Supporting Information

Engineering defect-rich Prussian blue analogs composite for enhanced Cs^+ removal performance

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1. Experimental

Reagents: Sodium chloride (NaCl), anhydrous potassium carbonate (K_2CO_3), magnesium chloride ($MgCl_2$) and potassium ferricyanide ($K_3Fe(CN)_6$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Zinc chloride ($ZnCl_2$), calcium chloride ($CaCl_2$), cesium chloride (CsCl), ammonium chloride (NH_4Cl) and hydrochloric acid (HCl) were purchased from Aladdin. Potassium citrate ($K_3C_6H_5O_7$) and ammonium citrate ($(NH_4)_3C_6H_5O_7$) were supplied by Macklin.

All regents used in our experiments were of analytical grade and without further purification. For security, non-radioactivity $^{133}Cs^+$ (*i.e.,* CsCl) instead of radioactive $^{137}Cs^+$ was used for experiments.

Characterization: The nitrogen adsorption and desorption data was performed by an adsorption equipment (Micromeritics APSP2460, USA), and the specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were proceeded through TESCAN MIRA scanning electron microscope. The FT-IR spectra was acquired with a Thermo Scientific Nicolet iS20 in the range of 4000 - 400 cm^{-1}. The thermogravimetric analysis was measured by a Rigaku TG-DTA8122 at a heating rate of 10 °C/min in the range of 30 - 800 °C. XRD patterns were obtained by powder X-ray diffraction (RIKEN SmartLab-SE, Japan) using Cu-Kα rays with the diffraction range of 10° - 80°. X-ray photoelectron spectroscopy (XPS) was carried out using a K-Alpha equipped with a micro-focused monochromator X-ray source (Thermo Scientific, ESCALAB 250Xi, America). The ratio of K, Fe, Zn elements in both Zn-PBA and Zn-PBA/NPC was measured by ICP-OES: Agilent 5110 after digestion. Electron paramagnetic resonance (EPR, Billerica, MA) spectra were obtained using an EPR spectrometer.

Synthesis of NPC: NPC was prepared by the improved self-assembly method[1-2]. First, NaCl (4.0 g), K_2CO_3 (1.3 g) and $(NH_4)_3C_6H_5O_7$ (3.0 g) were dissolve completely in the deionized water (140 mL). Then, the solution above was freeze-dried for 36 h.

As a result, the salts were coated with $(NH_4)_3C_6H_5O_7$. Subsequently, these white particles were heated to 700 °C at 5 °C/min for 30 min at a nitrogen atmosphere. At this step, the $C_6H_5O_7^{3-}$ was carbonized into carbon and the N served by NH_4^+ doped onto this carbon material. Finally, after washing with1 mol/L HCl (3×10 mL) and deionized water (5×10 mL) and subsequently dried at 60 ℃ for 12 h , the black NPCs were obtained.

Synthesis of Zn-PBA/NPC: The obtained NPC (0.11 g) was poured into $K_3Fe(CN)_6$ solution (4 mmol, 100 mL) to form a black suspension, which was recorded as solution A. Solution B was composed of $ZnCl_2$ (0.82 g, 6 mmol), $K_3C_6H_5O_7$ (0.97 g, 3 mmol) and 100 mL deionized water. $C_6H_5O_7^{3-}$ could coordinate with Zn^{2+}, leading to the controlled nucleation and crystal growth of Zn-PBA. Then, slowly added solution A into solution B with continuous stirring for 6 h. The gray Zn-PBA/NPC was obtaining by aging, centrifuging, washing and drying. For comparison, the Zn-PBA powder without support was also prepared with the similar method.

Adsorption experiment: Typical adsorption experiment proceeded in a 250 mL beaker containing 50 mg adsorbent and 100 mL solution containing Cs^+ with known concentration. After stirring for certain time at certain temperature, the supernatant was filtered out through a 0.22 μm syringe filter. Then, the concentration of Cs^+ was measured by ICP-OES. In order to improve the measurement precision, every experiment proceeded three times and took the average.

Adsorption selectivity experiment: In order to investigate the adsorption selectivity of Zn-PBA/NPC, a series of binary solutions containing 20 mg/L Cs^+ and Na^+/ K^+/ Ca^{2+}/ Mg^{2+} (50 - 200 mg/L) were respectively prepared. The experiments proceeded using 50 mg Zn-PBA/NPC and 100 mL above binary solution under 298.15 K with a pH of 7.

Recyclability: After adsorption using 100 mg/L Cs^+ and 50 mg Zn-PBA/NPC under 298.15 K with a pH of 7, the Cs-laden Zn-PBA/NPC was eluted using 0.4 mol/L NH_4Cl solution. After washing with distilled water (3×10 mL), this regenerated Zn-

PBA/NPC was directly used for the next adsorption-desorption process.

2. Equations used in this work

The adsorption capacity (q_t, mg/g), adsorption efficiency (E,%) and distribution coefficient (K_d, mL/g) were calculated by the following Eqs. S1-S3.

$$q_t = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \tag{2}$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} = \frac{q_e}{C_e} \tag{3}$$

Where C_0, C_t and C_e (mg/L) are the concentrations of Cs^+ at initial, time t and equilibrium, respectively. V (L) is the volume of the solution used for adsorption and m (g) is the weight of the adsorbent.

The thermodynamic parameters including enthalpy (ΔH^0, kJ·mol^{-1}), entropy (ΔS^0, J·mol^{-1}·K^{-1}) and Gibbs free energy (ΔG^0, kJ·mol^{-1}) could be calculated by Eqs. S4-S5 as followings:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T} \tag{4}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5}$$

where K_d is the equilibrium distribution coefficient, T (K) is the temperature, R (8.314 J·mol^{-1}·K^{-1}) is the ideal gas constant, respectively.

Langmuir, Freundlich and Dubinin–Radushkevich isothermal adsorption equations and the equations of their parameters:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{6}$$

$$R_L = \frac{1}{1 + K_L C_{0,\max}} \tag{7}$$

$$q_e = k C_e^{1n} \tag{8}$$

$$\ln q_e = \ln q_{\max} - \beta\varepsilon^2 \tag{9}$$

$$\varepsilon = RT * \ln(1 + 1/C_e) \quad (10)$$

$$E = (2\beta)^{-1/2} \quad (11)$$

Where q_e (mg/g) is the equilibrium adsorption capacity, q_m (mg/g) is the maximum adsorption capacity, $C_{0,max}$ (mg/L) is the maximum initial Cs^+ concentrations, C_e (mg/L) is the equilibrium concentrations of Cs^+, K_L is Langmuir constant, and the R_L (L/mg) is separation factor. k and 1/n are constants representing the adsorption capacity and intensity, respectively. ε corresponds to the Polanyi potential, β corresponds to the activity coefficient that associated to the mean free energy E (kJ·mol^{-1}). If the magnitude of E is below 8 kJ·mol^{-1}, physisorption is envisaged.

3. Characterizations of NPC and Zn-PBA/NPC.

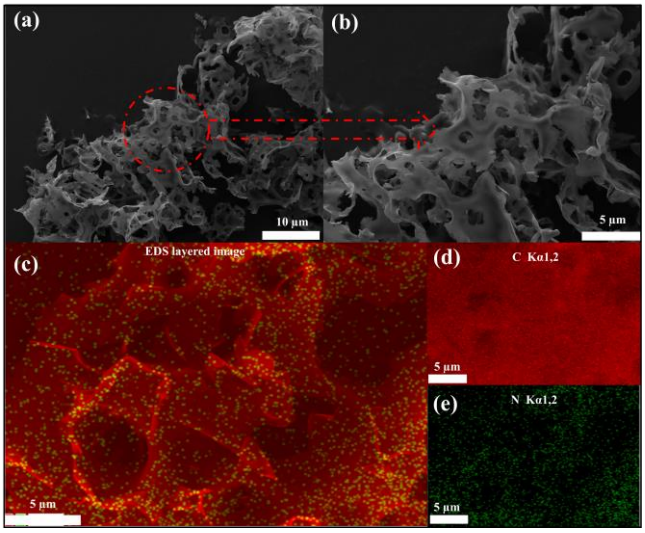

Figure S1. The SEM-EDS image of NPC, (a-b) the SEM image of NPC at different magnifications, (c-e) EDS of NPC.

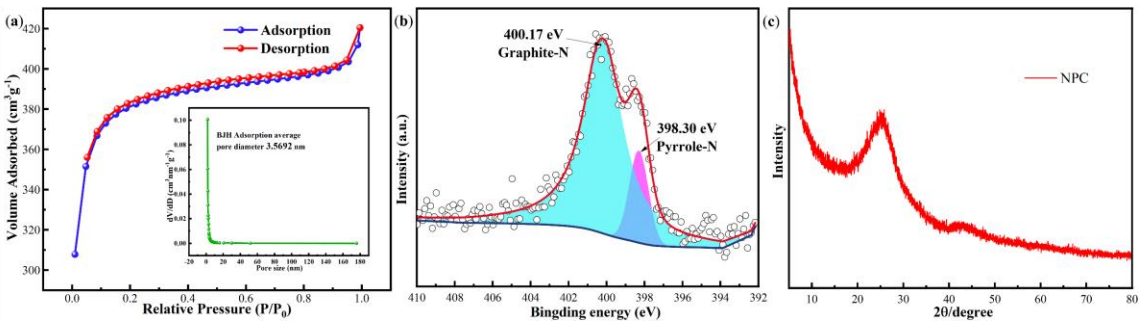

Figure S2. (a) Nitrogen adsorption and desorption curve and pore size distribution of NPC, (b) XPS spectra of N 1s, (c) XRD.

Table S1 BET parameters of NPC.

	BET Surface Area (m^2/g)	BJH Adsorption cumulative volume of pores (cm^3/g)	BJH Adsorption average pore diameter (nm)
NPC	556.05	0.15	3.72

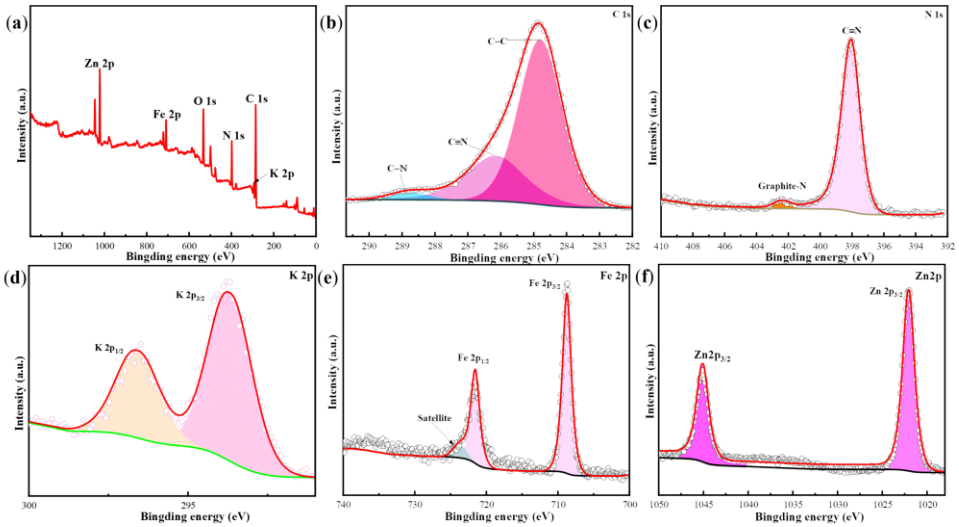

Figure S3. XPS spectra of Zn-PBA/NPC, (a) full spectra, (b) C 1s, (c) N 1s, (d) K 2p, (e) Fe2p, (f) Zn 2p.

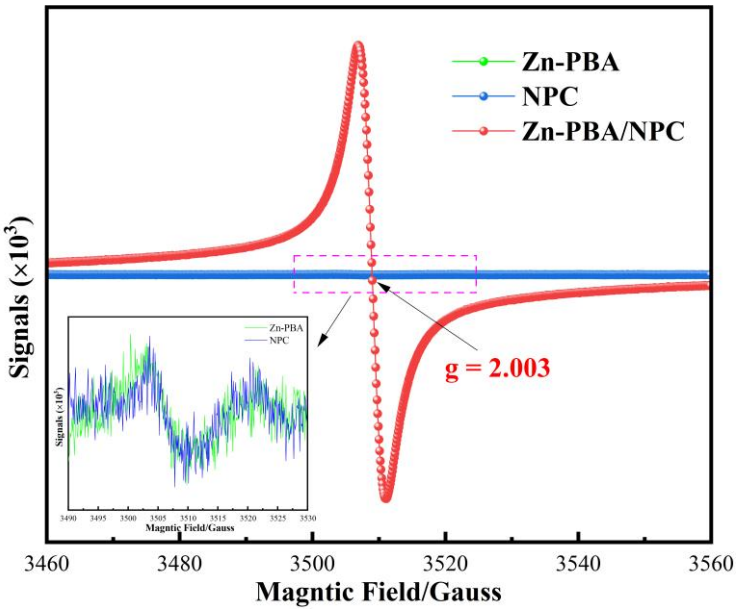

Figure S4. EPR spectra of NPC, Zn-PBA and Zn-PBA/NPC.

4. The element analysis results measured by ICP.

According to the reported method[3], we calculated the molecular formula of Zn-PBA in the Zn-PBA/NPC and Zn-PBA.

Table S2 The element analysis results measured by ICP and TG.

	K	Fe	Zn	H_2O
Zn-PBA/NPC	2.01	2.25	3.53	6.49
Zn-PBA	1.12	3.63	5.28	2.79

5. Adsorption kinetics.

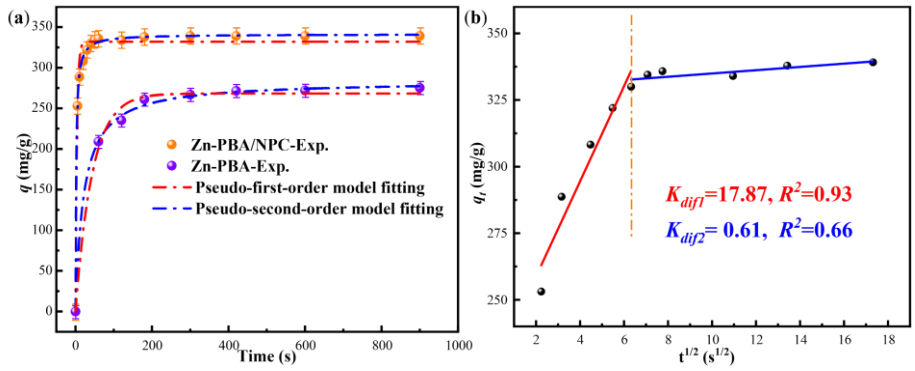

Figure S5. (a) Kinetics curves of Cs^+ adsorption onto Zn-PBA and Zn-PBA/NPC, (b) Intraparticle diffusion model.

Table S3 Pseudo-first-order and Pseudo-second-order model kinetic parameters.

Type	q_e(exp) (mg·g^{-1})	pseudo-first-order model			Pseudo-second-order model		
		q_e (mg·g^{-1})	K_1 (s^{-1})	R^2	q_e (mg·g^{-1})	K_2 (s^{-1})	R^2
Zn-PBA/NPC	339.2	329.4	0.266	0.9887	342.1	1.62×10^{-3}	0.9991
Zn-PBA	275.2	269.7	0.023	0.9933	282.9	1.64×10^{-4}	0.9980

6. Adsorption isotherms.

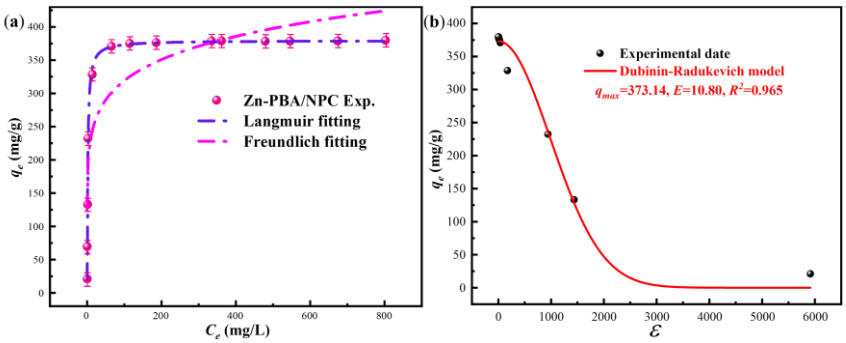

Figure S6. (a) Langmuir and Freundlich isothermal adsorption model fitting of Zn-PBA/NPC, (b) D-R model fitting. (C_0 = 20 - 1000 mg/L, pH = 7, m/V = 0.5 g/L, T = 298.15 K, 60 s)

Table S4 Fitting parameters of four isothermal adsorption models

Type	Langmuir	q_{max} (mg/g)	379.78
		K_L (L/mg)	0.5807
		R^2	0.9817
	Freundlich	K_F ((mg/g)·(L/mg)$^{1/n}$)	169.86
		$1/n$	0.1369
		R^2	0.8163
	D-R	q_{max} (mg/g)	373.14
		β (mol^2/kJ^2)	0.00429
		R^2	0.965
		E (kJ/mol)	10.80

7. Adsorption thermodynamic.

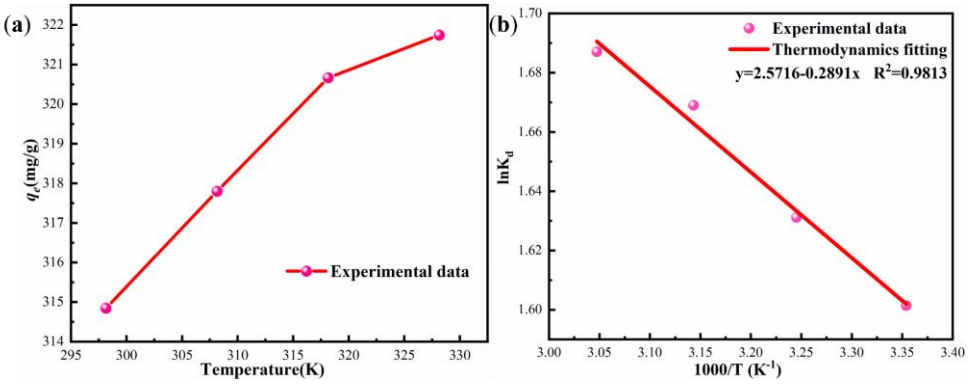

Figure S7 (a) Effect of temperature on Cs^+ equilibrium adsorption capacity, (b) Thermodynamic fitting curve of lnK_d as a function of 1000/T. (C_0 = 220 mg/L, pH = 7, m/V = 0.5 g/L, T = 298.15 - 328.15 K, 60 s)

Table S5 Thermodynamic parameters of Zn-PBA/NPC adsorption

	T (K)	ΔG^0 (kJ·mol^{-1})	ΔH^0 (kJ·mol^{-1})	ΔS^0 (J·mol^{-1}·K^{-1})
Zn-PBA/NPC	298.15	-3.97	2.40	21.38
	308.15	-4.18		
	318.15	-4.40		
	328.15	-4.61		

8. The effects of eluent on the desorption efficiency.

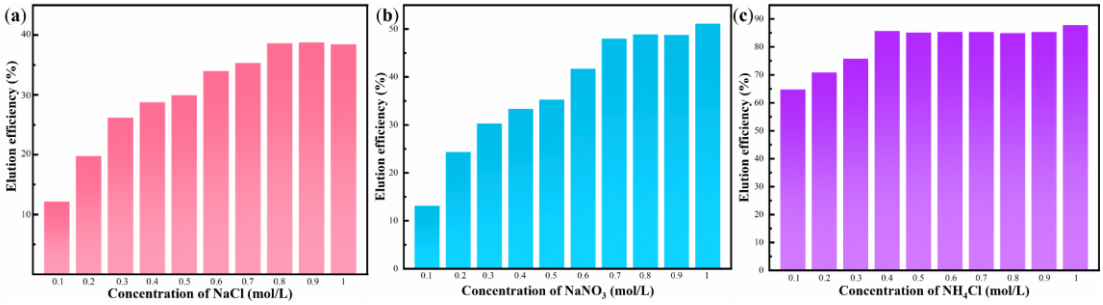

Figure S8. The effects of eluent on the desorption efficiency (a) NaCl, (b) $NaNO_3$, and (c) NH_4Cl

9. Adsorption selectivity.

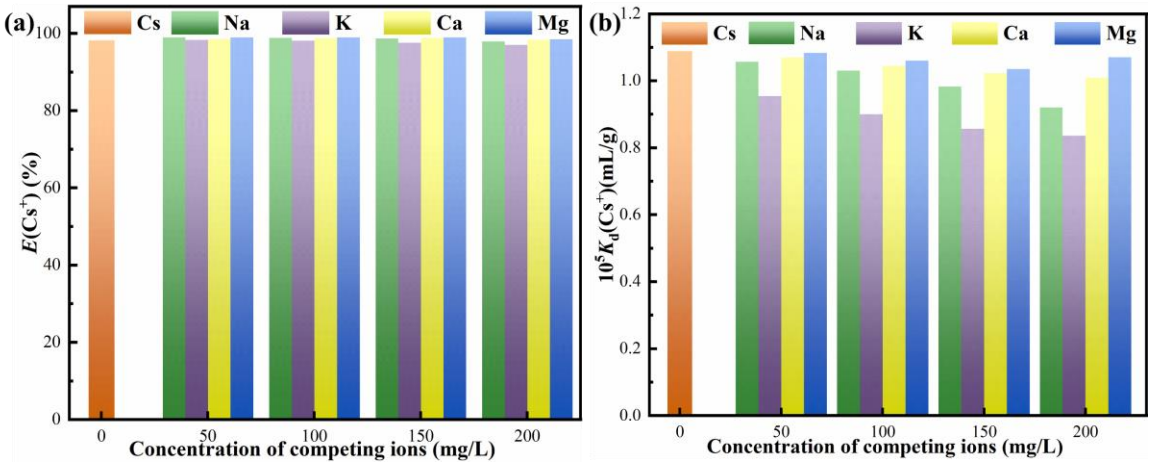

Figure S9. Adsorption selectivity of Zn-PBA/NPC in the presence of competing cations (a) adsorption efficiency E (%), (b) distribution coefficients K_d (mL/g). (20 mg/L Cs^+, pH = 7, m/V = 0.5 g/L, T = 298.15 K, 60 s)

10. Adsorption mechanism.

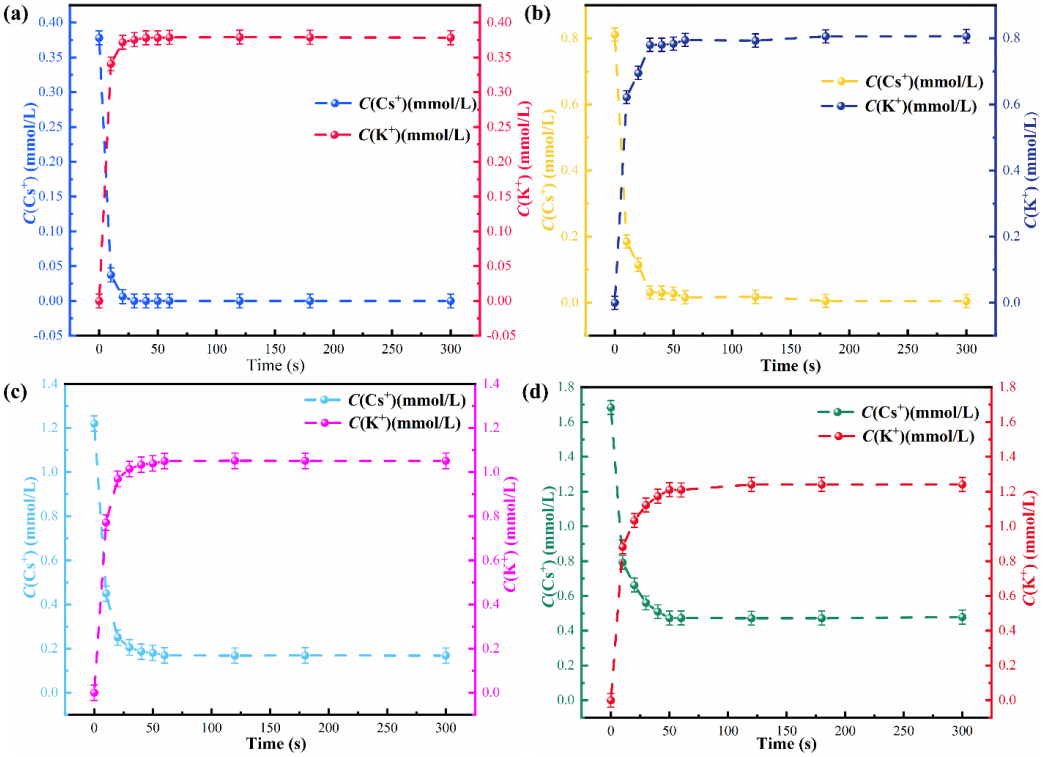

Figure S10. The changes of Cs^+ and K^+ with time. (a) 0.38 mmol/L Cs^+, (b) 0.82 mmol/L Cs^+, (c) 1.21 mmol/L Cs^+, (d) 1.69 mmol/L Cs^+. (pH = 7, m/V = 0.5 g/L, T = 298.15 K and 300 s)

11. XPS of Zn-PBA/NPC after adsorption.

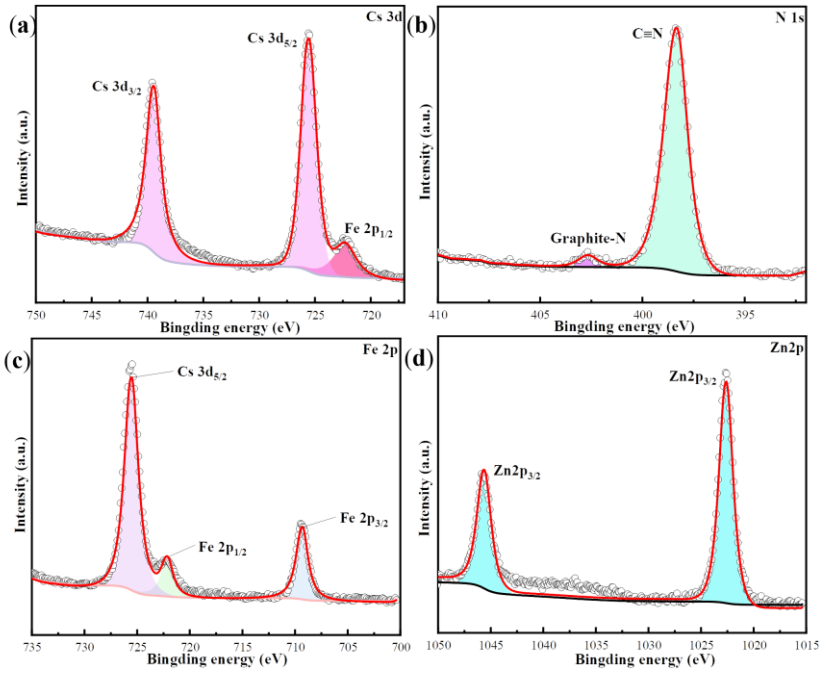

Figure S11. XPS spectra of Zn-PBA/NPC after adsorption, (a) Cs 3d, (b) N 1s, (c) Fe 2p, (d) Zn 2p.

12. Comparison of various adsorbents for Cs^+ adsorption.

Table S6 The absorption performance of Cs^+ by various absorbents.

Entry	Adsorbents	Equilibrium time (min)	q_{max} (mg/g)	Ref.
1	ZnHCF-ZDC	45	204.9	[4]
2	VMT/ZnHCF	300	378.8	[5]
3	PB/AC	30	207.2	[6]
4	PB/NHPC	120	125.3	[7]
5	3D RGO/PBAs	1440	204.9	[8]
6	NiHCF/RGO	4	320.0	[9]
7	CuHCF/chitosan fiber	90	70.3	[10]
8	PVA-SA-KCuHCF	90	113.6	[11]
9	PB@PAAm	60	374.0	[12]
10	PBA-CFs	30	175.6	[13]
11	NiFe-AH	90	117.7	[14]
12	PAN/PB	1	152.7	[15]
13	Zn-PBA/NPC	1	379.8	This work

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