Supplementary material

Fabrication of functional groups-rich monolith for magnetic field-assisted in-tube solid phase microextraction of inorganic selenium species in water samples followed by online chromatographic determination

Xiaochong Song [a], Siyu Luo [a], Jun Liu [a], Yuanfei Wu [b], Xiaojia Huang*

[a] Key Laboratory of the Ministry of Education for Coastal and Wetland Ecosystems;

Fujian Key Laboratory of Coastal Pollution Prevention and Control; College of the

Environment and Ecology, Xiamen University, Xiamen 361005, China

[b] College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

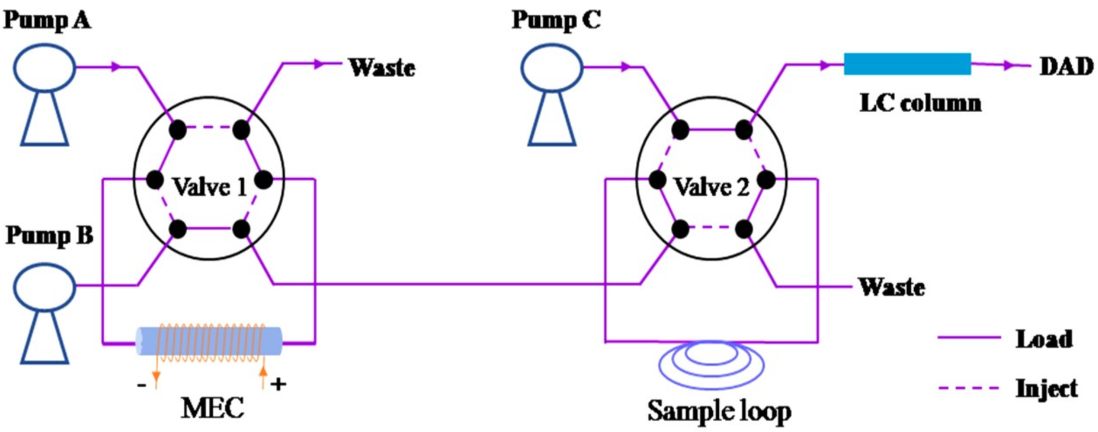

Fig. S1. The schematic of the developed online MEC-MFA/IT-SPME-HPLC/DAD system for the analysis of Se(IV) and Se(VI)

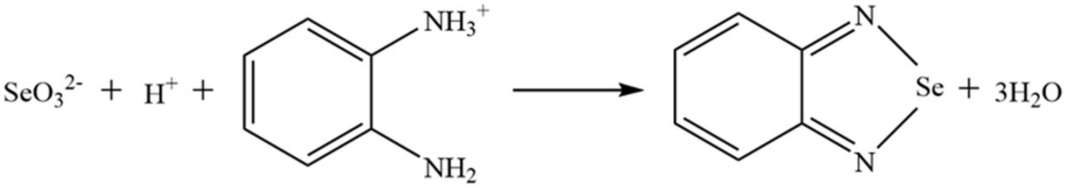

Fig. S2. The coordination reaction of Se(IV) with OPA

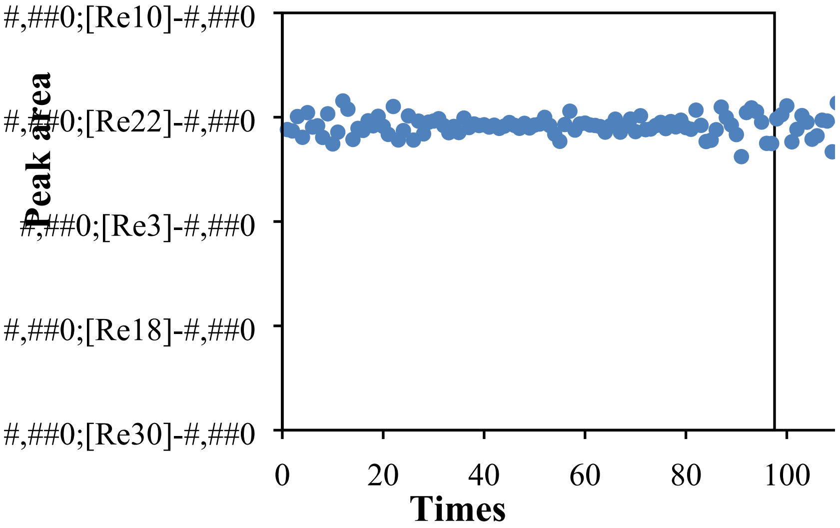

Fig. S3. Reusability of MEC-MFA/IT-SPME for the extraction of Se(IV)-OPA complex

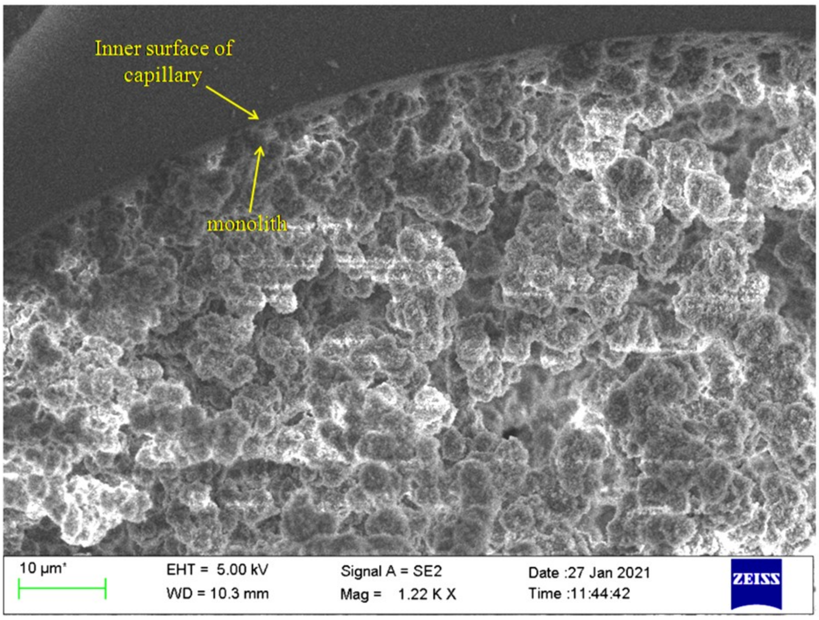

Fig. S4. SEM image of MEC at low magnification

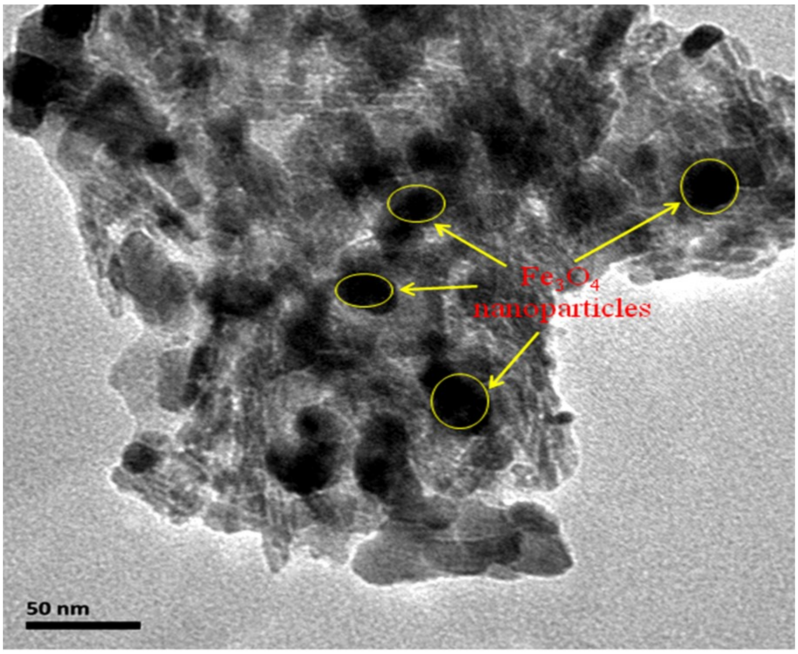

Fig. S5. TEM image of MEC

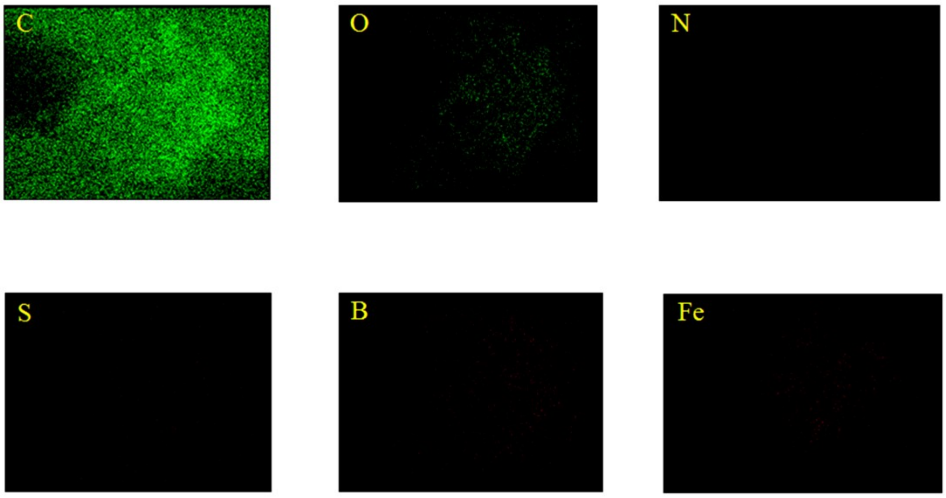

Fig. S6. Elemental mapping of C, O, N, S, B and Fe in MEC

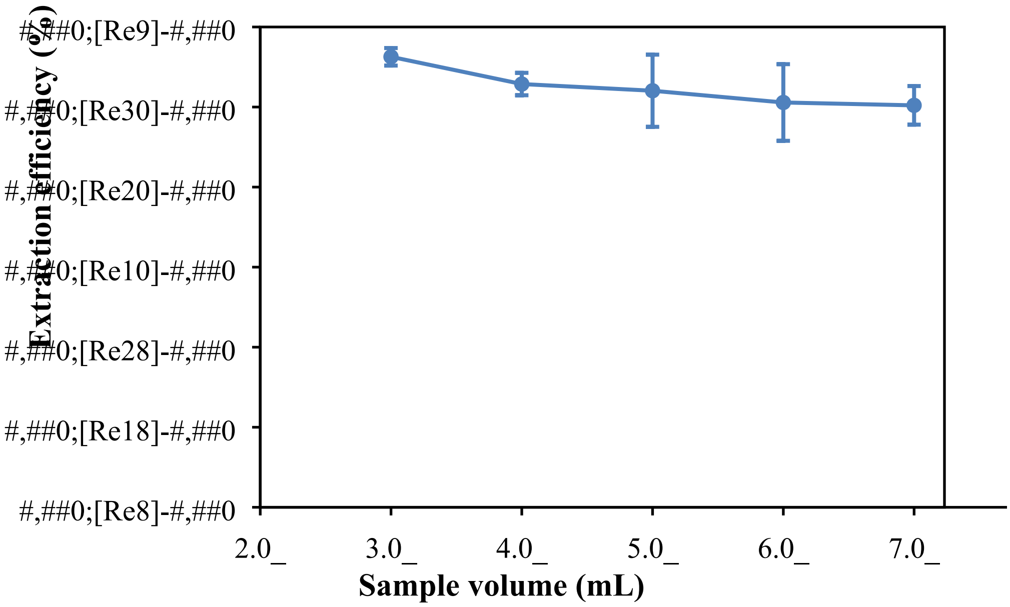

Fig. S7. Effect of sample volume on extraction efficiency

Conditions: magnetic field intensities in adsorption and desorption periods were 30 Gs and 50 Gs, respectively; sample flow rate was 0.10 mL/min; volume and flow rate of eluting solvent were 100 µL and 0.06 mL/min separately; sample pH did not be adjusted; the spiked concentration for Se(IV) was 50.0 µg/L.

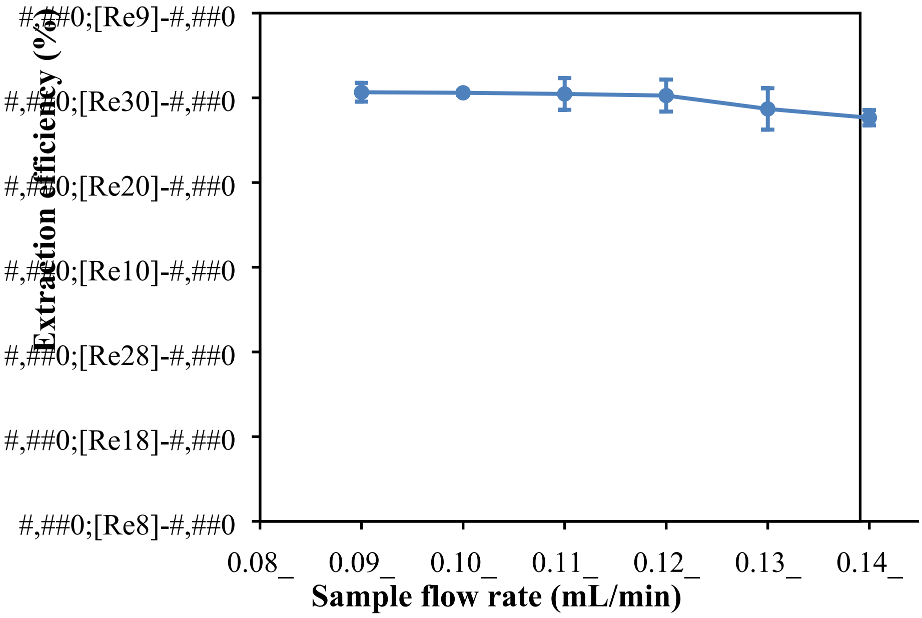

Fig. S8. Effect of sample flow rate on extraction efficiency

Conditions: sample volume was 6.0 mL/min; the other conditions were the same as in Fig. S7.

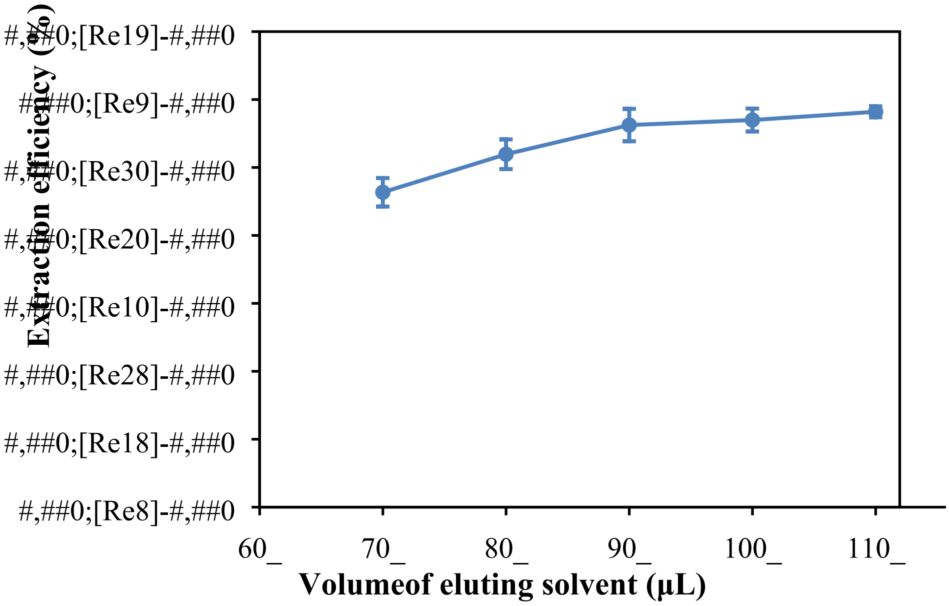

Fig. S9. Effect of volume of eluting solvent on extraction efficiency

Conditions: sample flow rate was 0.12 mL/min; the other conditions were the same as in Fig. S8.

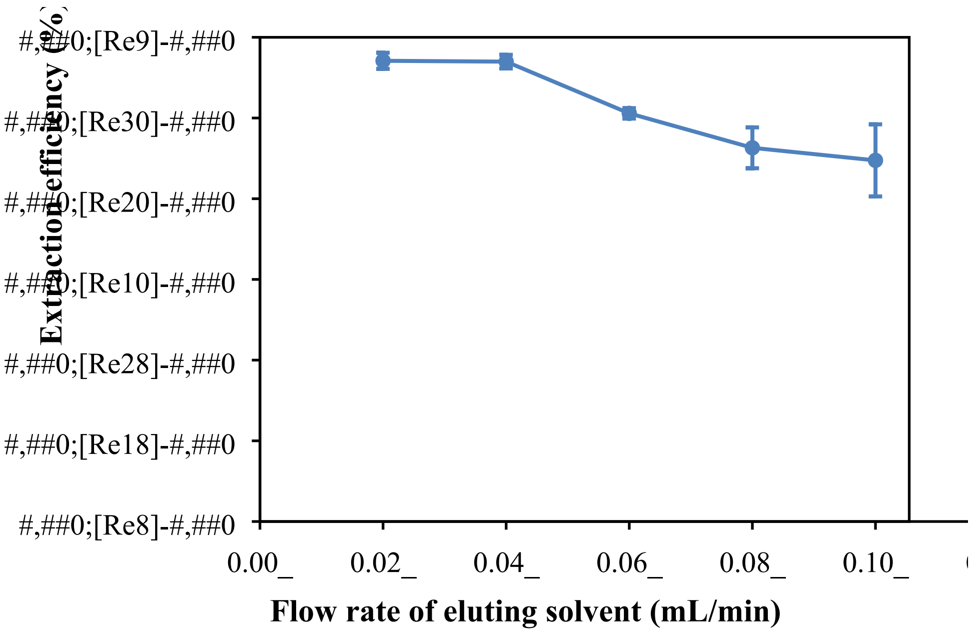

Fig. S10. Effect of flow rate of eluting solvent on extraction efficiency
Conditions: volume of eluting solvent was 90 μL; the other conditions were the same as in Fig. S9.

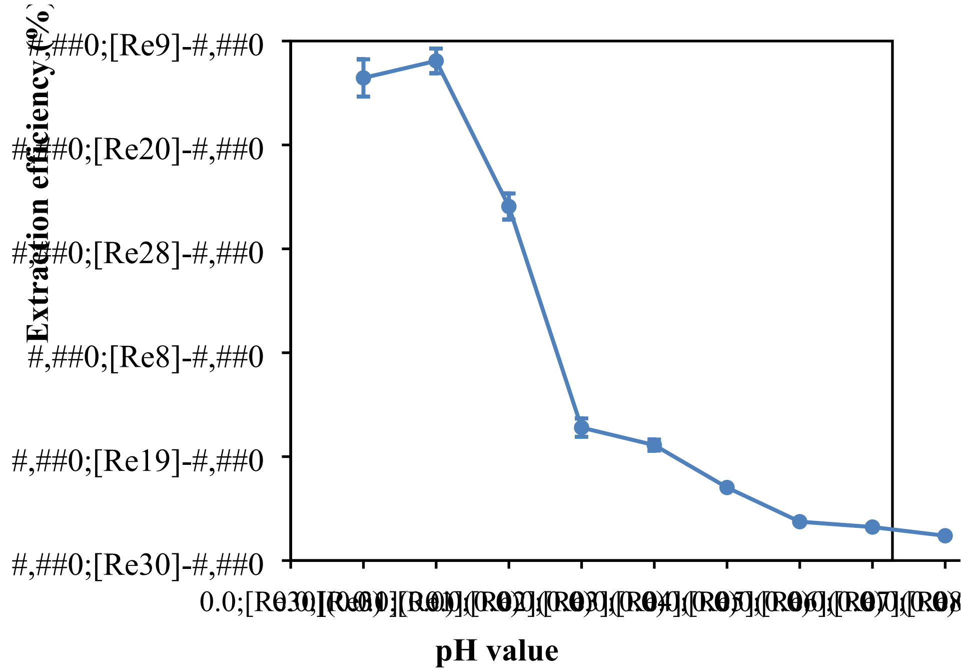

Fig. S11. Effect of solution pH value on extraction efficiency
Conditions: flow rate of eluting solvent was 0.04 mL/min; sample pH value was adjusted with 0.1 mol/L HCl and 0.1 mol/L NaOH; the other conditions were the same as in Fig. S10.

Table S1. Extraction performance of different MECs towards Se(IV)-OPA complex

MEC	Monomers (%, w/w)		Cross-linkers (%, w/w)		Monomer mixture (%, w/w)		Polymerization mixture (%, w/w)		Peak area [a]	Pressure [b] (MPa)
	MAT	ABA	DVB	EDMA	Monomers	Cross-linkers	Monomer mixture	Porogenic solvent		
1	70	30	50	50	40	60	30	70	1041	1.1
2	60	40	50	50	40	60	30	70	1053	1.8
3	50	50	50	50	40	60	30	70	1067	2.0
4	40	60	50	50	40	60	30	70	1065	6.7
5	50	50	70	30	40	60	30	70	1100	1.5
6	50	50	60	40	40	60	30	70	1095	1.8
7	50	50	40	60	40	60	30	70	1067	2.0
8	50	50	30	70	40	60	30	70	/	∞ [c]
9	50	50	70	30	50	50	30	70	1042	5.0
10	50	50	70	30	45	55	30	70	1100	3.7
11	50	50	70	30	35	65	30	70	1097	1.6
12	50	50	70	30	40	60	25	75	1041	1.2
13	50	50	60	40	40	60	35	65	/	∞
14	50	50	60	40	40	60	40	60	/	∞

[a] Ultrapure water was used as sample matrices, and the spiked concentration was 200 μg/L.

[b] Methanol passed through the capillary microextraction column with 0.10 mL/min flow rate.

[c] Under this ratio, the column pressure was too high and methanol solution could not pass through the MEC.

Table S2. The TCRs of coexisting ions

Interfering ions	Added as	TCRs	Concentrations of coexisting ion (μg/L)
K^+	KCl	1000	50000
Ca^{2+}	$CaCl_2$	1000	50000
Na^+	$NaCl$	1000	50000
Mg^{2+}	$MgSO_4$	1000	50000
Hg^{2+}	$Hg(NO_3)_2$	100	5000
Zn^{2+}	$Zn(NO_3)_2$	100	5000
Mn^{2+}	$MnSO_4 \cdot H_2O$	100	5000
Co^{2+}	$Co(NO_3)_2$	100	5000
Ni^{2+}	$NiSO_4$	100	5000
Sn^{4+}	$SnCl_4$	100	5000
Pb^{2+}	$Pb(NO_3)_2$	20	1000
Cd^{2+}	$CdSO_4$	20	1000
Cu^{2+}	$Cu(NO_3)_2$	20	1000

Concentration for Se(IV) was 50 μg/L.

Table S3. Comparison with other methods for the determination of selenium species in water samples

Methods	Sample volume (mL)	Eluent volume	Linear ranges (μg/L)	LODs (μg/L)	Extraction efficiency (%)	Extraction time (min)	Ref.
UALPME-ETAAS	25	0.5 mL choline chloride-phenol	0.2-8	0.0046	100	13	12
DLLME-ETAAS	15	0.5 mL THF-0.05 mL chloroform	10-50	0.97	100	23	15
MSPE-ETAAS	250	1.1 mL 0.64 mol/L HCl	0.03-10	0.01	96.8	25.5	30
D-μ-SPE-ETAAS	10	0.6 mL ethyl acetate	0.0047-3.8	0.0014	90	30.2	27
SPME-HGAAS	42	4.5 mL 0.1 M NaCl	0.012-200	0.004	75	20	31
SPE-HGAFS	1.0	0.1 mL NaOH (1.0%, m/v)	0.05-2.5	0.009	97	2.2	17
SPE-LEP/OES	500	0.6 mL 1.5 mol/L KOH	7.8-78	2.5	98.3	110	32
HF-LPME-HPLC/UV	22	0.025 mL MeOH	0.05-200	0.02	22.2	36.2	13
DLLME-UV/Vis	5.0	0.7 mL deep eutectic solvents	2.0-100	0.76	/[a]	5.5	28
DLLME-UV/Vis	5.6	0.15 mL 1-undecanol	20-300	3.4	/	12	33
CPE-UV/Vis	10	1.0 mL MeOH	5.0-400	9	/	65	16
PVG[b]-UV/Vis	10	/	10-400	7	/	48.3	34
MFA/IT-SPME-HPLC/DAD	6.0	0.09 mL MeOH	0.05-200	0.012	97	52	Current study

[a] Relevant values did not been given in the article;

[b] photochemical vapor generation.

Suppliers of chemicals and materials used in the study

1-Allyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide (MAT) (≥99%) was supplied by Shanghai Dibai Chemical Technology Co., Ltd. (Shanghai, China). (3-Acrylamidophenyl)boronic acid (ABA), divinylbenzene (DVB) (80%) and *o*-phenylenediamine (OPA) were obtained from Macklin Biochemical Co. (Shanghai, China). Ethylene dimethacrylate (EDMA) (97%) was bought from Alfa Aesar Biochemical Co. (Tianjin, China). n-Propyl alcohol (≥99.5%), 1,4-butanediol and azobisisobutyronitrile (AIBN, 97%) were got from Xilong Chemical Co. (Guangzhou, China). HPLC-grade acetonitrile (ACN) and methanol were purchased from Thermo Fisher Sci. (Shanghai, China). Water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA). The fused silica capillary (320 μm i.d.) was bought from Ruifeng Instrumental Co. (Hebei, China).

Detailed information about characterization instruments

The morphology and size of MEC were characterized by SEM (IEISS SUPRA 55, German) and TEM (JEOL 2011 microscope, Japan). The FI-IR (Shimadzu, Japan) and PPMS-9 VSM (QUANTOM, USA) were used to analyze the chemical structure and magnetic properties of prepared MEC. The contents of C, H, N and S in MEC were measured by elemental analysis (EA) (PerkinElmer-Model PE 2400, USA). Elemental mapping was conducted on OXFORD X-MaxN EDS system (Oxford, England). BET analysis was carried out on micromeritics ASAP 2020-physisorption analyzer (Micromeritics Instrument Corporation, Shanghai, China).

The relationship of intensity of magnetic field with current

The intensity of magnetic field (B) is calculated as follows：

$$B=\mu_0 nI$$

μ_0: permeability of vacuum, the value is$4\pi\times10^{-7}$ $N\cdot A^{-2}$;

n: coil number in per unit length, m^{-1}, the value is 5000 m^{-1} at present study;

I: current, A;

The unit of B is Tesla (T), $1T=1\ N\cdot A^{-1}\ m^{-1}=10^4$ Gs

For example, if we want to apply a magnetic field with the intensity of 30 Gs, the needed current is calculated as follows:

$$30\times10^{-4}\ \mathrm{N\cdot A^{-1}\ m^{-1}}=4\pi\times10^{-7}\ \mathrm{N\cdot A^{-2}}\times5000\ \mathrm{m^{-1}}\times I$$

$$I=0.48\ \mathrm{A}$$

Reference:

[1] Edit by J.J. Mao, M. Gu, *Phycics for University (Volume One),* Higher education press, Beijing, 2006.1