Electronic Supplementary Information for

Efficient immobilization of uranium (VI) by modified dendritic fibrous nanosilica (DFNS) using mussel bioglue

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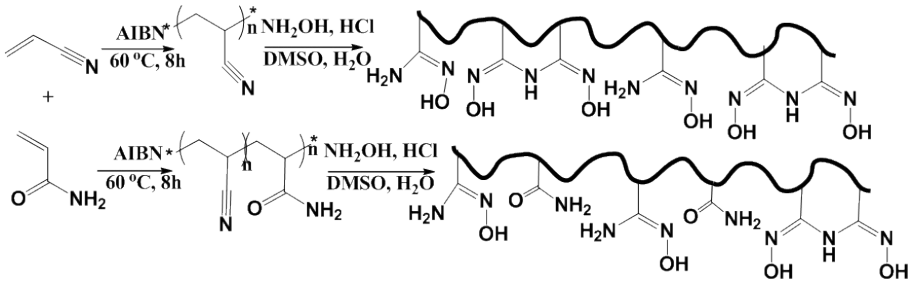
SI.1 Materials and methods



Scheme S1. Proposed schematic diagram of AOPNI and AOPNI-NH_2 composites.

SI.2 Morphological performance

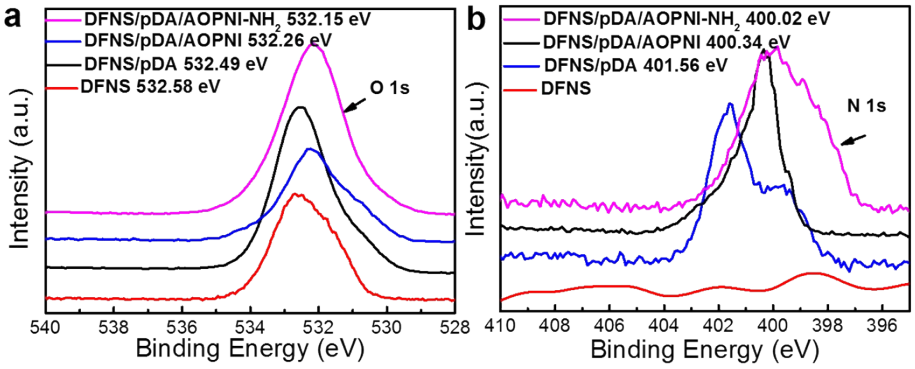


Figure S1. XPS spectroscopy patterns of O 1s (a), N 1s (b) of DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 composites.

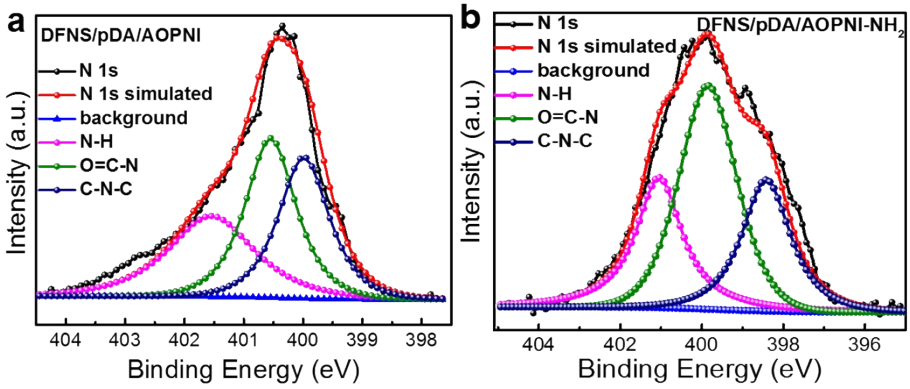


Figure S2. The high resolution N 1s XPS spectra of DFNS/pDA/AOPNI (a) and DFNS/pDA/AOPNI-NH_2 composites (b).

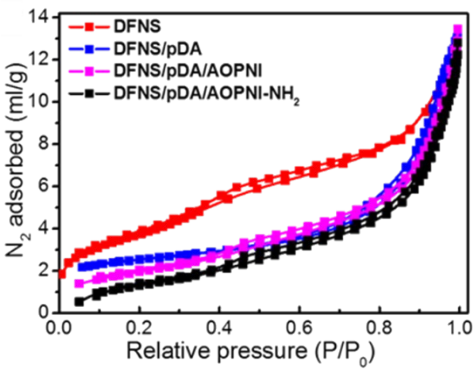


Figure S3. N_2 adsorption/desorption isotherms of DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2.

SI.3 Adsorption studies

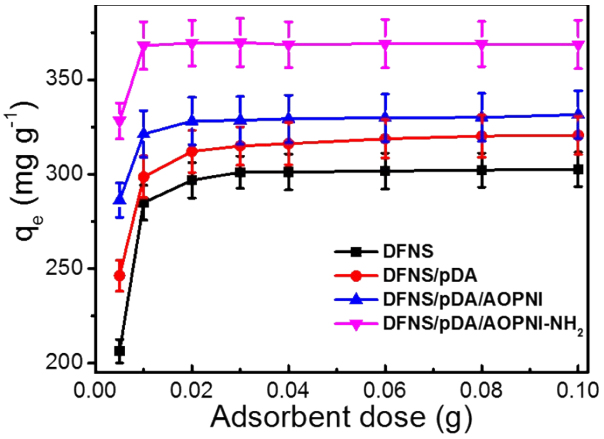


Figure S4. Effects of adsorbent dose on U(VI) adsorption by DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2.

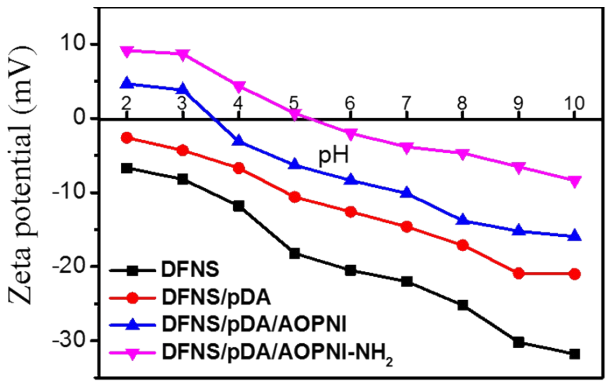


Figure S5. ζ -potential of DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH2 at different pH values.

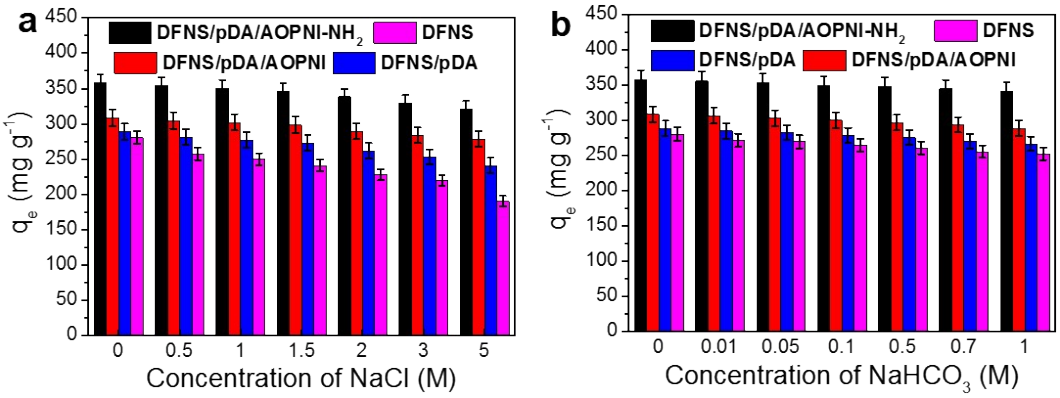


Figure S6. Effects of solution ionic strength on U(VI) adsorption by DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2.

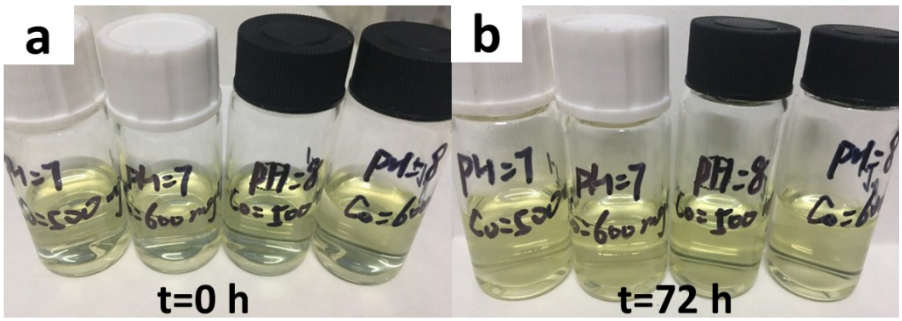


Figure S7. The digital photos of 500 mg g^{-1} and 600 mg g^{-1} uranium solution at pH=7, 8 for 72 h.

SI.4 Kinetics study

As the sorption kinetics govern the residence time of the sorption reaction and determine the solute uptake rate or the efficiency of the reaction, the following pseudo-first-order, pseudo-second-order and Weber-Morris (W-M) models are employed to interpret the mechanism controlling the sorption process. The linear form of the two models can be expressed by the following Eqs. S1-S3:

$$\ln\left(q_e - q_t\right) = lnq_e - k_1 t \quad \text{(S1)}$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad \text{(S2)}$$

$$q_e = K_{ip}\sqrt{t} + C \quad \text{(S3)}$$

Where q_t and q_e (mg g^{-1}) are the capacity of U(VI) at time t (min) and at equilibrium, K_{ip} is Internal diffusion constant, respectively, and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the respective rate constants.

Table S1 Kinetic parameter for adsorption of U (VI)

Kinetics model	U(VI) initial concentration	Materials	K	q_e^{exp}	q_e^{cal}	R^2
Pseudo-first order	500 mg g^{-1}	DFNS	0.0081	615	142.8	0.47106
		DFNS/pDA	0.0083	620	160.6	0.88988
		DFNS/pDA/AOPNI	0.0084	650	165.4	0.56698
		DFNS/pDA/AOPNI-NH_2	0.0085	653	171.5	0.59466
Pseudo-second order	500 mg g^{-1}	DFNS	$1.5*10^{-4}$	615	636	0.99965
		DFNS/pDA	$1.5*10^{-4}$	620	645	0.99971
		DFNS/pDA/AOPNI	$1.4*10^{-4}$	650	685	0.99961
		DFNS/pDA/AOPNI-NH_2	$1.5*10^{-4}$	653	667	0.99962

Table S2 Morris-Weber model parameter for adsorption of U (VI)

Materials	K^1_{ip}	K^2_{ip}	C^1	C^2
DFNS	38.64	0.086	185	620
DFNS/pDA	38.85	0.468	190.9	621
DFNS/pDA/AOPNI	39.9	0.589	198.4	641
DFNS/pDA/AOPNI-NH_2	40.1	0.865	205.7	655

SI.5 Isotherms study

In order to probe the maximum adsorption capacity and the progress of adsorption, the adsorption isotherms was studied. The adsorption of U (VI) on the DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2

composites increased with increasing temperature and the Langmuir and Freundlich models were applied to simulate experimental data.

$$C_e/q_e = 1/b \cdot q_m + C_e/q_m \quad \text{(S4)}$$

$$\ln q_e = \ln k + 1/n ln C_e \quad \text{(S5)}$$

Where C_e (mg L^{-1}) is the equilibrated U (VI) concentration, q_e (mg g^{-1}) is the amount of U (VI) adsorbed on the adsorbents capacity at equilibrium. K (L mg^{-1}) is a Langmuir constant related to the energy of the adsorbent and q_m (mg g^{-1}) is the saturation capacity at complete monolayer coverage.

Dubinin-Radushkevich (D-R) model was used to explain the U(VI) adsorption behaviour

$$\ln q_e = ln\, q_m - \beta\varepsilon^2 \quad \text{(S6)}$$

Where q_e (mg g^{-1}) is the amount of U (VI) adsorbed on the adsorbents capacity at equilibrium, β is activity and ε is the polanyi potential. In this formula, the ε was calculated by the following equations:

$$\varepsilon = RTln\,(1 + {}^{1}/_{C_e}) \quad \text{(S7)}$$

$$E = 1/\sqrt{2\beta} \quad \text{(S8)}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{(S9)}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad \text{(S10)}$$

$$K_d = \frac{q_e}{C_e} = \frac{(C_o - C_e)}{C_e} \cdot \frac{V}{m} \quad \text{(S11)}$$

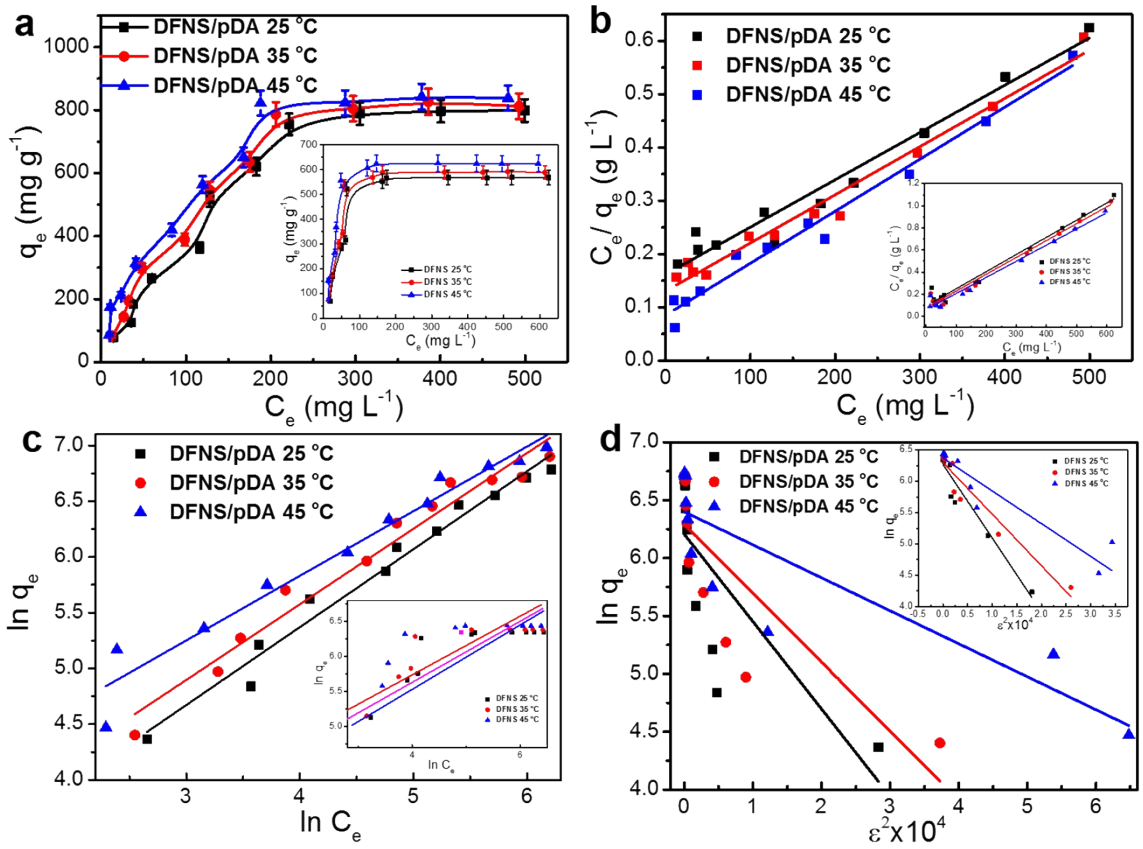


Figure S8. a) Isotherm model for DFNS (inset) and DFNS/pDA composites; b) Langmuir model; c) Freundlich model; d) Dubinin-Radushkevich model.

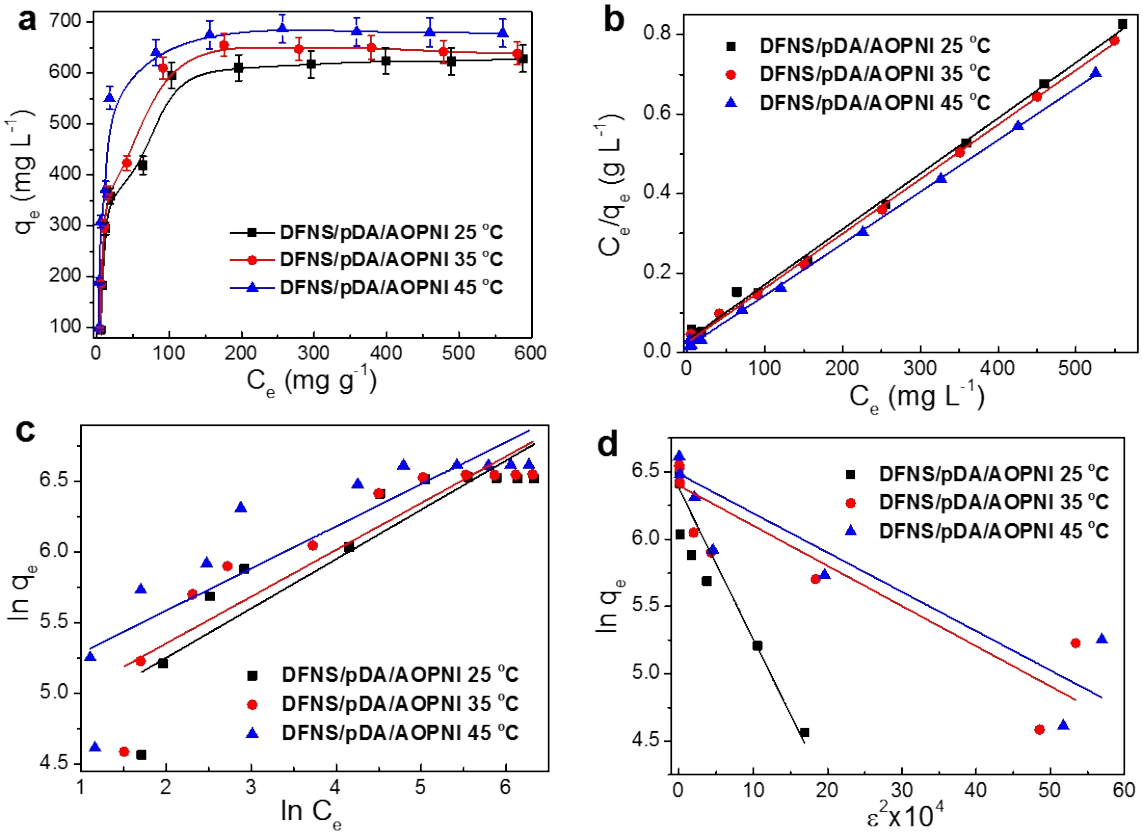


Figure S9. a) Isotherm model for DFNS/pDA/AOPNI composites; b) Langmuir model; c) Freundlich model; d) Dubinin-Radushkevich model.

Table S3 Isotherm parameter for adsorption of U (VI)

Materials	T (K)	Langmuir isotherm				Freundlich isotherm		
		q^{exp} (mg g^{-1})	q_o (mg g^{-1})	b (L mg^{-1})	R^2	K (L mg^{-1})	n	R^2
DFNS	298	567.14	645	0.0164	0.97023	40.26	2.18	0.66321
	308	589.69	653	0.0202	0.97933	48.93	2.29	0.65429
	318	625.11	684	0.0241	0.98024	58.35	2.39	0.64563
DFNS/pDA	298	620	723	0.0603	0.97751	13.15	1.43	0.92347
	308	632	702	0.0007	0.96288	17.51	1.47	0.95897
	318	653	726	0.0045	0.95491	33.52	1.73	0.88452
DFNS/pDA/AOPNI	298	675	714	0.0445	0.99672	298.29	2.86	0.81343
	308	684	730	0.0542	0.99877	327.42	3.02	0.81677

	318	745	769	0.0963	0.99932	377.97	3.35	0.75365
	298	657	712	0.0291	0.99337	71.59	2.56	0.78778
DFNS/pDA/AOPNI-NH_2	308	664	721	0.0342	0.99450	79.89	2.66	0.76255
	318	735	753	0.0465	0.99607	101.16	2.81	0.75796

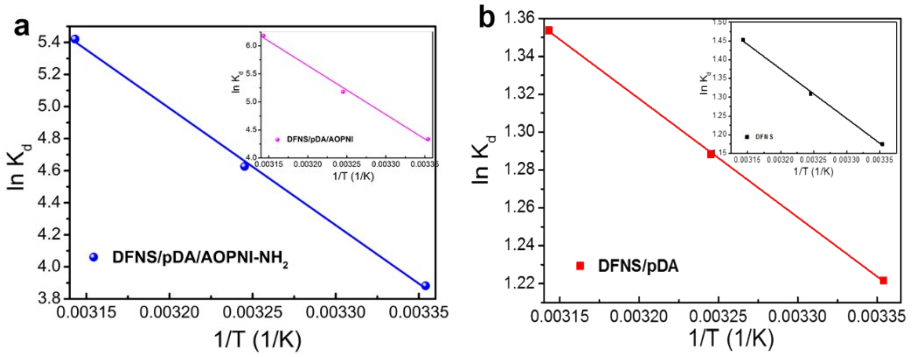


Figure S10. The influence of temperature on the U(VI) sorption on the a) DFNS/pDA/AOPNI (inset), DFNS/pDA/AOPNI-NH_2 and b) DFNS (inset), DFNS/pDA relationship curve between ln K_d and 1/T (1/K). pH= 8.0; T= 25 °C; amount of adsorbent 0.01 g and t= 180 min.

Table S4 The thermodynamic parameters of DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 for U(VI) adsorption

material	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})		
			298.15K	308.15K	318.15K
DFNS	10.96	46.51	-2.91	-3.37	-3.84
DFNS/pDA	5.199	27.59	-3.03	-3.31	-3.58
DFNS/pDA/AOPNI	72.52	279.02	-10.67	-13.46	-16.25
DFNS/pDA/AOPNI-NH_2	60.65	235.58	-9.59	-11.94	-14.3

SI.6 Effect of co-existing ions

Table S5 The concentrations of the competing cations.

Cations	U^{6+}	Ca^{2+}	K^+	Al^{3+}	Na^+	Zn^{2+}	Mg^{2+}	Sr^{2+}	Ni^{2+}
C_0 (mg L^{-1})	198.9	32.79	33.16	23.59	156.6	46.3	18.77	52.26	44.9

The selectivity coefficient (S_U) for U(VI), is defined as a specific term to describe the potency and degree of selectivity of the adsorbents as follows:

$$S_U = \frac{K_d^U}{K_d^M} \quad \text{(S12)}$$

Where K_d^U and K_d^M are the distribution ratio of the U(VI) ion and other competing ions in sorbent and solution, respectively.

Table S6 The selectivity coefficients ($S_{U/M}$) of U(VI) for different metal ions in water.

	K	Al	Na	Ca	Sr	Zn	Ni	Mg
DFNS $S_{U/M}$	118.2	4.03	10.3	114.2	44.3	48.4	100.32	9.9
DFNS/pDA $S_{U/M}$	128.8	1.67	69.6	126.4	887.5	118	109.3	20.1
DFNS/pDA/AOPNI $S_{U/M}$	447	4.8	2412	381	3667	592	229	80
DFNS/ pDA/AOPNI-NH_2 $S_{U/M}$	599.3	4.7	7817	1807	2361	605	184	79.8

SI.7 Adsorption-desorption experiments

SI.7.1 U (VI) desorption experiments

The recyclability and reuse of adsorbents play an important role in the extraction of U(VI) from seawater. The eluent agents of NaCl, Citric acid, HNO_3, $NaHCO_3$, and NaOH were first investigated for desorption of U(VI). The results from Figure S11a demonstrate that HNO_3 is the best eluent agent for reuse and recyclability of DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 adsorbents. Meanwhile, we observe that elution efficiency of DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 adsorbents are slightly lower than the others in the acid and base of aqueous solution, which means that strong chelation interactions by metal ions and the

DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2. Moreover, The desorption of DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 difficult in the process of extraction of U(VI) from weak base aqueous solution (pH=8.4). Based on the above data, when the absorbent is added to an aqueous solution of pH=8, the adsorption capacity is much greater than desorption. It means that the U(VI) can be saved on the surface of adsorbent, then we can use HNO_3 desorption for U(VI) in the lab, which opens up a possibility for the practical application of DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 adsorbents in seawater. Meanwhile, we examined the effect of different concentrations of HNO_3 for adsorption-desorption of U(VI) onto DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2. The results, given in Figure S11b, indicate that the change in eluent rate responds smoothly to increasing concentration of HNO_3, especially when nitrate concentrations are above 0.1 M. Taking into account these factors and cost issues, 0.1 M HNO_3 was used for the next step, which is the regeneration of DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 adsorbents for U(VI). In a typical experiment, 20 mg of sorbent with U (VI) ions was added into 50 mL eluent solution, which included in 0.1 M NaCl, 0.1 M Citric acid, 0.1 M HNO_3, 0.1 M $NaHCO_3$ and 0.1 M NaOH, respectively. The flasks were stirred for specified time (t, min) at room temperature, and then the solid phase was separated from the solution by centrifuge. The results were analysed with WGJ-III Trace Uranium Analyser to

obtain the concentrations of U (VI) ions. The elution rate of U (VI) ions was calculated.

SI.7.2 U (VI) adsorption-desorption cycle experiments

In a typical experiment, 20 mg of sorbent was added into 50 mL of U (VI) solution and stirred for 6 h at room temperature. The solid phase was separated from the solution by centrifuge. Then, the sorbent in the vacuum drying oven for 12 h. The dried sorbent was placed in the 50 mL eluent solution (0.1 M HNO_3) for the 6 h. After elution, the DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 composites was washed with abundant deionized water to remove residual H^+ and UO_2^{2+} until cannot detect UO_2^{2+} in the aqueous solutions. The DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 composites were regenerated by drying at 80 °C for 24 h and then reused. Eventually the elution efficiency of U (VI) ions was calculated. Repeat this experiment operation for five times.

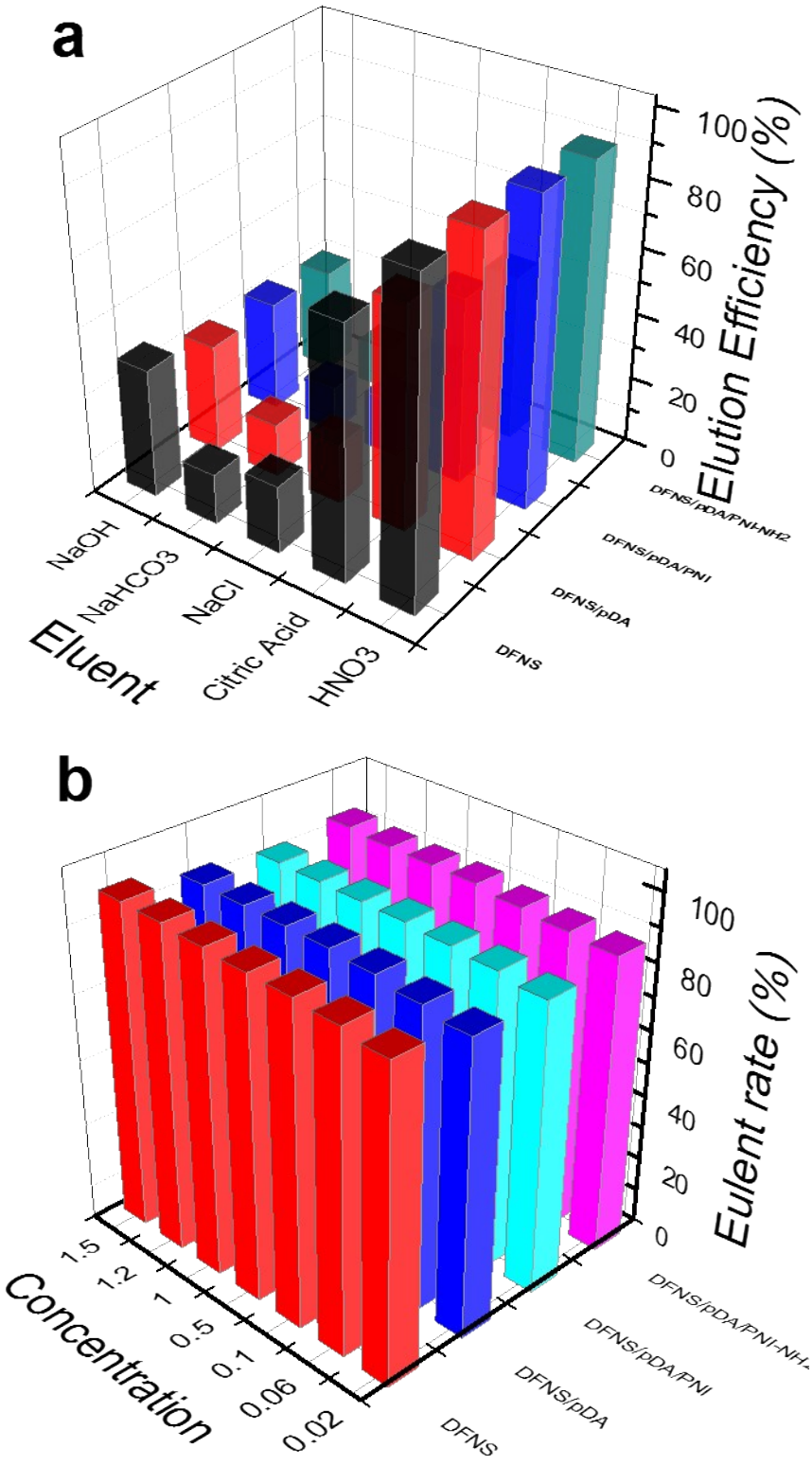


Figure S11. The effect of a) different eluent and b) different concentration eluent of HNO_3 on desorption of DFNS, DFNS/pDA, DFNS/pDA/AOPNI and DFNS/pDA/AOPNI-NH_2 composite

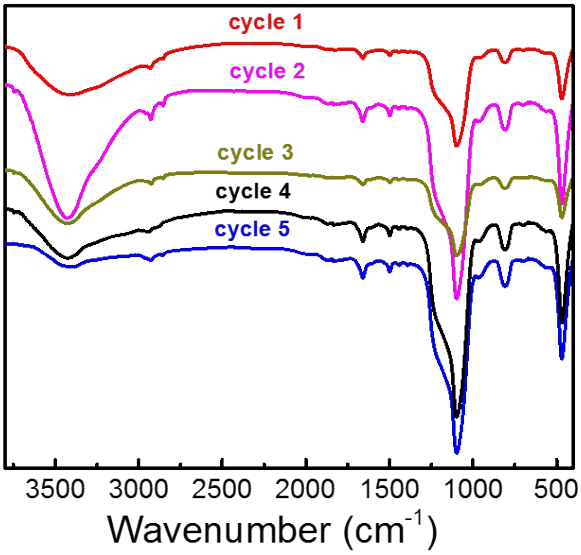


Figure S12. The FTIR spectra of DFNS/pDA/AOPNI-NH_2 composites after 5 cycles.

SI.8 Simulated seawater experiments

Table S7 Selected results of DFNS/pDA/AOPNI-NH_2 for the extraction of uranyl ions from simulated seawater

Elements	Ion concentration		Removal
	initial	final	(%)
U	3.524 μg L^{-1}	0.24 μg L^{-1}	93.1
Al	14.731 μg L^{-1}	8.125 μg L^{-1}	44.8
Ni	11.815 μg L^{-1}	10.563 μg L^{-1}	10.6
Ca	306.9 mg L^{-1}	287.42 mg L^{-1}	6.4
K	282.3 mg L^{-1}	266.81 mg L^{-1}	5.5
Mg	486.9 mg L^{-1}	415.92 mg L^{-1}	14.6
Na	2347.5 mg L^{-1}	1721.8 mg L^{-1}	26.6
Sr	5128.3 μg L^{-1}	4721.4 μg L^{-1}	7.9
Zn	38.87 μg L^{-1}	37.11 μg L^{-1}	4.5

Table S8 Selected results of DFNS/pDA/AOPNI for the extraction of uranyl ions from simulated seawater

Elements	Ion concentration		Removal
	initial	final	(%)
U	3.524 μg L^{-1}	0.401 μg L^{-1}	88.6
Al	14.731 μg L^{-1}	6.922 μg L^{-1}	53
Ni	11.815 μg L^{-1}	9.583 μg L^{-1}	19
Ca	306.9 mg L^{-1}	271.71 mg L^{-1}	11.5
K	282.3 mg L^{-1}	258.36 mg L^{-1}	8.5
Mg	486.9 mg L^{-1}	385.62 mg L^{-1}	20.8
Na	2347.5 mg L^{-1}	1565.31 mg L^{-1}	33.3
Sr	5128.3 μg L^{-1}	4621.01 μg L^{-1}	9.92
Zn	38.87 μg L^{-1}	35.91 μg L^{-1}	7.6

Table S9 Selected results of DFNS/pDA for the extraction of uranyl ions from simulated seawater

Elements	Ion concentration		Removal
	initial	final	(%)
U	3.524 μg L^{-1}	0.536 μg L^{-1}	84.7
Al	14.731 μg L^{-1}	6.547 μg L^{-1}	55.6
Ni	11.815 μg L^{-1}	9.883 μg L^{-1}	16.3
Ca	306.9 mg L^{-1}	263.91 mg L^{-1}	14.0
K	282.3 mg L^{-1}	249.85 mg L^{-1}	11.5
Mg	486.9 mg L^{-1}	358.15 mg L^{-1}	26.4
Na	2347.5 mg L^{-1}	1461.84 mg L^{-1}	37.7
Sr	5128.3 μg L^{-1}	4585.73 μg L^{-1}	10.6
Zn	38.87 μg L^{-1}	35.06 μg L^{-1}	9.8

Table S10 Selected results of DFNS for the extraction of uranyl ions from simulated seawater

Elements	Ion concentration		Removal
	initial	final	(%)
U	3.524 μg L^{-1}	0.611 μg L^{-1}	82.7
Al	14.731 μg L^{-1}	6.892 μg L^{-1}	53.2
Ni	11.815 μg L^{-1}	9.572 μg L^{-1}	19
Ca	306.9 mg L^{-1}	258.76 mg L^{-1}	15.7
K	282.3 mg L^{-1}	239.9 mg L^{-1}	15
Mg	486.9 mg L^{-1}	336.87 mg L^{-1}	30.8
Na	2347.5 mg L^{-1}	1443.04 mg L^{-1}	38.5
Sr	5128.3 μg L^{-1}	4555.3 μg L^{-1}	11.2
Zn	38.87 μg L^{-1}	33.5 μg L^{-1}	13.9