Electronic Supplementary Information

Porous g-C_3N_4 Modified with Phenanthroline Diamide for Efficient and Ultrafast Adsorption of Palladium from Simulated High Level Liquid Waste

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Characterization

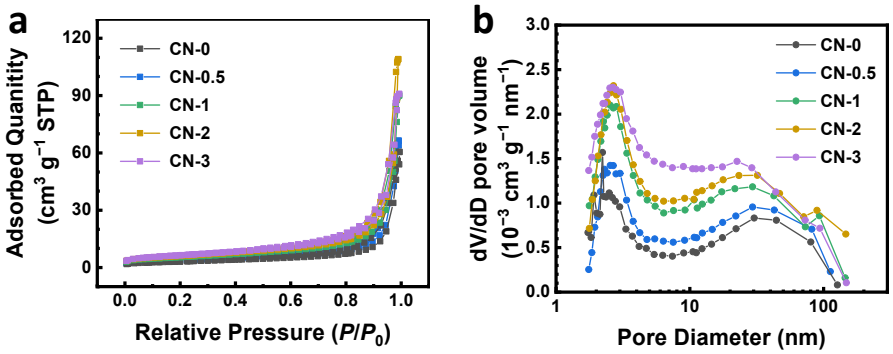


Fig. S1. N_2 adsorption–desorption isotherms (a) and the corresponding pore size distributions (b) of CN-x.

Table S1 The average pore width (nm) of the series of CN-x and CN-DAPhen.

	Average pore width (nm)
CN-0	16.00
CN-0.5	16.37
CN-1	16.83
CN-2	15.77
CN-3	15.38
CN-DAPhen	17.89

Table S2 Elemental analysis of CN-x.

	Mass conc. [%]				Atomic conc. [%]				
	N	C	H	O	N	C	H	O	C/N
CN-0	56.37	34.73	2.04	6.85	42.88	30.82	21.75	4.56	0.72
CN-0.5	59.15	35.04	1.90	3.91	45.47	31.43	20.47	2.63	0.69
CN-1	60.69	32.95	1.95	4.42	46.30	30.57	20.50	2.63	0.66
CN-2	60.08	33.85	1.90	4.17	46.27	30.41	20.51	2.81	0.65
CN-3	61.47	32.96	1.83	3.73	47.72	29.86	19.89	2.54	0.62

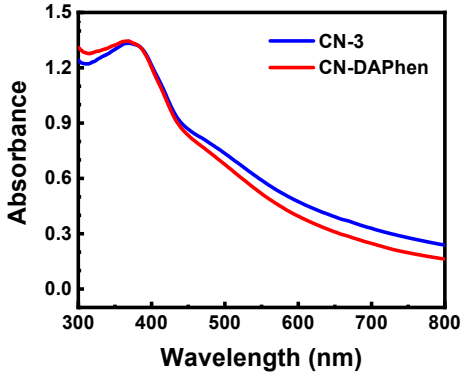


Fig. S2. UV–vis absorption spectra of CN-3 and CN-DAPhen.

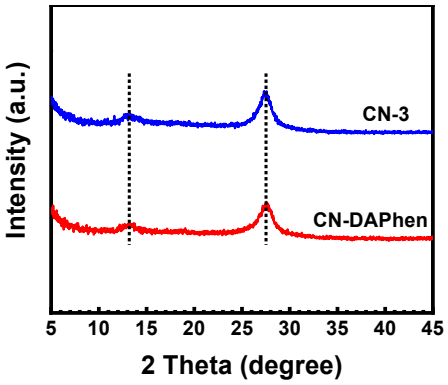


Fig. S3. Powder XRD patterns of CN-3 and CN-DAPhen.

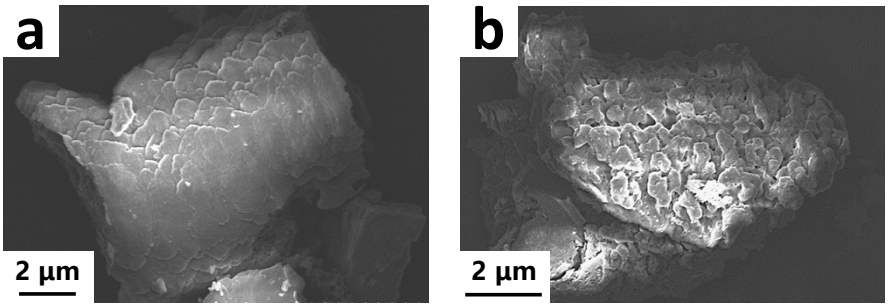


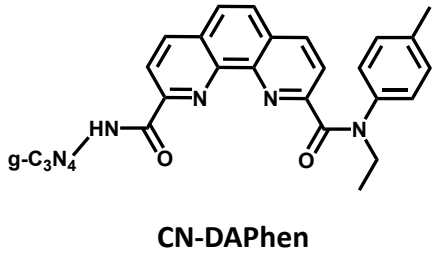
Fig. S4. SEM images of CN-0 (a) and CN-3(b).

The modification density of DAPhen groups

As shown in **Fig. S5**, there are 61/3 C atoms of C–C and 8/3 atoms of C–N in a DAPhen group. The modification density of DAPhen groups could be calculated according to the following **equations**:

$$n_{C(C-C\ in\ CN-3)}/n_{C(total\ in\ CN-3)} = [n_{C(C-C\ in\ CN-DAPhen)} - n_{C(C-C\ in\ DAPhen)}]/[n_{C(C-C\ in\ CN-DAP)} - n_{C(C-C\ in\ DAPhen)} + n_{C(C-N\ in\ CN-DAPhen)} + n_{C(C-N\ in\ DAPhen)}]$$

In CN-DAPhen, 100 mol C atoms correspond to x mol DAPhen groups. The mass of CN-DAPhen that had 100 mol C atoms was 2004 g. After entering the value of the corresponding part, the value of x is calculated to be 3.3164 mol, and the modified density is 3.3164 mol/2004 g, which is 1.655 mmol g^{-1}.



CN-DAPhen

Fig. S5. Chemical structures of CN-DAPhen.

Adsorption performance of CN-DAPhen and other adsorbents

Table S3 The maximum adsorption capacities (q_m) and the equilibrium adsorption times for Pd(II) adsorption on different functionalized materials.

Adsorbents	q_m (mg g^{-1})	Equilibrium time (min)	Adsorption conditions	Ref.
UiO-66-NH_2	167.0	＞180	T = 298 K, pH = 1.0	[1]
UiO-66-Pyta	294.1	5	T = 298 K, pH = 4.5	[2]
AP-XAD 16	8.0	30–45	T = 298 K, in 3M HNO_3	[3]
ASUiO-66	45.4	/	T = 298 K, in 3M HNO_3	[4]
ethylenediamine-modified magnetic chitosan nanoparticles	138.0	300	T = 298 K, pH = 5.7	[5]
chitosan/graphene oxide composite	216.9	720	T = 298 K, pH = 3.0–4.0	[6]
CN-DAPhen	390.63	< 5	T = 298 K, pH = 1.0	**This work**

DFT calculation

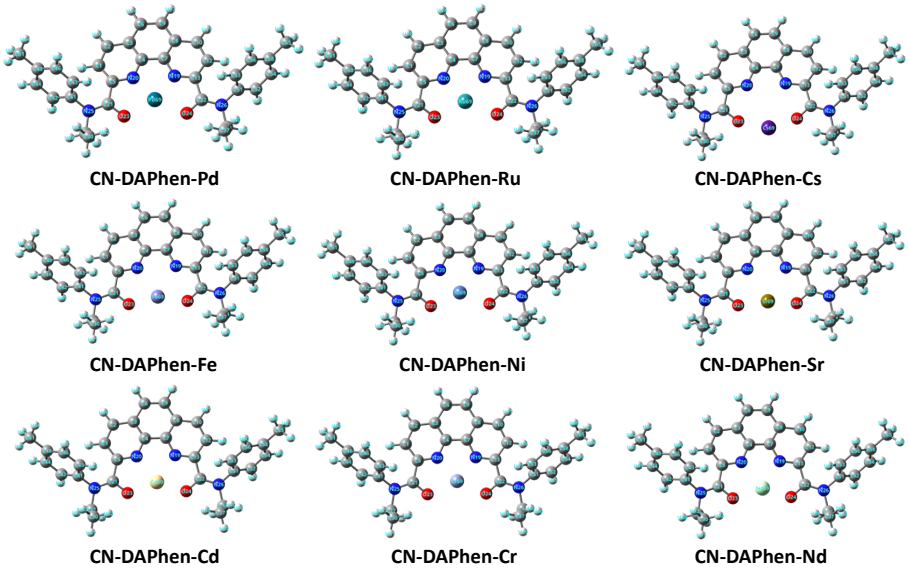


Fig. S6. The optimized structures of CN-DAPhen-M (M stands for different metal ions). Gray, light gray, red, blue, light blue, teal, light cyan, dark purple, purple, light purple, khaki, yellow, lavender and green spheres represent C, H, O, N, Pd, Ru, Cs, Fe, Ni, Sr, Cd, Cr, and Nd, respectively.

Table S4 Calculated bond distances (Å) and natural charges of complexes of CN-DAPhen with different metal ions (CN-DAPhen-M) (M stands for different metal ions).

	Bond length (Å)				Natural charges		
	M-N19	M-N20	M-O23	M-O24	Q_M	Q_N	Q_O
CN-DAPhen-Pd	1.887	1.886	1.982	1.990	2.032	-0.787	-0.548
CN-DAPhen-Ru	1.975	1.973	2.206	2.207	1.898	-0.702	-0.563
CN-DAPhen-Cs	2.078	2.083	2.143	2.141	0.922	-0.437	-0.497
CN-DAPhen-Fe	3.267	3.311	3.168	3.233	1.081	-0.413	-0.580
CN-DAPhen-Ni	2.484	2.484	2.029	2.022	1.062	-0.754	-0.538
CN-DAPhen-Sr	2.776	2.778	2.649	2.639	1.684	-0.546	-0.521
CN-DAPhen-Cd	2.391	2.395	2.396	2.351	1.512	-0.623	-0.509
CN-DAPhen-Cr	2.142	2.197	2.285	2.193	1.109	-0.750	-0.525
CN-DAPhen-Nd	2.257	2.291	2.118	2.055	1.436	-0.419	-0.563

Table S5 Changes in binding energy (ΔE), enthalpy (ΔH), Gibbs free energy (ΔG) (kJ/mol) for the complexation reaction of different metal ions and CN-DAPhen.

	ΔE (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
CN-DAPhen + Pd^{2+} → [CN-DAPhen-Pd]$^{2+}$	−599.07	−601.55	−546.65
CN-DAPhen + Ru^{3+} → [CN-DAPhen-Ru]$^{3+}$	−520.64	−523.12	−475.07
CN-DAPhen + Cs^{+} → [CN-DAPhen-Cs]$^{+}$	−79.55	−82.03	−26.68
CN-DAPhen + Fe^{3+} → [CN-DAPhen-Fe]$^{3+}$	−98.85	−101.61	−78.36
CN-DAPhen + Ni^{2+} → [CN-DAPhen-Ni]$^{2+}$	−360.08	−362.56	−310.82
CN-DAPhen + Sr^{2+} → [CN-DAPhen-Sr]$^{2+}$	−70.49	−72.97	−35.32
CN-DAPhen + Cd^{2+} → [CN-DAPhen-Cd]$^{2+}$	−161.66	−164.13	−122.25
CN-DAPhen + Cr^{3+} → [CN-DAPhen-Cr]$^{3+}$	−191.30	−190.80	−196.53
CN-DAPhen + Nd^{3+} → [CN-DAPhen-Nd]$^{3+}$	−157.20	−160.11	−125.05

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