

Electronic Supplementary Information

Gram-scale synthesis of monodisperse sulfonated polystyrene nanospheres for rapid and efficient sequestration of heavy metal ions

Bin Gong, Yaotian Peng, Ziyang Pan, Weiming Chen, Yi Shen, Kaijun Xiao*, and Ling Zhang*

E-mails: feyshen@scut.edu.cn (Y. Shen); fekjxiao@scut.edu.cn (K. J. Xiao)

Experimental Section

Materials: Sodium hydroxide ($\geq 96.0\%$), potassium peroxydisulfate ($\geq 99.5\%$) and anhydrous ethanol ($\geq 99.7\%$) were purchased from the Nanjing chemical reagent Co. Ltd., China. Sulfuric acid (98.0%), nitric acid ($\geq 68.0\%$), sodium dodecyl sulfate ($\geq 99.0\%$), nickel nitrate ($\geq 98.0\%$), potassium chloride ($\geq 99.5\%$), sodium chloride ($\geq 99.5\%$), calcium chloride (96.0%), iron nitrate 9 H₂O (98.5%), Co(NO₃)₂·6H₂O ($\geq 99.8\%$), sodium carbonate ($\geq 99.8\%$) and lead nitrate ($\geq 99.0\%$) are purchased for the Damao chemical reagent co. Ltd, Tianjin, China. Styrene (98%), Cu(NO₃)₂·3H₂O ($> 99.0\%$) and zinc chloride ($\geq 98.0\%$) are purchased from the Fuchen chemical reagent Co. Ltd. Tianjin, China. α -Fe₂O₃ (30 nm $\geq 99.5\%$) and γ -Fe₂O₃ (20 nm $\geq 99.5\%$) were provided from the Aladdin Bio-Chem Technology Co. Ltd. Shanghai, China. Macroporous acidic cation exchange resin was purchased from the Qinshi technology co. Ltd., Zhengzhou, China. Talapia-fish-scale derived collagen proteins (Mw 500~600 Da) is from Baiwei Co. Ltd. Guangdong, China. Activated carbon (Norit DLC Super 50 carbon, surface area 1534 m² g⁻¹) was provided from the Sigma Aldrich, China. All the reagents are of analytic grade. Graphene powder (surface area 247 m² g⁻¹) was synthesized via a chemical vapor deposition method and further purified by a sedimentation process as reported in our previous work.¹

Synthesis of sulfonated polystyrene nanospheres: Prior to synthesis, styrene was first extracted by NaOH aqueous solution (5 wt. %) and distilled water to remove any inhibitor and

further purified by reduced-pressure rotary evaporation at 60°C. PS nanospheres were synthesized via emulsion polymerization.² Typically, sodium dodecyl sulfate (0.2 g, 0.69 mmol) and Na₂CO₃ (0.1 g, 0.94 mmol) were dissolved into distilled water (300 mL). The resulting solution was transferred to three-neck flask. The flask was purged with nitrogen gas for 30 min. Subsequently, styrene (30 mL) was added into the solution by intense agitation and the solution was heated to 60°C. After 30 min, potassium persulfate aqueous solution (15 mL, 0.23 mmol L⁻¹) was introduced. The polymerization reaction was conducted at 75°C for 20 h. After cooling to room temperature, the product was alternately washed with ethanol and water, and dried at 60°C for further use. To obtain sulfonated PS nanospheres, PS powder (1 g) was dispersed into concentrated H₂SO₄ (40 mL, 98 wt. %) by ultrasonication. The sulfonation reaction was conducted at room temperature for 3 h. The product was thoroughly washed by water and ethanol, and dried at 60°C using a vacuum oven.

Determination of degree of sulfonation by titration: The content of sulfonic groups in the resulting sulfonated polystyrene nanospheres was determined by titration. The details of experimental procedures are listed as follows: 50 mg sulfonated polystyrene nanospheres were dispersed into 50 mL of NaOH standard solution with a concentration of 0.01 mol L⁻¹ by ultrasonication. Two droplets of phenolphthalein solution were added as an indicator. The solution was titrated by HCl solution with a concentration 0.01 mol L⁻¹. The consumed volume of HCl solution (V_{HCl}) was recorded. The degree of sulfonation (DS) was calculated by following equation: $DS = (0.05 \times 0.01 - V_{HCl} \times 0.01) / 0.05$

Characterization: The morphology of the samples was observed by field emission scanning electron microscopy (FESEM) (JSM-7600F, JEOL) and transmission electron microscopy (JEM2010, JEOL). X-ray diffraction (XRD) patterns were obtained by a diffractometer

(PW1830, Philips) equipped with Cu-K α radiation of 1.54 Å. The N₂ adsorption–desorption isotherm was obtained using the accelerated surface area porosimetry system (ASAP 2020, Micromeritics). An energy dispersive X-ray analyzer equipped in the FESEM/TEM and an axis-ultra X-ray photoelectron spectrometer (Kratos-Axis Ultra System) with monochromatized Al-K α radiation were used to analyze the elemental composition of the samples. Fourier transform infrared spectroscopy (FTIR) was recorded by an analyzed (Nicolet 6700, Thermo Scientific). A thermogravimetric analyzer (DTG-60H, Shimadzu) was used to investigate the thermal stability of the samples. The thermogravimetric analyses (TGA) were operated at a temperature range of 40 to 700°C using a heating rate of 20°C/min under air flow. The concentrations of metal ions were analyzed using an atomic absorption spectrometer (Z-2000 Hitachi).

Adsorption of heavy metal ions: Stock solution of metal solution (1000 mg L⁻¹) was supplied from National Institute of Metrology, Beijing, China. The stock solutions were diluted to the desired concentrations with deionized water. In a typical batch adsorption test, SPS powder was introduced into pollutant solutions and then agitated at 180 rpm using a mechanical shaker at 30°C. The variations in the concentration of metal ions as a function of time were monitored using an atomic absorption spectrometer (AAS) (Z-2000 Hitachi). The adsorption up-take per unit mass of adsorbent q_t (mg g⁻¹) at time t (min) was calculated using equation (1)

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 (mg L⁻¹) is the initial metal ion concentration and C_t (mg L⁻¹) is the concentration at time t (min) in the liquid phase, V (L) is the volume of the solution and W (g) is the weight of the sorbent.

To determine the equilibrium adsorption capacity q_e (mg g⁻¹), the sorbent was immersed in the pollution solution for at least 24 h to achieve the equilibrium state of adsorption. The adsorption isotherms were fitted by Langmuir equation (2)

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

where C_e (mg L⁻¹) is the equilibrium concentration, q_{\max} (mg g⁻¹) is the maximum adsorption capacity and b is the Langmuir isotherm constant, and Freundlich equation (3)

$$q_e = k C_e^{1/n} \quad (3)$$

where k and n are the Freundlich isotherm constant.

To study the kinetics of the adsorption of metal ions, three kinetic models including the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied to fit the experimental data. The pseudo-first-order kinetic model can be expressed by equation (4)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where k_1 (min⁻¹) is the adsorption rate constants of the first order kinetic model. The pseudo-second-order kinetic model is expressed by equation (5)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2 (g (mg·min)⁻¹) is the adsorption rate constants of the second order kinetic model. The intraparticle diffusion model is expressed by equation (6)

$$q_t = k_p t^{1/2} + C \quad (6)$$

where k_p (mg (g h^{1/2})⁻¹) is the intraparticle diffusion rate constant and C (mg g⁻¹) is a constant related to the thickness of the boundary layer.

To highlight the efficiency of SPS, several sorbents including activated carbon, graphene, α - Fe_2O_3 , γ - Fe_2O_3 and a commercial resin were also tested under identical conditions. The details of experimental procedures are: The sorbent (50 mg) was added into of Pb^{2+} solutions (100 mL) under agitation at 180 rpm using a mechanical shaker at 30°C. At given time intervals, aliquot (3 ml) was sampled and separated by centrifuge. The supernatant was filtered through a membrane filter with a pore size of 220 nm. The concentration of Pb^{2+} was analyzed by AAS.

To study the regeneration and recyclability of SPS, we conducted cyclic adsorption-desorption tests. SPS (100.4 mg) was added into Pb^{2+} solution (40 mL, 50.23 mg L^{-1}). After reaching to an equilibrium state, SPS was separated by centrifuge. The Pb^{2+} concentration of the supernatant was determined. The resulting Pb^{2+} -saturated SPS was regenerated by immersing into HNO_3 (1 mol L^{-1}). The regenerated SPS was employed again to remove Pb^{2+} from the pollutant solutions. This adsorption-desorption process was repeated for four times. The desorption kinetics was also investigated. The details of experimental procedures are as follows: SPS powder (100 mg) was added into Pb^{2+} solution (80 mL, 50 mg L^{-1}). After 3 h, the mixture was separated by centrifuge with an rpm of 10000 for 30 min. The supernatant was discarded. The precipitate was distributed into HNO_3 (100 mL, 1 mol L^{-1}). The concentration of released Pb^{2+} in the solution was recorded as a function of time.

For the practical application, SPS nanospheres were employed to extract heavy metals from Talapia-fish-scale derived collagen proteins. The experimental procedures are listed as follows: SPS (300 mg) was added into collagen protein solution (40 mL) by ultrasonication. The sorption process was conducted at 30°C for 3 h. Subsequently, collagen proteins were separated by centrifuge. The supernatant was filtered through a membrane filter. The concentrations of metal ions were determined accordingly.

References

1. Y. Shen, A. C. Lua, *Sci. Rep.* 2013, 3, 3037
2. D. Y. Liu, X. X. Peng, B. H. Wu, X. Y. Zheng, T. T. Chuong, J. L. Li, S. G. Sun, G. D. Stucky. *J. Am. Chem. Soc.*, 2015, 137, 9772.

Table S1 Fitting the equilibrium data using the Langmuir and Freundlich models

	Langmuir model			Freundlich model		
	q_{\max} (mg g ⁻¹)	b (L mg ⁻¹)	R ²	1/n	k	R ²
Pb ²⁺	83.6	0.16	0.9995	0.207	29.9	0.7281
Zn ²⁺	25.1	1.09	0.9875	0.249	12.7	0.9946
Cu ²⁺	19.3	3.29	0.9986	0.233	11.1	0.6943

Table R2 Comparison on adsorption capacities of sorbents based on polystyrene

Sample	Metal ions	Adsorption capacities (mg/g)	References
D001-Polyethyleneimine	Cu ²⁺	99	Chen <i>et al.</i> , Environ. Sci. Tech. 2010, 44, 3508-13.
Sulfonated crushed polystyrene	Pb ²⁺	60	Bekri-Abbes <i>et al.</i> , J. Polym. Environ. 2006, 14, 249-256.
Sulfonated polystyrene	Cu ²⁺	48.8	Wieslaw <i>et al.</i> , J. Appl. Poly. Sci. 2013, 128, 2611-2617.
Sulfonated expanded polystyrene	Cu ²⁺	49.5	Wieslaw <i>et al.</i> , J. Appl. Poly. Sci. 2013, 128, 2611-2617.
Sulfonated waste Styrofoam	Pb ²⁺	45.5 (pH=3)	Mahmoud <i>et al.</i> , ACS Sustain. Chem. Eng. 2015, 4, 819-827
SPS nanospheres	Pb ²⁺	83.6	This work
SPS nanospheres	Zn ²⁺	25.1	This work
SPS nanospheres	Cu ²⁺	19.3	This work

Table S3 Fitting the kinetic data using the pseudo-second-order, pseudo-first-order and Intra-particle diffusion equations

	Pseudo-second-order		Pseudo-first-order		Intra-particle diffusion	
	k_2 (g mg ⁻¹ min ⁻¹)	R ²	k_1 (min ⁻¹)	R ²	k_p (mg·g ⁻¹ ·min ^{-0.5})	R ²
Pb ²⁺	4.63	1	0.268	0.38089	2.13	0.21518
Zn ²⁺	0.066	0.99934	0.435	0.97606	2.96	0.60523
Cu ²⁺	0.067	0.9999	0.193	0.90633	2.68	0.65551

Table S4 Fitting the kinetic data obtained from different adsorbents using the pseudo-second-order equation.

Sample	Fitting equation	qe (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R ²
AC	Y=-0.38521+0.43824X	2.28	Na.	0.99807
α -Fe ₂ O ₃	Y=0.07177+0.08111X	12.3	0.0916	0.99994
Graphene	Y=0.33026+0.3182X	3.14	0.306	0.99983
Resin	Y=0.93766+0.03605X	14.8	0.0171	0.08938
γ -Fe ₂ O ₃	Y=0.10697+0.10639X	9.39	0.105	0.99992
SPS	Y=0.000581245+0.05188X	19.2	4.63	1

Table S5 Metal concentration (mg L⁻¹) in the collagen protein extracted from Talapia fish scale before and after SPS treatment. (Note: * indicates that the concentration is less than the detection limit of the instrument).

Sample	K ⁺	Na ⁺	Cu ²⁺	Zn ²⁺	Pb ²⁺	Ca ²⁺	Fe ³⁺	Ni ²⁺	Co ²⁺
Pristine collagen protein	2.43	4.27	1.4	1.6	1.15	1.32	3.57	0.104	1.11
Treated collagen protein	0.44	1.39	0.002*	0.01*	0.001	0.05*	0.001	0.035	0.002*

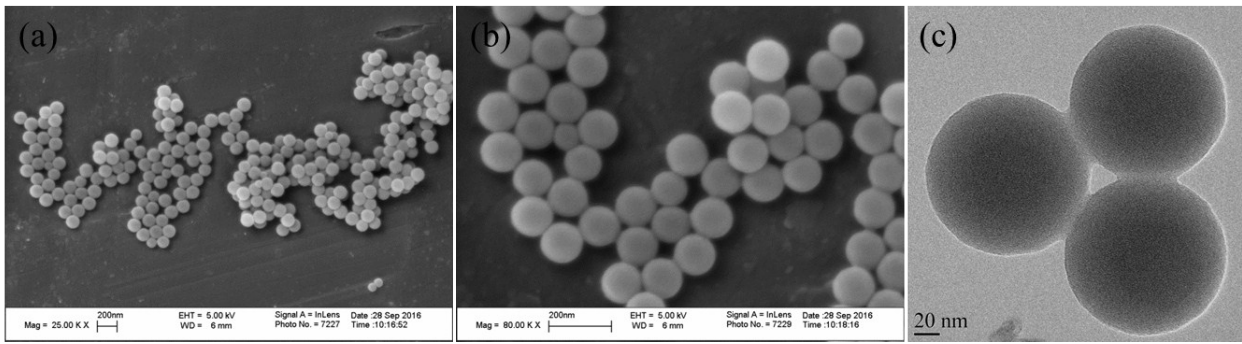


Fig. S1 (a, b) FESEM and (c) TEM images of PS nanospheres.

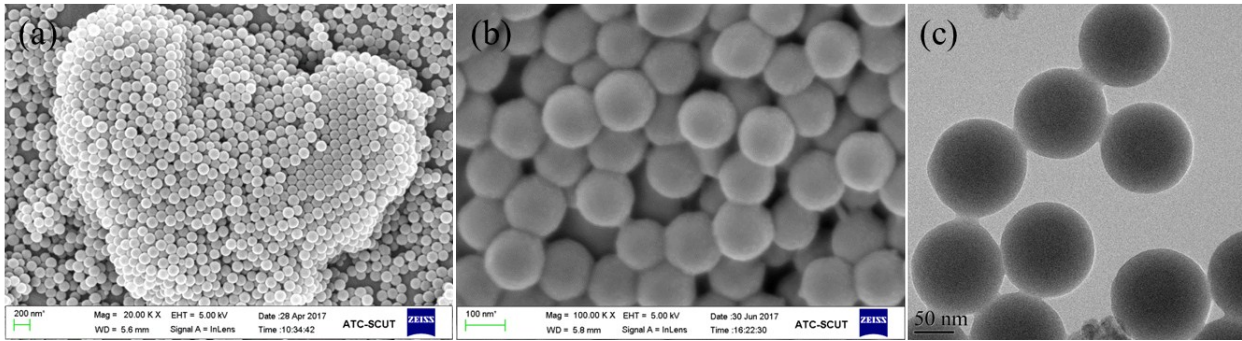


Fig. S2 (a, b) FESEM and (c) TEM images of SPS nanospheres.

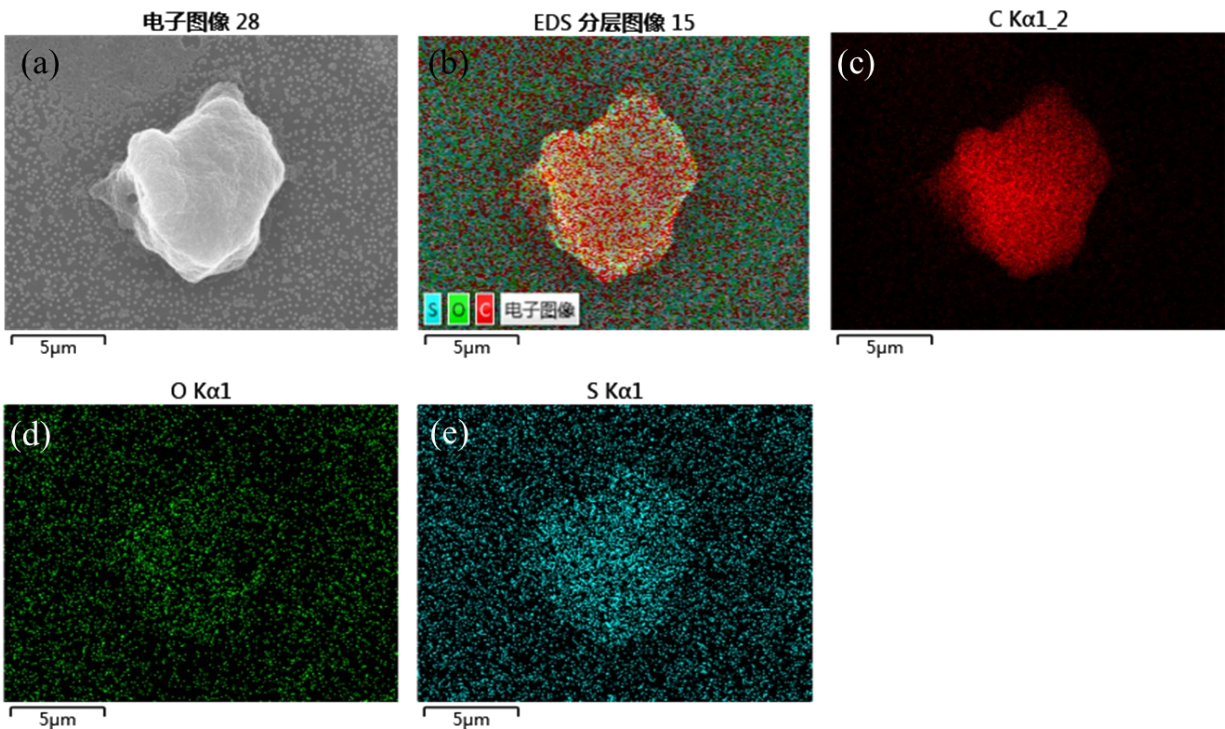


Fig. S3 (a) FESEM and corresponding EDS elemental mapping images of (b) overall, (c) carbon, (d) oxygen and (e) sulfur element of SPS nanospheres.

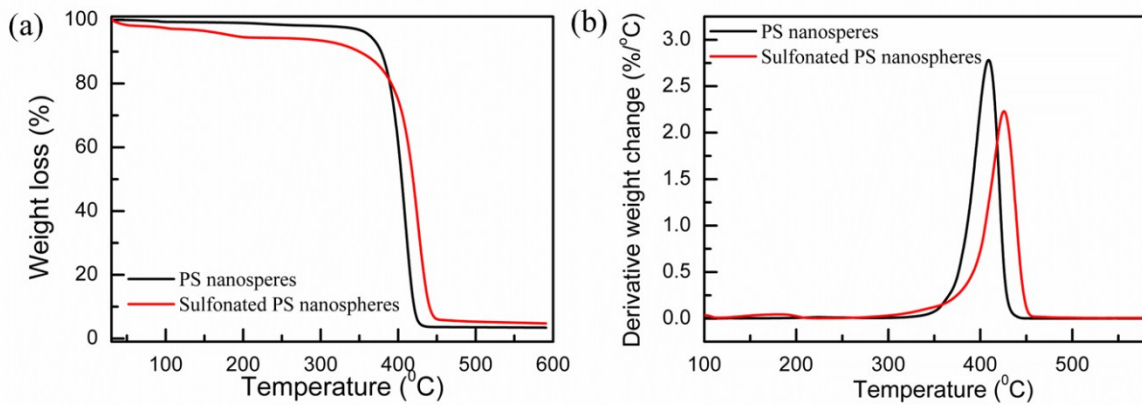


Fig. S4 TG curves (a) and corresponding derivative curves of PS and SPS nanospheres.

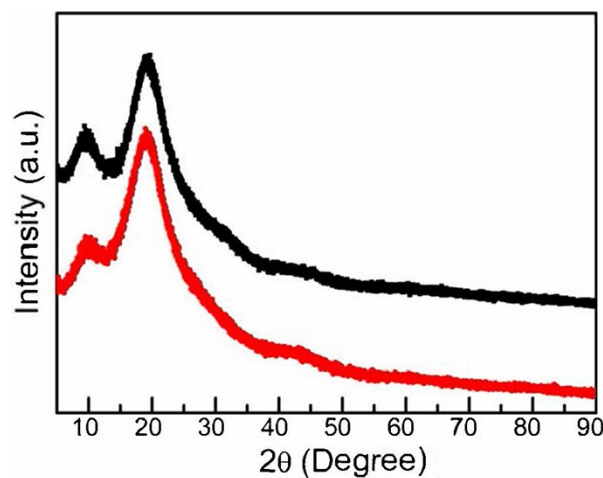


Fig. S5 XRD patterns of PS (black line) and SPS (red line) nanospheres

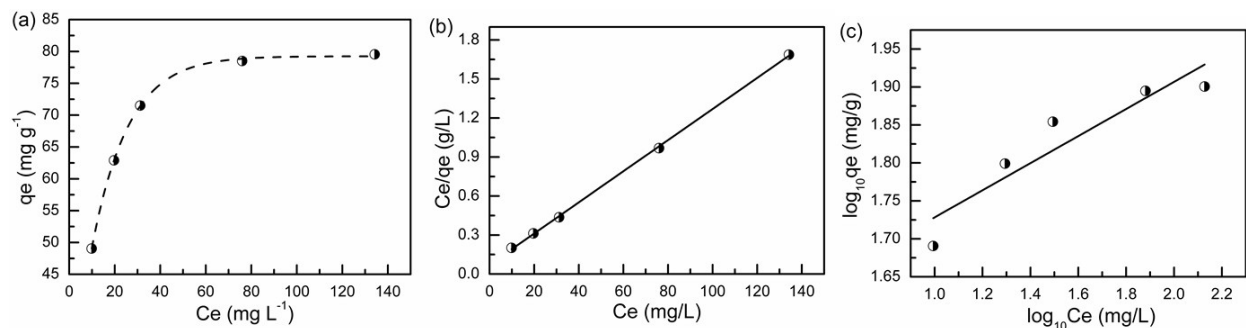


Fig. S6 (a) adsorption isotherms of Pb^{2+} onto SPS, and fitting curves (b) by the Langmuir model and (c) Freundlich model.

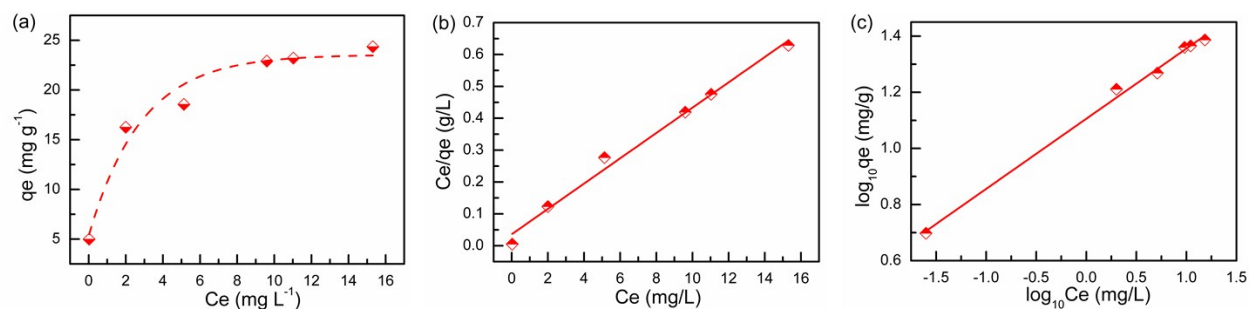


Fig. S7 (a) adsorption isotherms of Zn^{2+} onto SPS, and fitting curves (b) by Langmuir model and (c) Freundlich model.

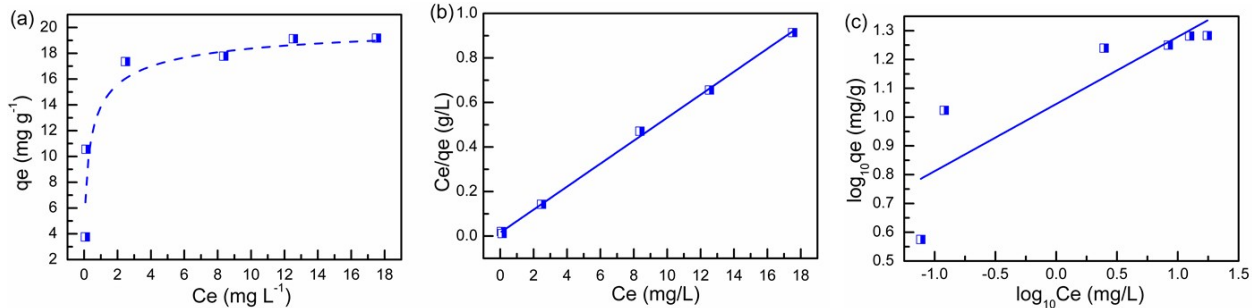


Fig. S8 (a) adsorption isotherms of Cu^{2+} onto SPS, and fitting curves (b) by Langmuir model and (c) Freundlich model.

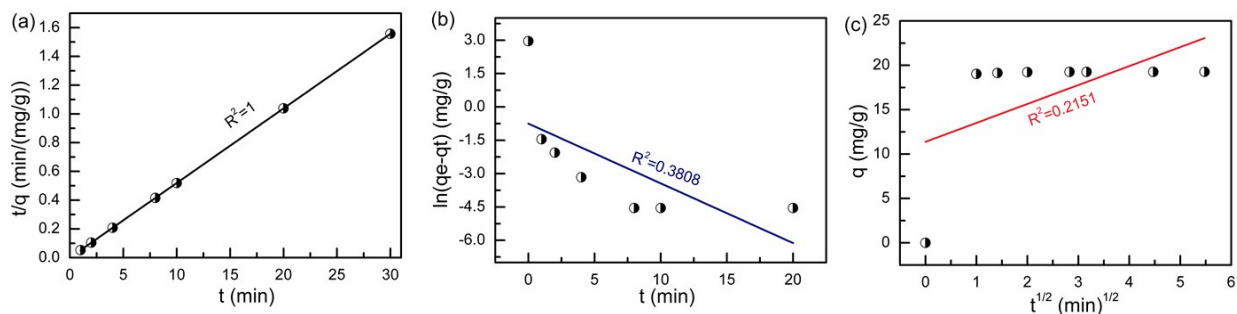


Fig. S9 Fitting the adsorption kinetics of Pb^{2+} onto SPS using (a) pseudo-second-order, (b) pseudo-first-order, and (c) intra-particle diffusion equations. $[\text{Pb}^{2+}]_0=10 \text{ mg L}^{-1}$

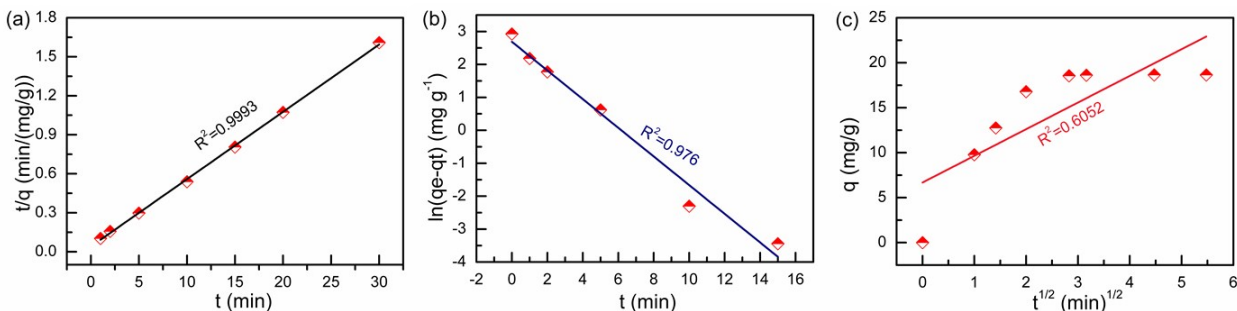


Fig. S10 Fitting the adsorption kinetics of Zn^{2+} onto SPS using (a) pseudo-second-order, (b) pseudo-first-order, and (c) intra-particle diffusion equations. $[\text{Zn}^{2+}]_0=10 \text{ mg L}^{-1}$

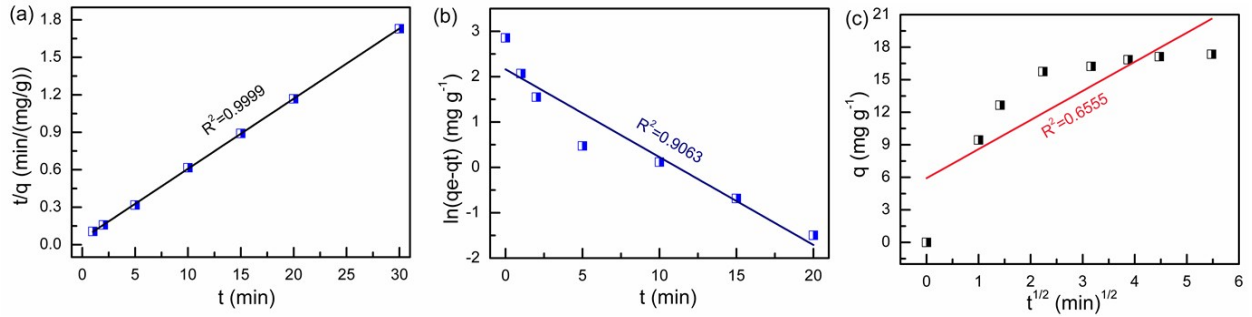


Fig. S11 Fitting the adsorption kinetics of Cu²⁺ onto SPS using (a) pseudo-second-order, (b) pseudo-first-order, and (c) intra-particle diffusion equations. [Cu²⁺]₀=10 mg L⁻¹

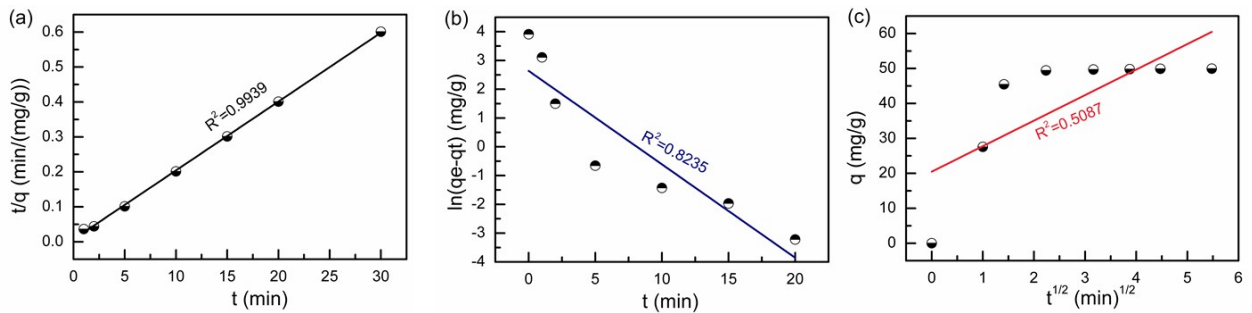


Fig. S12 Fitting the adsorption kinetics of Pb²⁺ onto SPS using (a) pseudo-second-order, (b) pseudo-first-order, and (c) intra-particle diffusion equations. [Pb²⁺]₀=25 mg L⁻¹

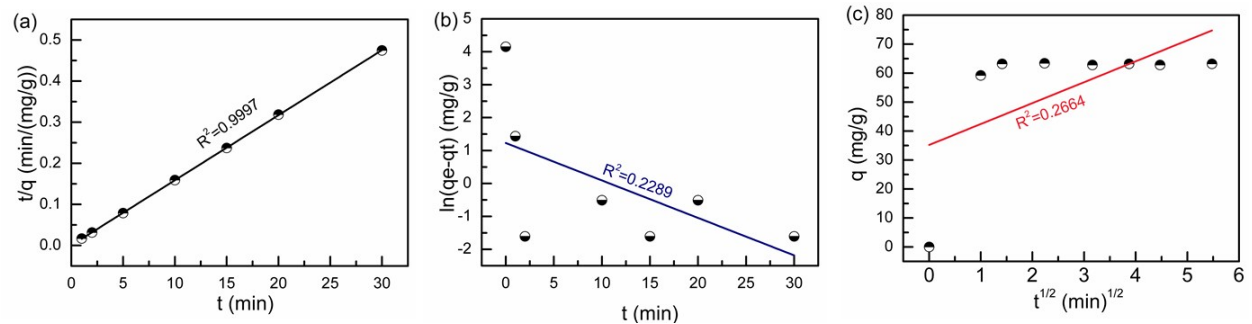


Fig. S13 Fitting the adsorption kinetics of Pb²⁺ onto SPS using (a) pseudo-second-order, (b) pseudo-first-order, and (c) intra-particle diffusion equations. [Pb²⁺]₀=100 mg L⁻¹

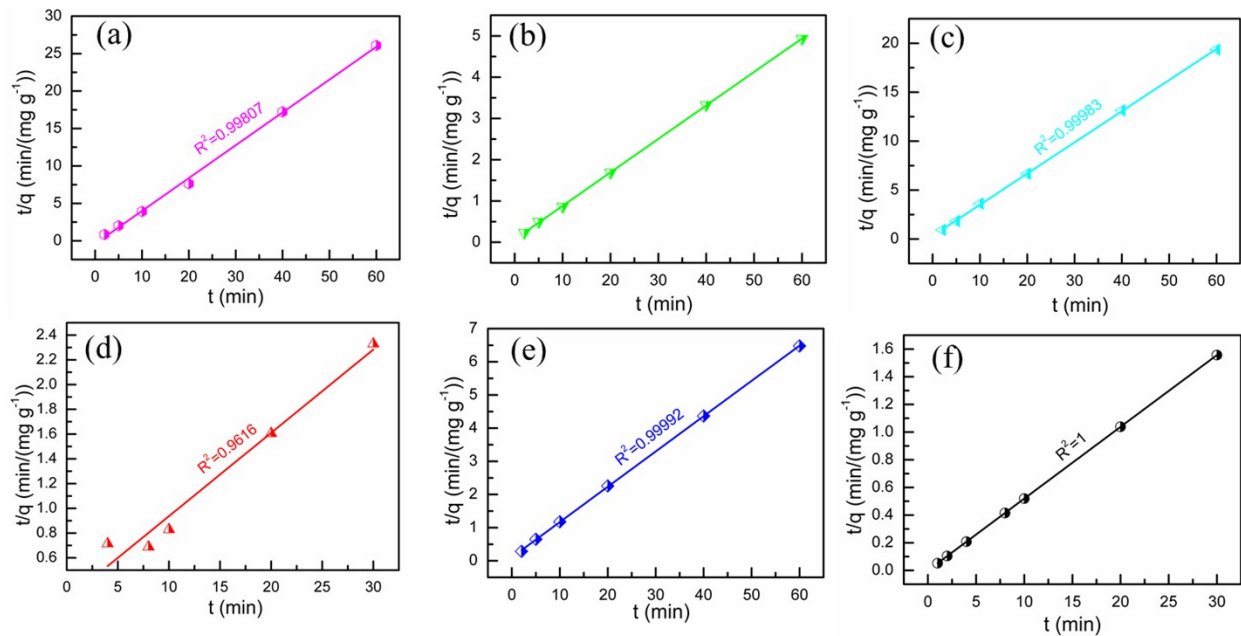


Fig. S14 Fitting the adsorption kinetics of Pb^{2+} onto (a) AC, (b) $\alpha\text{-Fe}_2\text{O}_3$, (c) graphene, (d) commercial resin, (e) $\gamma\text{-Fe}_2\text{O}_3$ and (f) SPS using the pseudo-second-order model.

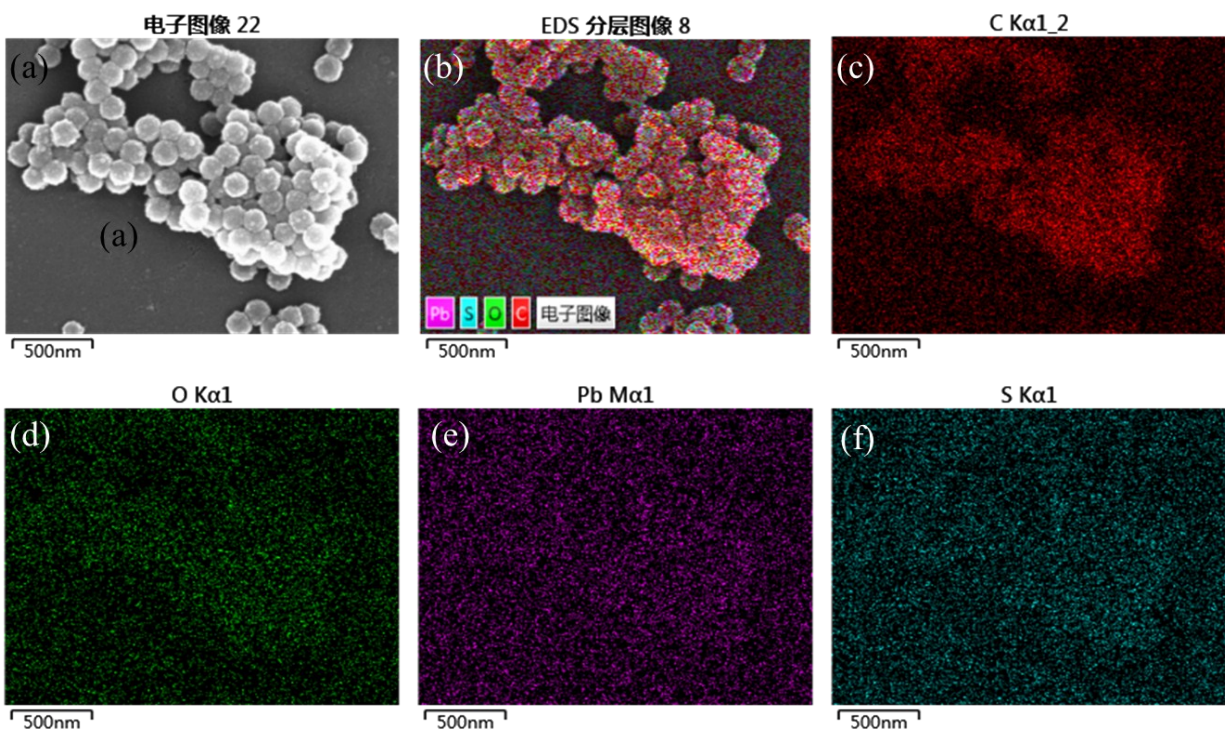


Fig. S15 (a) FESEM image of Pb^{2+} -adsorbed SPS and corresponding EDS elemental mapping images of (b) overall, (c) carbon, (d) oxygen, (e) lead, and (f) sulfur element.

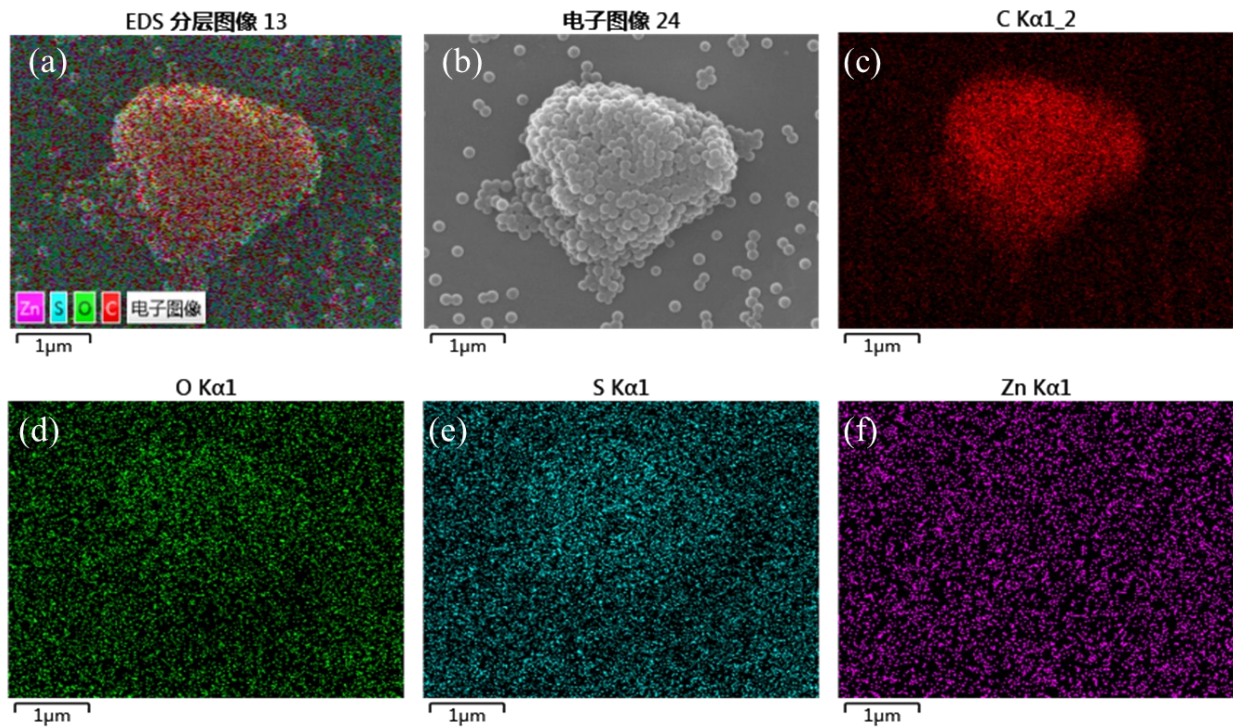


Fig. S16 (a) FESEM image of Zn²⁺-adsorbed SPS and corresponding EDS elemental mapping images of (b) overall, (c) carbon, (d) oxygen, (e) sulfur, and (f) zinc element.

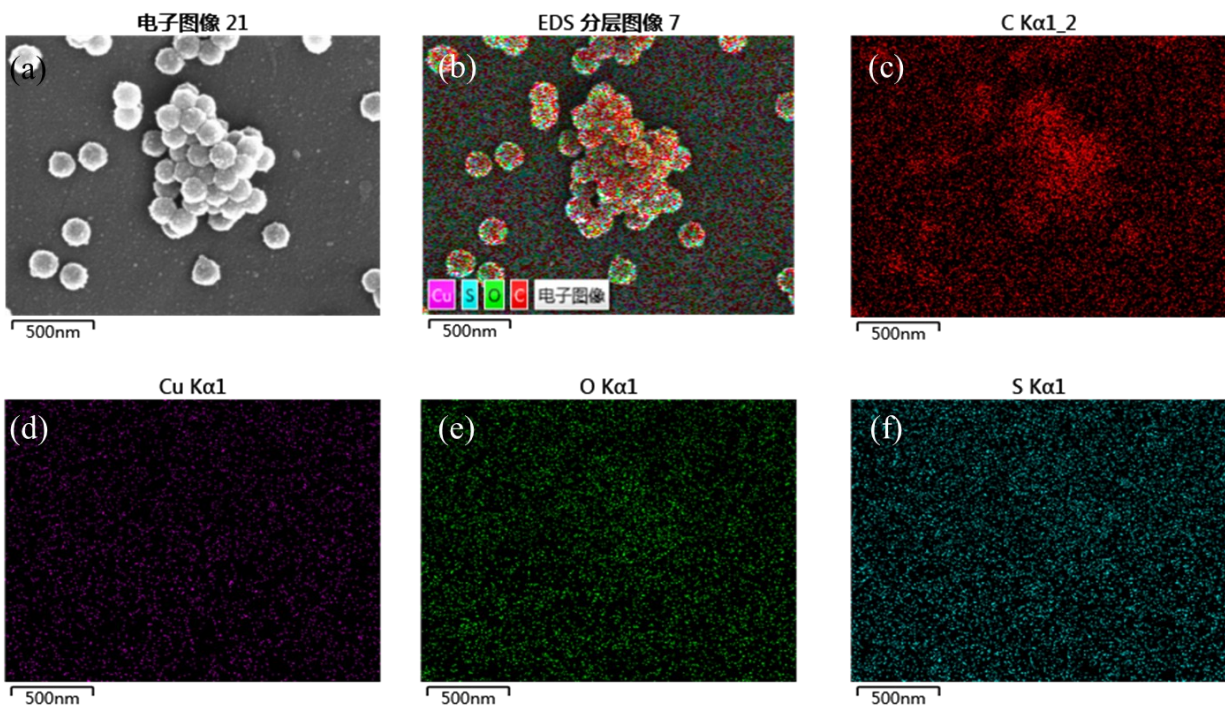


Fig. S17 (a) FESEM image of Cu²⁺-adsorbed SPS and corresponding EDS elemental mapping images of (b) overall, (c) carbon, (d) copper, (e) oxygen, and (f) sulfur element.

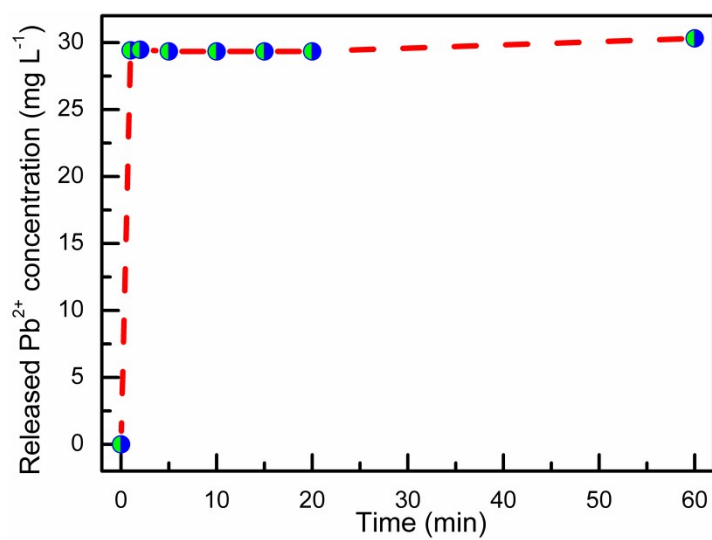


Fig. S18 Pb²⁺ concentrations recorded during desorption experiment as a function of time.

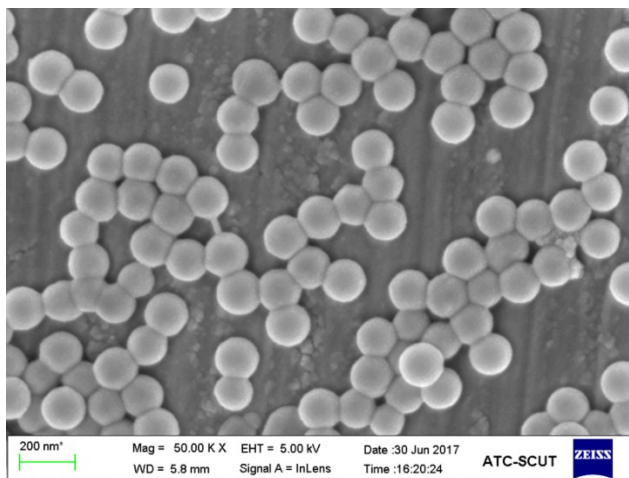


Fig. S19 FESEM image of spent SPS nanospheres after cyclic tests.