Supporting Information

Electrochemical Fabrication of Copper-Containing Metal–Organic Framework Films as Amperometric Detectors for Bromate Determination

Erbin Shi[a], Xiaoqin Zou[b], Jia Liu[c], Huiming Lin[a], Feng Zhang[a], Shaoxuan Shi[a], Fenghua Liu[a], Guangshan Zhu[b], and Fengyu Qu*[a]*

a College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin, Heilongjiang 150025 (P.R. China)

b Key Laboratory of Polyoxometalate Science of the Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, Jilin 130024 (P.R. China)

c College of Chemistry, Jilin University, Changchun, Jilin 130012 (P.R. China)

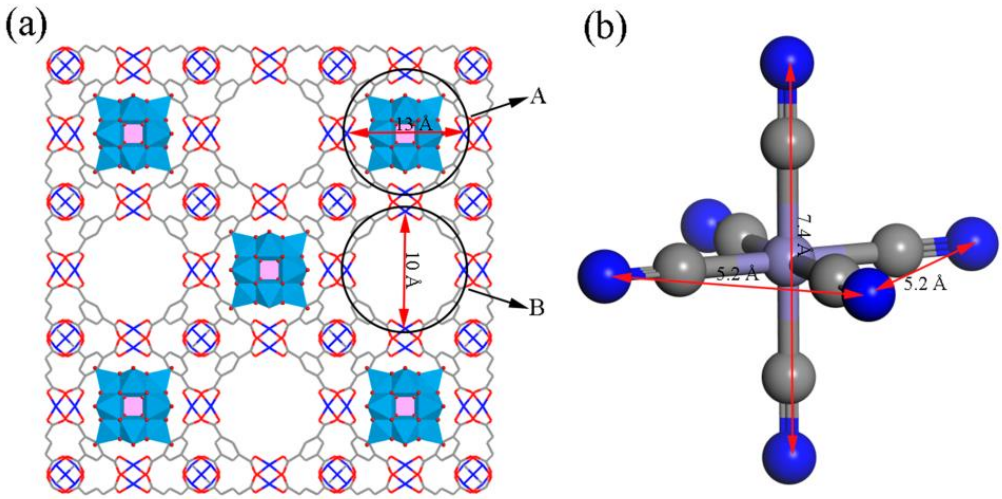

Figure S1. (a)View of a (001) sheet with two kinds of pores, A and B, in NENU-3, and (b) the structure of potassium ferricyanide ($[Fe(CN_6)]^{3-}$).

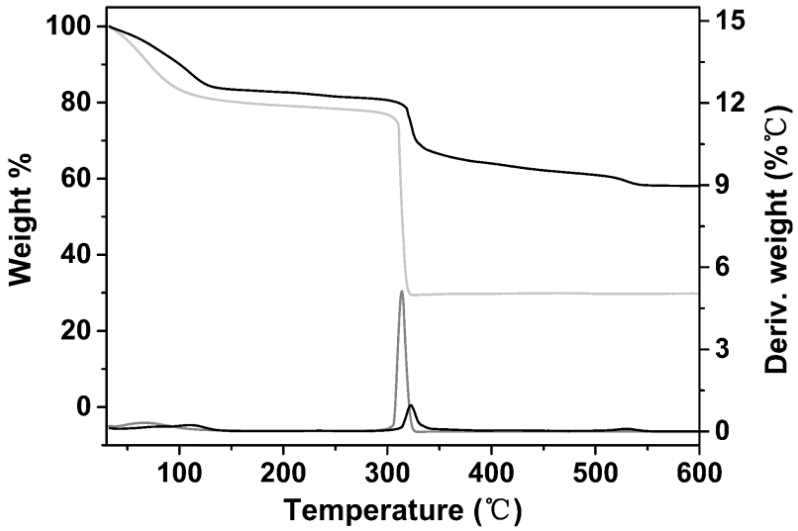

Figure S2. The thermogravimetric (TGA) and DTG analysis curves of $Cu_3(BTC)_2$ (gray) and NENU-3 (black).

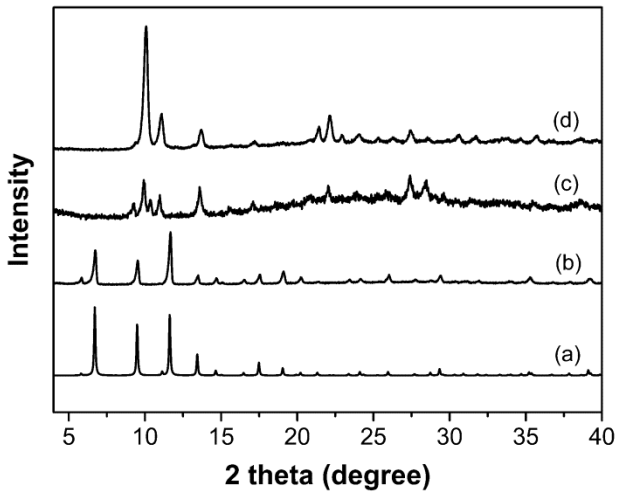

Figure S3. PXRD patterns for (a) the simulated $Cu_3(BTC)_2$ material, (b) the as-made $Cu_3(BTC)_2$ powders, and the $Cu_3(BTC)_2$ after the immersion in water at room temperature for (c) 15 min and (d) 24 h.

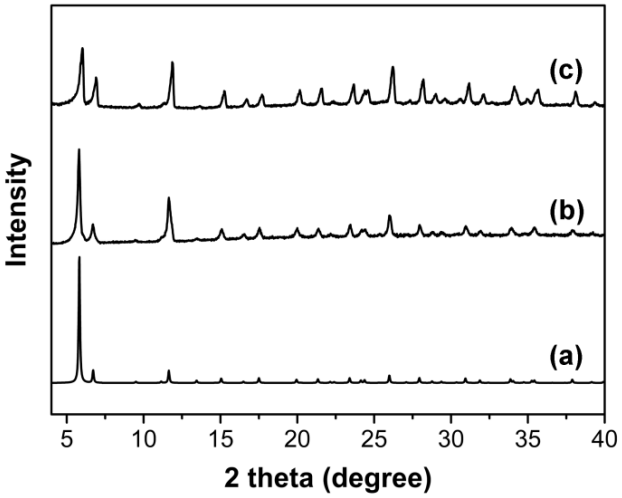

Figure S4. PXRD patterns for (a) the simulated NENU-3 material, (b) the NENU-3 film and the NENU-3 film after the immersion in water at room temperature for (c) 24 h.

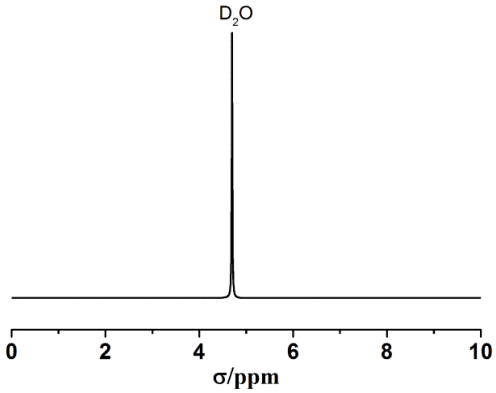

Figure S5. ^{1}H NMR spectrum of the aqueous after soaking NENU-3 for 24 hours.

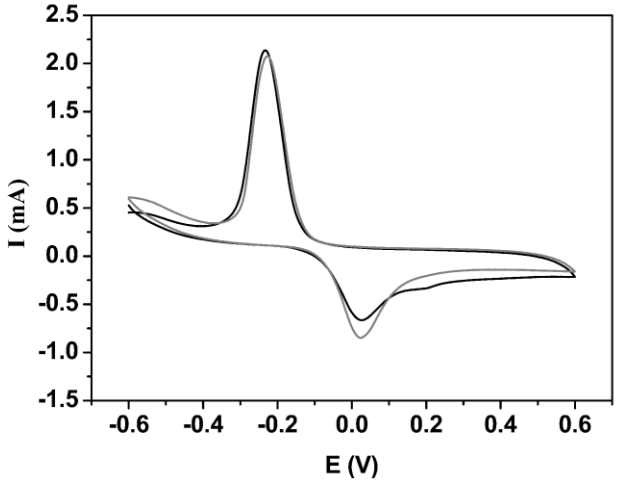

Figure S6. Cyclic voltammetric curves of bare copper substrate measured in the B-R buffer solution (pH 6.5) at a scan rate of 50 mV s^{-1} before (black) and after (gray) adding 0.3 mM of bromate.

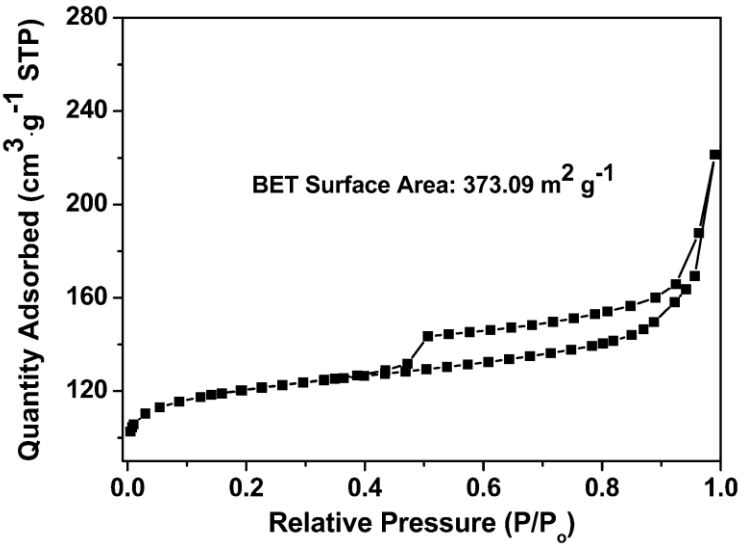

Figure S7. N_2 adsorption-desorption isotherm of the NENU-3 material.

The sample was pretreated in vacuum at 120 °C overnight and the sorption analysis was performed on Micromeritics Tristar II.

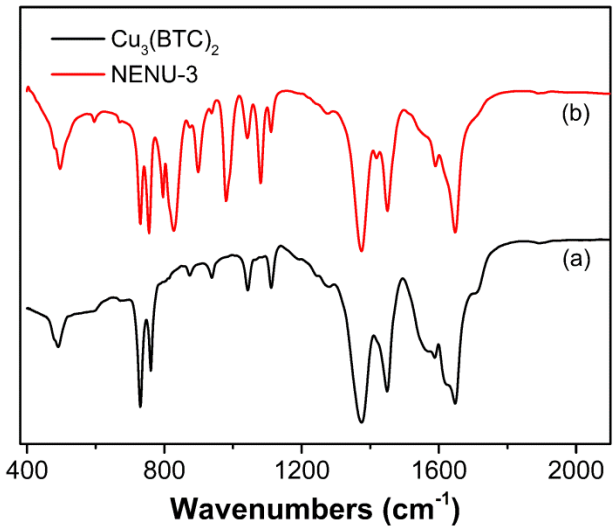

Figure S8. FT-IR spectra of (a) $Cu_3(BTC)_2$ and (b) NENU-3.

Adsorption procedure:

The BrO_3^-, Cl^-, and Br^- stock solutions (1 g L^{-1}) were prepared by dissolving $NaBrO_3$, NaCl, and NaBr in deionized water, and the desired anions concentrations were obtained by diluting the stock solutions with water. The adsorption of the different inorganic anions by the NENU-3 material was performed by mixing the dried NENU-3 (50 mg) and BrO_3^-, Cl^-, and Br^- solutions (20 mL). The mixtures were left in a stirred operating at room temperature for 12 h to reach equilibrium. After reaching adsorption equilibrium, the supernatant and the solid were separated by centrifugation at 12,000 rpm for 20 min. The concentrations of BrO_3^- and Br^- were measured by the UV-vis spectra and the concentrations of Cl^- were recorded by the potentiometric titration.

Analytical procedure of bromate concentrations

Standard solutions for calibration were prepared by adding 1.0 mL of H_2SO_4 solution (6 M) and 3.0 mL of KI solution (3 mM) as reducing agent to 10 mL brown volumetric flasks.[1, 2] After the homogenization, the solutions were left to stand for 10 min. The absorbances of the solutions were final recorded at 350 nm using the Ultraviolet-spectrophotometer (UV 2600, Shimadzu).

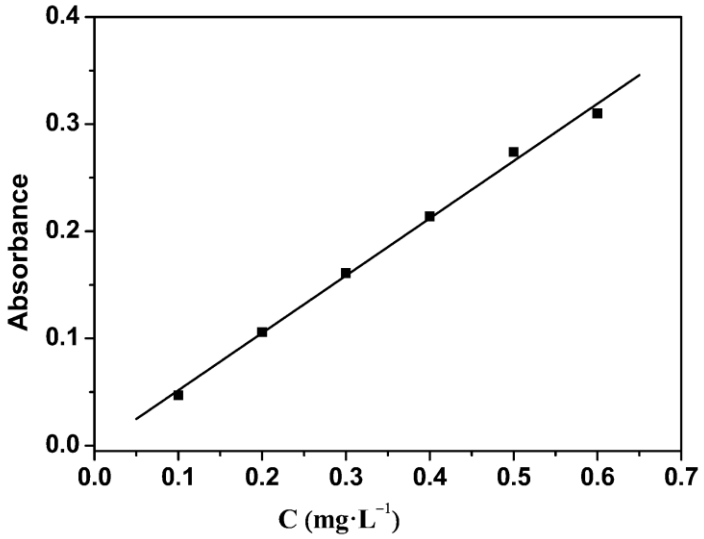

Figure S9. Standard curve of UV absorbance of the BrO_3^- solutions in the function of concentrations in water.

The supernatant solution containing different BrO_3^- concentrations after removing the NENU-3 material were diluted 100 fold in 10 mL brown volumetric flasks with KI solution (3.0 mL, 3.0

mM) and H_2SO_4 solution (1.0 mL, 6 M), and then the concentrations were estimated by monitoring the absorbances at 350 nm using a UV–vis spectrophotometer. The amount of BrO_3^- was verified by using the standard curve of BrO_3^- solutions.

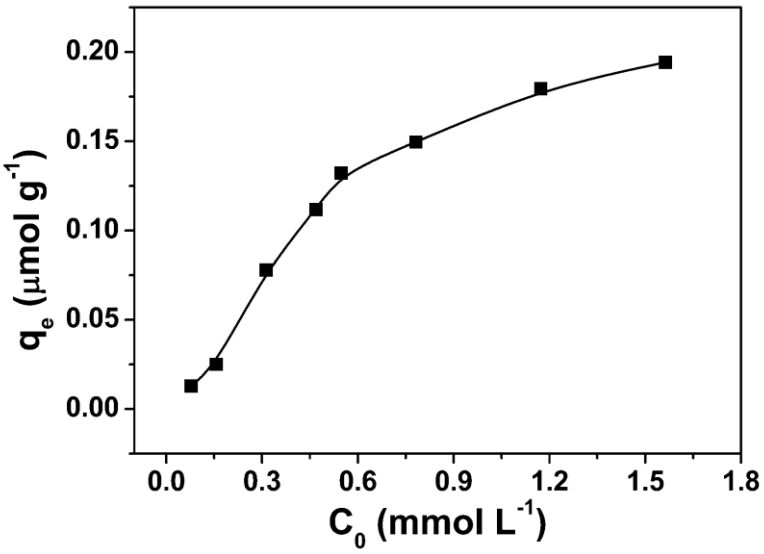

Figure S10. Adsorption isotherm for BrO_3^- on NENU-3.

Analytical procedure of Cl^- concentrations

The $AgNO_3$ solution (1 L, 14 mM) containing the concentrated nitric acid (2 mL, 14 M) was prepared at the dark condition. The standard solution of NaCl (14.1 mM) was used as the titrant. The concentration of $AgNO_3$ solution was recorded by an automatic potentiometric titration instrument (Model ZDJ-4A, Shanghai Precision & Scientific Instrument Corporation, China).[3, 4] A chloride ion-selective electrode, a calomel electrode outer chamber filled with 2 M $NaNO_3$ and a silver electrode were used as working electrode, reference electrode and as counter electrode, respectively. The titrator made a sound automatically when the titration reached the end-point, and the corresponding volume was given by the end of the titration. Five replicates were performed for each sample. The concentration of $AgNO_3$ solution was calculated equal to 12.7 mM.

The supernatant concentrations of chloride ions after the adsorption of the NENU-3 material were determined by using $AgNO_3$ (12.7 mM) as titrant.

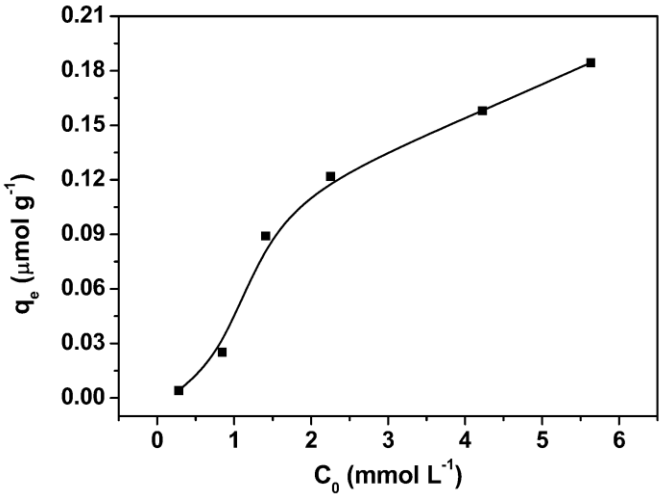

Figure S11. Adsorption isotherm for Cl^- on NENU-3.

Analytical procedure of Br^- concentrations

Standard solutions for calibration were prepared by following process[5, 6]: in a brown volumetric flask (25.00 mL), a given amount of Br^- solution was treated with 1.00 mL of acetate buffer solution (pH 4.6). Then 0.25 mL of phenol red solution (0.24 g L^{-1}) and 1.00 mL of chloramine-T solution (2.0 g L^{-1}) were added, and the solution was shaken. Exactly two minutes later, 1.00 mL of sodium thiosulphate solution (50 g L^{-1}) was added into the above solution to decompose the excess of chloramine-T, and diluted with water to 25.00 mL. After five minutes, the absorbance of the solution was recorded at 590 nm using the Ultraviolet-spectrophotometer (UV 2600, Shimadzu).

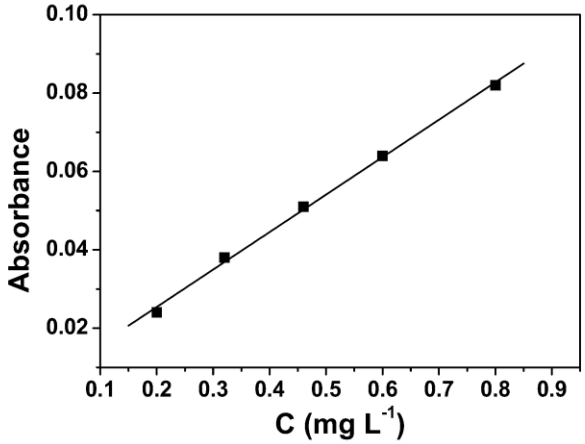

Figure S12. Standard curve of UV absorbances of Br^- solutions in function of concentrations.

The supernatant solution (2.00 mL) containing the different Br^- concentrations after removing the NENU-3 material were duplicated the procedure of standard solution for calibration. Then the concentrations were estimated by monitoring the absorbances at 590 nm using a UV–vis spectrophotometer. The amount of Br^- was calculated by using the standard curve of Br^- solutions.

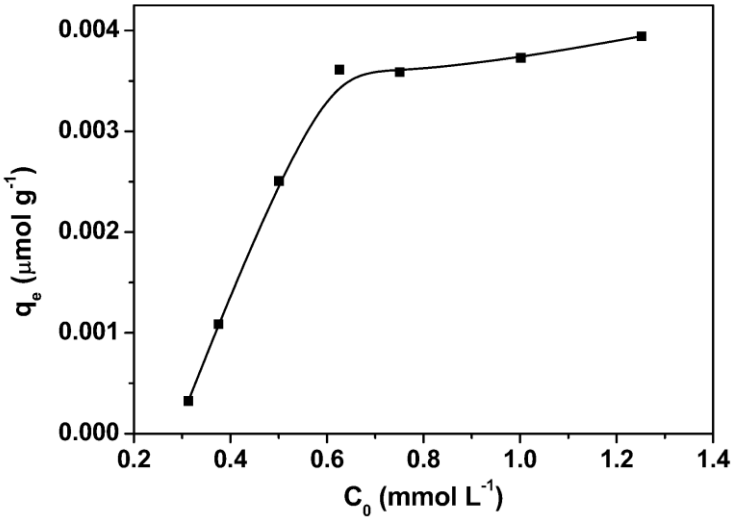

Figure S13. Adsorption isotherm for Br^- on NENU-3.

Table S1 Analytical parameters for bromate determination using different modified electrodes

Method	Material	Detection limit ($\mu mol\ L^{-1}$)	Linear Range ($\mu mol\ L^{-1}$)	Sensitivity ($\mu A\ cm^{-2}\ mM^{-1}$)	Reference
AP	P_2Mo_{18}/OMC/GC	0.922	2.77–4000	-	7
AP	$CoW_{11}Co$/PVP/TiO_2/GCE	5	20–4400	-	8
CV	tungsten oxide films	100	300-45000	6200	9
AP	$[SiNi(H_2O)W_{11}O_{39}]^{6-}$/ cysteamine/Au	14.88	14-13580	-	10
CV	$(EMIM)_3PMo_{12}O_{40}$(1)/CPE	-	1250–7500	-	11
AP	(MWCNT-PLL)/Hb	0.96	15-6000	7.56	12
AP	Ag/MWNTs	-	500–4000 4000–20000	580.33 121.44	13
AP	PMo_{12}/CNTs/PEDOT	-	100–2000	32	14
AP	NENU-3 film	12	50 – 19100 19100 – 72740	11.2 5.08	This work

Reference

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