Supplementary Information (SI) for RSC Advances.

MOF-Derived MoO_2/C Composites as High-Performance Electrodes for Electrochemical Uranium(VI) Removal

Hongyan Zhou[a] Ranran Jiao[b] Xiaotong Ma[a] Suyuan Zeng[a,*] Yuwei Mi[a,*]

[a] School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China

[b] National Synchrotron Radiation Laboratory, Anhui Provincial Engineering Laboratory of Advanced Functional Polymer Film, CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei 230026, China

[*] Corresponding author.

E-mail: drzengsy@163.com (S. Zeng), luckyyuweimi@163.com (Y. Mi)

Tel: +86-635-8230614, Fax: +86-635-8230196

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Experimental

1.1 Materials and reagents

All reagents were purchased from commercial suppliers and used without further purification. Acetylene black was obtained from Hefei Kejing Materials Technology Co., Ltd. Activated carbon was sourced from Fujian Yihuan Carbon Industry Co., Ltd. Copper(II) acetate was procured from Tianjin Bodi Chemical Co., Ltd. Phosphomolybdic acid was supplied by Sinopharm Chemical Reagent Co., Ltd. L-Glutamic acid was acquired from Shanghai Chemical Reagent Procurement Supply Station Reagent Factory. Trimesic acid was purchased from Beijing Qimi Wo Technology Co., Ltd. Absolute ethanol was obtained from Tianjin Fuyu Fine Chemical

Co., Ltd. Uranyl nitrate hexahydrate ($UO_2(NO_3)_2.6H_2O$,99%), polyvinylidene fluoride (PVDF), N-methylpyrrolidone (NMP), and nitric acid (HNO_3) were all sourced from Sigma-Aldrich Reagent Co., Ltd.

1.2 Characterization

Powder X-ray diffraction (XRD) data were collected on a Riagku Smartlab 9 diffractometer with Cu Kα radiation (λ=1.5405 Å). Electron microscopy characterizations of the samples were conducted using high-resolution transmission electron microscopy (HRTEM, Thermo Fischer, Talos F200x, 200 kV). X-ray photoelectron spectra (XPS) of the samples were determined using an ESCALAB 250 instrument (Thermo Fischer, EACALAB 250Xi). Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Perkin-Elmer TGA 7 infrared spectrometer to identify the functional groups on the surface of samples. Nitrogen adsorption–desorption isotherm experiments were carried Micromeritics ASAP 2460 instrument (Missouri, USA) to obtain BET surface area and Barrett–Joyner–Halenda (BJH) size distributions.

1.3 Preparation and Detection of U(VI) Solution

The U(VI) solution was prepared by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ tothe deionized water. For measuring the concentration U(VI) ions accu-rately, extracted the samples (0.5 mL) each time, and then measured it atthe wavelength of 669 nm by the Dichlorphosphonoazo III method usingspectrophotometer. For expressing the adsorption performances, wecalculated the removal ratio (%) and adsorption capacity (Q_e) as follow: $\text{Removalratio (\%)} = (C_0 - C_e)/C_0$ (S1)

$$Q_e = (C_0 - C_e)\,V/m \qquad \text{(S2)}$$

Where C_0 (mg L^{-1}) is the initial concentration; C_e (mg L^{-1}) is the final concentration; m (g) and V (mL) represent the mass of adsorbent and the volume of the suspension, respectively. And the experimentaldata were the averages of triplicate determinations.

1.4 Energy consumption calculations

Energy-normalized removed U(VI) (ENRU, mg J^{-1}) and electric energy consumption per unit mass of U (E, kWh/kg U) were calculated by Eqs. S3 and S4 as follows,

$$ENRU = \frac{(C_0 - C_e)V}{\int I V_{cell} \, \mathrm{d}t} \quad (S3)$$

$$E = \frac{V_{Ce_{ll}} \int i \, \mathrm{d}t}{(C_0 - C_t) \cdot V \cdot 3600} \quad (S4)$$

C_0 (g L^{-1}) and C_e (g L^{-1}) are the initial and a certain time concentration of uranium, respectively; V are the solution volume (L), i is the applied current (A), t is time of electrosorption (s), V_{cell} is the cell voltage (V).

1.5 Langmuir and Freundlich models

Langmuir (Eq. (S5)) and Freundlich (Eq. (S6)) models were employed to fit the electrosorption isotherms:

$$q_e = \frac{k_L q_m C_e}{1 + k_L C_e} \equiv \frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m k_L} \quad (S5)$$

$$q_e = K_F C_e^{\frac{1}{n}} \equiv \log q_e = n \log C_e + \log k_F \quad (S6)$$

where q_m (mg g^{-1}) is the maximum electrosorption capacity of adsorbents, C_e is the equilibrium concentration of U(VI) in solution, k_L (L mg^{-1}) represents energy of electrosorption, k_F (mg g^{-1} (mg $L^{-1})^n$) is a constant which is indicative of the electrosorption capacity of the adsorbent, (1/n) represents the electrosorption intensity or surface heterogeneity.

1.6 Kinetic models

To Fig. out the electrosorption mechanism as well as the rate-controlling steps during the electrosorption process, the pseudo-first-order kinetic (Eq. (S7), PFO), pseudo-second-order kinetic (Eq. (S8), PSO), and Weber-Morris (Eq. (S9), W&M) models were employed to fit the kinetic data:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \equiv \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (S7)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \equiv \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(S8)}$$

$$q_t = k_{W\&M} t^{\frac{1}{2}} + c \quad \text{(S9)}$$

where q_t (mg/g) is the amount of U(VI) adsorbed at t time (min), q_e (mg/g) is the amount of U(VI) adsorbed at equilibrium, k_1 (min^{-1}), k_2 (min^{-1}), and $k_{W\&M}$ (mg g^{-1} $min^{-0.5}$) are the electrosorption rate constants for PFO, PSO and W&M models, respectively.

1.7 Electrochemical measurements

The active materials (MoO_2/C), acetylene black (AB), and polyvinylidene fluoride (PVDF) were weighed to form a homogeneous slurry with a nickel foam substrate as the current collector at a mass ratio of 8:1:1, and then dried at 70 °C for 12 h.

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV)were performed in a mixed solution of 60 mg L^{-1} uranyl nitrate and 0.5 M Na_2SO_4 using an electrochemical workstation (GAMRY reference 600+) in a three-electrode system with a Pt counter electrode and a saturated calomel electrode (SCE) reference electrode. In the EIS experiment, a frequency range of 0.01-100,000 Hz was employed. Calculate the specific capacitance according to CV using the following equation,

$$C = \frac{\int_{V_2}^{V_1} I dV}{2mv(V_1 - V_2)} \quad \text{(S10)}$$

where C is the specific capacitance (F/g), I is the current intensity (A), and m is the mass of the active material. m is the mass of the active materials (g), *v* is the potential scan rate (V/s), V is the electrode potential (V), V_1 and V_2 are the high and low potential limits of CV curves, respectively

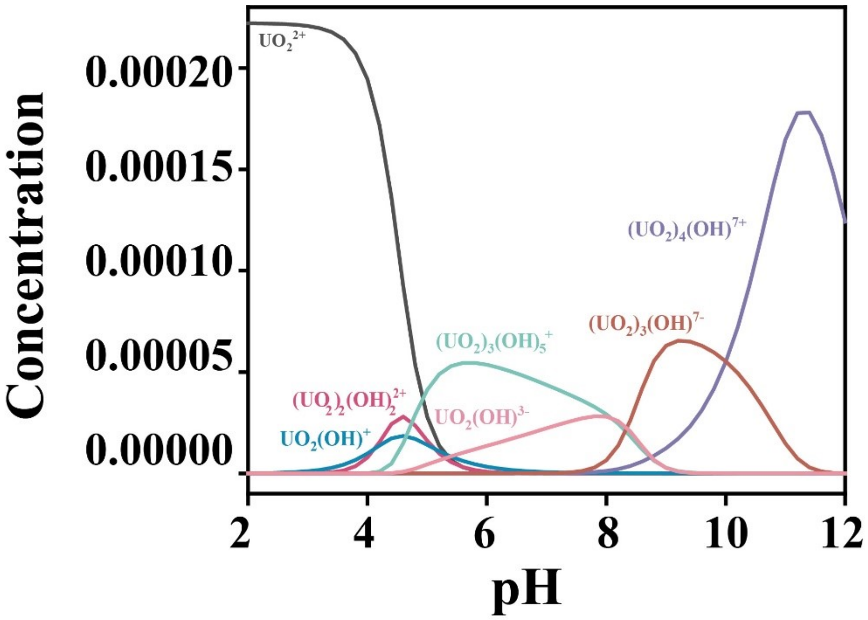

Fig. S1 The species distribution of U(VI) at different pH values

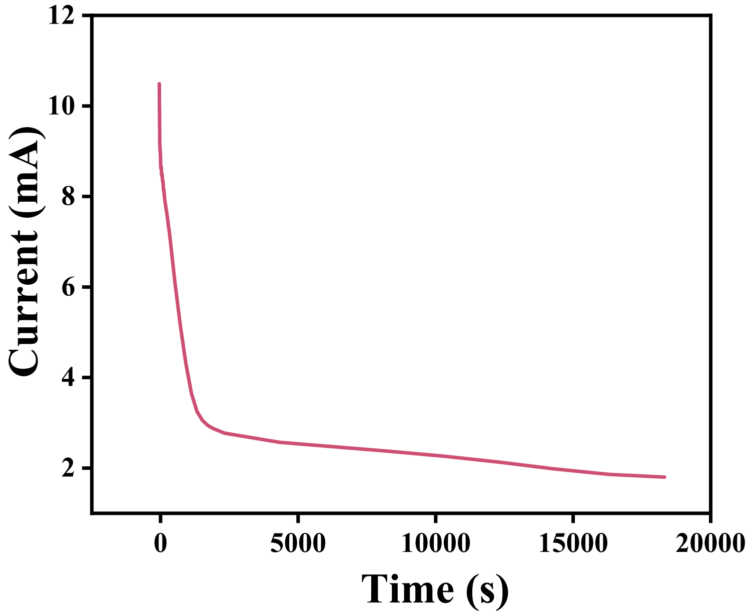

Fig. S2 The i-t curve during the constant voltage test of the MoO_2/C (applied potential of 1.2 V, pH = 4.0, T = 298 K, $C_0(U)$ = 140mg L^{-1}, 5 h running time)

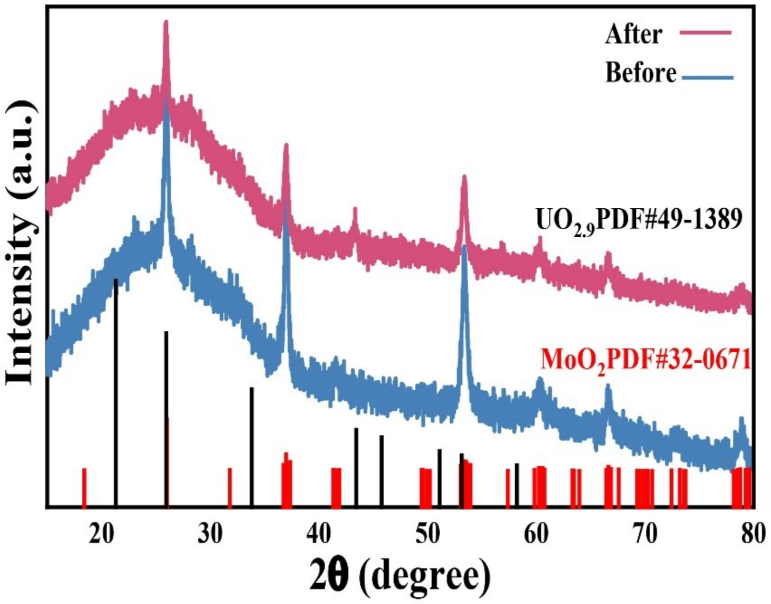

Fig.S3. XRD patterns comparation of MoO_2/C before after electrosorption

Table. S1. Isotherms Parameters for Langumir and Freundlich models.

Models	Parameters		
Langumir	R^2	q_m (mg g^{-1})	k_L (L mg^{-1})
	0.9845	1018	0.0458
Freundlich	R^2	n	k_F (mg L^{-1})
	0.9931	1.1219	32.1

Table.S2 Isotherm parameters for Langumir and Freundlich models at different temperatures.

		Langmuir			Freundlich		
	T (K)	q_m (mg/g)	K_L(L/mg)	R^2	K_F (L/mg)	n	R^2
MoO_2/C	298 K	1018	0.0351	0.98	32.1	1.12	0.99
	308 K	1175	0.0316	0.90	31.8	1.08	0.99
	318K	1196	0.0328	0.93	34.2	1.10	0.99

Table. S3 Comparison of maximum adsorption capacity of U (VI) from different reports.

Sample	TK	PH	C0(mg/L)	V(Ml)	Q_m(mg/g)	References
low-cost MOF@ cotton fibre	298	3	5-150	-	241.28	[1]
MIL-101-AO	298	7	1-300	50	613.5	[2]
CeO_2@UiO-66(Ce)	298	6	50-400	-	239	[3]
Cu-BTC	298	6-7	0.2-5	-	16.91	[4]
MIL-101(Fe, Cu)/GO-5%	298	5.5	10-80	40	358.61	[5]
MoO_2/C	**298**	**4**	**300**	**50**	**806.79**	**This work**

Table S4. Kinetic parameters of the electrosorption of U(VI).

Models	R^2	Parameters	
PFO	0.9472	k_1 (min^{-1})	$q_{e\ cal}$ (mg g^{-1})
		0.00732	8.9136
PSO	0.9891	k_2 (g mg^{-1} min^{-1})	$q_{e\ cal}$ (mg g^{-1})
		0.000103	203.2520
		$k_{W\&M}$	c
W&M-1	0.9999	13.3241	13.3241
W&M-2	0.9970	12.2553	20.6108
W&M-3	0.9257	1.5120	147.0451

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