Supporting Information on

Plasma Induced Grafting Polyacrylamide on Graphene Oxide Nanosheets for Simultaneous Removal of Radionuclides

Wencheng Song, Xiangxue Wang, Qi Wang, Dadong Shao, and Xiangke Wang*

This updated version of the Electronic Supplementary Information (published on 02 Jan 2020) replaces the original version first published on-line on 03 Nov 2014.

Procedure of potentiometric acid-base titration

0.05g PAM/GO nanosheets was spiked into 0.01 mol/L NaCl background electrolyte at *T* = 295 K, and purged with argon gas for 2 h under vigorous stirring to exclude atmospheric CO_2. The initial pH of suspension was adjusted to pH 3.0 by adding 1 mol·L^{-1} of HCl, and then the suspension was titrated to pH 11.0 with 0.05 mol·L^{-1} of NaOH at a variable increment (0.008-0.15 mL). The equilibrium value was taken when showing a drift less than 0.03 mV per minute. The data sets of pH versus the net consumption of H^+ or OH^- were used to obtain intrinsic acidity constants.

Dielectric barrier discharge (DBD) plasma

The reactor was a quartz tube with an inside diameter of 4 mm and a length of 170 mm. A copper wire with a diameter of 0.75 mm was installed into the quartz tube as an electrode. The DBD plasma treatment was carried out at room temperature for 30 min with the voltage of 120 V and power of 240 W. After the DBD plasma treatment, the resulted material was rinsed with Milli-Q water thoroughly to remove residual acrylamide monomer and homopolymer, and then the suspension was dried by vacuum freeze-drying technique.

Mechanisms of Plasma Polymerization

The mechanism of plasma polymerization, a subject of some controversy, was discussed as being either in the layer adsorbed on the substrate, or in the gas phase. An ionic chain mechanism was proposed,[1] but most often a radical mechanism.[2] The plasma-induced polymerization is a chemical process which is initiated by radicals, which are produced by exposure to the plasma, similar to radiation-initiated polymerization, which is started by photons, electrons, or alpha particles.[3] Under the plasma-induced polymerization process, the PAM and GO are activated by photons, electrons, or alpha particles. The both activated PAM and GO form strong chemical bonds and thereby results in the grafting of PAM on GO.

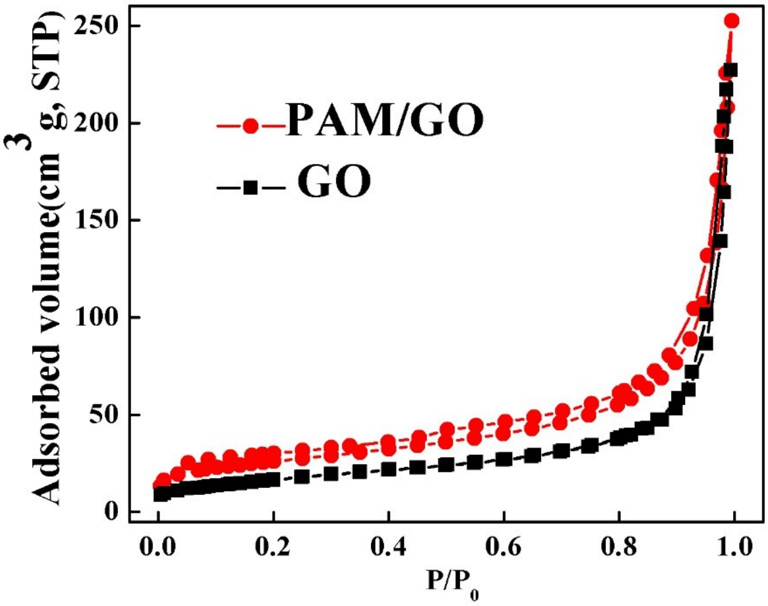

Figure S1 N_2 adsorption-desorption isotherms of GO and PAM/GO

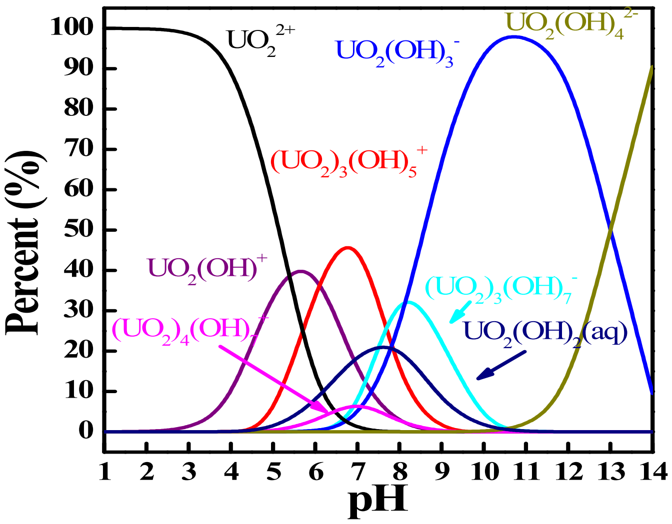

Figure S2 Relative distribution of U(VI) species as a function of pH based on the equilibrium constants. C $_{\text{initial}}$ [U(VI)] = 10 mg/L.

Table S1. Equilibrium constants (logK_a) of U(VI) hydrolysis reactions.

hydrolysis reactions	logK_a[4]
$UO_2^{2+} + H_2O = UO_2OH^+ + H^+$	-5.20
$UO_2^{2+} + 2H_2O = UO_2(OH)_2 + 2H^+$	-12.10
$UO_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	-19.20
$UO_2^{2+} + 4H_2O = UO_2(OH)_4^{2-} + 4H^+$	-33.00
$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+$	-15.55
$3UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^- + 7H^+$	-28.34
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	-16.94
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	-21.60

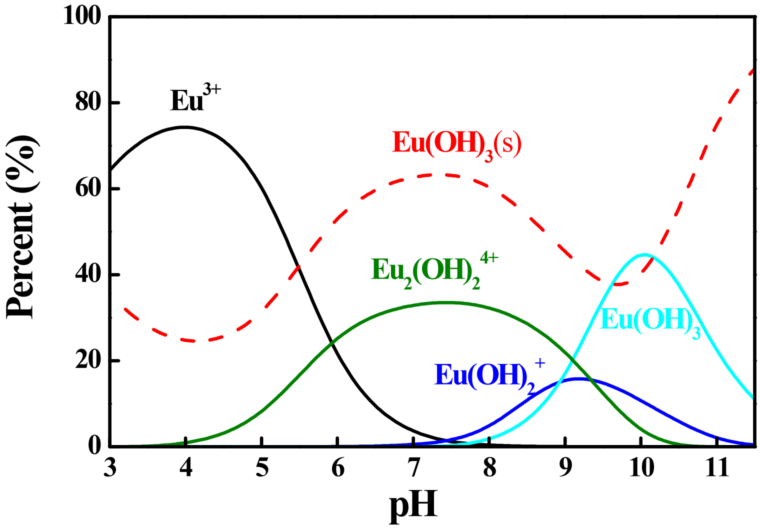

Figure S3 Relative distribution of Eu(III) species as a function of pH based on the equilibrium constants. C $_{\text{initial}}$ [Eu(III)] = 10 mg/L.

Table S2. Equilibrium constants (logK_a) of Eu(III) hydrolysis reactions.

hydrolysis reactions	logK_a[5]
$Eu^{3+} + H_2O = EuOH^{2+} + H^+$	-7.91
$Eu^{3+} + 2H_2O = Eu(OH)_2^+ + 2H^+$	-14.86
$Eu^{3+} + 3H_2O = Eu(OH)_3 + 3H^+$	-24.13
$Eu^{3+} + 4H_2O = Eu(OH)_4^- + 4H^+$	-36.60
$2Eu^{3+} + 2H_2O = Eu_2(OH)_2^{4+} + 4H^+$	-6.92

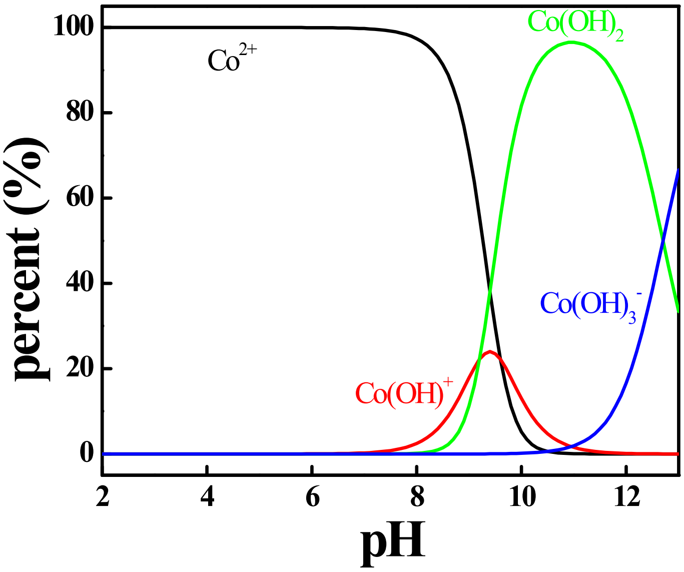

Figure S4 Relative distribution of Co(II) species as a function of pH based on the equilibrium constants. C $_{\text{initial}}$ [Co(II)] = 10 mg/L.

Table S3. Equilibrium constants (logK_a) of Co(II) hydrolysis reactions.

hydrolysis reactions	logK_a[6]
$Co^{2+}+OH^- = Co(OH)^+$	-9.6
$Co^{2+}+2OH^- = Co(OH)_2^0$	-9.2
$Co^{2+}+3OH^- = Co(OH)_3^-$	-12.7

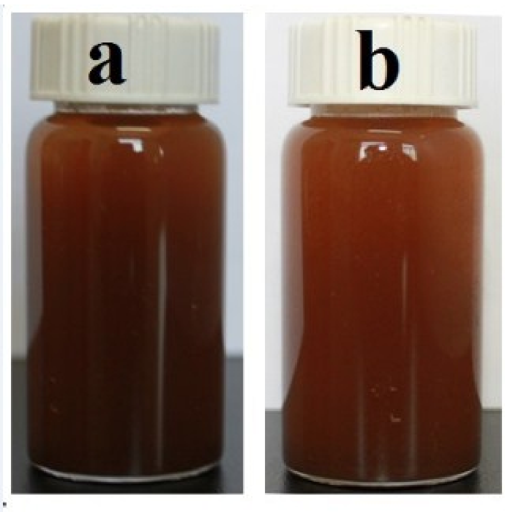

Figure S5 Photograph of PAM/GO suspensions of initial (a) and after 4 days of aging time (b)

We put two bottles of PAM/GO suspensions. One is the initial; the other is after 4 days of aging time. From the photograph, it is clear that there is no obvious difference between the two bottles, demonstrating that the PAM/GO has high dispersion properties in aqueous solutions.

Table S4. Comparison of maximum adsorption capacities of radionuclides on various adsorbents

Sorbents	Experimental conditions	C_{smax} (mmol/g)	Reference
		U(VI)	
plasma functionalized MWCNTs	pH=5.6, T = 303 K	0.315	[7]
Magnetic $Fe_3O_4@SiO_2$	pH = 6.0, T = 298 K	0.218	[8]
Amidoximated hydrogel	pH = 3.0, T = 298 K	0.166	[9]
Modified carbon CMK-3	pH = 4.0, T = 295 K	0.315	[10]
Graphene oxide nanosheets	pH = 5.0, T = 293 K	0.41	[11]
PAM/GO nanosheets	pH = 5.0, T = 295 K	0.698	This tudy
		Eu(III)	
Bare TiO_2	pH = 4.5, T = 298 K	0.0099	[12]
Na-montmorillonite	pH = 5.0, T = 298 K	0.0067	[13]
MWCNTs	pH = 4.5, T = 298 K	0.306	[14]
Activated carbon	pH = 4.5, T = 298 K	0.132	[15]
Graphene oxides	pH = 4.5, T = 298 K	1.06	[15]
PAM/GO nanosheets	pH = 5.0, T = 295 K	1.245	This study
		Co(II)	
β–CD/GO	pH = 6, T = 303 K	1.229	[16]
lemon peel	pH = 6, T = 298 K	0.435	[17]
GO	pH = 6, T = 303 K	0.804	[16]
Magnetite/GO	pH = 6, T = 303 K	0.22	[18]
Magnetic MWCNT/IO composites	pH = 6.4, T = 293 K	0.15	[19]
PAM/GO nanosheets	pH = 5.0, T = 295 K	1.621	This study

Table S5. Atomic contents (%) of PAM/GO and PAM/GO-radionuclide calculated from the XPS data

Type	C	O	N	U	Eu	Co
PAM/GO	56.39	30.16	13.45			
PAM/GO-U	56.34	28.41	12.42	2.83		
PAM/GO-Eu	56.32	27.63	11.54		4.51	
PAM/GO-Co	55.35	28.91	12.12			3.64

Table S6. Curve fitting results of XPS U 4f, O 1s, and N 1s spectra

Type		Peak	BE (eV)	FWHM (eV)	%
PAM/GO-U	U 4f	1	382.50	2.25	84.02
		2	381.10	2.15	15.98
	O 1s	1	533.4	1.48	26.13
		2	531.89	1.54	60.01
		3	531.18	1.45	13.86
	N 1s	1	401.64	1.05	11.74
		2	399.94	1.29	67.31
		3	398.99	1.17	20.96
PAM/GO-Eu	Eu 3d	1	1134.81	2.01	40.59
		2	1136.69	1.95	59.41
	O 1s	1	530.62	1.14	8.38
		2	531.86	1.57	63.31
		3	533.40	1.52	28.31
	N 1s	1	398.70	1.96	7.16
		2	399.75	1.44	88.57
		3	401.44	1.39	4.27
PAM/GO-Co	Co 2p	1	780.45	1.91	68.34
		2	782.16	1.98	31.66
	O 1s	1	533.39	1.27	25.99
		2	531.89	1.48	59.43
		3	530.89	1.11	14.58
	N 1s	1	401.64	2.06	8.22
		2	399.74	1.37	84.12
		3	398.79	1.93	7.66
PAM/GO	O 1s	1	531.89	1.83	78.06
		2	533.39	1.47	21.94
	N 1s	1	399.92	1.88	93.54
		2	401.52	1.56	6.46
		3	401.44	1.39	4.27

References

1 (a) A. R. Westwood, *Eur. Polym. J.,* 1971, 7, 363; (b) L. F. Thompson, K. G. Mayhan, *J. Appl. Polym. Sci.,* 1972, **16**, 2291.

2 (a) M. J. Vasile, G. Smolinsky, *J. Electrochem. Soc.,* 1972, **119**, 451; (b) H. Kobayashi, A. T. Bell, M. Shen, *J. Appl. Polym. Sci.,* 1973, **17**, 885; (c) H.

Kobayashi, A. T. Bell, M. Shen, *Macromolecules*, 1974, **7**, 277.

3 W. Stiller, J. Friedrich, *Z. Chem.,* 1981, **21**, 91.

4 J. A. Davis, D. E. Meece, M. Kohler and G. P. Curtis, *Geochim. Cosmochim. Acta,* 2004, **68**, 3621.

5 Y. B. Sun, Q. Wang, C. L. Chen, X. L. Tan and X. K. Wang, *Environ. Sci. Technol.,* 2012, **46**, 6020.

6 H. Yüzer, M. Kara, E. C. Sabah, M. S. Celik and *J. Hazard. Mater.,* 2008, **151**, 33.

7 M. M. Song, Q. Wang, Y. D. Meng, *J. Radioanal. Nucl. Chem.,* 2012, **293**, 899.

8 F. L. Fan, Z. Qin, J. Bai, W. D. Rong, F. Y. Fan, W. Tian, X. L. Wu and L. Zhao, *J. Environ. Radioact.,* 2012, **106**, 40.

9 N. Seko, A. Katakai, M. Tamada, T. Sugo and F. Yoshii, *Sep. Sci. Technol.,* 2004, **39**, 3753.

10 J. H. Kim, H. I. Lee, J. W. Yeon, Y. Jung and J. M. Kim, *J. Radioanal. Nucl. Chem.,* 2010, **286**, 129.

11 G. X. Zhao, T. Wen, X. Yang, S. B. Yang, J. L. Liao, J. Hu, D.D. Shao and X. K. Wang, *Dalton Trans.,* 2012, **41**, 6182.

12 X. L. Tan, M. Fang, J. X. Li, Y. Lu and X. K. Wang, *J. Hazard. Mater.,* 2009, **168**, 458.

13 T. Okada, Y. Ehara and M. Ogawa, *Clays Clay Miner.,* 2007, **55**, 348.

14 H. M. H. Gad and N. S. Awwad, *Sep. Sci. Technol.,* 2007, **42**, 3657.

15 Y. B. Sun, Q. Wang, C. L. Chen, X. L. Tan and X. K. Wang, *Environ. Sci. Technol.*, 2012, **46**, 6020.

16 W. C. Song, J. Hu, Y. Zhao, D. D. Shao and J. X. Li, *RSC Adv.,* 2013**, 3**, 9514.

17 A. Bhatnagar, A. K. Minocha and M. Sillanpaa, *Biochem. Eng. J.,* 2010, **48**, 181.

18 M. C. Liu, C. L. Chen, J. Hu, X. L. Wu and X. K. Wang, *J. Phys. Chem. C,* 2011, **115**, 25234.

19 Q. Wang, J. X. Li, C. L. Chen, X. M. Ren, J. Hu and X. K. Wang, *Chem. Eng. J.,* 2011,**174**, 126.