Efficient recovery of gold from solution with thiocyanate-modified Zr-MOF: adsorption properties and DFT calculations

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Supporting Information

1.Experimental section

1.1 Materials

Zirconium tetrachloride ($ZrCl_4$), 2-amino-terephthalic acid, ethanol, and dimethylformamide (DMF) were purchased from Shanghai Aladdin Reagent Co., LTD. $HAuCl_4 \cdot 3H_2O$ was obtained from Anaiji Chemical Technology Co., LTD. Analytical-grade reagents were available without additional purification. We used deionized water to prepare all solutions.

1.2 Equipment and Characterization

Bruker TENSOR27 was used on the collection Fourier transform infrared (FT-IR) data. The produced materials' surface morphology and specific surface area were observed using scanning electron microscopy (SU8010, SEM) and ASAP 2020 PLUS HD88, respectively. Data on the distribution and composition of elements were gathered using X-ray photoelectron spectroscopy (XPS) a Thermo ESCALAB 250 XI. Utilizing inductively coupled plasma atomic emission spectroscopy (ICP-OES, AGILENT 5100, USA), precise amounts of all metals ion were confirmed.

1.3 Relevant calculation formulas

The adsorption capacity value at equilibrium (q_e) of Zr-MOF might be calculated by Eqn. (S1). adsorption efficiency might be calculated by Eqn. (S2) Where C_0 and C_e (mg/L) represented the initial and equilibrium Au(III)

contents, respectively, V (L) and m (g) represented reaction liquid volume, and the mass of Zr-MOFs, respectively.

$$q_e = \frac{C_0 - C_e}{m} V \qquad \text{Eqn. (S1)}$$

$$\text{adsorption efficiency} = \frac{C_0 - C_e}{C_e} \times 100\% \qquad \text{Eqn. (S2)}$$

In Eqn. (S3) and (S4) , k_1 (min^{-1}) and k_2 ($g \cdot min^{-1} \cdot mg^{-1}$) denoted the rate constants of the pseudo-first-order and pseudo-second-order models, respectively; t (min) represented the adsorption time, q_e and q_t (mg/g) represented the amount of Au(III) at the adsorption equilibrium and anytime;

$$q_t = q_e(1 - e^{-k_1 t}) \qquad \text{Eqn. (S3)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{Eqn. (S4)}$$

The adsorption behavior has been estimated based on models of Langmuir and Freundlich isotherms by Eqn. (S5) and (S6),where q_m was the saturated adsorption capacity, k_L and K_F denoted the binding constant of the Langmuir and the Freundlich isothermal adsorption systems. C_e is the residual concentration of Au (III). $1/n$ between 0 and 1, indicates easy adsorption.

$$q_e = \frac{k_L q_m C_r}{1 + k_L C_e} \qquad \text{Eqn. (S5)}$$

$$q_e = K_F C_e^{1/n} \qquad \text{Eqn. (S6)}$$

The thermodynamic data were fitted via Eqn (S7) and (S8), including b(the adsorption equilibrium constant), R (8.314 J/mol/K), T (temperature, K), ΔG (Gibbs free energy) , ΔH (Enthalpy change), and ΔS (Entropy change).

$$\lg b = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \qquad \text{Eqn. (S7)}$$

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eqn. (S8)}$$

Q represented the adsorption amount of different ions, C_i and C_e are the initial and equilibrium ions concentration, and m was the mass of Zr-MOF. V was the

solution volume.The relative affinity between the ions and Zr-MOF could be expressed as an adsorption distribution coefficient (K_Q) and selectivity coefficient (K), which can be found in Eqn S(9) and S(10)

$$K_Q = \frac{Q}{C_e} = \frac{C_i - C_e}{C_e} \cdot \frac{V}{m} \qquad \text{Eqn. (S9)}$$

$$K = \frac{K_Q(Au^{3+})}{K_Q(coexisting\ ions)} \qquad \text{Eqn. (S10)}$$

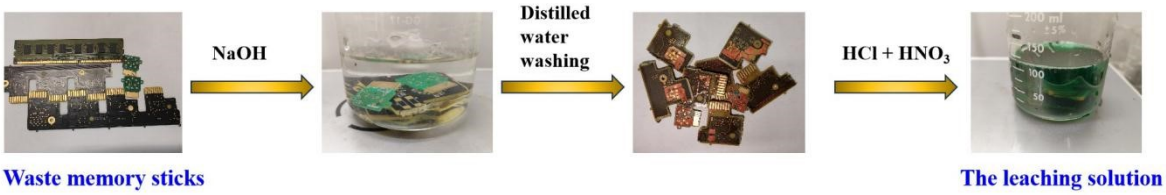
The Dmol3 module of Material Studio 2020 was utilized to execute the DFT analyses. The interactions between the core and electrons were described using the Perdew-Burke-Ernzerhof (PBE) function in the generalized gradient approximation (GGA) approach. The criteria for force and energy convergence were established at 0.002 Ha $Å^{-1}$ and 10^{-5} Ha, correspondingly.

ΔE，which is the binding energy, was calculated with the equation shown in Eqn. (S11)

$$\Delta E(kcal/mol) = 627.5 \times [E_{total}(Ha) - E_{MOF}(Ha) - E_{AuCl_4^-}(Ha)] \qquad \text{Eqn. (S11)}$$

E_{total}, E_{MOF}, and E_{AuCl4}^- are the energy of system, UiO-66-NCS and $AuCl_4^-$, respectively.

2. Characterizations



Scheme.S1 The treatment processes of actual e-waste

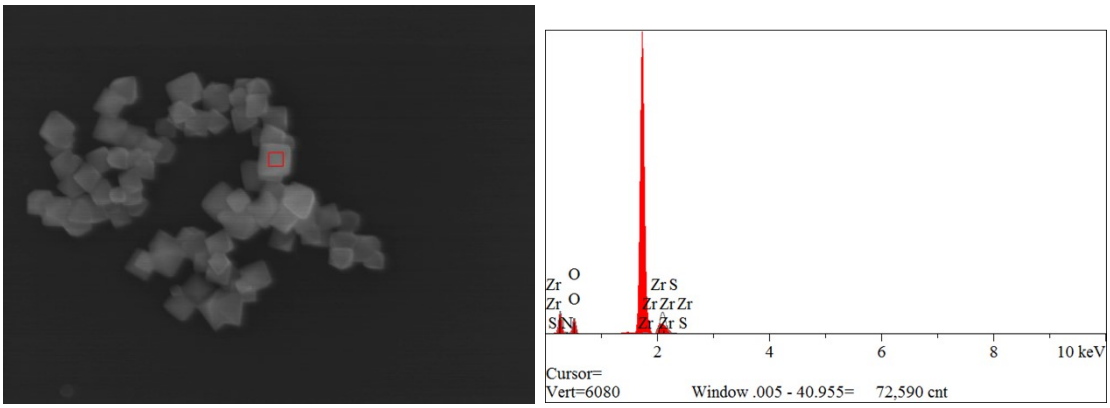


Fig. S1. EDS analysis of UiO-66-NCS

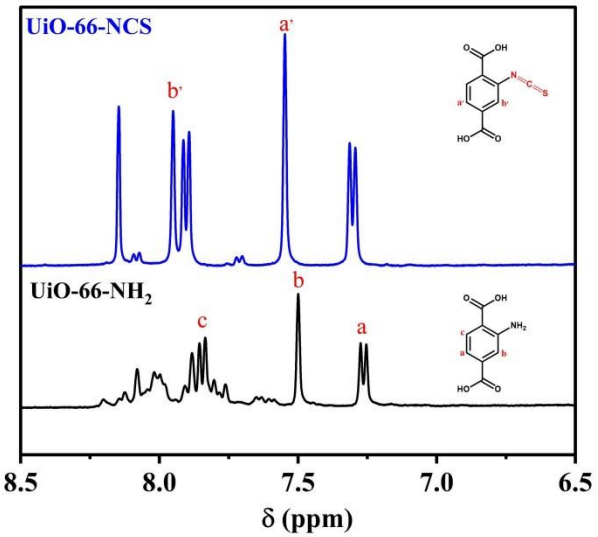


Fig. S2. HNMR analysis of UiO-66-NCS and UiO-66-NH_2

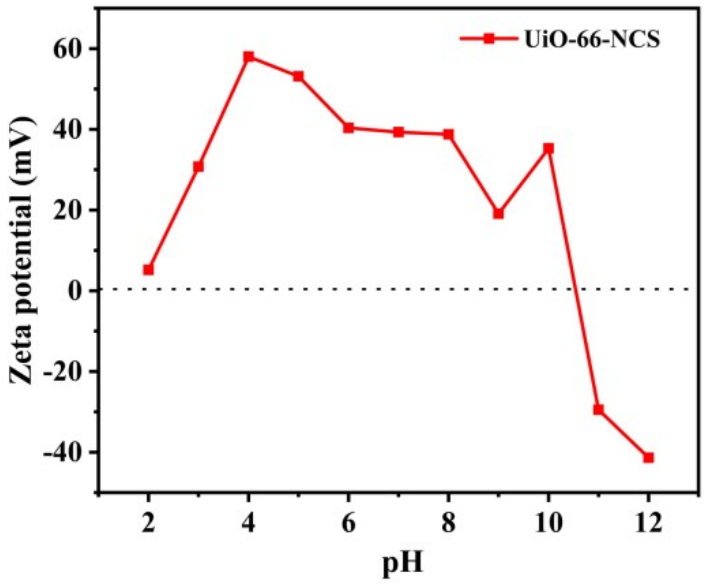


Fig. S3. Effects of pH on the zeta potential of UiO-66-NCS

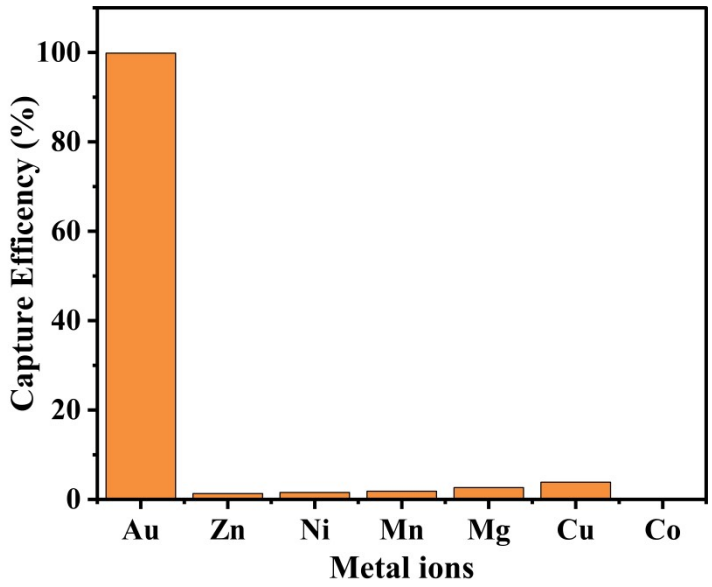


Fig.S4 The efficiency to capture Au(III) from the mixed metal ions in simulated the leach solution.

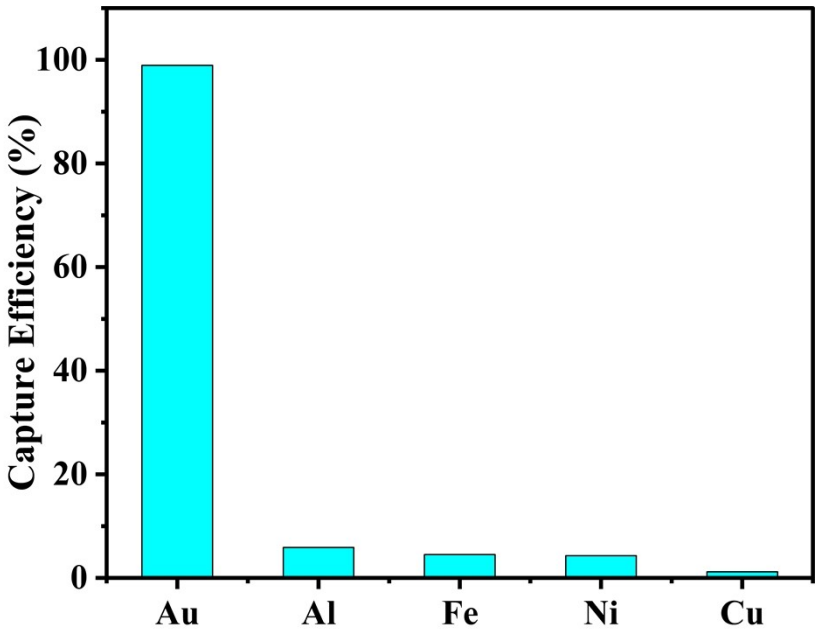


Fig.S5. The efficiency to capture Au(III) from actual e-waste leaching solution by UiO-66-NCS

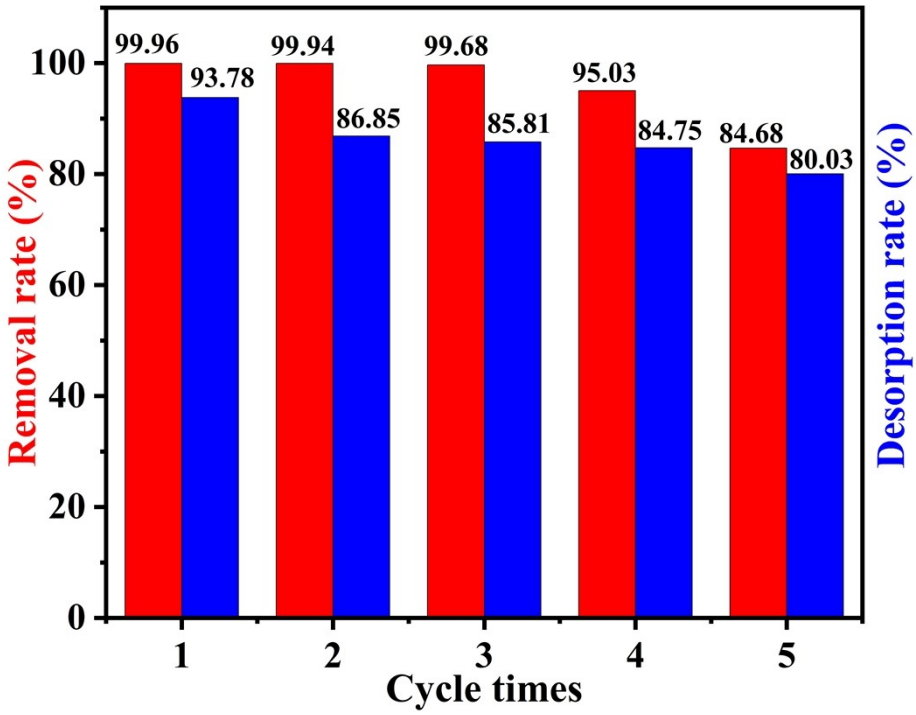


Fig.S6. reusability of UiO-66-NCS

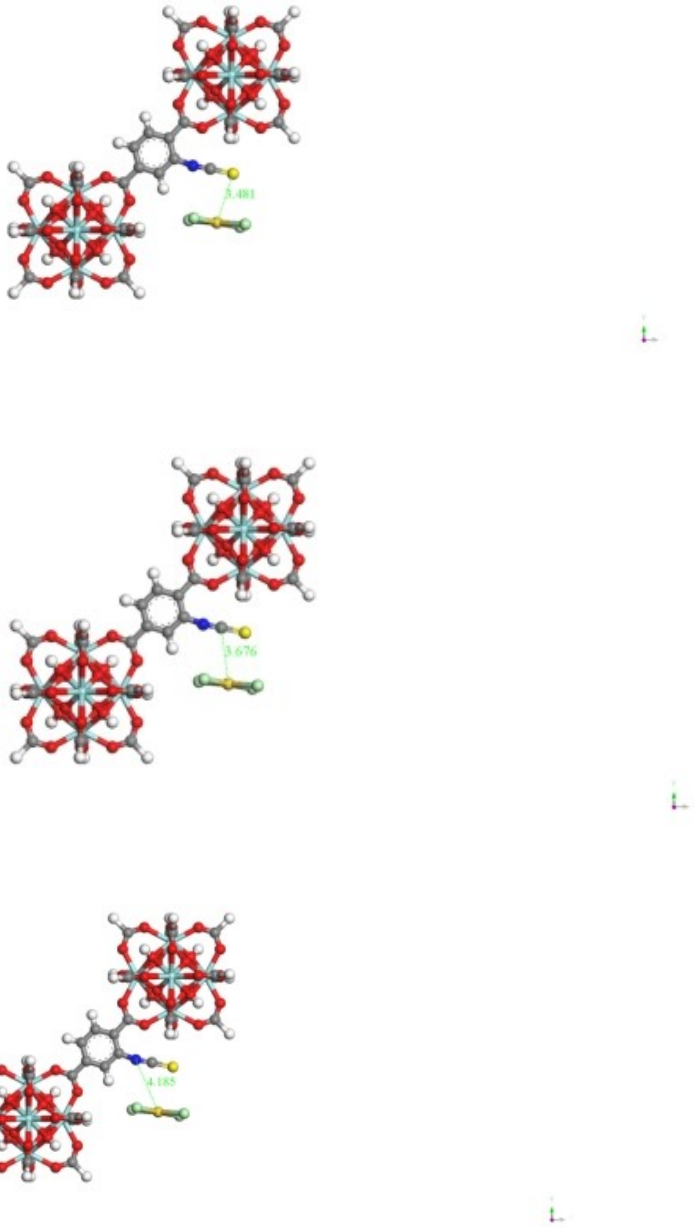


Fig.S7 The optimized geometries of the complexes and the binding energy, as well as the bond length.The grey, white, red, blue, yellow and yellow with green corresponds to C, H, O, N, S and Au,Cl atoms, respectively.

Table. S1 BET surface area and Pore characteristics of UiO-66-NH_2 and UiO-66-NCS

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore width (nm)
UiO-66-NH_2	709.80	0.39	2.08
UiO-66-NCS	620.61	0.34	2.11

Table. S2 The fitting parameters of dynamic models

Kinetic models	Parameters	Values
Pseudo first-order	q_e	194.33
	k_1	0.03627
	R^2	0.986
Pseudo second-order	q_e	202.43
	k_2	0.000305
	R^2	0.999

Table S3. Comparison of the Adsorption Capacities of Au(III) onto Various Adsorbents

Adsorbents	pH	t (min)	T (K)	Q_e (mg/g)	Ref
UiO-66-ATU	3	1440 min	298	227.68	[44]
UiO-66-MTD	6	180 min	298	301.5	[20]
ZT-MOF	7	480 min	298	333.34	[18]
UiO-66-TA	2	240 min	298	372	[19]
FSUN-50	5.54	1440 min	298	463.85	[31]
FSUN-10	5.58	1440 min	298	611.818	[31]
DONA-MOF	9.17	120 min	303	637.5	[45]
UiO-66-NH_2/CTS	5	720 min	298	671	[46]
UiO-66-BTU	2	720 min	308	680.2	[22]
UiO-66-NCS	4	1440 min	298	675.53	This work

Table S4 The fitting parameters of isotherm models

Isotherm model	Parameters	Values
Langmuir	q_m	665.643
	K_L	0.72682
	R^2	0.908
	R-χ2	2975.82
Freundlich	K_F	358.161
	1/n	0.12461
	R^2	0.854
	R-χ2	4697.13

Table S5 Thermodynamic modelling parameters of UiO-66-NCS

T (K)	*b*	ΔG (kJ/mol)	ΔH (kJ/mol·K)	ΔS (kJ/mol)
298	1.82326	-0.9269		
308	1.99043	-2.3349		
318	3.50045	-3.7429	41.0315	0.1408
328	6.8125	-5.1509		
338	11.62626	-6.5589		

Table S6 The distribution coefficient (KD) and selectivity coefficient (K) of Au^{3+} over other cations.

metal ion	UiO-66-NCS		
	R(%)	K_Q (L/g)	K
Zn	1.30	0.0132	50429.55
Ni	1.55	0.0157	42399.36
Mn	1.85	0.0188	35407.978
Mg	2.65	0.0272	24473.16
Cu	3.85	0.04	16641.75
Co	0.05	$5*10^{-4}$	1331340
Au	99.85	665.67	-

Table S7 Ionic radii, electronegativity and covalency index of metal ions

metal ion	ionic radius	electronegativity	covalent index	atomic weight
Zn	0.74	1.81	2.42	65.38
Ni	0.69	1.91	2.52	58.69
Mn	0.67	1.55	1.61	54.94
Mg	0.72	1.31	1.24	24.31
Cu	0.73	1.90	2.64	63.55
Co	0.74	1.88	2.62	58.93
Au	0.85	2.54	5.48	196.97

Table. S8. Elemental composition and content of metal ions in actual e-waste leaching solution

Element(mg/L)	Au	Al	Fe	Ni	Cu
Original content	100.220	254.110	42.690	1027.910	29678.510
Remaining content	1.04	239.17	40.76	983.82	29324.64
Capture efficiency (%)	98.96	5.88	4.52	4.29	1.19

Table S9 the binding energy of related models

E_{total}(Ha)	E_{mof}(Ha)	E_{AuCl4-}(Ha)	ΔE(kcal/mol)
-68665.06682	-48955.56428	-19709.48879	-8.63