frac{2}{3}}\nu^{\frac{-1}{6}}\omega^{\frac{1}{2}}}$$

where j is the current density, j_L and j_K are the diffusion and kinetic-limiting current densities, respectively, ν is the kinematic viscosity of the solution ($0.01 \text{ cm}^2\cdot\text{s}^{-1}$), F represents the Faraday constant ($96485 \text{ C}\cdot\text{mol}^{-1}$), k is the electron transfer rate constant, C_0 is the O_2 concentration in the bulk of electrolyte ($1.2\times 10^{-6} \text{ mol}\cdot\text{cm}^{-3}$), D_0 is the diffusion coefficient of O_2 in the electrolyte ($1.8\times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$), and ω is the rotation rate ($\text{rad}\cdot\text{s}^{-1}$).

3. Results and discussion

We synthesized Co/N-ZTCs according to Fig. 1. The first step is to anchor Co/2-methylimidazole complex into HY zeolite as a precursor of Co/N-ZTC by complexing Co ion with 2-methylimidazole in HY zeolite. The next step is chemical vapor deposition (CVD) using methanol as a carbon source, followed by carbonization process. The last step is base and acid treatments to remove HY zeolite and aggregated Co particles. As a control experiment, the same CVD process was also conducted for HY, Co/HY and NaY as zeolites.

To confirm that Co/2-methylimidazole is anchored into HY zeolite, it is important to observe the color of the sample. The color of HY zeolite changed from pink into purple

after Co ion exchange and 2-methylimidazole coordination as shown in Fig. S1 (Supplementary Material). The color of the complex composed of Co and 2-methylimidazole like ZIF-67 is well known to be purple. [40] Thus, Co/2-methylimidazole complex was likely to be successfully anchored into HY zeolite. After the CVD process, the color of the samples changed into black for CVD-HY, CVD-Co/HY and CVD-Co/N/HY since carbon was successfully deposited. Meanwhile, the color of CVD-NaY did not change to black after the same CVD process; the amount of deposited carbon was probably very small. This is because NaY zeolite has less amount of strong acid sites to catalyze the carbon deposition. In fact, after the base and acid treatments to remove zeolite template, CVD-HY, CVD-Co/HY and CVD-Co/N/HY gave ZTCs whereas CVD-Na-Y did not.

SEM images demonstrates that the morphologies and sizes of HY-ZTC, Co-ZTC and Co/N-ZTC are similar to that of the Y zeolite template as shown in Fig. 2 (a-d); HY zeolite could work as a template. XRD pattern shows a sharp peak around 6.6 degree for each of HY-ZTC, Co-ZTC and Co/N-ZTC as shown in Fig. 2 (e). The peak is likely to be typical of the (111) structural regularity of FAU zeolite; Y zeolite is one of FAU zeolite [41]. Hence, the prepared ZTCs are expected to have the same porous structures as HY, Co/HY, and Co/N/HY.

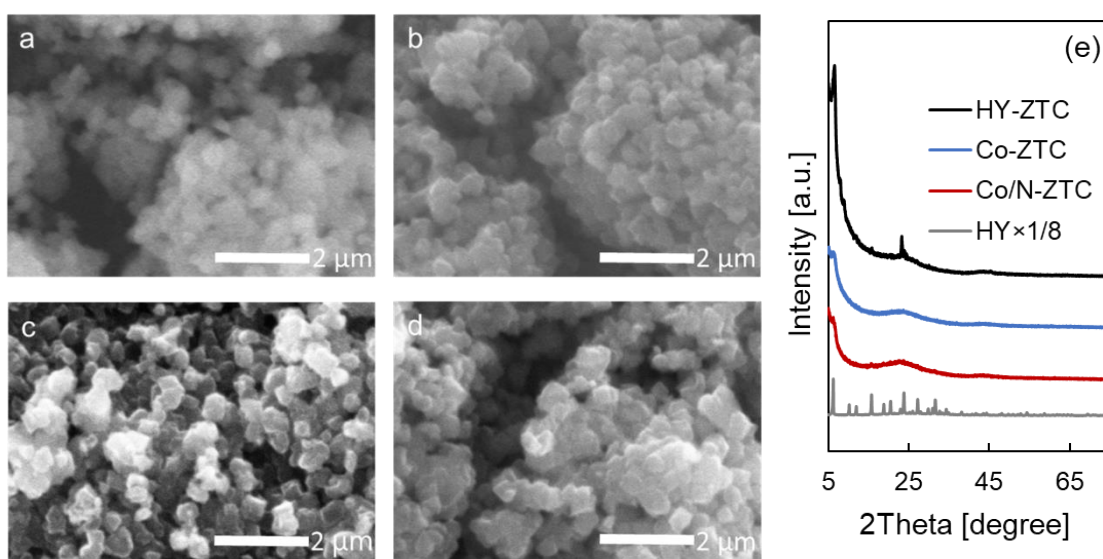


Fig. 2 SEM images of (a) HY, (b) HY-ZTC, (c) Co-ZTC and (d) Co/N-ZTC. X RD patterns of the (e) HY-ZTC, Co-ZTC, Co/N-ZTC samples and HY.

To confirm that the porous structure of the templates is transferred to the obtained ZTCs, we measured N₂ adsorption-desorption isotherms of HY-ZTC, Co-ZTC and Co/N-ZTC at 77 K. All the isotherms are similar as shown in Fig. 3 (a); the obtained ZTCs should have similar porosity. In fact, the analysis of the isotherms suggests that these ZTC samples have uniform micropore size distributions centered in the range from 1 to 2 nm as shown in Fig. 3 (b) and that BET surface areas of HY-ZTC, Co-ZTC and Co/N-ZTC were 1790, 1660 and 2030 m²/g, respectively, as listed in Table 1. These values look high, but ZTCs are known as carbon materials with high surface area up to 4000 m²/g due to their microporosity. [25] This could be because some pores are clogged. EDX

measurements indicated that HY-ZTC, Co-ZTC and Co/N-ZTC contain SiO₂ and Al₂O₃ from the zeolite template. Therefore, we can conclude that some micropores in HY-ZTC, Co-ZTC and Co/N-ZTC are partially blocked by residual SiO₂ and Al₂O₃ of the Y zeolite templates in the base and acid treatments. More severe condition in the base and acid treatments might be better to obtain ZTCs with higher BET surface area. To decide the condition, we have to check if the obtained ZTCs contain enough amount of Co species for electrocatalysis.

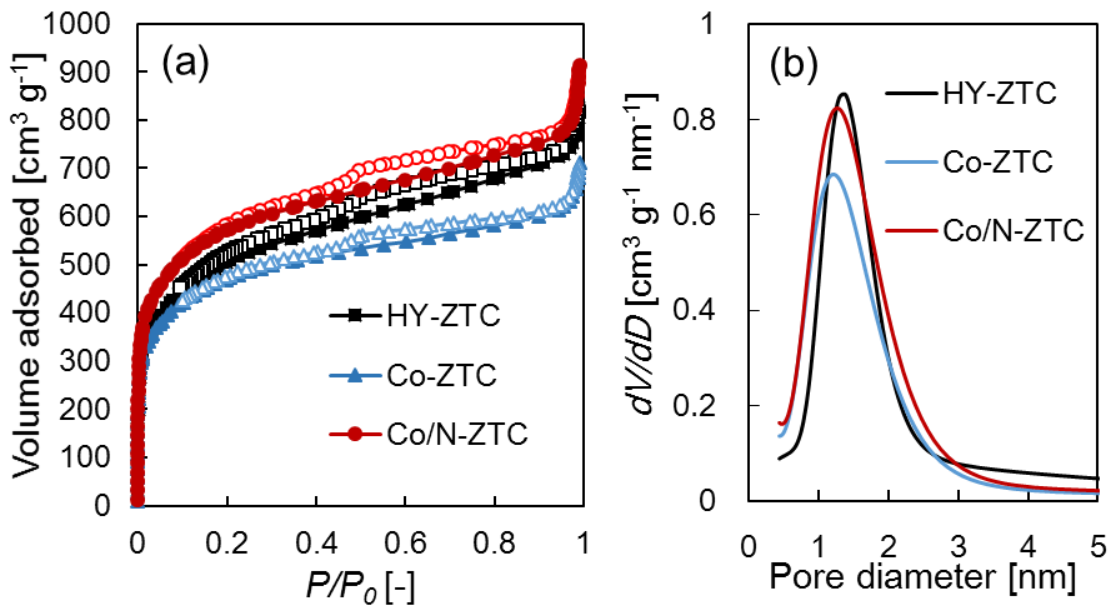


Fig. 3 Results of N₂ adsorption-desorption measurements; (a) N₂ adsorption-desorption isotherms of HY-ZTC, Co-ZTC and Co/N-ZTC samples, and (b) pore size distribution (DFT method using slit shaped pores) of HY-ZTC, Co-ZTC and Co/N-ZTC samples.

Table 1 Elemental contents and structural properties of ZTC samples.

Catalysts	Co (wt.%)	N (wt.%)	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)
HY-ZTC	--	--	1790	1.28	0.74
Co-ZTC	0.27	--	1660	1.09	0.55
Co/N-ZTC	0.06	0.42	2030	1.40	0.74

ICP measurements show that the Co content of Co-ZTC and Co/N-ZTC is 0.27 wt% and 0.06 wt%, respectively. These values are quite small. Co species is likely to be partially dissolved during the acid treatment. TEM images for the samples before and after the base and acid treatments indicate that some cobalt nanoparticles observed before the base and acid treatments disappear after the treatments as shown in Fig. S2 (Supplementary Material). Single atomic Co was observed in STEM images of Co-ZTC and Co/N-ZTC after the treatments as shown in Fig. 4. This result confirmed that single atomic Co was fabricated on both Co-ZTC and Co/N-ZTC. Thus, the current condition is likely to achieve a good balance between high BET surface area and the formation of CoN_x species. Then, we also check if Co/N-ZTC has CoN_x species.

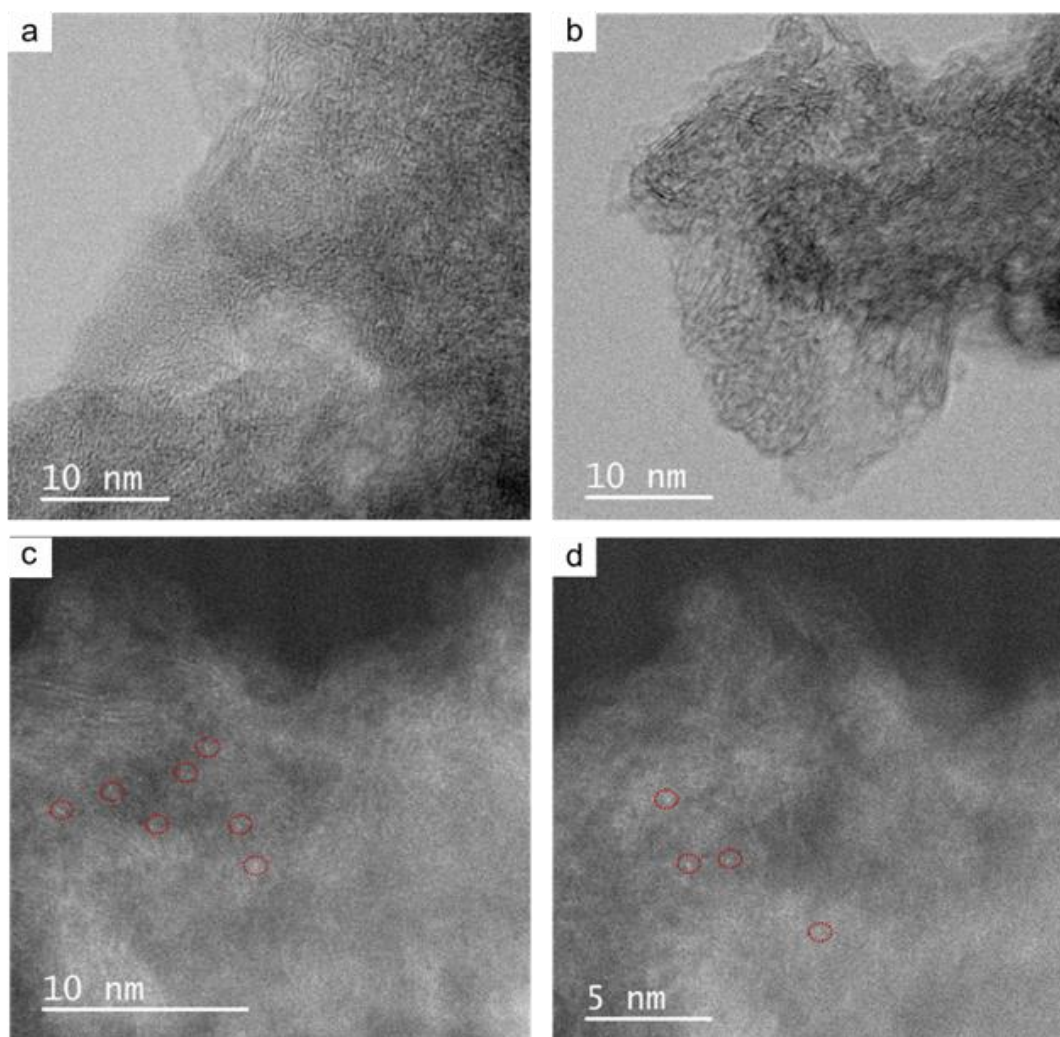


Fig. 4 Bright field TEM images and HAADF-STEM images of (a, c) Co-ZTC and (b, d) Co/N-ZTC.

Elemental analysis (CHN) of Co/N-ZTC shows the N content is 0.42 wt % (Table 1). To determine the CoN_x structure of Co/N-ZTC sample, Co K-edge XANES spectra for Co-ZTC and Co/N-ZTC were measured. The spectra exhibit peaks at 7727 eV and 7723 eV for Co/N-ZTC and Co-ZTC, respectively as shown in Fig. 5. The shift of the Co K-edge

peak is consistent with the formation of CoN_x species in Co/N-ZTC [42-44]. These results of STEM and XANES imply that highly-dispersed CoN_x can be successfully introduced to ZTC by complexing Co ion with 2-methylimidazole in HY zeolite.

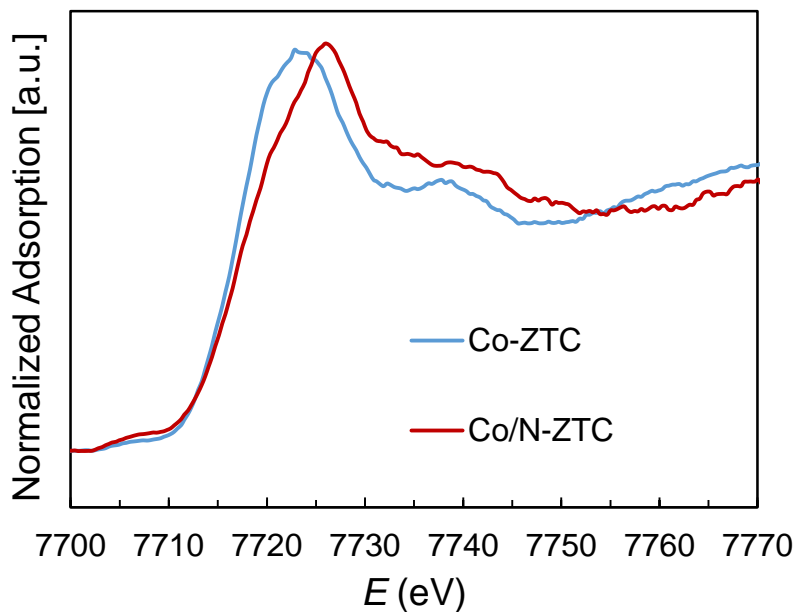


Fig. 5 The normalized XANES spectra at the Co K-edge of ZTC samples.

Finally, we examined ORR measurements over the obtained ZTCs. Co/N-ZTC showed much higher onset potential (0.93 V vs. RHE) than the others. The porosity of HY-ZTC, Co-ZTC and Co/N-ZTC were similar as mentioned above. In addition, both Co-ZTC and Co/N-ZTC have single atomic Co as mentioned above. As a lot of researchers reported that CoN_x species on the carbon matrix is more active for ORR than the other moieties, and therefore, it contributes to the higher onset potential of Co/N-ZTC. In addition, we

performed ORR measurements over Co/N-ZTC treated by base and acid using different concentrations of NaOH and HCl. 2 M NaOH and 0.1 M HCl treatments seems to be optimized as shown in Fig. S3 (Supplementary Materials). To improve the current density of Co/N-ZTC, we carried out second carbonization for Co/N-ZTC. The current density increased after the second carbonization. This is because the conductivity improves after second carbonization. The current density of the two-times carbonized Co/N-ZTC (rec-Co/N-ZTC) at 0.7 V vs. RHE is comparable to that of Pt/C with a 20 wt% Pt; rec-Co/N-ZTC must have been an excellent catalyst for ORR. In addition, the rec-Co/N-ZTC exhibited almost the same LSV curve even in the presence of methanol as shown in Fig. 6 (b); the methanol tolerance of rec-Co/N-ZTC is very high. In fact, only small negative shift was observed after 10000 cycles. These results exhibit that rec-Co/N-ZTC is an excellent catalyst with high durability. To gain further insights into the reaction kinetics, rotating disk electrode (RDE) measurements with rotating speeds ranging from 1200 rpm to 2400 rpm were conducted. All K-L plots derived from LSV curves show good linearity with stable slopes as shown in Fig. 6 (c). The results demonstrated a direct 4-electron transfer pathway as shown in Fig. 6 (d). The 4-electron transfer pathway is favorable for ORR; an ideal reaction path occurs during the ORR over rec-Co/N-ZTC.

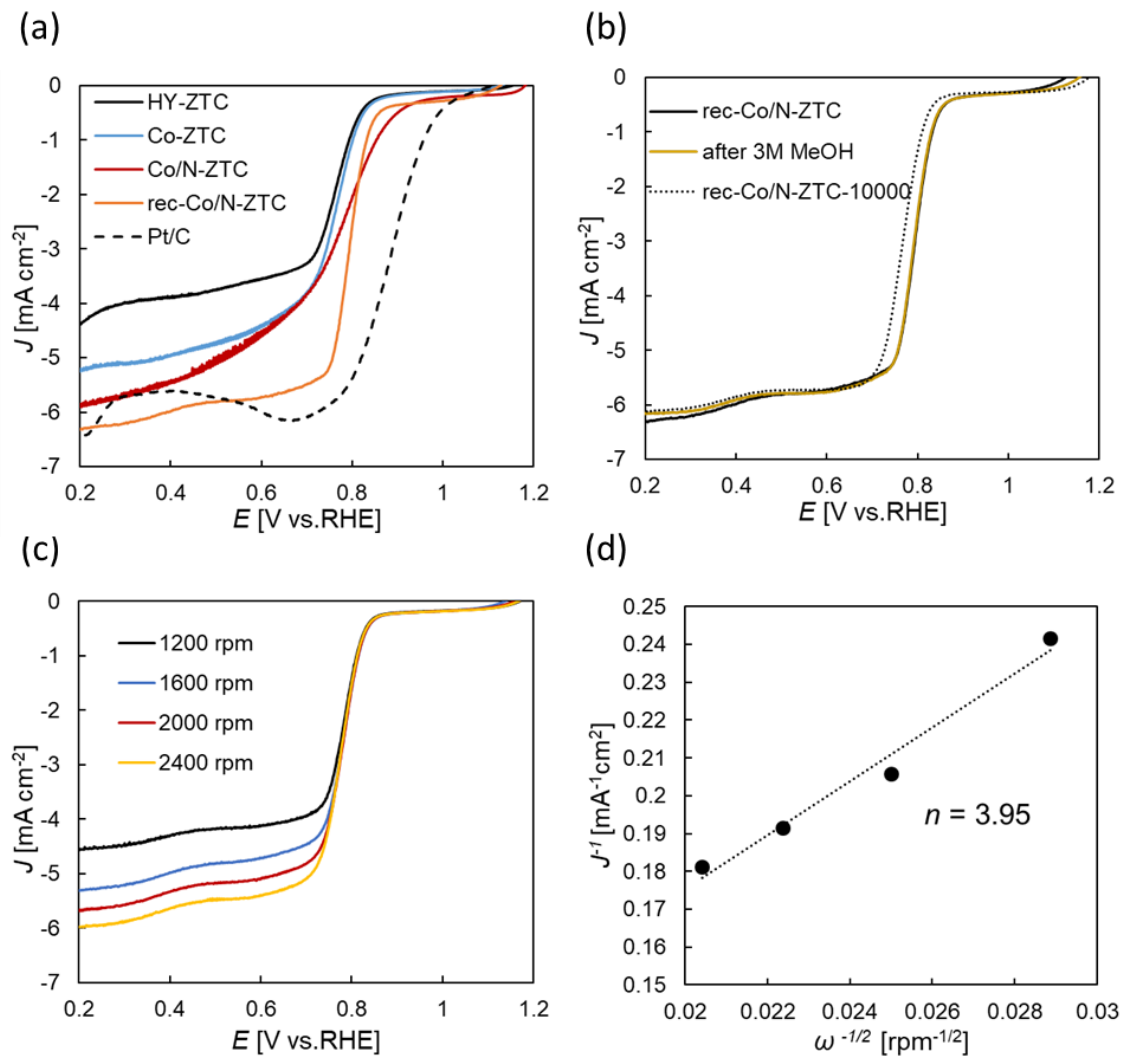


Fig. 6 (a) LSV curves over various ZTC catalysts and 20 wt% Pt/C in O₂-saturated 0.1 M KOH electrolytes at 1600 rpm, (b) Durability and methanol tolerance tests of rec-Co/N-ZTC, (c) LSV curves over rec-Co/N-ZTC with different rotating speed and (d) Koutecky-Levich (K-L) plot.

4. Conclusion

We synthesized Co/N-ZTC with a high surface area and highly dispersed CoN_x species by complexing Co ion with 2-methylimidazole in Y zeolite as a template. Co/N-ZTC shows excellent catalytic performance on ORR due to its high microporosity and single atomic Co species in CoN_x moieties. Our synthetic strategy can be applied to synthesize other TM/Het-ZTCs. Thus, this work provides a new direction for the design of ZTCs and expands the further utilization of ZTCs.

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Supplementary Material

Single atomic Co coordinated with N in microporous carbon for oxygen reduction reaction obtained from Co/2-methylimidazole anchored to Y zeolite as a template

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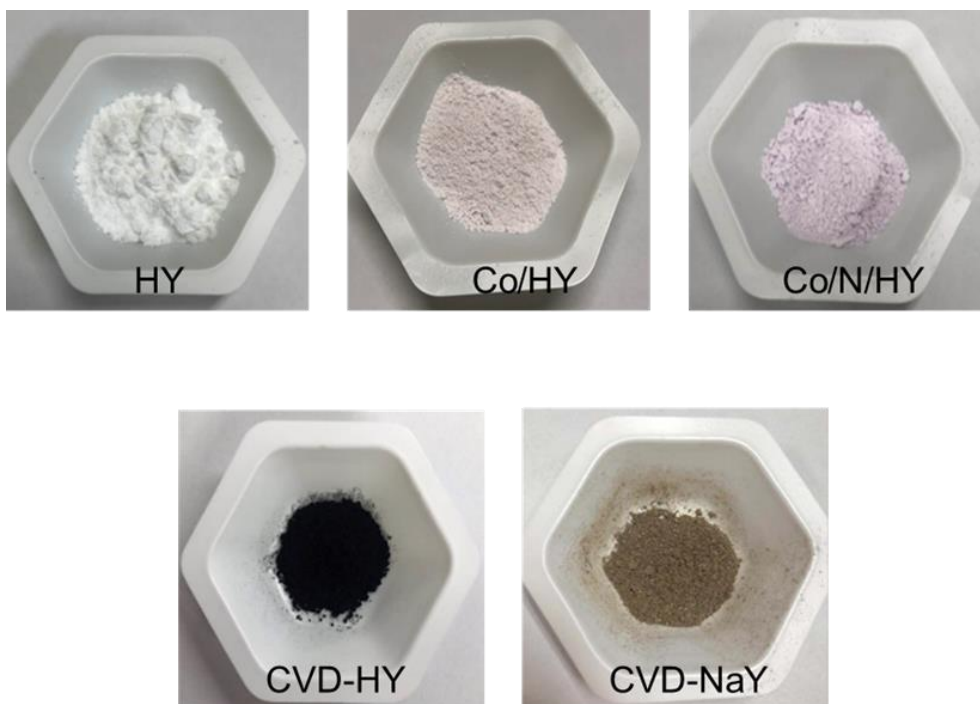


Fig. S1 Pictures of the precursors.

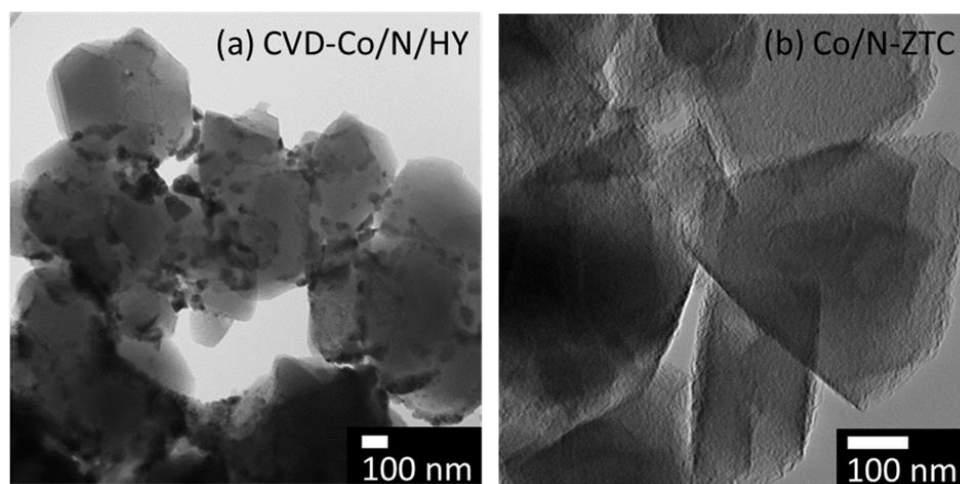


Fig. S2 TEM images of (a) CVD-Co/N/HY and (b) Co/N-ZTC.

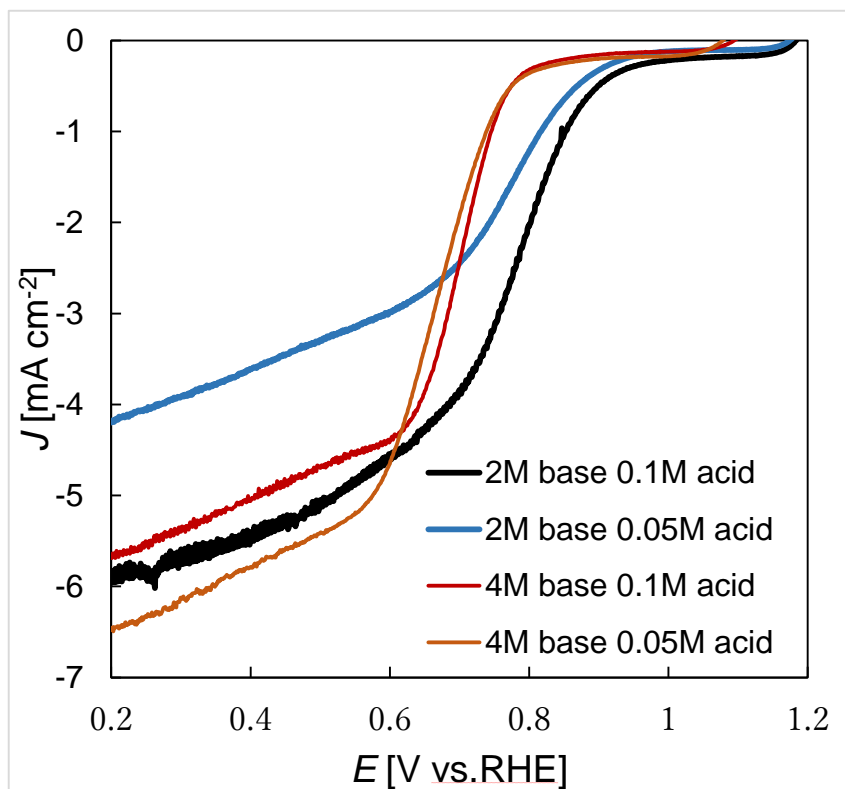


Fig. S3 LSV curves over Co/N-ZTC treated by base and acid using different concentrations of NaOH and HCl in O₂-saturated 0.1 M KOH electrolytes at 1600 rpm.

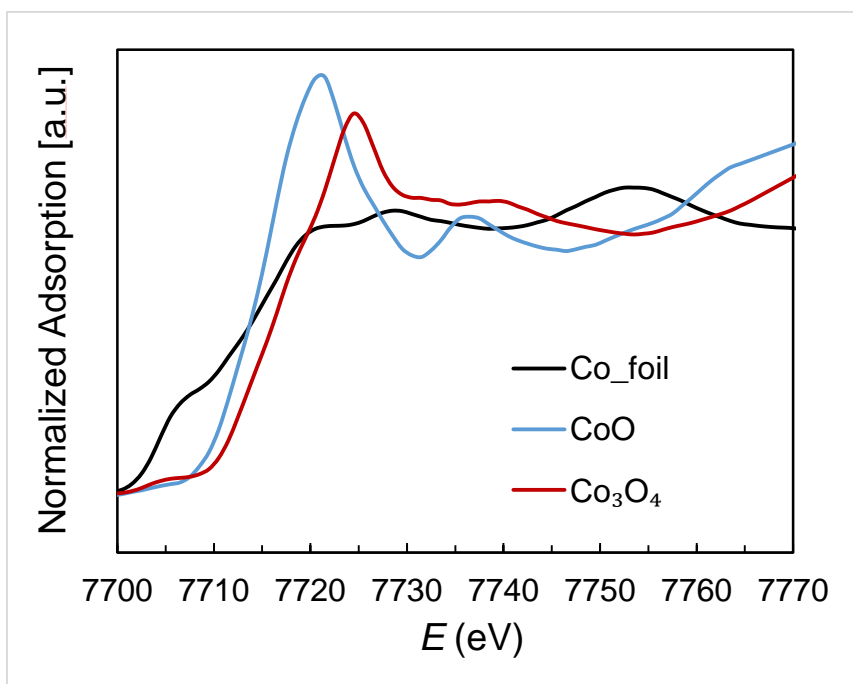


Fig. S4 The normalized XANES spectra at the Co K-edge of Co_foil, CoO and Co₃O₄.

There is no conflict of interest to declare.