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Controllable Self-catalytic Fabrication of Carbon Nano Materials Mediated from Nickel Metal Organic Framework

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E-mail: weili@nankai.edu.cn In the beginning of the study, three kinds of homologous metal-organic frameworks were prepared under the same experimental conditions (ESI Fig. S1). The FT-IR spectra of the MOFs were also obtained (ESI Fig. S3). The result was consistent with the MOFs prepared by CE.



Figure S1 Photo of the MOFs. (a) $Zn_2(bdc)_2dabco$, (b) $Ni_2(bdc)_2dabco$, (c) $Co_2(bdc)_2dabco$



Figure S2 X-ray pattern spectrum of MOF Ni₂(bdc)₂dabco



Figure S3 FT-IR spectra of the MOFs. (a) $Zn_2(bdc)_2dabco$, (b) $Ni_2(bdc)_2dabco$, (c) $Co_2(bdc)_2dabco$

Because the unreacted H₂bdc lowers the surface areas of the MOFs and blocks the pores of the framework, post-processing by washing with DMF and ethanol is very important for removal of residual ligands. Nonspecific physical adsorption of the MOFs was carried out to measure the total surface area and the pore size distribution. The specific surface areas of the MOFs $Zn_2(bdc)_2dabco$, $Ni_2(bdc)_2dabco$ and $Co_2(bdc)_2dabco$ were 2065, 2004 and 978 m² g⁻¹ with the pore volume of 0.782, 0.996 and 0.406 cm³ g⁻¹, respectively (Table S1). As illustrated by the N₂ isotherm of the MOFs (ESI, Fig. S4), it is a type I adsorption isotherm, indicating a microporous material. And pore size was uniformity.

Table S1 Determination of pore characteristics using nitrogen adsorption isotherms of the MOFs

Sample	Specific	Pore volume	^o Average pore
	surface	$(cm^3 g^{-1})$	diameter ^c (Å)
	area ^a (m ² g ⁻¹))	
$Zn_2(bdc)_2dabco^{1*}$	2065	0.782	15.14
Ni ₂ (bdc) ₂ dabco ^{1*}	2004	0.996	19.89
$Co_2(bdc)_2dabco^{1*}$	978	0.406	16.61

^aSpecific surface areas were calculated by Brunauer-Emmett-Teller method.

^b Pore volumes were calculated by Dubinin-Radushkevitch method.

^c Average pore diameter was measured by BJH equation.

^{1*} Reaction time was 1 min.

*The other reaction conditions were the same.



Figure S4 N₂ isotherm of MOFs prepared by MW at 120 °C for 1 min under the same conditions. (a) $Zn_2(bdc)_2dabco$, (b) $Ni_2(bdc)_2dabco$, (c) $Co_2(bdc)_2dabco$

Fig. S5A shows that using MW does not decrease the yield of the MOF for crystallization times of 1 to 15 min. However, when using CE the yield of MOF decreases as reaction time increases. Because of the long crystallization times (12-48)

h), the crystals remain in contact with the solvent for a much longer period. Conversely, when using MW the heating is fast and uniform, creating nuclei throughout the solution that quickly grows into crystals. The nucleation and crystallization were accelerated initially. Thermal stability was studied using TG (Fig. S5B), which again shows that MOFs M₂(bdc)₂dabco prepared by both CE and MW are similar. The first step in the TG curves is associated with the loss of crystal water and the remaining solvent (DMF). The MOFs began to decompose at 350 °C when unreacted bdc oxidizes. The organic linker of the MOFs started to decompose slowly and finally the frameworks were completely destroyed around 550 °C. It was also stable in the air. Therefore, the MOFs have good thermal stability.



Figure S5 Characterization of the MOFs. (A) The XRD patterns of the MOF $Zn_2(bdc)_2dabco$ formed with change in reaction time. (B) TG curves of the MOFs. (a) $Zn_2(bdc)_2dabco$ (b) $Ni_2(bdc)_2dabco$ (c) $Co_2(bdc)_2dabco$.The testing procedure was carried out from 30 to 700 °C, at a heating rate 10 °C min⁻¹.

Z-Average size of $Zn_2(bdc)_2dabco$, $Ni_2(bdc)_2dabco$ and $Co_2(bdc)_2dabco$ were 2121, 1073 and 939.2 nm, respectively (Table S2). And PDI was 0.843, 00.137 and 0.712, respectively. They were all monodisperse system referring to the dispersion of the dispersed phase a singlespecies, and very narrow particle size distribution.

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Sample	Z-Average Size	PDI	
	(d. nm)		
$Zn_2(bdc)_2dabco$	1089	0.843	
Ni ₂ (bdc) ₂ dabco	2121	0.137	
Co ₂ (bdc) ₂ dabco	2441	0.712	

Table S2 Z-Average size and PDI determination of MOFs

Dispersant: ethanol; 0.01 g MOF dispersed into 20 mL ethanol.