Supporting Information

SnS Micro/Nanocrystals with Urchinlike Architectures for Capture of Au(III), Pt(IV), and Pd(II)

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Experimental section

Reagents

Polyvinyl pyrrolidone (PVP, M = 40000), Pluronic F-127 (F127, average molecular weight 12600), and thioacetamide (CH_4N_2S) were provided by Sigma-Aldrich. Tin (II) chloride dehydrate ($SnCl_2$) and ethylene glycol were purchased from Aladdin Co. (Shanghai, China). Hydrochloric acid (HCl), and absolute ethyl alcohol were obtained from Beijing Chemical Corp. (China).

Standard stock solutions (1000 mg L^{-1}) of Au^{3+}, Pd^{2+}, and Pt^{4+} containing 1.5 mol L^{-1} HCl, were purchased from Aladdin Co. The stock solutions (1000 mg L^{-1}) of Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, and Na^{+} were separately prepared by standard methods from $PbCl_2$, $CdCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $MnCl_2$, $FeCl_3$, $CaCl_2$, $MgCl_2$, and NaCl. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. All the reagents used were of analytical grade or better. All glass vessels used for analysis were cleaned before use by soaking them in 10 % nitric acid solution for at least 24 h and then rinsed thoroughly with ultrapure water.

Apparatus

The measurements of metal ion were performed by a flame atomic absorption spectrometry (FAAS, TAS-990, Beijing Purkinje General Instruments Co. Ltd., China). Operational parameters of wavelength of Au^{3+}, Pd^{2+}, and Pt^{4+} were 242.8 nm, 244.8 nm and 265.9 nm, respectively, while that was recommended by the manufacturer for the determination of other metal ions.

A PB-10 digital pH meter (Sartorius Corporation, Germany) was carried out for the pH

measurements. Adjustment of pH was under taken using HCl and NaOH. Deionized water used throughout all experiments was purified with the Millipore system (Millipore, Milford, MA, USA).

Synthesis of urchinlike SnS microcrystals

Urchinlike SnS was prepared according to a one-pot hydrothermal synthesis. 0.2888 g of $SnCl_2$ and 0.0962 g of thioacetamide were dissolved in 1.6 mL of ethylene glycol, respectively. 500 mg of PVP (M.W. 40000) was added to 25 mL of ethylene glycol under stirring to obtain a homogeneous solution. Afterwards, the above $SnCl_2$ and thioacetamide solution were added to the prepared PVP-ethylene glycol solution, and the obtained solution was well dispersed by sonication for 10 min. Finally, the mixture was transferred into an autoclave and reacted at 160 °C for 12 h in an oven. The resultant product was collected by centrifugation, washed seven times with deionized water and anhydrous ethanol, respectively, and dried at 50 °C overnight under vacuum.

The preparation process of product using F127 is similar to the above method, except for the addition of F127. The synthesis procedure for different product with PVP is same to that for the synthesis of urchinlike SnS microcrystals except that varied amount (0.01 – 6.0 g) of PVP is added into the starting reaction mixture.

Material characterization

X-ray diffraction (XRD) was obtained using a powder diffractometer (Bruker D8 Advanced Diffractometer System) with a Cu Ka (1.5418 Å) source. Scanning electron microscope (SEM) measurements were carried out on a FEI Nova Nano SEM-450 equipped with an energy dispersive X-ray spectrometer (EDX) by an accelerating voltage of 10 kV.

Raman spectra were measured on a HORIBA Raman microscope with 532 nm laser excitation. A FEI Tecnai G2 Spirit Bio was used to obtain the Transmission electron microscopy (TEM) images on operating at 80 kV. Power samples were prepared by drop-drying a diluted suspension of the samples in ethanol onto a holey carbon copper grid that was dried under ambient conditions before the measurements. High-resolution TEM (HRTEM) and selected area electron diffraction (SAED) pattern were performed on FEI TF-20 at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was taken on a VG Multilab 2000 X-ray photoelectron spectrometer with Al Kα radiation. Nitrogen adsorption/desorption curves were determined using a Micromeritcs ASAP 2010 surface area analyzer with Brunauer-Emmett-Teller (BET) measurement. Thermogravimetric curves (TGA) were collected using a DSC-TGA thermogravimetric analyzer (TGA/DSC 3+, METTLER). The temperature scanning scope was from room temperature to 1000 °C with a heating rate of 10 °C min^{-1} and the atmosphere was N_2.

Batch adsorption experiments

10 mL of certain concentration metal ions were added to 2 ± 0.2 mg of urchinlike SnS as an adsorbent in a vial (50 mL), followed by stirring in a rotary shaker to attain equilibrium. After the adsorption equilibrium, the aqueous phase was filtered and then concentration of residual metal ions was analyzed by FAAS. All the adsorption experiments were performed at ambient condition unless otherwise stated. To research the effect of adsorbent dosage on the uptake of the SnS, the amount of the adsorbent was in the range of 2 – 20 mg. For pH test, the initial pH value of the metal ions was adjusted using 2 M HCl and 2 M NaOH. For kinetic studies, a typical adsorption experiment was performed under 150 mg L^{-1} of Au^{3+}, 25 mg L^{-1}

of Pd^{2+}, and 25 mg L^{-1} of Pt^{4+} with 2 ± 0.2 mg of adsorbent addition for Au^{3+}, Pd^{2+}, and Pt^{4+}, and the three metal ions concentration at different time intervals was determined. Adsorption isotherm experiments were conducted by adding 2 ± 0.2 mg of adsorbent into Au^{3+}, Pd^{2+}, and Pt^{4+} solution with concentrations ranging from 20 to 300 mg L^{-1}.

The adsorbed amount (q_e, mg g^{-1}) and the distribution coefficient (K_d) were calculated according to following Eq. (1) and (2).

$$q_e = \frac{(C_i - C_e) \times V}{m} \quad (1)$$

$$K_d = \left(\frac{C_i - C_e}{C_e} \right) \times \frac{V}{m} \quad (2)$$

In Eq. (1) and (2), C_i is the initial concentration of metal ions (mg L^{-1}), and C_e is final equilibrium concentrations of metal ions (mg L^{-1}). m (g) and V (L) are the adsorbents' weight and the volume of the initial metal ion solution respectively.

Desorption experiment

The desorption of metal ions on urchinlike SnS was carried out by washing the adsorbent with deionized water several times, then adding the mixture of 1.0 M HCl and 0.5 M thiourea solution to the adsorbent and leaving for 30 min to achieve complete desorption. The recovery of the SnS adsorbents for 150 mg L^{-1} of Au^{3+}, 25 mg L^{-1} of Pd^{2+}, and 25 mg L^{-1} of Pt^{4+} was tested over six cycles to evaluate their reusability.

Adsorption isotherm

The Langmuir, Freundlich and Temkin isotherm models were expressed linearly as Eq.3–5:

Langmuir model $$\frac{C_e}{q_e} = C_e \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \quad (3)$$

Freundlich model $$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Temkin model $q_e = B\ln A + B\ln C_e$ (5)

where C_e (mg L^{-1}) is the equilibrium concentration of the solute, q_e is the amount adsorbed at equilibrium (mg g^{-1}), q_{max} is the maximum adsorption at monolayer coverage (mg g^{-1}), K_L is the adsorption equilibrium constant (L mg^{-1}), K_f is the Freundlich isotherm constants, and n is the Freundlich exponent. For the Langmuir isotherm model, q_{max} and K_L could be obtained from the slope and intercept of the linear plot of C_e/q_e *vs.* C_e. For the Freundlich isotherm model, K_f and n can be calculated by the slope and intercept of the linear plot of log q_e *vs.* log C_e.

Adsorption kinetics

Conventional kinetic models, e.g. pseudo-first-order, pseudo-second-order, and intra-particle diffusion model, were used to fit the experimental data in this work. The pseudo-first-order and pseudo-second-order models after transformation into linear form were expressed in as Eq. 6 and 7,

Pseudo-first-order $\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$ (6)

Pseudo-second-order $\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t$ (7)

where q_t and q_e (mg g^{-1}) are the amounts of metal ions adsorbed at any time t (min) and at equilibrium, respectively, and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constants of pseudo-first-order and pseudo-second-order adsorption. k_1 was determined by plotting log ($q_e - q_t$) *vs.* t in the pseudo-first-order model. Similarly, k_2 and q_e were calculated from pseudo-second-order model by plotting t/q_t *vs.* t.

Adsorption thermodynamics

The effect of the temperature on the adsorption of Au^{3+}, Pd^{2+}, and Pt^{4+} for MoS_2 was studied at different temperatures ranging from 278 K to 308 K. The thermodynamic parameters associated with the sorption viz., free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$), were calculated as follow equation (8 and 9).

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R}\frac{1}{T} \tag{8}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{9}$$

Where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), and T (K) is the absolution temperature. $\Delta H°$ and $\Delta S°$ could be calculated from the slope and intercept of the linear plot of $\ln K_d$ *versus* $1/T$. $\Delta G°$ was obtained from equation (9).

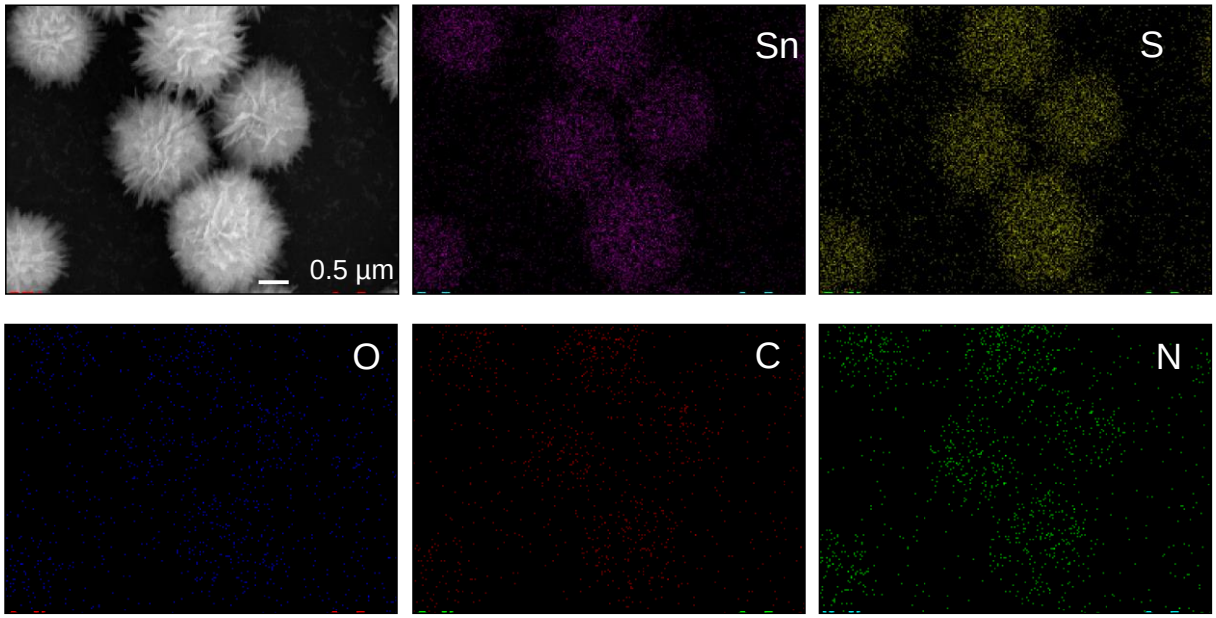

Figure S1. SEM image and the corresponding EDX mapping images of the urchinlike SnS microcrystals

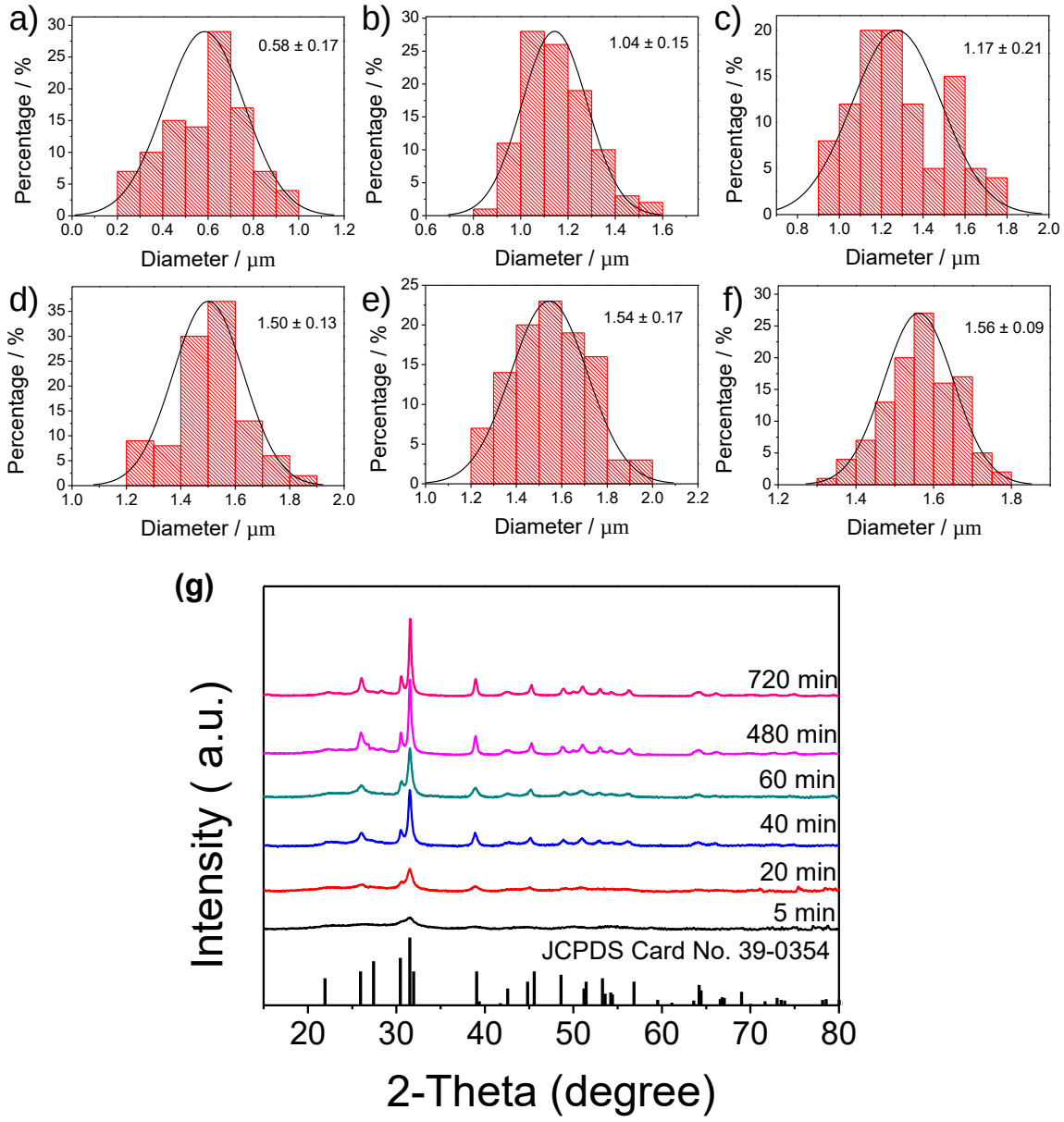

Figure S2. (a-f) Diameter graph and (g) XRD patterns of the samples prepared at 5 min, 20 min, 40 min, 60 min, 480 min, and 720 min, respectively.

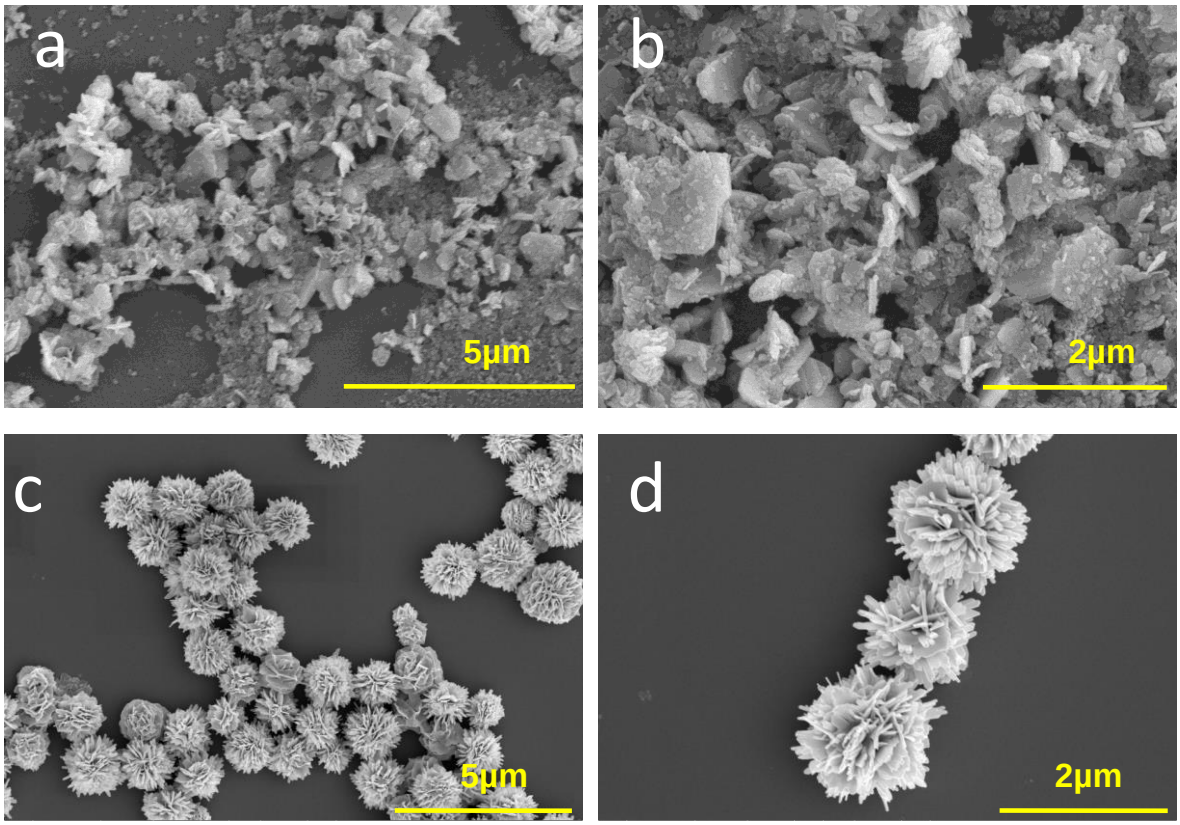

Figure S3. SEM image of urchinlike SnS microcrystals synthesized by the same hydrothermal method without (a, b) and with PVP (c, d).

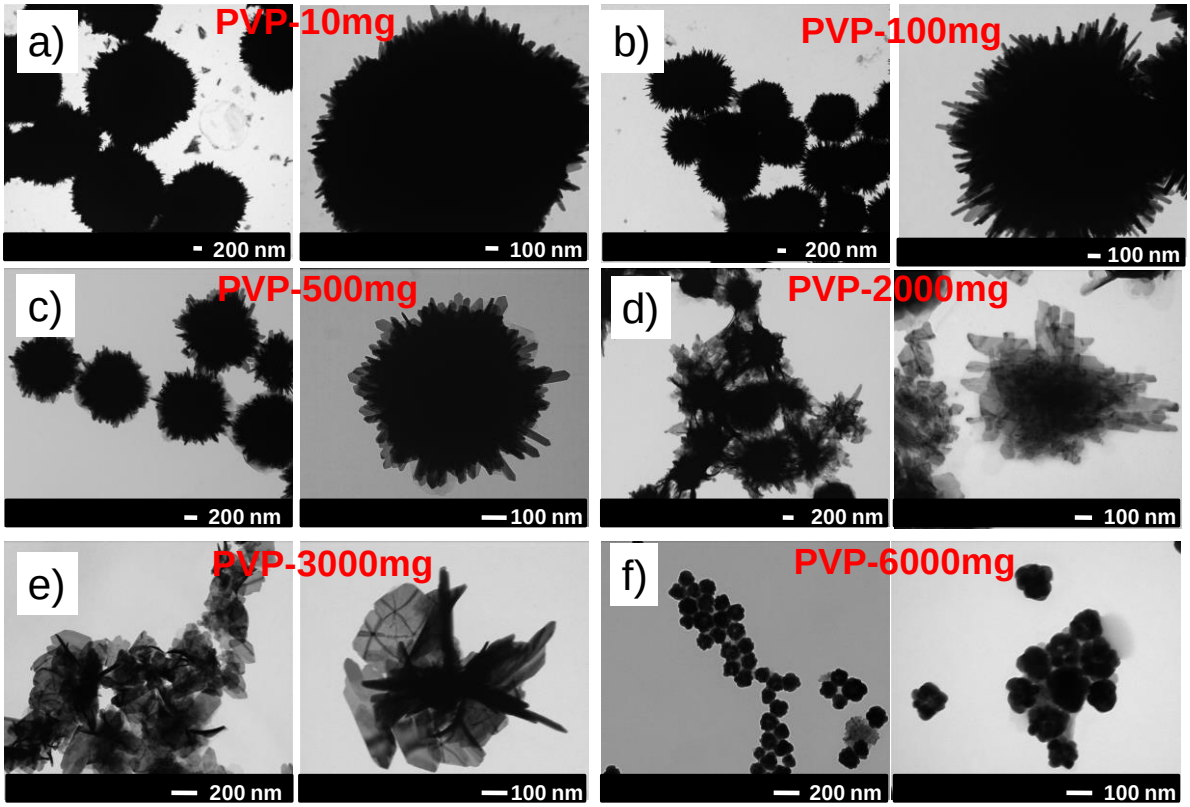

Figure S4. TEM images of the samples prepared with different PVP amount in the synthesis system.

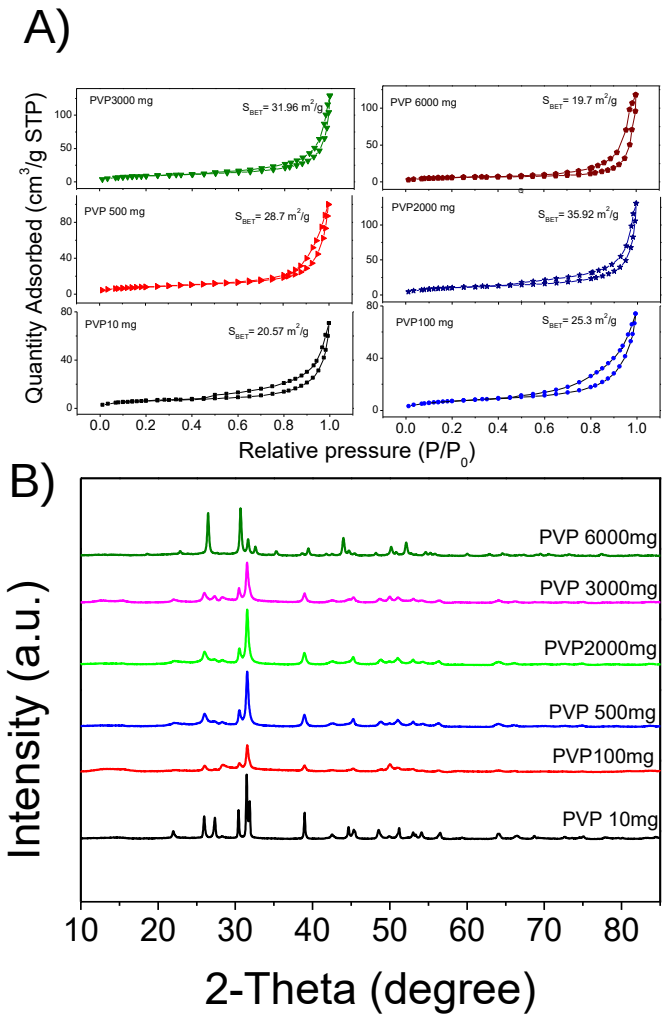

Figure S5. (A) N_2 adsorption-desorption curves and (B) XRD patterns of the samples prepared with different PVP amount.

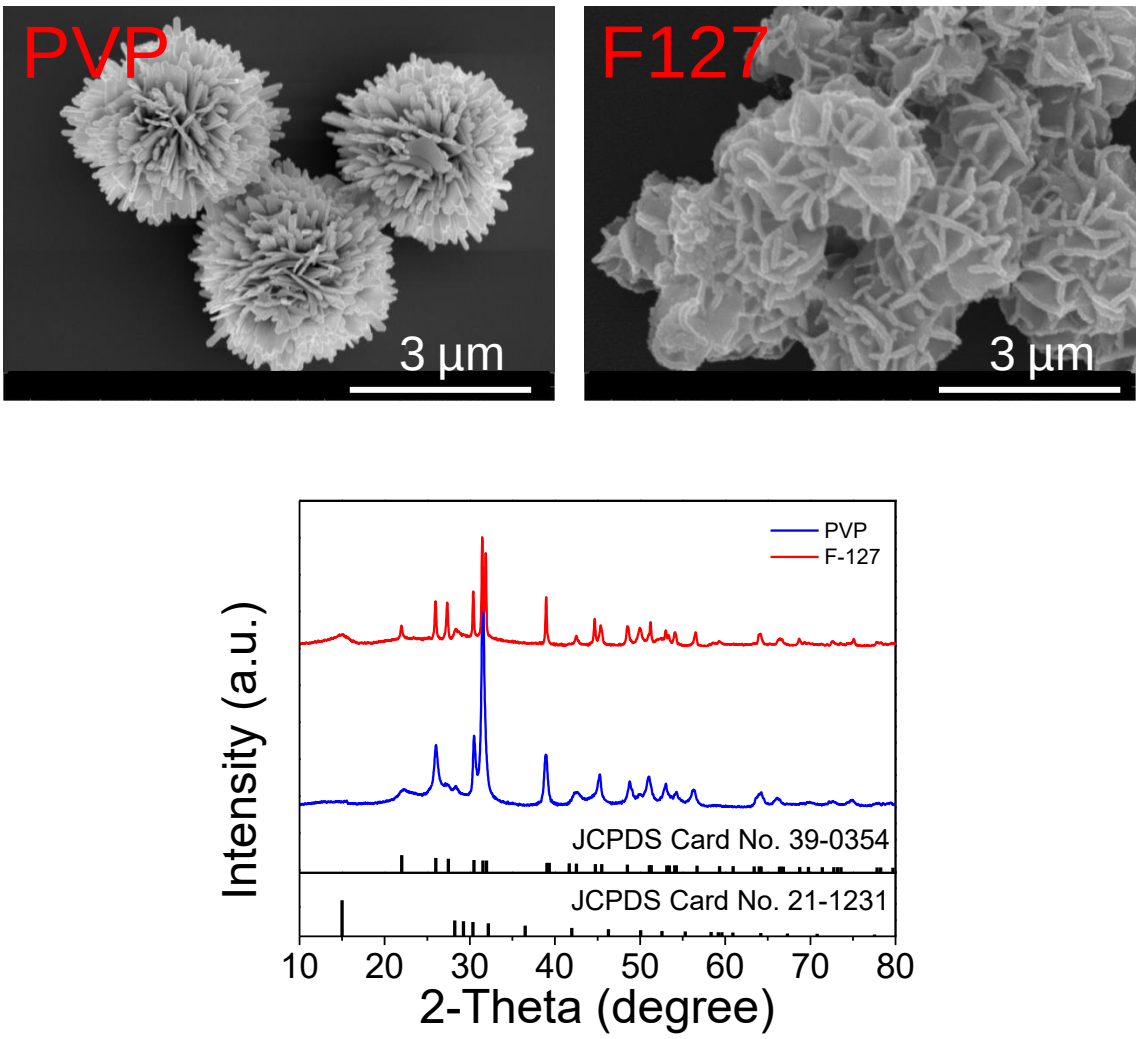

Figure S6. SEM images and XRD patterns of the samples prepared with PVP and F127.

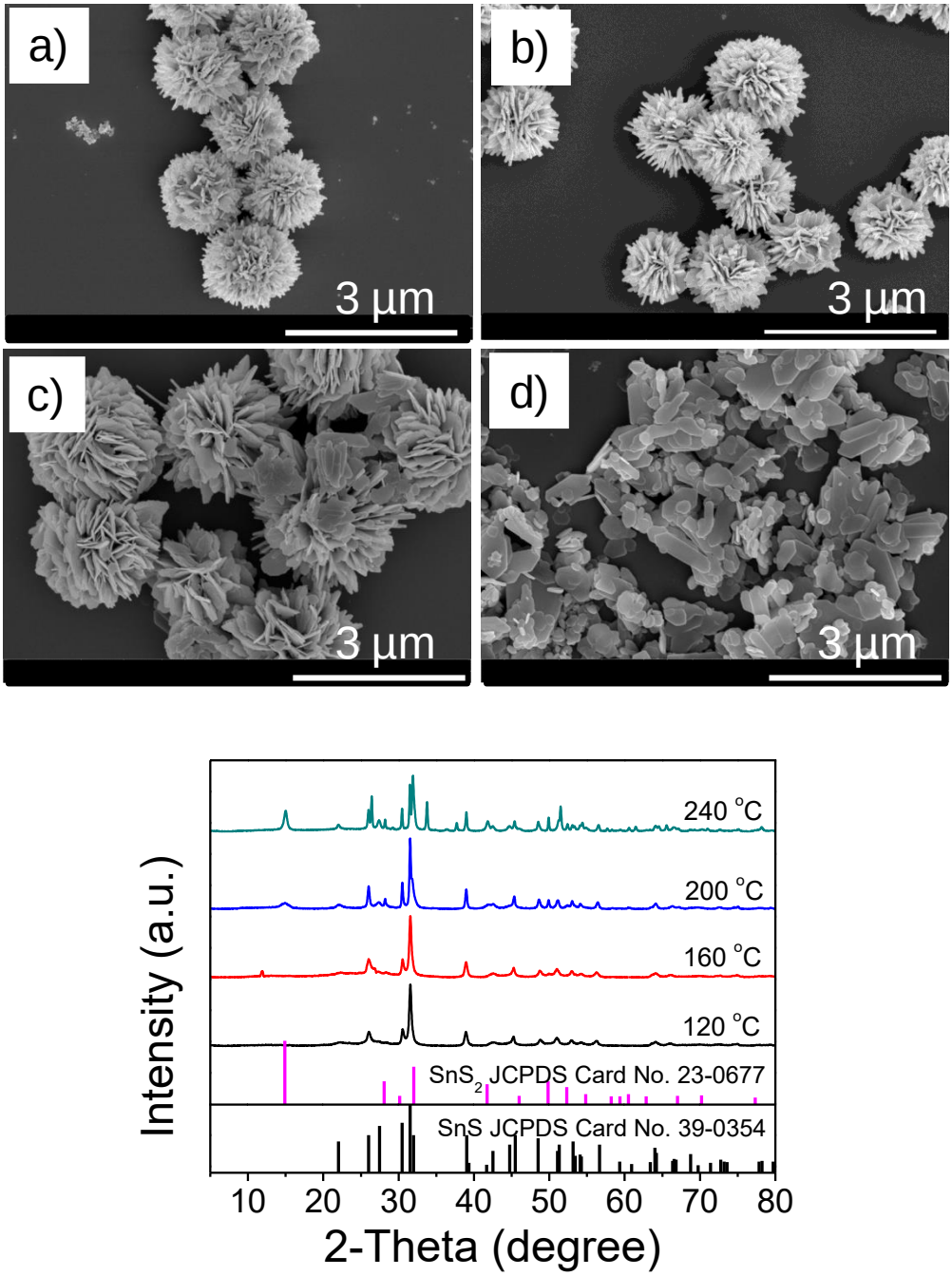

Figure S7. SEM images of the SnS products synthesized at various reaction temperatures, (a) 120 °C, (b) 160 °C, (c) 200 °C and (d) 240 °C for 12 h; (e) XRD patterns of the products synthesized at various temperatures for 12 h.

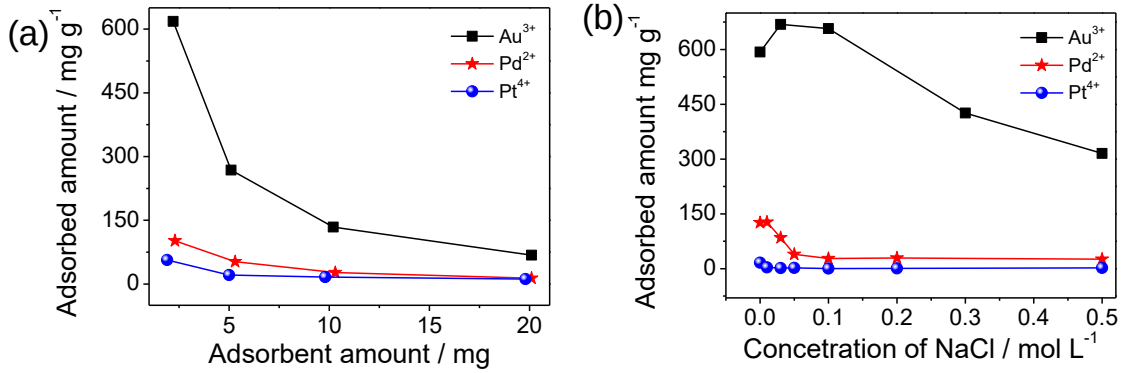

Figure S8. (a) Effect of adsorbent on the capture of Au^{3+}, Pd^{2+}, and Pt^{4+} with urchinlike SnS (C_i = 150 mg L^{-1} of Au^{3+}, 25 mg L^{-1} of Pd^{2+} and Pt^{4+}; pH=1.13 of Au^{3+}, Pd^{2+}, and Pt^{4+}; V = 10 mL; t = 150 min; T = 298 K). (b) Effect of the ionic strength on the capture of Au^{3+}, Pd^{2+}, and Pt^{4+} with urchinlike SnS (m = 2 ± 0.3 mg; C_i = 150 mg L^{-1} for Au^{3+}, 25 mg L^{-1} for Pd^{2+} and Pt^{4+}; V = 10 mL; pH=1.13 of Au^{3+}, Pd^{2+}, and Pt^{4+}; t = 150 min; T = 298 K).

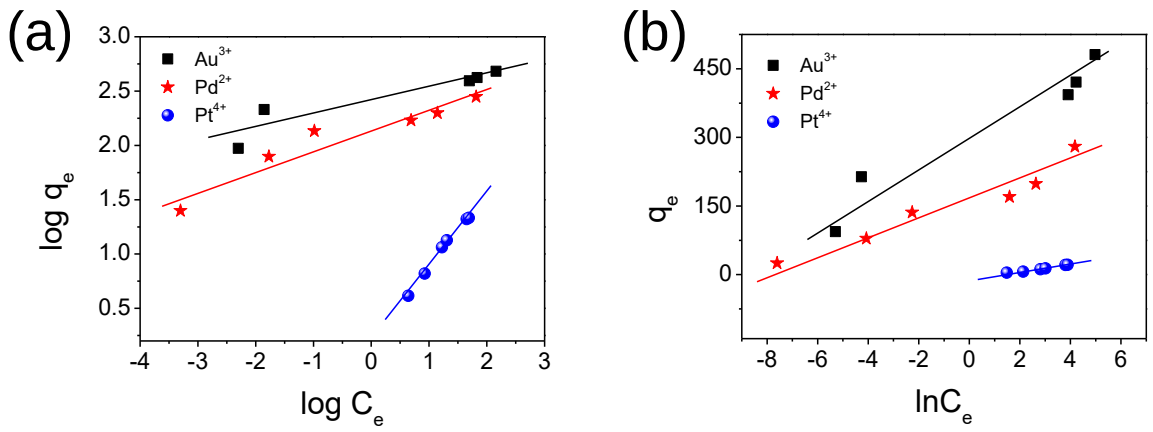

Figure S9. (a) Adsorption isotherm curves fitted to Freundlich models and (b) Temkin models of Au^{3+}, Pd^{2+}, and Pt^{4+} capture on urchinlike SnS microcrystals.

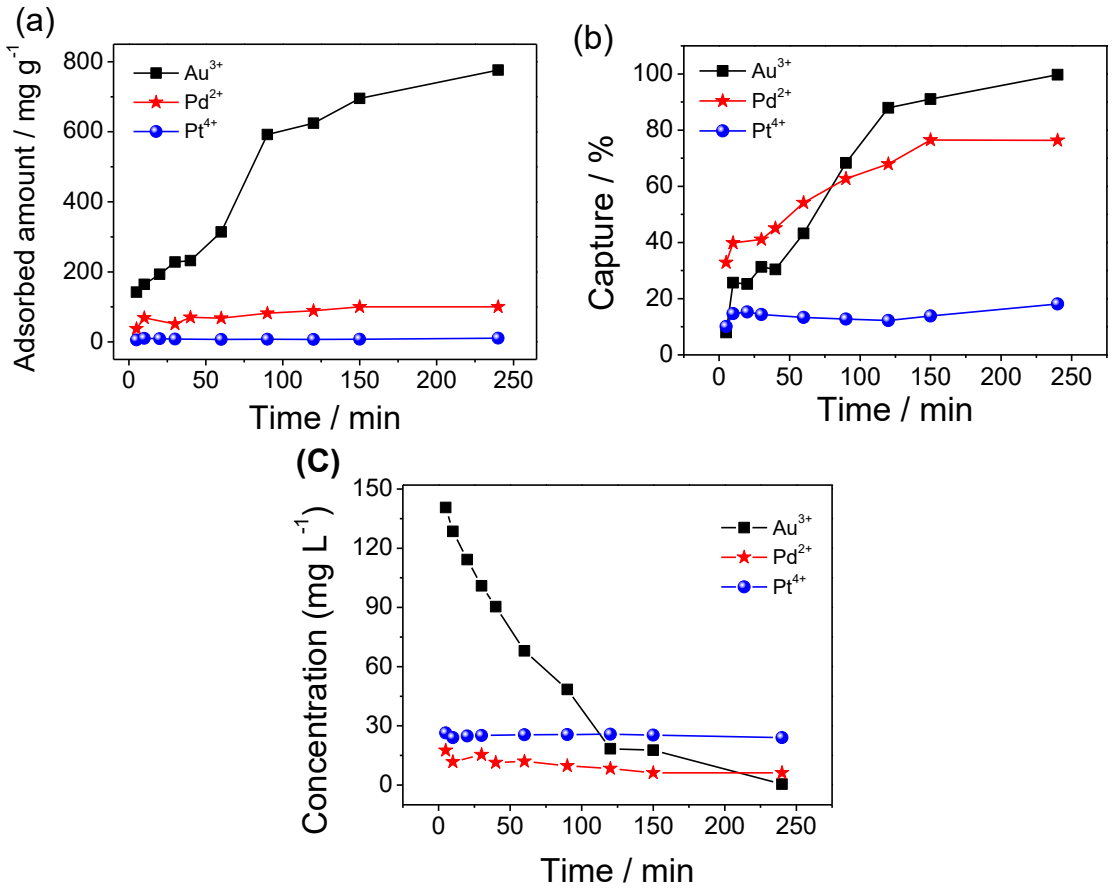

Figure S10. (a) Sorption capacity with contact time, (b) capture percentages as a function of contact time, and (c) ion concentration change following contact time. (Condition: adsorbent dosage m = 2 ± 0.2 mg; C_i=150 mg L^{-1} of Au^{3+}, 26 mg L^{-1} of Pd^{2+}, and 29 mg L^{-1} of Pt^{4+}; V = 10 mL; pH = 1.13 of Au^{3+}, Pd^{2+}, and Pt^{4+}; T = 298 K).

Table S1. Parameters obtained from two kinetics models at 298K.

Kinetic model	Kinetic parameters	Metal ions		
		Au^{3+}	Pd^{2+}	Pt^{4+}
	$q_{e,\,exp}$ (mg g^{-1})	**777.2**	**100.0**	**9.624**
Pseudo-first-order	$q_{e,\,cal}$ (mg g^{-1})	1097	81.10	4.256
	k_1(min^{-1})	0.0184	0.0161	4.606×10^{-3}
	R^2	0.9050	0.9800	0.929
Pseudo-second-order	$q_{e,\,cal}$ (mg g^{-1})	**783.4**	**105.2**	**9.475**
	k_2 (g mg^{-1} min^{-1})	9.103×10^{-6}	4.402×10^{-4}	1.872×10^{-2}
	R^2	0.993	0.9930	0.9930

Table S2. Thermodynamic parameters of the adsorption Au^{3+}, Pd^{2+}, and Pt^{4+} on urchinlike SnS microcrystals.

Metal ions	$\Delta G°$ (KJ mol^{-1})				$\Delta H°$	$\Delta S°$	R^2
	278K	288K	298K	308K	(KJ mol^{-1})	(J mol^{-1} K^{-1})	
Au^{3+}	−0.22	−8.45	−17.13	−25.80	241.3	867.2	0.9930
Pd^{2+}	−3.15	−4.82	−6.50	−8.17	43.39	167.4	0.9910
Pt^{4+}	1.72	0.97	0.22	−0.53	22.56	74.96	0.9960

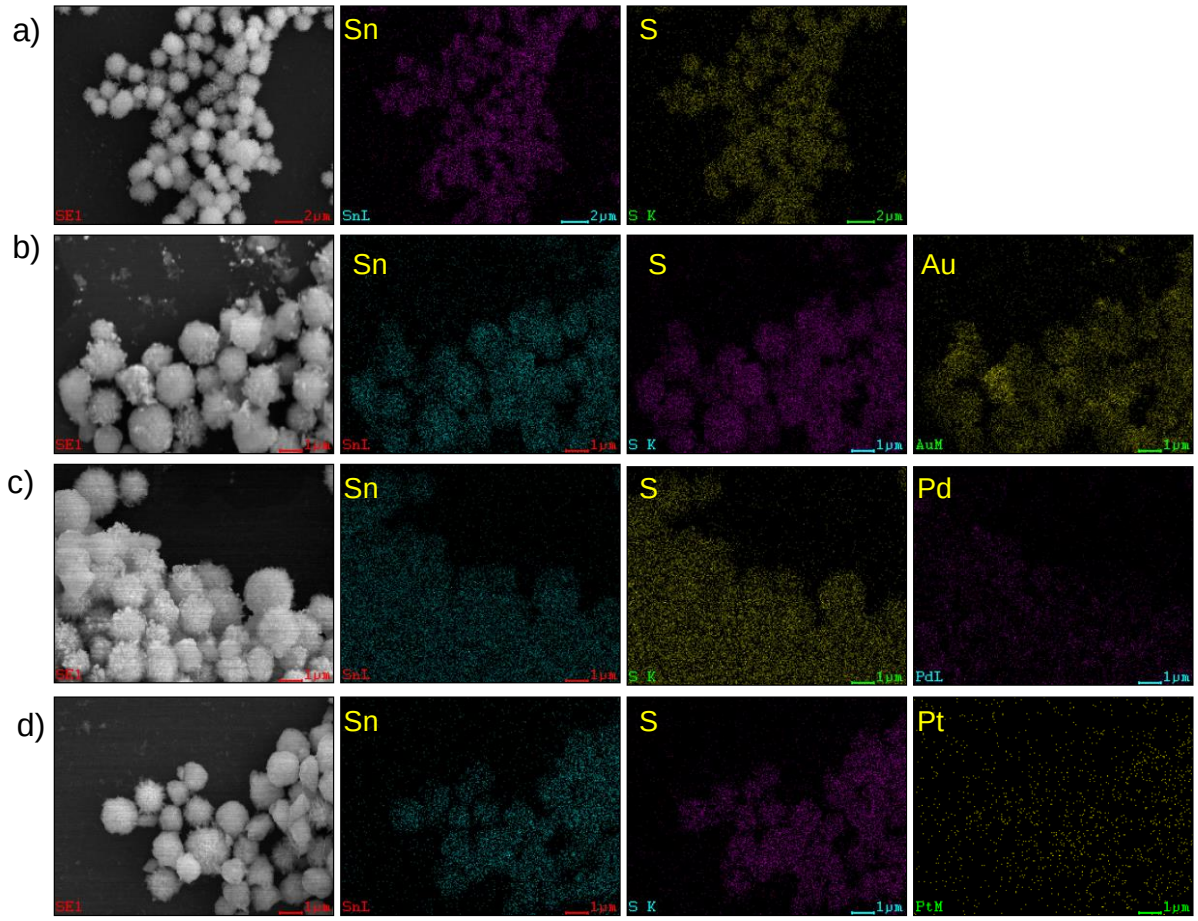

Figure S11. SEM image and the corresponding EDX mapping images of the urchinlike SnS microcrystals (a) before and (b-d) after capture Au^{3+}, Pd^{2+}, and Pt^{4+}.

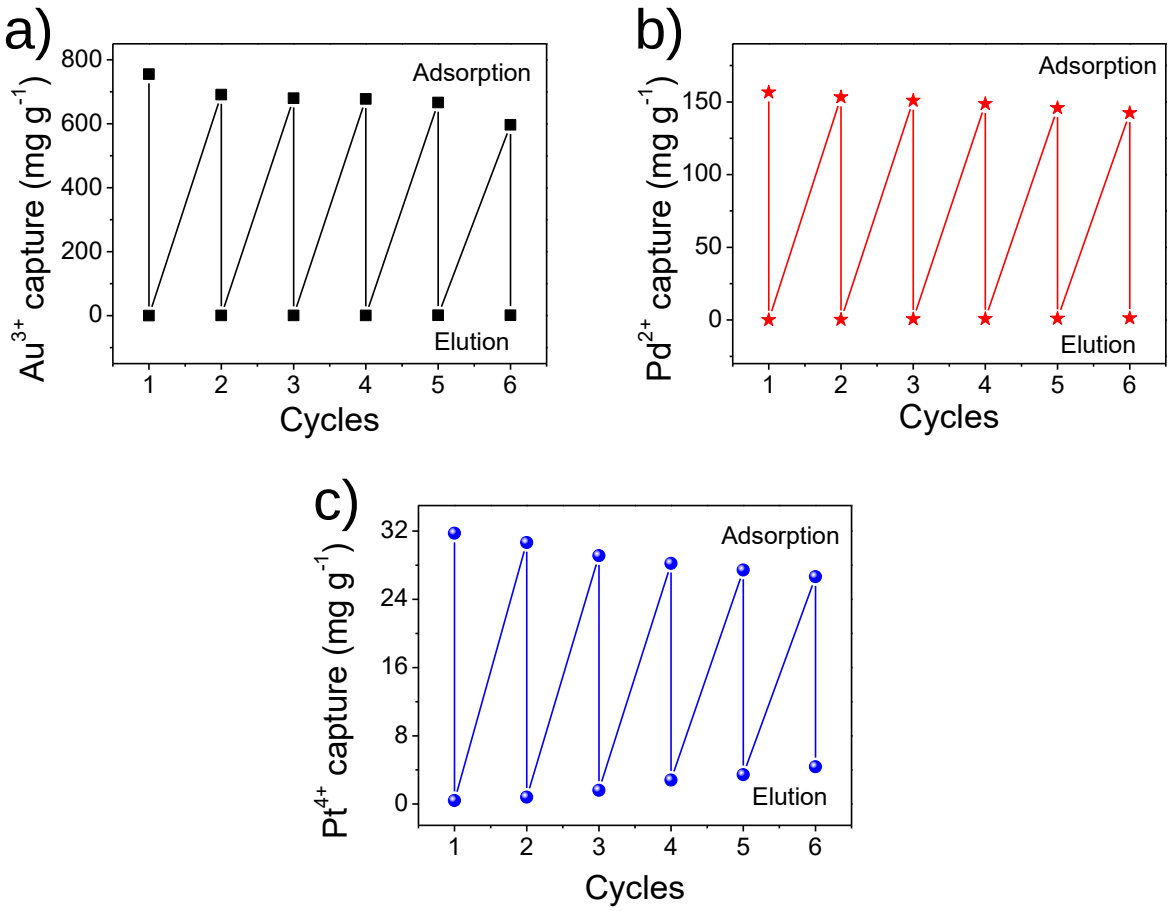

Figure S12. Reusability of urchinlike SnS microcrystals for the capture of Au^{3+} (a), Pd^{2+} (b), and Pt^{4+} (c).