

## Supplementary Information

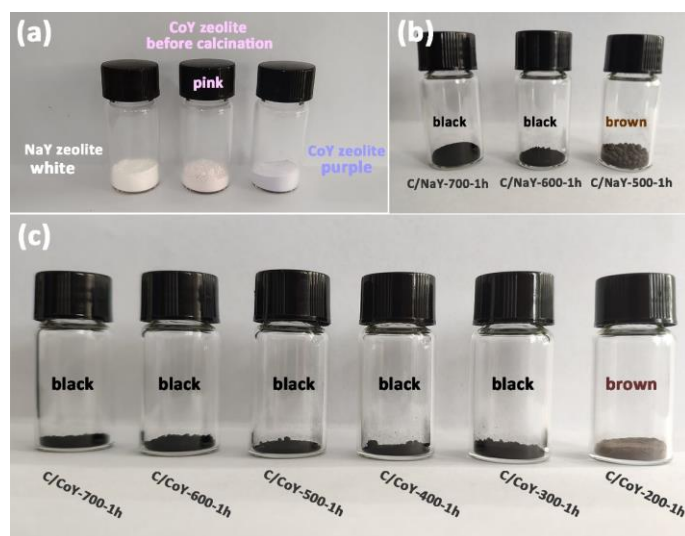
### Large-scale synthesis of 3D ordered microporous carbon at low temperature using cobalt ions exchanged zeolite Y as a template

ZHAO Hong-wei<sup>1</sup>, LI Li-xiang<sup>1,2,\*</sup>, ZUO Huai-yang<sup>1</sup>, QU Di<sup>1</sup>, ZHANG Han<sup>1</sup>, Tao Lin<sup>1</sup>, SUN Cheng-guo<sup>1,3</sup>, JU Dong-ying<sup>2</sup>, AN Bai-gang<sup>1,2,\*</sup>

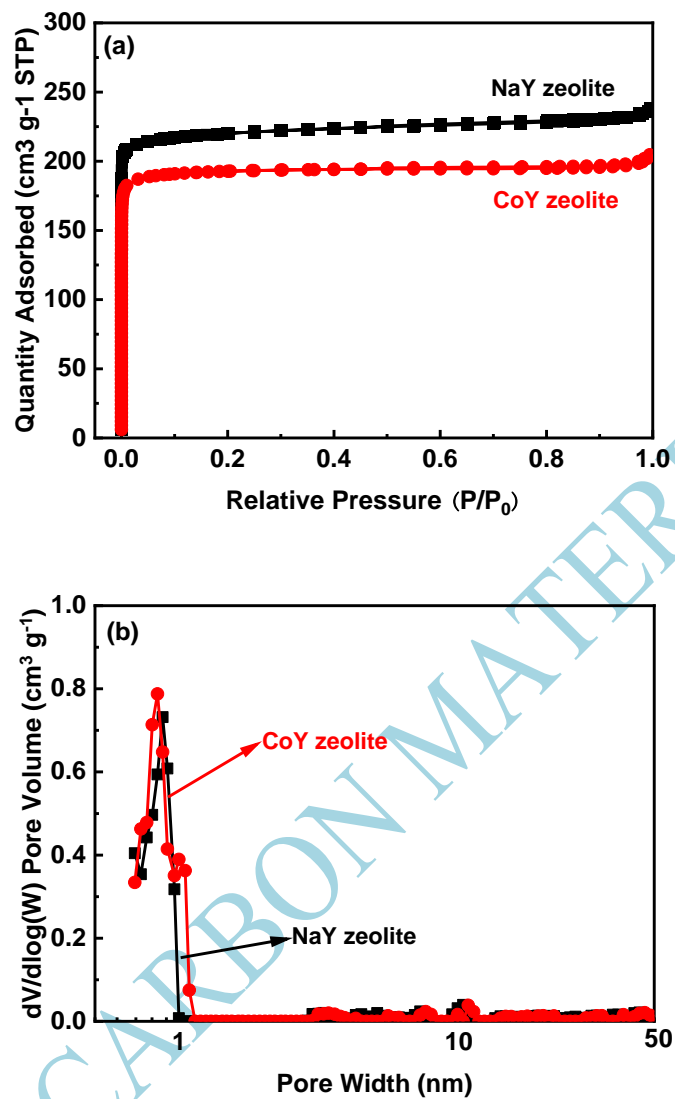
(1. Key Laboratory of Energy Materials and Electrochemistry Research Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China;  
2. Hainan Provincial Key Lab of Fine Chemistry, School of Chemical Engineering and Technology, Hainan University, Haikou 570228, China.;  
3. School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.)

Corresponding author: LI Li-xiang, Professor. E-mail: lxli2005@126.com;  
AN Bai-gang, Professor. E-mail: bgan@ustl.edu.cn

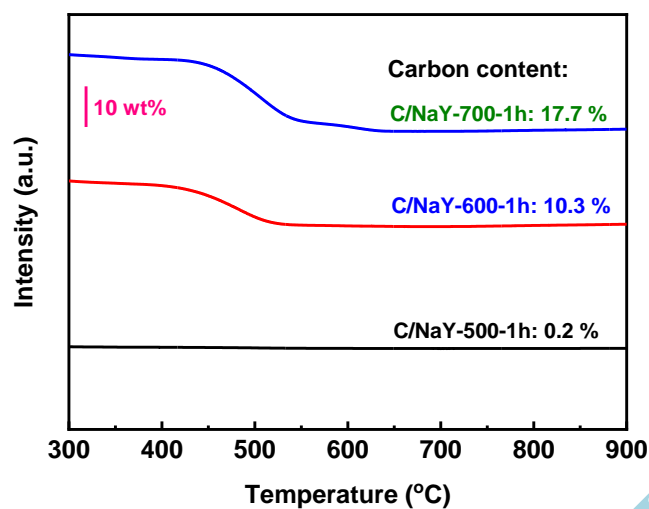
NEW CARBON MATERIALS

**Results and Discussion**

**Fig. S1.** (a) Photos of white NaY zeolite powders, pink CoY zeolite (before calcination) and purple CoY zeolite powders, (b) NaY zeolite and (c) CoY zeolite after CVD process at the different CVD temperature, respectively.



**Fig. S2.** (a)  $N_2$  adsorption-desorption isotherms, (b) PSD calculated using the NLDFT model of the NaY and CoY zeolite.



**Fig. S3.** Carbon deposition was calculated by the thermogravimetric analysis curves. TGA curves of the C/NaY-A-1h samples prepared at different CVD temperatures. The condition of the TGA test was that the sample was heated from room temperature to 900 °C in high-purity air with heating rate of 10 °C min<sup>-1</sup>. Since the samples contain varying amounts of water, the water content needed to be excluded. The calculation TGA curves started at 300 °C.

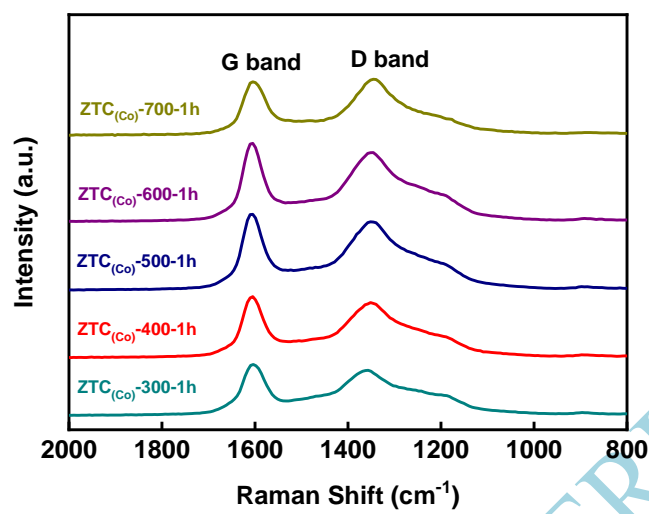
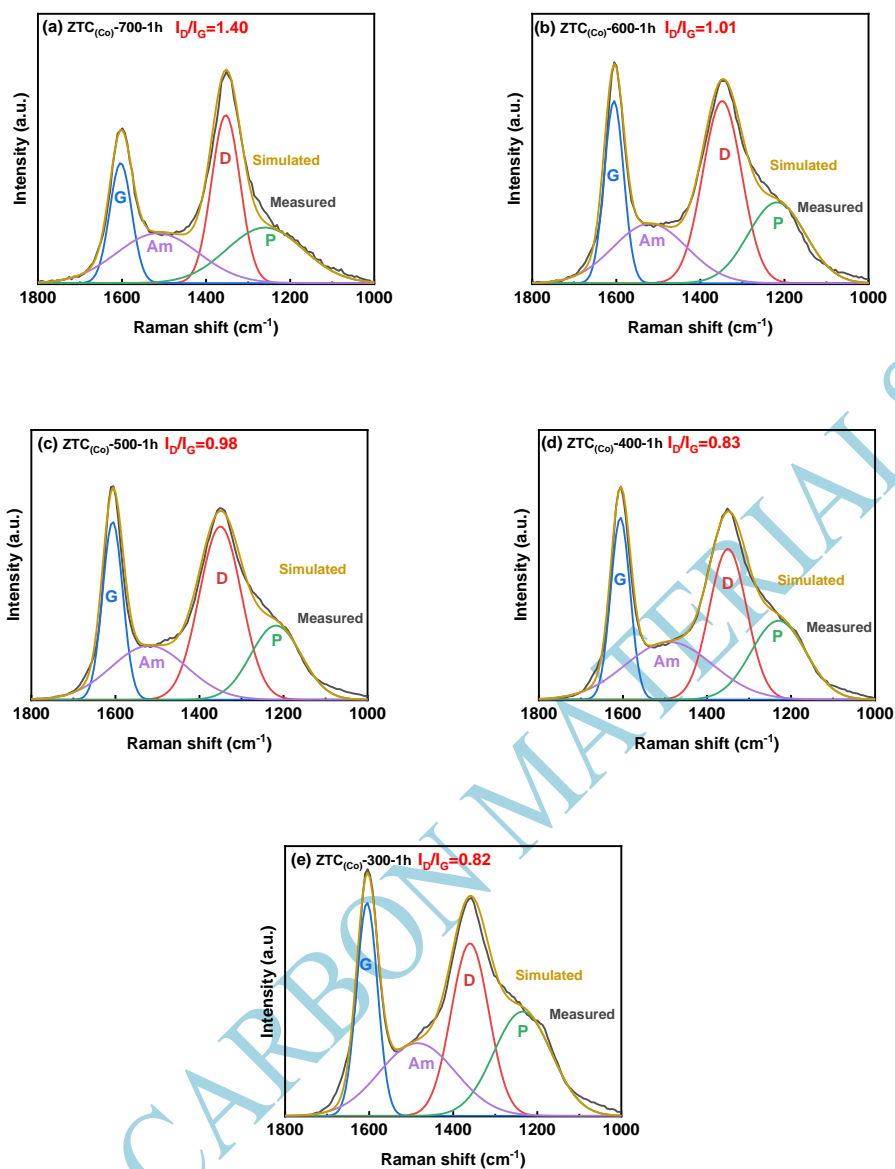
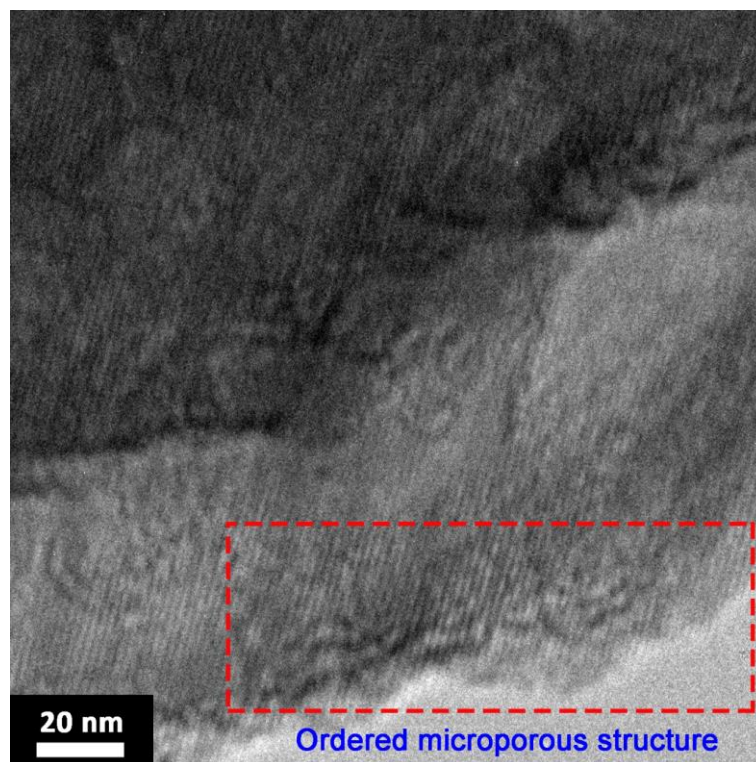


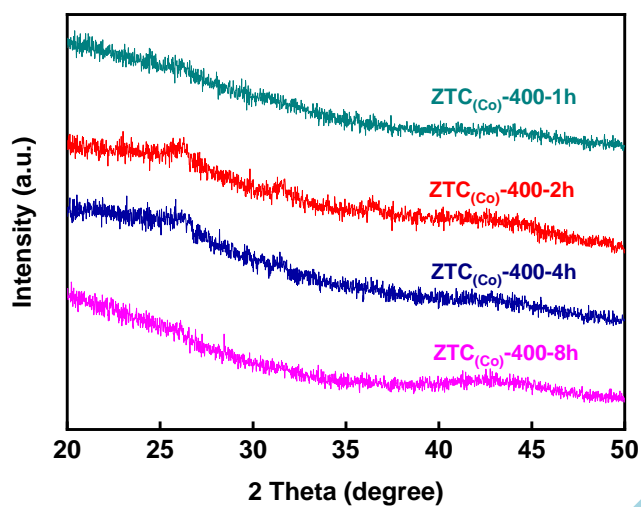
Fig. S4. Raman spectra of ZTC<sub>(Co)</sub>-A-1h samples prepared at different CVD temperatures.



**Fig. S5.** (a)~(e) Deconvoluted components (D, G, P, Am), fitting result and the values of I<sub>D</sub>/I<sub>G</sub> are shown for ZTC(C<sub>60</sub>)-A-1h samples. The graphitic peak (G band) at ca. 1600 cm<sup>-1</sup>; the disorder peak (D band) at ca. 1300 cm<sup>-1</sup>; the peak ascribed to amorphous carbon (Am peak) at ca. 1515 cm<sup>-1</sup>; the peak ascribed to sp<sup>3</sup>-bonded carbon atoms (P peak) at ca. 1200 cm<sup>-1</sup> [1].



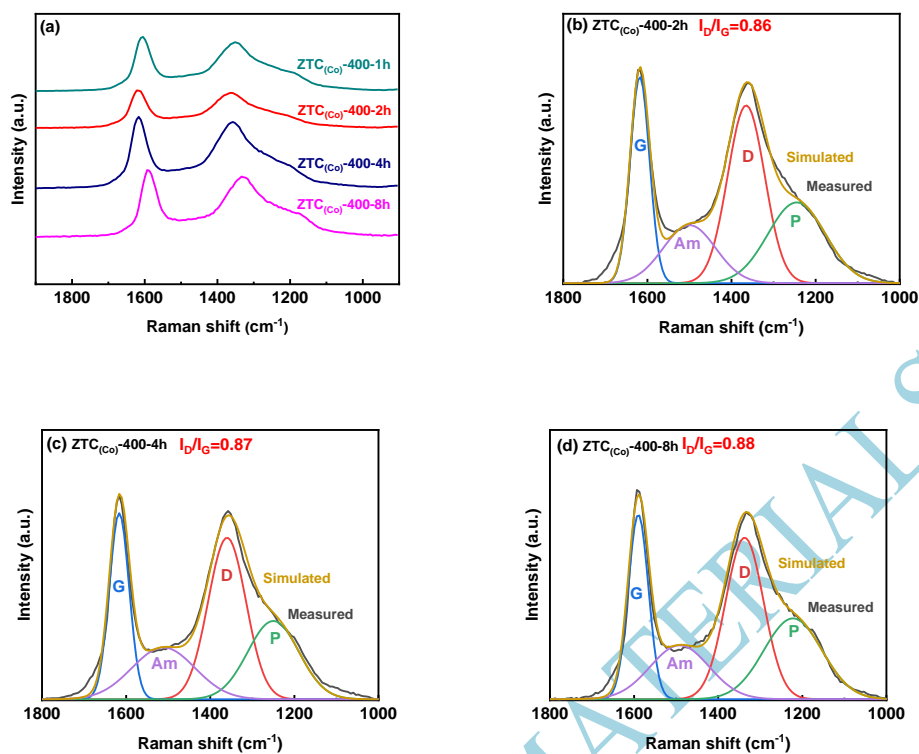
**Fig. S6.** TEM image of ZTC<sub>(C<sub>60</sub>)-400-1h</sub>.



**Fig. S7.** Wide-angle XRD patterns of ZTC<sub>(Co)</sub>-400-1h, ZTC<sub>(Co)</sub>-400-2h, ZTC<sub>(Co)</sub>-400-4h and ZTC<sub>(Co)</sub>-400-8h.

NEW CARBON MATERIALS





**Fig. S8.** (a) Raman spectra of all samples. (b)-(e) Deconvoluted components (D, G, P, Am), fitting result, the values of  $I_D/I_G$  are shown for ZTC<sub>(Co)</sub>-400-2h, ZTC<sub>(Co)</sub>-400-4h and ZTC<sub>(Co)</sub>-400-8h. The graphitic peak (G band) at ca. 1600 cm<sup>-1</sup>; the disorder peak (D band) at ca. 1300 cm<sup>-1</sup>; the peak ascribed to amorphous carbon (Am peak) at ca. 1515 cm<sup>-1</sup>; the peak ascribed to sp<sup>3</sup>-bonded carbon atoms (P peak) at ca. 1200 cm<sup>-1</sup> [1].

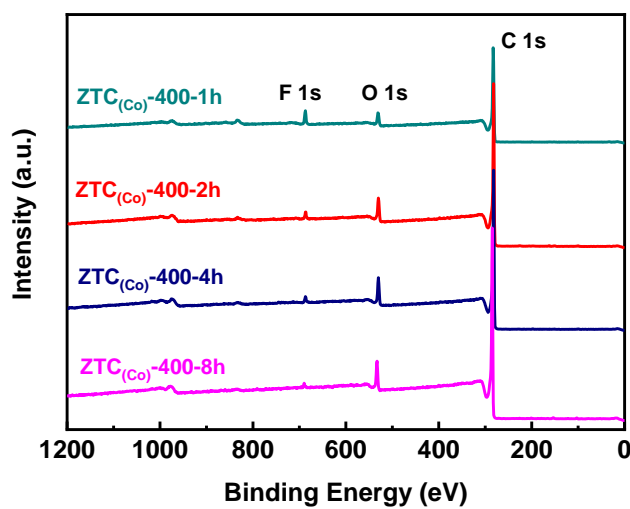
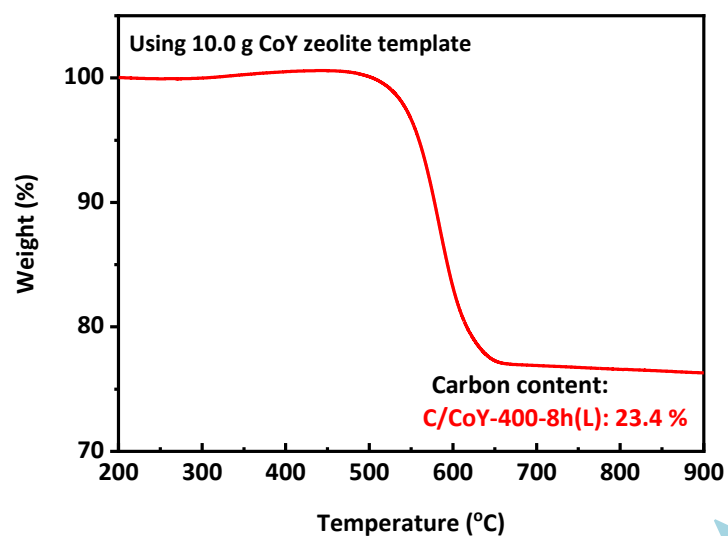
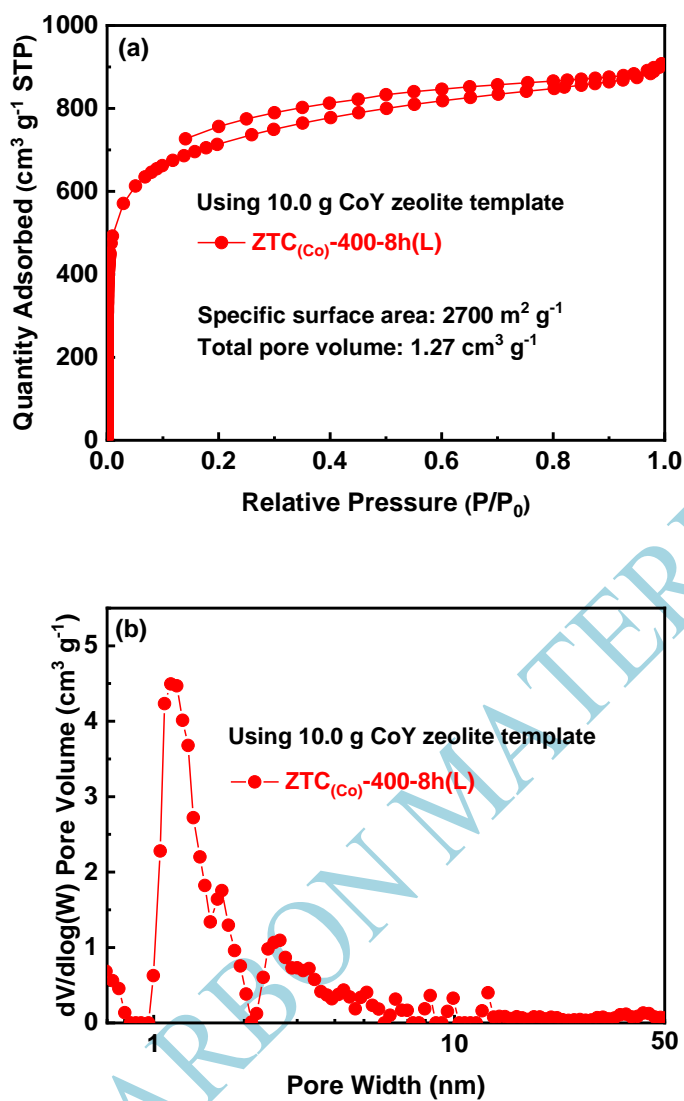


Fig. S9. XPS survey spectra of ZTC<sub>(Co)</sub>-400-1h, ZTC<sub>(Co)</sub>-400-2h, ZTC<sub>(Co)</sub>-400-4h and ZTC<sub>(Co)</sub>-400-8h.

NEW CARBON MATERIALS



**Fig. S10.** Carbon deposition of C/CoY-400-8h(L) was calculated by the thermogravimetric analysis curves. The preparation conditions of C/CoY-400-8h(L) are as follows: the 10.0 g of CoY zeolite was placed in a large horizontal quartz reactor, and the air was purged by pure Ar gas flow at room temperature for 1 h in the reactor. The CVD temperature of the synthesis device was heated up to 400 °C under pure Ar gas flow with a heating rate of 5 °C min<sup>-1</sup>. Then acetylene gas (50 % in Ar, acetylene: 30 sccm; Ar: 30 sccm) was passed through the reactor for 8 h. After the carbonaceous deposition, the graphitization temperature was increased to 900 °C and was maintained for 1 h under pure Ar gas again. Cooling to room temperature, the carbon compounds are indicated as C/CoY-400-8h(L).



**Fig. S11.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) NLDFT pore size distribution of ZTC<sub>(Co)</sub>-400-8h(L).

**Table S1.** Summary of SSA and pore volume from the N<sub>2</sub> adsorption-desorption isotherms at -196 °C and synthesis condition for each sample.

Samples	Temperature <sup>a</sup>	SSA <sup>b</sup>	V <sub>1</sub> <sup>c</sup>	V <sub>2</sub> <sup>d</sup>
NaY	-	650	0.33	0.16
CoY	-	570	0.28	0.22
ZTC <sub>(Co)</sub> -700-1h	700	1370	0.67	0.46
ZTC <sub>(Co)</sub> -600-1h	600	1480	0.87	0.48
ZTC <sub>(Co)</sub> -500-1h	500	2060	0.94	0.71
ZTC <sub>(Co)</sub> -400-1h	400	2200	1.00	0.80
ZTC <sub>(Co)</sub> -300-1h	300	1400	0.67	0.47

Temperature<sup>a</sup>: CVD temperature (°C), SSA<sup>b</sup>: BET specific surface area, m<sup>2</sup> g<sup>-1</sup>, V<sub>1</sub><sup>c</sup>: total pore volume, cm<sup>3</sup> g<sup>-1</sup>, V<sub>2</sub><sup>d</sup>: micropore volume, cm<sup>3</sup> g<sup>-1</sup>.

**Table S2.** Surface elements content (at%) of the ZTC<sub>(Co)</sub>-400-1h, ZTC<sub>(Co)</sub>-400-2h, ZTC<sub>(Co)</sub>-400-4h and ZTC<sub>(Co)</sub>-400-8h.

Samples	C 1s	O 1s	F 1s
ZTC <sub>(Co)</sub> -400-1h	90.2	5.8	4.0
ZTC <sub>(Co)</sub> -400-2h	92.6	6.1	1.3
ZTC <sub>(Co)</sub> -400-4h	92.3	6.5	1.2
ZTC <sub>(Co)</sub> -400-8h	92.8	6.7	0.5

**Table S3.** A list of ZTCs prepared by CVD methods.

Zeolite	Method	Mass <sup>a</sup>	Carbon Source	T <sup>b</sup> (°C)	SSA <sup>c</sup> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>1</sub> <sup>d</sup> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>2</sub> <sup>e</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Ref. <sup>f</sup>
CoY zeolite	CVD	1.0 g	Acetylene	400	3000	1.33	1.03	This work
CoY zeolite	CVD	10.0 g	Acetylene	400	2700	1.27	0.92	This work
β zeolite	CVD	-	Propylene	800	2025	1.30	0.90	2
β zeolite	CVD	0.5 g	Acetonitrile	850	2272	1.96	0.45	3
NaY zeolite	CVD	-	Propylene	800	2300	1.50	0.51	4
NaY zeolite	CVD	-	Benzene	650	1511	0.92	0.36	5
β zeolite	CVD	0.3 g	Acetonitrile and H <sub>2</sub> O vapor	750	1860	-	1.4	6
HY zeolite	CVD	0.8 g	Acetonitrile	750	1322	0.84	0.47	7
LaY zeolite	CVD	-	Ethylene and H <sub>2</sub> O vapor	600	-	1.40	1.20	8
CaX zeolite	CVD	0.3 g	Ethylene and H <sub>2</sub> O vapor	600	2770	1.32	1.05	9
CaX zeolite	CVD	200 g	Ethylene and H <sub>2</sub> O vapor	600	2400	1.16	1.00	9
CoY zeolite	CVD	1.0 g	Ethylene and H <sub>2</sub> O vapor	600	1613	1.18	0.82	10
CaY zeolite	CVD	0.3 g	Nitrogen-containing precursor and H <sub>2</sub> O vapor	600	2540	1.25	1.00	11

Mass<sup>a</sup>: the mass of zeolite templates used; Temperature<sup>b</sup>: CVD temperature (°C); SSA<sup>c</sup>: BET specific surface area, m<sup>2</sup> g<sup>-1</sup>; V<sub>1</sub><sup>d</sup>: total pore volume, cm<sup>3</sup> g<sup>-1</sup>; V<sub>2</sub><sup>e</sup>: micropore volume, cm<sup>3</sup> g<sup>-1</sup>; Ref<sup>f</sup>: References.

## Reference

- [1] Tang R, Taguchi K, Nishihara H, et al. Insight into the origin of carbon corrosion in positive electrodes of supercapacitors [J]. *Journal of Materials Chemistry A*, 2019, 7(13): 7480-7488.
- [2] Kyotani T, Ma Z X, Tomita A. Template synthesis of novel porous carbons using various types of zeolites [J]. *Carbon*, 2003, 41(7): 1451-1459.
- [3] Yang Z X, Xia Y D, Mokaya R. Hollow shells of high surface area graphitic N-doped carbon composites nanocast using zeolite templates [J]. *Microporous and Mesoporous Materials*, 2005, 86(1-3): 69-80.
- [4] Armandi M, Bonelli B, Bottero I, et al. Synthesis and characterization of ordered porous carbons with potential applications as hydrogen storage media [J]. *Microporous and Mesoporous Materials*, 2007, 103(1-3): 150-157.
- [5] Song X H, Teo W S, Wang K. Synthesis and characterization of activated carbons prepared from benzene CVD on zeolite Y [J]. *Journal of Porous Materials*, 2011, 19: 211-215.
- [6] Kim K, Lee T, Kwon Y, et al. Lanthanum-catalysed synthesis of microporous 3D graphene-like carbons in a zeolite template [J]. *Nature*, 2016, 535: 131-135.
- [7] Zhao H W, Li L X, Liu Y Y, et al. Synthesis and ORR performance of nitrogen-doped ordered microporous carbon by CVD of acetonitrile vapor using silanized zeolite as template [J]. *Applied Surface Science*, 2020, 504(28): 144438.
- [8] Kwon Y, Kim K, Ryoo R. N-doped zeolite-templated carbon as a metal-free electrocatalyst for oxygen reduction [J]. *RSC Advances*, 2016, 6(49): 43091-43097.
- [9] Kim K, Kwon Y, Lee Y, et al. Facile large-scale synthesis of three-dimensional graphene-like ordered microporous carbon via ethylene carbonization in CaX zeolite template [J]. *Carbon* 2017, 118: 517-523.
- [10] Moon G H, Bähr A, Tüysüz H. Structural engineering of 3D carbon materials from transition metal ion-exchanged Y zeolite templates [J]. *Chemistry of Materials*, 2018, 30(11): 3779-3788.
- [11] Han S W, Bang J, Ko S H, et al. Variation of nitrogen species in zeolite-templated carbon by low-temperature CVD of pyrrole and the effect on oxygen reduction activity [J]. *Journal of Materials Chemistry A*, 2019, 7(14): 8353-8360.