Electronic Supplementary Information (ESI)

Bayberry Tannin immobilized Bovine Serum Albumin Nanospheres: Characterization, Irradiation Stability and Selective Removal Uranyl Ion from Radioactive Wastewater

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S1. Batch adsorption

Effect of pH on UO_2^{2+} adsorption. 0.02g of BSA-BT-NSs was immersed into 50 mL of 100 mg L^{-1} UO_2^{2+} solution. The pH of the solutions, ranged from 2 to 6, was adjusted using diluted 0.1 M NaOH solution and 0.1 M HNO_3 solution. The adsorption process was conducted at 298 K with constant stirring for 24 h. Then, the suspension was filtered and the concentration of UO_2^{2+} in filtrate was analyzed by UV-Vis (UV-3900, Hitachi Corp., Tokyo, Japan; the limit of analytical detection of uranium is 0.1 mg L^{-1}) at 650 nm with arsenazo (III) as the complex agent (Fig.S1A). The UO_2^{2+} concentrations were measured using a calibration curve (Fig.S2B) (Y = 0.24071X − 0.00255, where X is the concentration of UO_2^{2+} in mg L^{-1} and Y is the absorbency; R^2 = 0.999). The linear equation was established from the known concentration of standard UO_2^{2+} solutions (0, 0.4, 0.8, 1.6, 2.4, 3.2, and 4 mg L^{-1}, respectively) [13]. The adsorption capacity of UO_2^{2+} onto BSA-BT-NSs was calculated from the concentration difference of UO_2^{2+} before and after the adsorption.

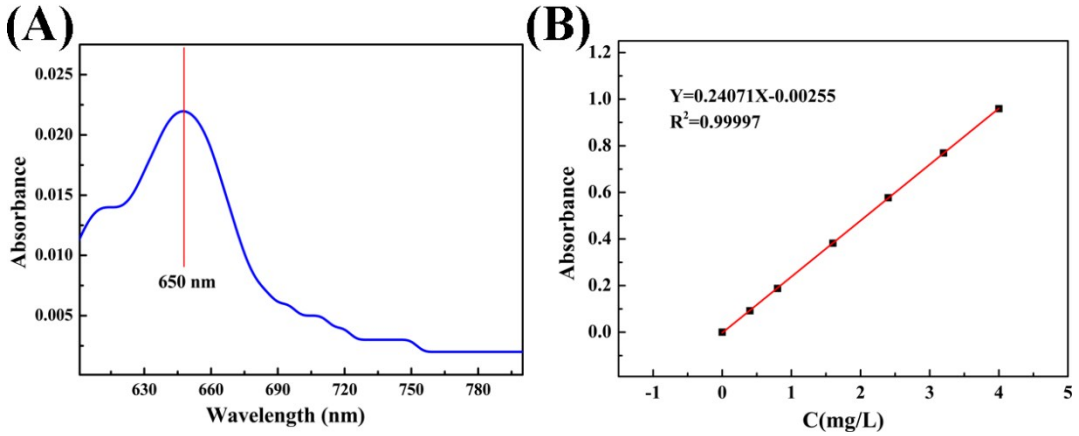

Fig. S1 Absorption spectra of uranium-Arsenazo III complex (A) and standard curve of uranium (B)

Effects of the temperature and the initial UO_2^{2+} concentration. 0.02g of BSA-BT-NSs was immersed into 50 ml of UO_2^{2+} solution, where the initial concentration of UO_2^{2+} ranged from 20 mg L^{-1}, 100 mg L^{-1}, 180 mg L^{-1}, 260 mg L^{-1}, 340 mg L^{-1}, 420 mg L^{-1}. The pH of solutions was 5.0 and the adsorption processes were conducted with constant stirring for 24 h at 288 K, 298 K, 308 K, 318 K and 328 K, respectively. The concentrations of UO_2^{2+} in residual solutions after adsorption were analyzed by UV-Vis with arsenazo (III) as the complex agent.

Adsorption kinetics. 0.02 g of BSA-BT-NSs was suspended in 50 mL of 100 mg L^{-1} UO_2^{2+} solutions. The pH of the solution was adjusted to 5.0 and the adsorption process was conducted at 298 K with constant stirring. The concentration of UO_2^{2+} was analyzed at a regular interval during adsorption process by UV-Vis. The adsorption capacities at time t (min) were obtained by mass balance calculation and were denoted as q_t (mg g^{-1}).

S2. Preparation of BSA-BT-NSs.

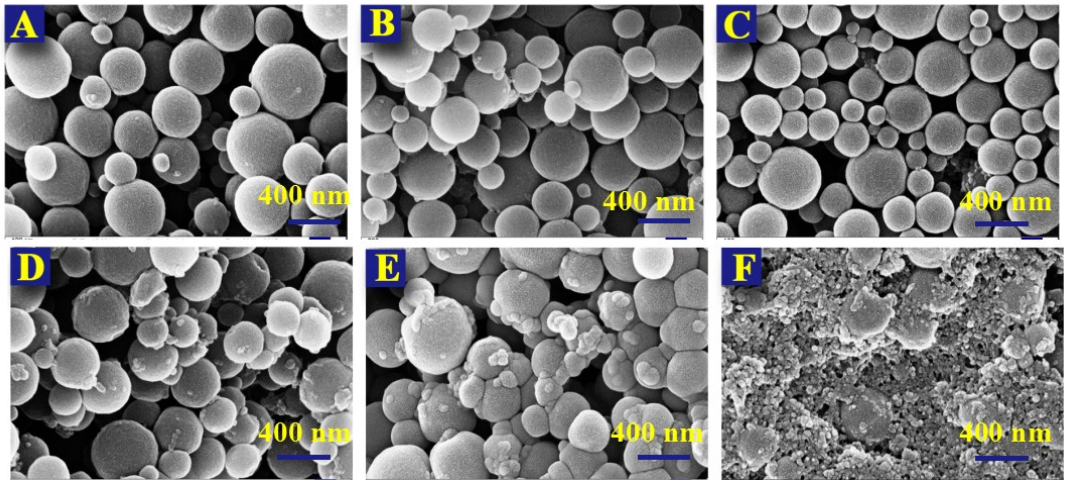

Fig. S2 SEM images of BSA-BT-NSs using difference amount tannin to immobilization (A-10%, B-20%, C-30%, D-40%, E-50% and F-60%)

S3. Thermal analysis

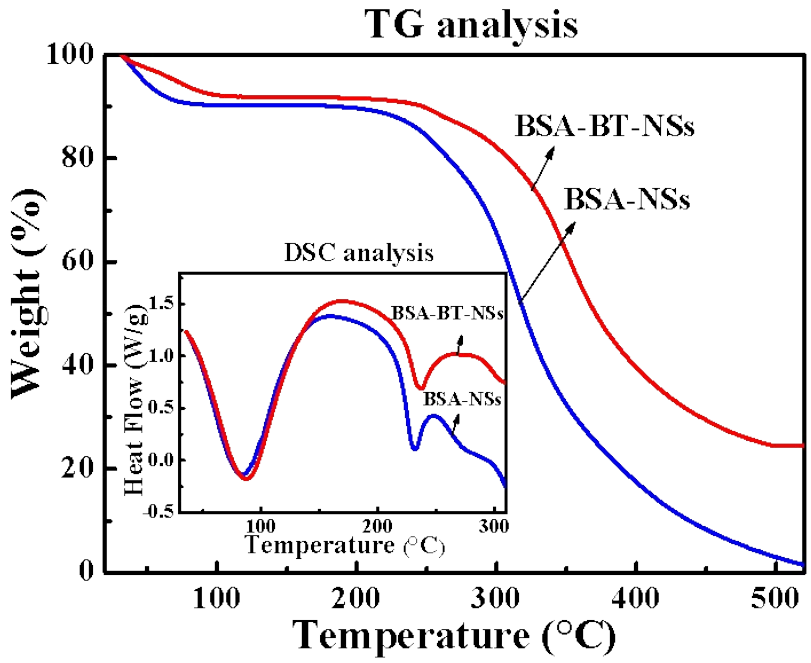

Fig. S3 The thermal analysis of BSA-NSs and BSA-BT-NSs

S4. Uranyl ion removal

Thermodynamics: Three basic thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated using following equations.

$\Delta G^0=\Delta H^0 - T\Delta S^0$ (1)

$\ln K_L=\Delta S^0/R - \Delta H^0/RT$ (2)

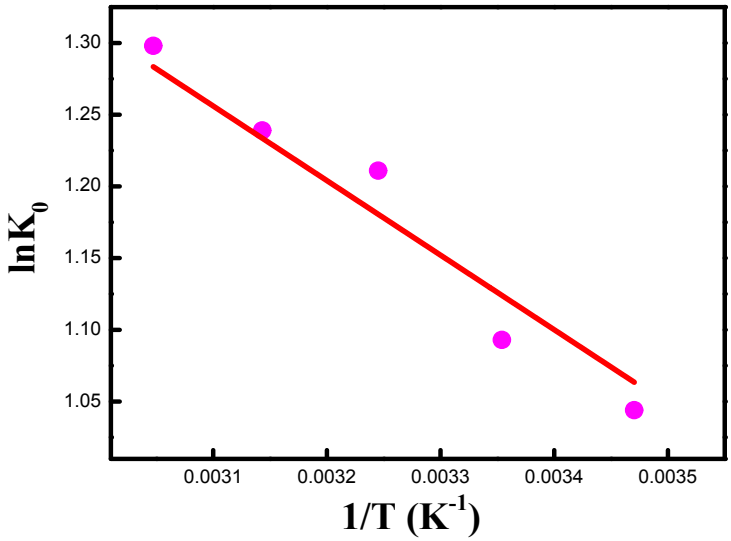

Fig.S4 The liner relationship between $\ln K_L$ and 1/T for U(VI) adsorption on BSA-BT-NSs

Isotherm model: Experimental data was fitted by Langmuir and Freundlich models. The linear and non-linear form of Langmuir isotherm equation can be written as:

$$\frac{C_e}{q_e}=\frac{1}{K_L q_{max}}+\frac{C_e}{q_{max}} \quad \text{(linear)} \qquad (3)$$

$$q_e=\frac{q_{max} K_L C_e}{(1+K_L C_e)} \quad \text{(non-linear).} \qquad (4)$$

The Freundlich Model can be expressed as linear and non-linear forms:

$$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e \quad \text{(linear)} \qquad (5)$$

$$q_e=K_F C_e^{\frac{1}{n}} \quad \text{(non-linear)} \qquad (6)$$

where q_e (mg g^{-1}) represents the equilibrium adsorption of uranium (VI) on the adsorbent, C_0 and C_e (mg L^{-1}) are initial and equilibrium uranium(VI) concentration,

respectively.

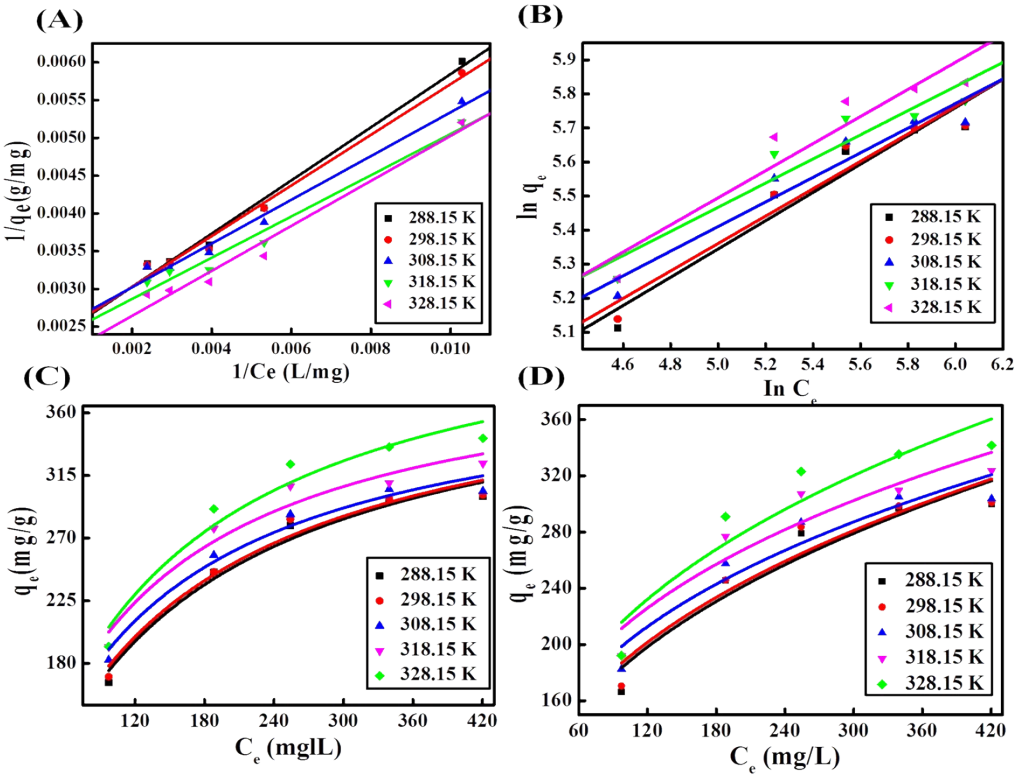

Fig.S5 The linear (A) and non-linear (C) fitting of Langmuir model of UO_2^{2+} adsorption on BSA-BT-NSs; The linear (B) and non-linear (D) fitting of Freundlich model of U(VI) adsorption on BSA-BT-NSs

Table S1 Characteristic parameters obtained from Langmuir and Freundlich equations

Type	T (K)	Langmuir			Freundlich		
		q_m(mg g^{-1})	K_L(L mg^{-1})	R^2	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	n	R^2
Linear model	288	431.034	0.007	0.983	26.287	2.409	0.911
	298	423.729	0.007	0.983	28.449	2.484	0.910
	308	409.836	0.008	0.981	36.736	2.767	0.900
	318	431.034	0.008	0.966	40.183	2.819	0.871
	328	487.805	0.008	0.966	33.304	2.513	0.870
Non-linear model	288	404.626	0.008	0.966	33.272	2.682	0.892
	298	402.446	0.008	0.963	35.406	2.753	0.889
	308	392.336	0.010	0.963	44.304	3.051	0.880
	318	408.260	0.010	0.945	49.227	3.142	0.852

328	451.059	0.009	0.943	43.302	2.851	0.849

Table S2 Equilibrium parameters R_L

T(K)	Uranium(VI) concentration (mg L^{-1})									
	100		180		260		340		400	
	Linear	Non-liner	Linear	Non-liner	Linear	Non-liner	Linear	Non-liner	Linear	Non-liner
288	0.610	0.568	0.447	0.405	0.374	0.335	0.309	0.274	0.265	0.233
298	0.594	0.558	0.430	0.395	0.359	0.325	0.295	0.265	0.253	0.226
308	0.550	0.516	0.387	0.355	0.318	0.290	0.259	0.234	0.220	0.198
318	0.548	0.504	0.385	0.345	0.317	0.280	0.257	0.226	0.219	0.190
328	0.562	0.543	0.399	0.381	0.330	0.313	0.269	0.254	0.229	0.216

Adsorption kinetics. Two kinetic models, pseudo-first-order and pseudo-second-order, were employed to evaluate the rate-controlling mechanism of the adsorption process. The linear and non-linear forms of the equations are given as follows:

$$\lg(q_e - q_t) = \lg q_e - K_1 t \quad (11)$$

$$\frac{\mathrm{t}}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (12)$$

The non-linear forms of pseudo-first-order and pseudo-second-order kinetic models can be written as:

$$\mathrm{q}_t = q_e(1 - \exp(-K_1 t)) \quad (13)$$

$$\mathrm{q}_t = \frac{K_2 t q_e^2}{(1 + K_2 t q_e)} \quad (14)$$

where t (min) is the contact time, q_e and q_t (mg g^{-1}) are the adsorption capacity at any time t and equilibrium, respectively, and K_1(g mg^{-1} min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the rate constants of pseudo-first-order and pseudo-second-order adsorption.

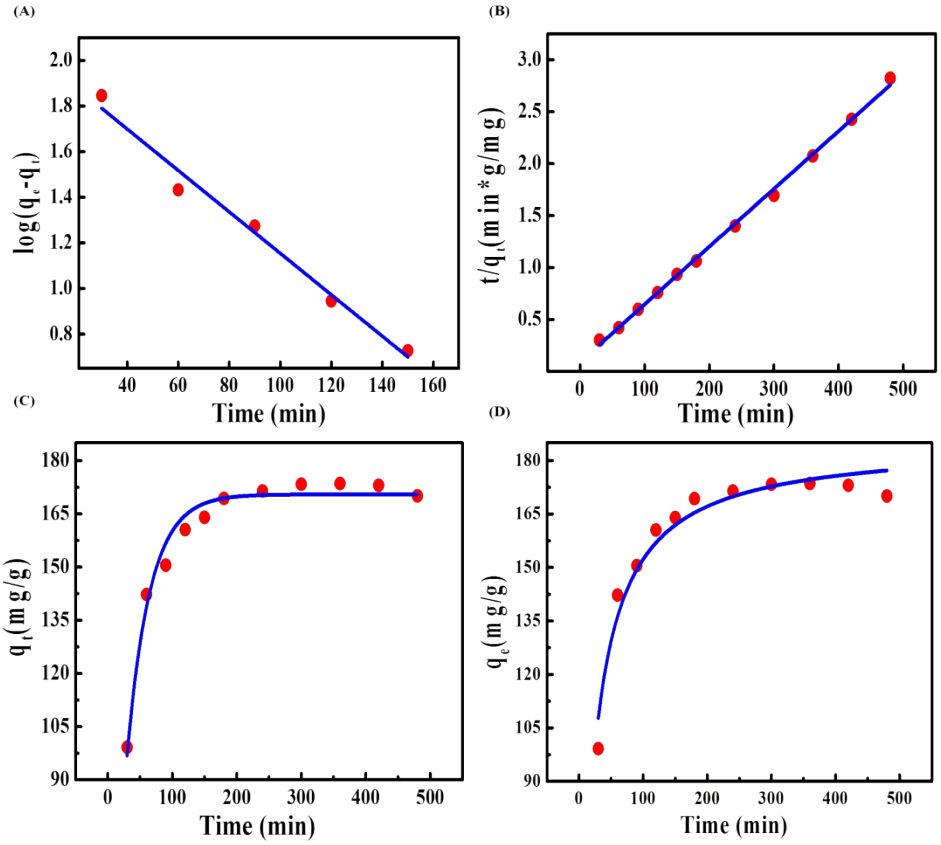

Fig.S6 The linear (A) and non-linear (C) fitting of pseudo-first-order kinetic of UO_2^{2+} adsorption on BSA-BT-NSs; the linear (B) and non-linear (D) fitting of pseudo-second-order kinetic model of UO_2^{2+} adsorption on BSA-BT-NSs.

Table S3 Parameters of Pseudo-first-order kinetics and Pseudo-second-order kinetics for U(VI) adsorption on BSA-BT-NSs.

Model	Pseudo-first-order			Pseudo-second-order		
Parameter	q_e (mg g^{-1})	k1(g/mg*min)	R^2	q_e (mg/g)	k2(g/mg*min)	R^2
Linear	7.864	9.080×10^{-3}	0.978	179.856	3.440×10^{-4}	0.998
Non-linear	170.483	2.800×10^{-2}	0.974	185.144	2.507×10^{-4}	0.953

S5. Theory calculation

Table S4 Binding energy of corresponding geometric models.

Geometric Models	PC-U	PC-U-PC	BT-U	BT-U-BT
E_B (KJ mol^{-1})	693.132	979.315	799.964	1157.846