Zinc-modulated Fe-Co Prussian blue analogues with well-controlled morphology for cesium adsorption

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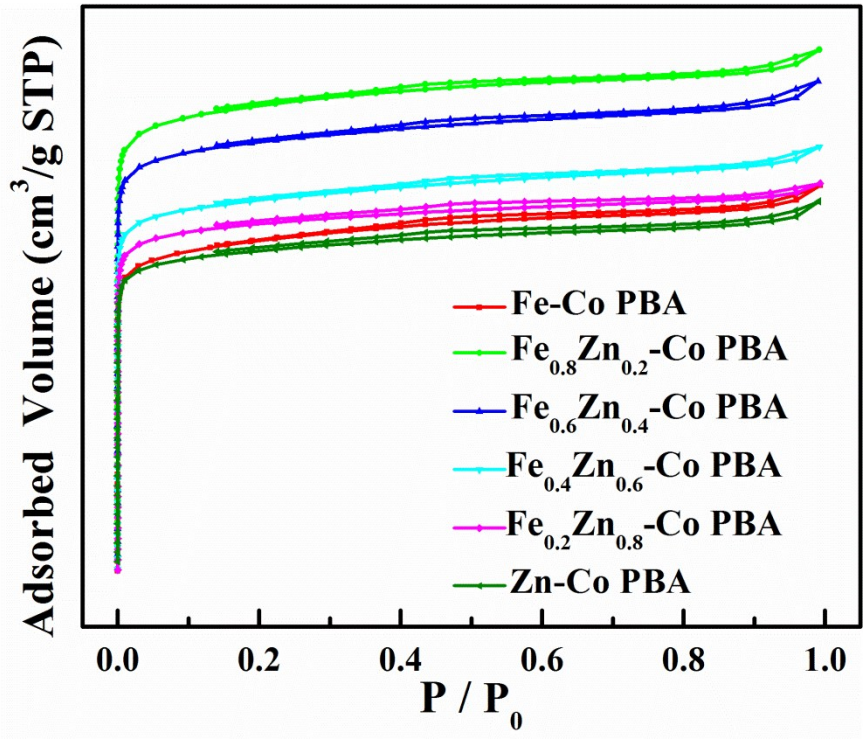

Fig. S1 N_2 adsorption/desorption isotherm of Fe_xZn_{1-x}-Co PBAs

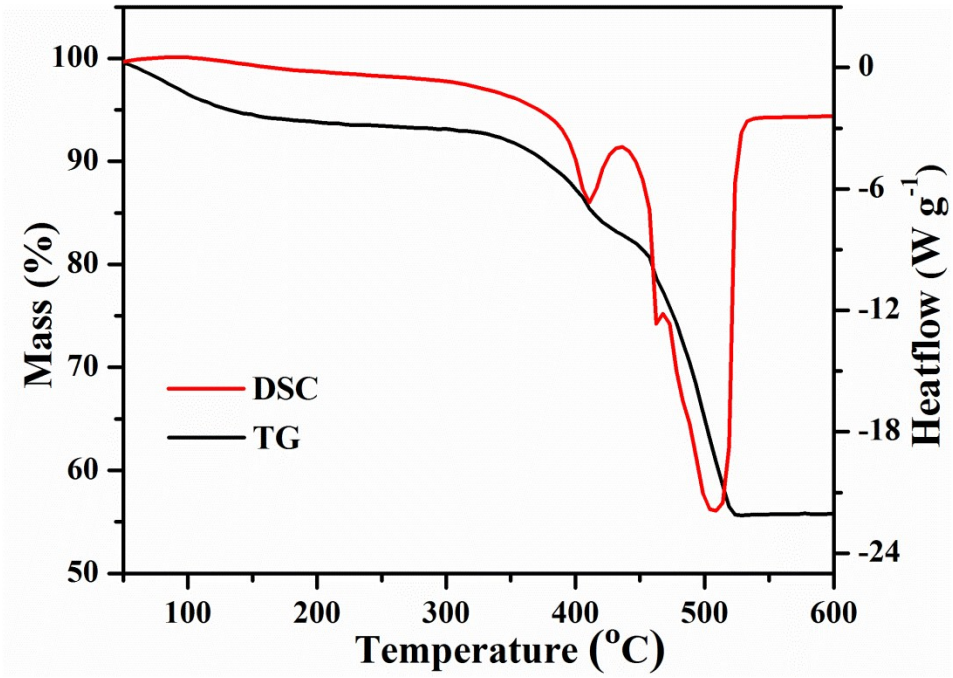

Fig. S2 TG and DSC curves of Zn-Co PBA

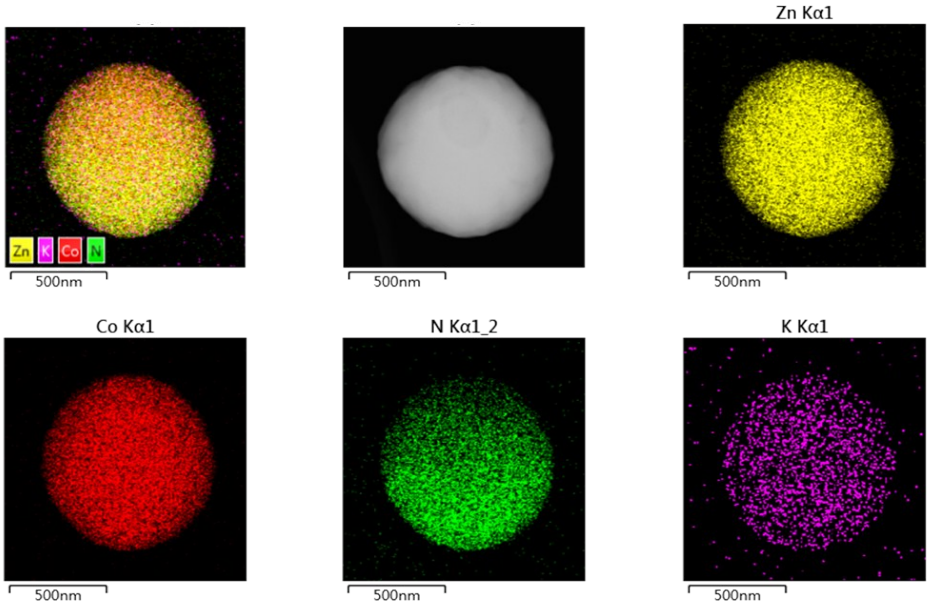

Fig. S3 Elemental mappings of Zn-Co PBA

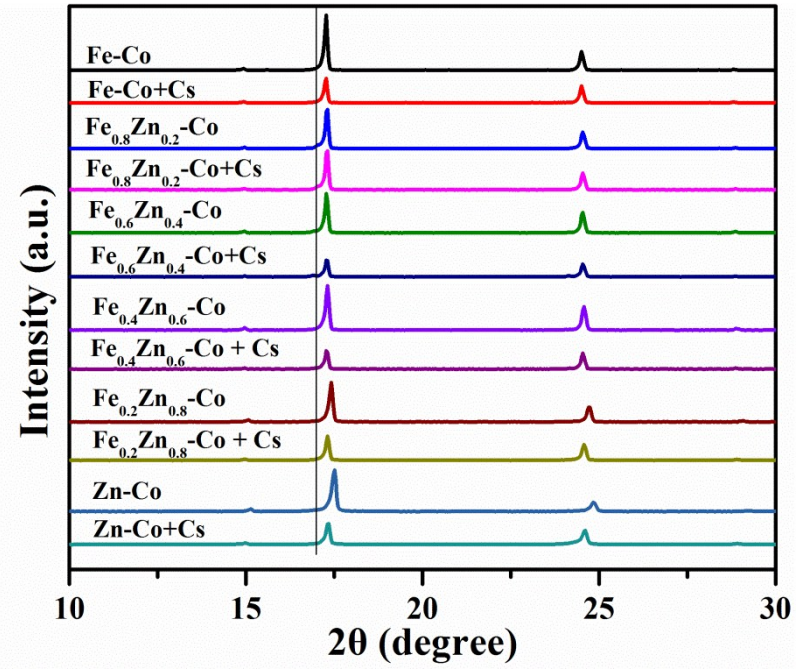

Fig. S4 Comparison of XRD patterns of the series of Fe_xZn_{1-x}-Co PBAs before and after adsorption

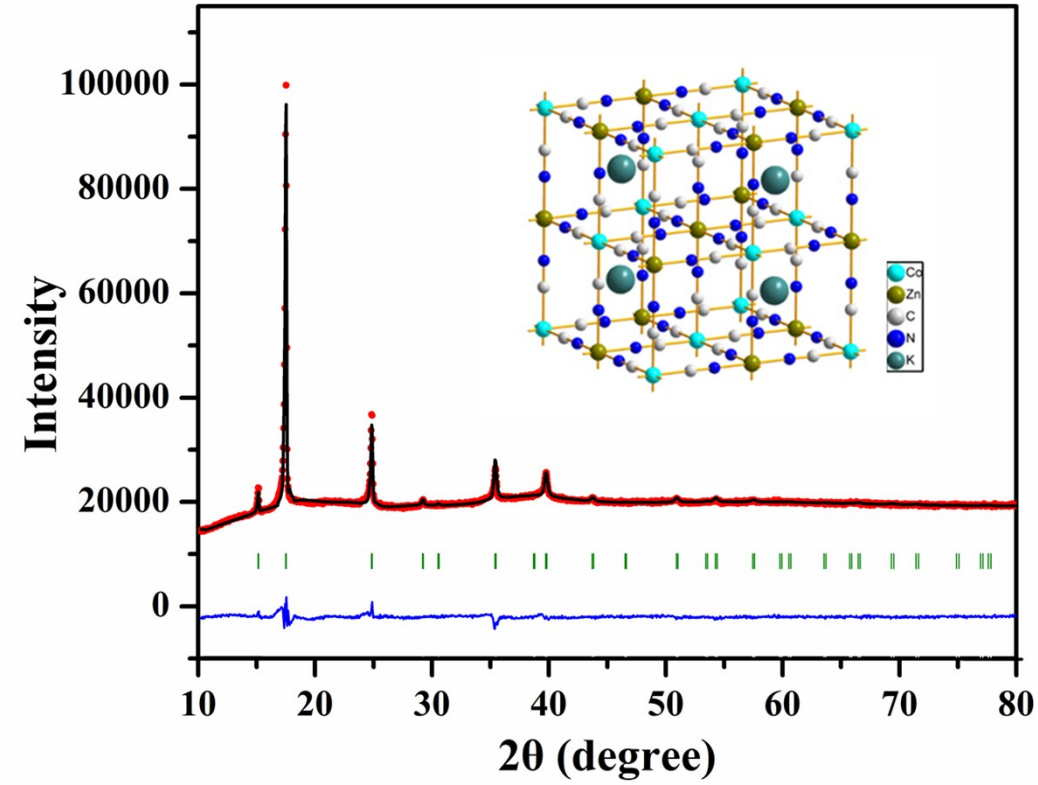

Fig. S5 The Rietveld structural refinement result of Zn-Co PBA (XRD powder patterns observed in red, calculated in black and difference profile in blue; a = 10.137 Å, space group Fm-3m, R_{wp} = 15.8%, R_{exp} = 7.93%. Inset: Crystal structure model of Zn-Co PBA, the water molecules are omitted.)

Table S1 BET surface area, pore size and micropore volume of the Fe_xZn_{1-x}-Co PBAs

material	Fe-Co	$Fe_{0.8}Zn_{0.2}$-Co	$Fe_{0.6}Zn_{0.4}$-Co	$Fe_{0.4}Zn_{0.6}$-Co	$Fe_{0.2}Zn_{0.8}$-Co	Zn-Co
BET(m^2 g^{-1})	569.49	754.65	697.19	604.25	549.64	507.71
H-K median pore width (nm)	0.6140	0.6139	0.6087	0.6106	0.6117	0.6096
micropore volume (cm^3 g^{-1})	0.1867	0.2753	0.2554	0.2192	0.2089	0.1907

Table S2 Isotherm parameters for the adsorption of Cs^+ using Zn-Co PBA

Langmuir model			Freundlich model		
k_L (L mg^{-1})	Q_m (mmol g^{-1})	R^2	K_F (L mg^{-1})	n	R^2
23.34	1.92	0.96	1.80	5.26	0.87

Table S3 pH of the solution before and after adsorption

Adsorbent	pH of CsCl solution (0.001M)	pH after adsorption
Fe-Co	6.74	5.28
$Fe_{0.8}Zn_{0.2}$-Co		5.38
$Fe_{0.6}Zn_{0.4}$-Co		5.57
$Fe_{0.4}Zn_{0.6}$-Co		5.37
$Fe_{0.2}Zn_{0.8}$-Co		5.26
Zn-Co		5.44

Table S4 Fractional atomic coordinates and occupancies of Zn-Co PBA.

Wyckoff	Atom	x	y	z	Occ	U, Å^2
4a	Co	0	0	0	0.47	0.035(12)
4b	Zn	0.5	0.5	0.5	1	0.28(2)
8c	O_1	0.25	0.25	0.25	0.45	0.45(18)
8c	K	0.25	0.25	0.25	0.06	0.45(18)
24e	C	0.19	0	0	0.47	0.4(8)
24e	N	0.31	0	0	0.47	0.12(7)
24e	O_2	0.21	0	0	0.52	0.24(13)

O_1: crystal water, O_2: coordinated water.

Table S5 Room temperature ^{57}Fe Mössbauer parameters of Fe-Co and $Fe_{0.6}Zn_{0.4}$-Co PBAs before and after sorption

Sample	Parameter	Fe(III) HS	Fe(II) HS		
			site 1	site 2	site 3
Fe-Co (before)	IS (mm s^{-1})	0.33	1.11	1.11	1.13
	QS (mm s^{-1})	0.72	0.88	1.52	1.97
	Area (%)	26.4	19.9	30.9	22.8
Fe-Co (after)	IS (mm s^{-1})	0.33	1.1	1.12	1.13
	QS (mm s^{-1})	1.05	0.92	1.53	2.08
	Area (%)	47.7	15.4	21.8	15.1
$Fe_{0.6}Zn_{0.4}$-Co (before)	IS (mm s^{-1})	0.33	1.23	1.15	1.1
	QS (mm s^{-1})	0.72	0.6	1.21	1.89
	Area (%)	44	3.2	21.3	31.5
$Fe_{0.6}Zn_{0.4}$-Co (after)	IS (mm s^{-1})	0.33	1.23	1.15	1.1
	QS (mm s^{-1})	0.72	0.55	1.9	2.06
	Area (%)	60.5	6.1	18.2	15.2

Table S6 Concentration of M^A and M^B released

M^A-M^B PBA	**Co-Fe**	**Cu-Fe**	**Mn-Co**	**Ni-Co**
$C_M{}^A$ (ppm)	8.139	10.25	9.579	19.33
$C_M{}^B$ (ppm)	0.0588	0.3731	1.868	0.9338

M^A-M^B PBA represents $M^A{}_3[M^B(CN)_6]_2$