Supporting Information

A novel amino and carboxyl functionalized mesoporous silica as an efficient adsorbent for nickel(II)

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1.Sampling and preparation

Synthesis of MSS**.** 0.6 g CTAB and 0.4 g gelatin were dispersed in a homogeneous solution using 240 ml deionized water and 80 ml isopropyl alcohol. After 0.3 g kalium chloratum (KCl), 10 ml ammonia, and followed 1.7 ml 1,3,5-Trimethyl benzene (TMB) were added, the temperature was up to 65 ℃ and stirred 30 min to mix TMB uniformly. Then the mixture of methanol and ethyl silicate (6 m1TEOS and 12 ml methanol) was added dropwise stirring at 65 ℃ for 3.5 h. After aging 2 h, filtrated and washed with deionized water and ethanol several times, the white solid was drying in the blast air oven at 80 ℃ overnight. The surfactant was removed by refluxed at the mixture of ethanol and hydrochloric acid (ethanol: hydrochloric acid = 5:1) for 36 h. The final white samples called MSS were obtained after filtration, washing and drying.

Synthesis of MSS@NH_2@CN**.** 1.1 g MSS was dispersed in 50 ml anhydrous toluene. After stirring for 10 min, 1.3 ml NQ-62 was added. The mixture was heated to 100 ℃ and reflux for 11 h. Then, added 1.8 ml CTES and refluxed for 24 h at 100 ℃. MSS@NH_2@CN were obtained followed by filtration, washing with toluene and drying in vacuum oven at 60 ℃ overnight.

Synthesis of MSS@NH_2@COOH. 1.8 g MSS@NH_2@CN was dispersed in 80 ml absolute ethyl alcohol and stirring 15 min. Then the volume ratio of 50% dilute sulfuric acid (v/v) was added and refluxed 5 h. After filtration and washing with ethanol many times, the samples were dried in vacuum oven at 35 ℃ for 24 h. The final products were called MSS@NH_2@COOH.

2.Characterization Methods.

The structural properties of mesoporous silica materials were examined by Scanning electron microscope (SEM, ΣIGMA, Germany) and Transmission electron microscope (TEM, JEM-2100, Japan). X-ray diffraction (XRD) patterns of the silica were obtained by XRD diffractometer (D8 ADVANCE, BRUKER, Germany) which was operated at an acceleration voltage of 40 kV by using Cu Kα radiation. Analysis and identification of material molecules and functional groups were carried out with Fourier transform infrared spectra (FTIR, VERTEX 70, BRUKER, Germany) and XPS (Esca Lab 250Xi, Thermo Fisher Scientific) . The textural properties of the MSS and MSS@NH_2@COOH including surface area, pore volume, and pore size distribution were determined by nitrogen adsorption-desorption isotherms (ASAP2460, USA). The surface areas and pore sizes were calculated by the Brunauer-Emmet-Teller (BET) equation and Barrot-Joyner-Halender (BJH), respectively. Thermo-gravimetric/Differential scanning calorimetry TG/DSC was carried out for the samples using STA 449C Jupiter analyzer in the range of 30-1000 ℃ under air.

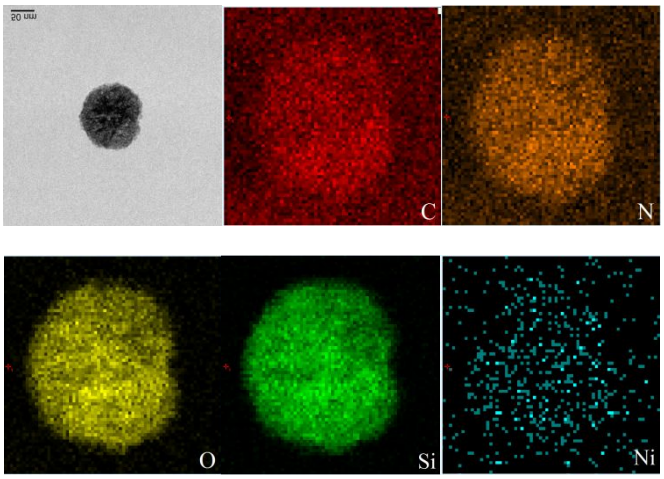

Figure S1. TEM image of one single MSS@NH_2@COOH nanoparticle and energy-dispersive X-ray spectroscopy element mapping of C, N, O, Si elements in one MSS@NH_2@COOH nanoparticle after removal of Ni(II).

Table S1. MSS and MSS@NH_2@COOH of EDS Scan Data.

	Element	Weight(%)	Atom(%)		Element	Weight(%)	Atom(%)
MSS	C K	57.61	65.52	MSS@NH_2@COOH	C K	23.93	31.1
	O K	37.71	32.2		N K	5.81	6.47
	Si K	4.68	2.28		O K	55.67	54.32
					Si K	14.6	8.11
	Quantity	100			Quantity	100	

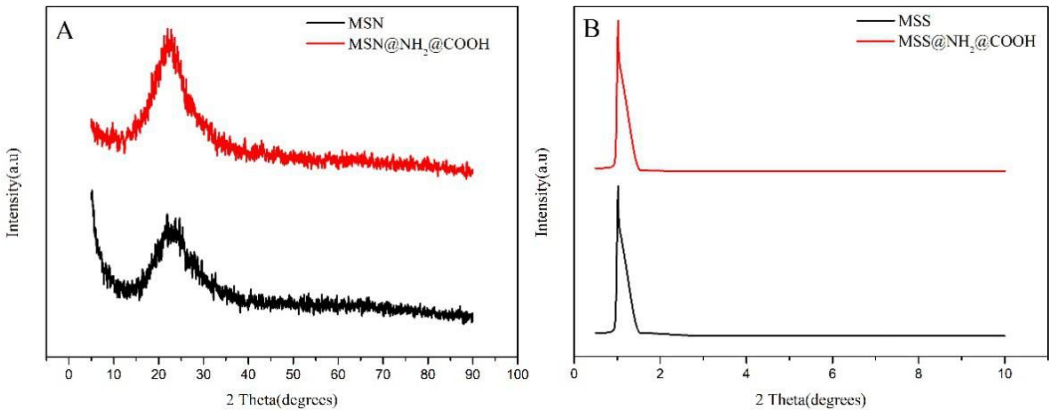

Figure S2. The XRD(A) and SAXS(B) analysis diagram of MSS and MSS@NH_2@COOH.

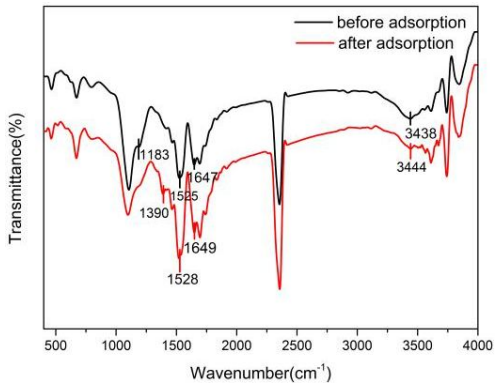

Figure S3. The infrared spectra of MSS@NH_2@COOH before and after adsorption of nickle ion.

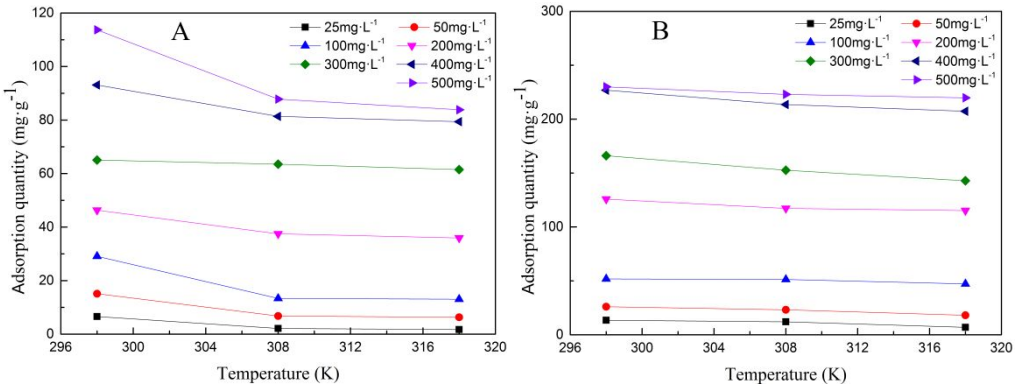

Figure S4. Effect of different temperatures on Ni(II) ions adsorption quantity of MSS (A) and MSS@NH_2@COOH (B).

Table S2. Comparison of the optimized adsorbent dose reported in this work and literatures.

Adsorbent	Functionalized group	Adsorption quantity ($mg \cdot g^{-1}$)	Adsorption conditions	optimized adsorbent dose(mg)	Reference
MCM-41/TMSPDETA	TMSPDETA	58.47	pH=6,t=120min,T=25℃,C_0=30mg/L	50	[1]
NiIMS2, NiIMS1	AAPTS	20.8,22.9	pH=6 and 3,t=120min,T=30℃,C_0=250mg/L	10	[2]
PEI/MCM-41	PEI	139.7	pH=6,t=300min,T=30℃,C_0=50mg/L	500	[3]
NH_2-MCM-41	APTMS	12.36	pH=5,t=120min,T=25℃,C_0=50mg/L	500	[4]
IIP/CTAB	MAA	33,31	pH=7.25,t=20min,T=25℃,C_0=50mg/L	50	[5]
MSS@NH_2@COOH	NQ-62,CTES	125.57	pH=5,t=120min,T=25℃,C_0=200mg/L	40	This work

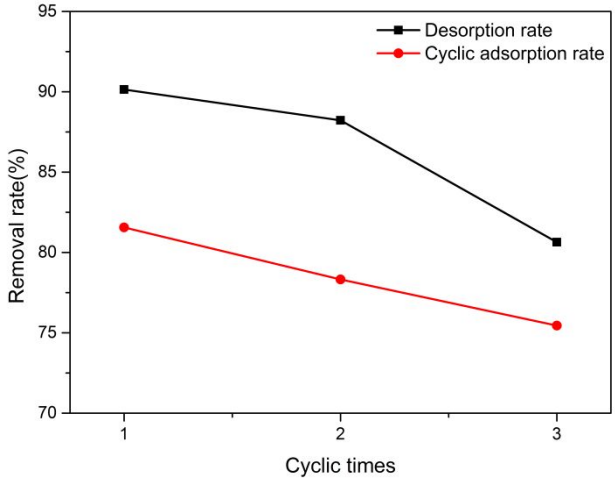

Figure S5. Cyclic times of Ni(II) ions.

Table S3. Kinetic, Isotherm, and Thermodynamic Data and Related Relative Standard Deviations (RSDs) for MSS and MSS@NH_2@COOH.

		MSS								MSS@NH_2@COOH							
kinetic	time/min	5	15	30	50	70	90	120	180	5	15	30	50	70	90	120	180
	Q/($mg \cdot g^{-1}$)	25.85	30.34	37.43	41.99	43.96	46.55	46.61	46.48	68.08	89.6	102.46	112.56	119.34	124.99	125.37	125.57
	%removal	34.46	35.12	37.91	55.98	58.61	62.08	62.14	61.98	45.39	51.14	53.97	59.71	67.71	83.33	83.58	83.71
	RSD	2.35	3.08	2.27	1.56	2.68	3.32	4.13	3.87	1.65	2.79	4.11	2.09	2.53	1.27	2.12	3.05
isotherm	C_0/($mg \cdot L^{-1}$)	25	50	100	200	300	400	500		25	50	100	200	300	400	500	
	Q/($mg \cdot g^{-1}$)	6.56	15.09	29.91	46.298	6.06	93.09	113.71		13.59	26.05	51.85	125.82	166.12	226.82	229.99	
	%removal	35	40.23	38.79	61.73	57.83	62.01	60.64		72.46	69.47	69.15	83.4	73.83	75.61	61.33	
	RSD	2.24	3.16	1.85	1.05	2.49	2.63	1.58		1.38	2.44	2.47	1.15	3.09	2.16	1.77	
thermodynamic	T/K	298	308	318						298	308	318					
	InKd	5.44	5.23	5.19						6.44	6.37	6.36					
	RSD	0.87	1.23	1.37						0.95	1.18	1.22					

Referances

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