Supporting Information

Polypyrrole/cobalt ferrite/multiwalled carbon nanotubes as an adsorbent for the removal of uranium ions from aqueous solutions

Qi Liu,*[a] Jiahui Zhu,[a] Lichao Tan,[a] Xiaoyan Jing,[a] Jingyuan Liu,[a] Dalei Song,[a] Hongsen Zhang,[a] Rumin Li,*[a, b] G.A. Emelchenko,[d] and Jun Wang,*[a, b, c]

[a] Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, China. Fax: +86 451 8253 3026; Tel: +86 451 8253 3026; E-mail address: zhqw1888@sohu.com

[b] Harbin Shipbuilding Engineering Design & Research Academy, Harbin, 150001, China.

[c] Institute of Advanced Marine Materials, Harbin Engineering University, 150001, China.

[d] Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, 142432, Russia.

* Corresponding author: Tel.: +86 451 8253 3026; Fax: +86 451 8253 3026; E-mail: zhqw1888@sohu.com.

Chemicals

All the chemicals were of reagent grade and all the solutions were prepared in deionized water. $FeSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, ethylene glycol, ethanol, ammonia solution, ammonium persulfate，pyrrole and multiwalled carbon nanotubes (MWCNTs) were purchased from Tianjin Kemiou Chemical Reagent Company and used without further purification. Uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ was acquired from Aladdin Reagent Limited. A stock solution of uranium (VI) ($1000 mgL^{-1}$) was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in deionized water.

Preparation of uranium solution

Uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (2.110 g) were dissolved in deionized water (100 ml). After stirring for 20 min, the above solution was transferred into a 1000 ml volumetric flask and added deionized water. The resulting solution is 1000 mg / L of uranium solution. Working solutions were prepared by appropriate dilution of the stock solution with deionized water.

Desorption and recycle experiments

Uranium adsorption experiments were carried out the following procedure: 0.02 g of PPy/$CoFe_2O_4$/MWCNTs was put in contact with 50 mL uranium (VI) ions in the conical flask. The conical flask was placed in a thermostatic water shaker at speed of 150 rpm for 360 min. After saturated adsorption, desorption was carried out by washing the adsorbents with distilled water several times, and then the solution containing 50 mL of different concentrations of $NaHCO_3$ was added to the adsorbed uranium (VI) ions adsorbents for 360 min. The concentrations of uranyl ions in the supernatant and $NaHCO_3$ solution were determined by ICP, respectively. Before the second adsorption, the adsorbent was treated with 0.5 mol L^{-1} $NaHCO_3$ solution for 360 min. The samples were separated from the solution by magnetic separation. The above procedure was repeated three times to test the reusability of the PPy/$CoFe_2O_4$/MWCNTs.

Effect of other metallic ions

Competitive adsorption of the binary mixtures of U(VI)/Na(I), U(VI)/K(I), U(VI)/Mg(II) and U(VI)/Ca(II) with a molar ratio 1:1 were investigated in an equilibration–adsorption batch systems. The selectivity experiment of PPy/$CoFe_2O_4$/MWCNTs for uranium (VI) was carried out by stirring 50 mL aqueous

solution containing 0.02g PPy/$CoFe_2O_4$/MWCNTs, of which the initial uranium (VI) concentration is 50 mg L^{-1}. The concentrations of these ions in solution were measured by ICP after adsorption.

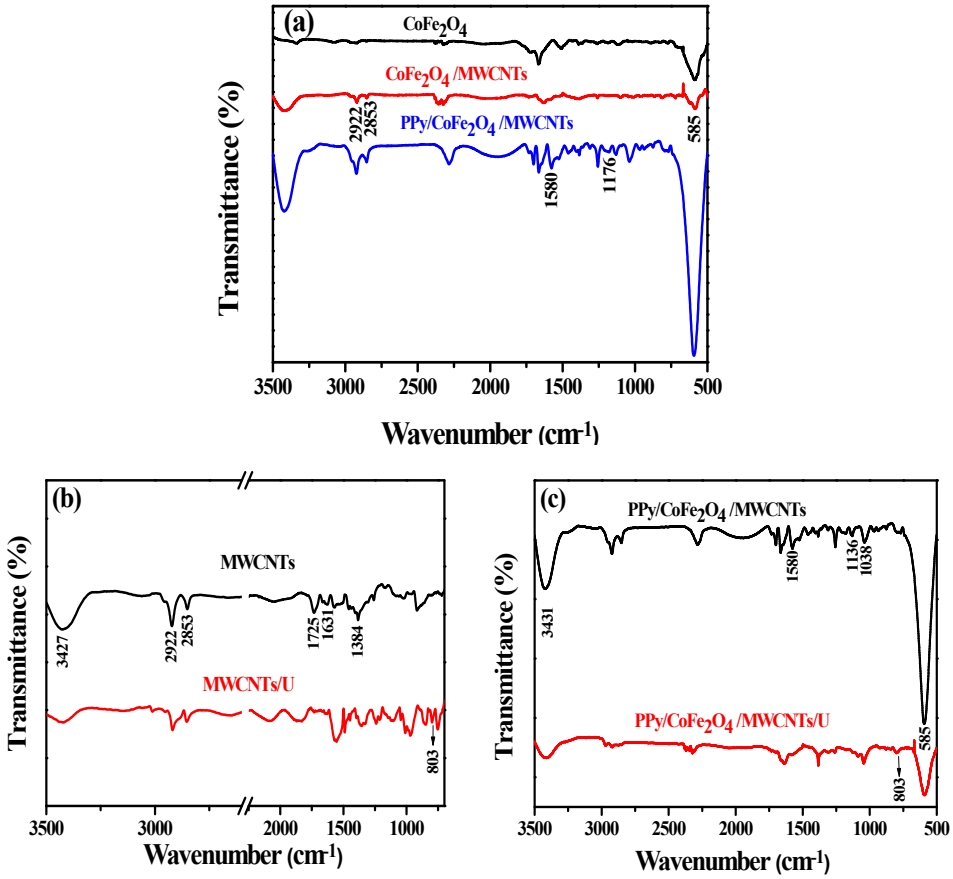

Fig. S1 (a) FT-IR spectra of $CoFe_2O_4$, $CoFe_2O_4$/MWCNTs and PPy/$CoFe_2O_4$/MWCNTs, (b) FT-IR spectra of MWCNTs and MWCNTs/U, (c) FT-IR spectra of PPy/$CoFe_2O_4$/MWCNTs and PPy/$CoFe_2O_4$/MWCNTs/U.

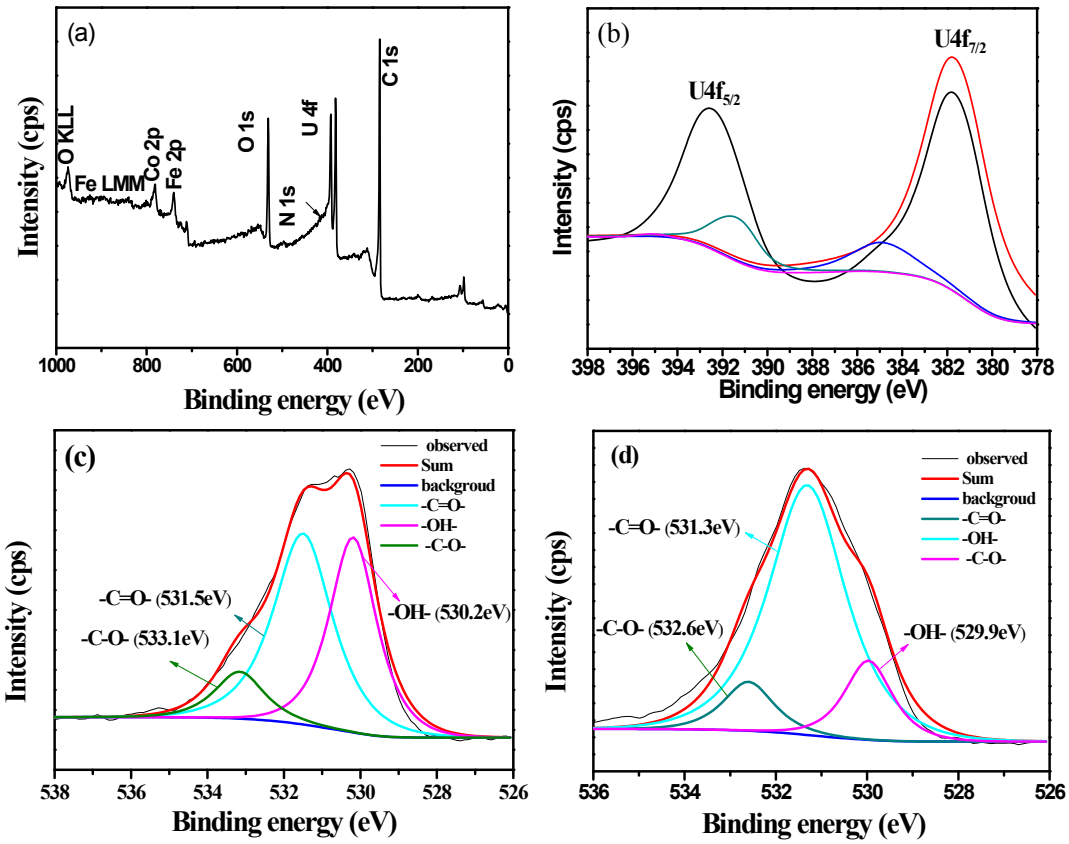

Fig. S2 (a) the survey spectra, (b) U4f$_{7/2}$ and U4f$_{5/2}$ of PPy/CoFe$_2$O$_4$/MWCNTs/U, and O1s for (c) PPy/CoFe$_2$O$_4$/MWCNTs and (d) PPy/CoFe$_2$O$_4$/MWCNTs/U.

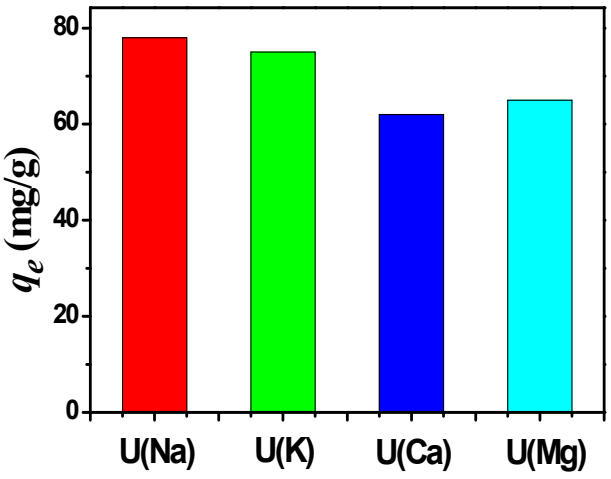

Fig. S3 Competitive adsorption of coexistent ions onto PPy/CoFe$_2$O$_4$/MWCNTs magnetic composite [uranium(VI)]. Initial = 50 mg L^{-1}; pH =7.0; T=25^{o}C; metal/uranium molar ratios 1:1

Table. S1 Isotherm constants and values of R^2 for PPy/$CoFe_2O_4$/MWCNTs

T(K)	Langmuir isotherm			Freundich isotherm		
	q_m（mg • g^{-1}）	b（L·mg^{-1}）	R^2	K（L·g^{-1}）	n	R^2
298	148.81	0.237	0.979	39.65	2.82	0.978
308	159.49	0.258	0.979	42.87	2.75	0.975
318	163.67	0.359	0.965	60.11	3.71	0.9

Table. S2 The maximum adsorption capacity of different adsorbents for uranium (VI).

Adsorbents	Maximum adsorption capacity	Ref.
Activated carbon (Merck)	28.3 mg/g	[1]
magnetic illite	17.71 mg/g	[2]
AgOH-NPs–MWCNTs	125 mg/g	[3]
Manganese oxide coated zeolite	15.1 mg/g	[4]
acylamide- and carboxyl-functionalized metal–organic framework	125.944 mg/g	[5]
HNTs-Fe_3O_4	88.32 mg/g	[6]
ACF-Sal	142.8 mg/g	[7]
SBA-15 (DMS)	196 mg/g	[8]
PPy/$CoFe_2O_4$/MWCNTs	148.8 mg/g	this work

References

1 A. Mellah, S. Chegrouche, M. Barkat, *J. Colloid Interface Sci.,* 2006, **296**, 434–441

2 Y. Du, Z. Yin, H. Wu, P. Li, W. Qi and W. Wu, *J. Radioanal. Nucl. Chem.*, 2015, **304**, 793-804.

3 F. Zare, M. Ghaedi, A. Daneshfar, S. Agarwal, I. Tyagi, T. A. Saleh and V. K. Gupta, *Chem. Eng. J.,* 2015, **273**, 296-306.

4 R. P. Han, W. H. Zou, Y. Wang, L. Zhu, *J. Environ. Radioactiv.,* 2007, **93**, 127–143.

5 L. L. Wang, F. Luo, L. L. Dang, J. Q. Li, X. L. Wu, S. J. Liu and M. B. Luo, *J. Mater. Chem. A,* 2015, **3**, 13724-13730.

6 W. He, Y. Chen, W. Zhang, C. Hu, J. Wang and P. Wang, *Korean J. Chem. Eng.*, 2016, **33**, 170-177.

7 S. Mishra, J. Dwivedi, A. Kumar and N. Sankararamakrishnan, *RSC Adv.*, 2015, **5**,

33023-33036.
8 J. K. Gao, L. A. Hou, G. H. Zhang and P. Gu, *J. Hazard. Materi.*, 2015, **286**, 325-333.