

Inversed vulcanised sulfur polymer nanoparticles prepared by antisolvent precipitation

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Experimental

Materials

Sulfur (S₈, sublimed powder, reagent grade, ≥ 99.5 %, Brenntag UK & Ireland), dicyclopentadiene (DCPD > 96.0 %, Sigma-Aldrich), (S)-(-)-perillyl alcohol (≥ 95 %, Sigma Aldrich) mercury (II) chloride (ACS, 99.5% MIN, Alfa Aesar UK), Chloroform-d (99.8 atom % D, Sigma Aldrich). Chloroform (Stabilized with amylene, Fisher Scientific), Ethanol (≥ 99.5 %, Sigma-Aldrich), 1,3-diisopropenyl benzene (> 97.0 %(GC), TCI), Trace Metal Certified Reference Material (QC3132-500ML, Lot LRAC5492, Sigma-Aldrich). All chemical precursors were used as received without any further purification. Deionized water was used in filtration and washing steps of the resultant materials.

Synthesis of inversed vulcanised sulfur polymers

Poly(Sulfur-Perillyl Alcohol-Dicyclopentadiene)

Reactants (sulfur and crosslinkers (used as received), 10 g in total, specific ratio for different samples are indicated by X, Y, Z in sample name, SPD-X,Y,Z, presenting the mass percentage of sulfur, PA, and DCPD, respectively) were mixed in 40 mL volume glass vials. The mixture was stirred at 175 °C in aluminium blocks and stirred (800 rpm) by magnetic stirrer bars. The reaction time depended on the ratio of reactants. When the reaction had changed to thick dark brown liquid, the prepolymer was transferred into a silicone mould and moved into an oven at 140 °C for 18 hours.

Poly (sulfur-diisopropenyl benzene)

Reactants (sulfur and crosslinkers (used as received), 1:1 in weight ratio, 10 g in total) were mixed in 40 mL volume glass vials. The mixture was stirred at 175 °C in aluminium blocks and stirred by magnetic stirrer bars. The reaction time depended on the ratio of reactants. When the reaction had changed to thick dark brown liquid, the prepolymer was transferred into a silicone mould and moved into an oven at 140 °C for 18 hours. The sample generated was named SDIB-50,50.

Partly cured poly(Sulfur - dicyclopentadiene)

Reactants (sulfur and dicyclopentadiene (used as received), 1:1 in weight ratio, 10 g in total) were mixed in 40 mL volume glass vials. The mixture was stirred at 175 °C in aluminium blocks and stirred by magnetic stirrer bars. The reaction time depended on

the ratio of reactants. When the reaction had changed to thick dark brown liquid, the prepolymer was transferred into a silicone mould and moved into an oven at 140 °C for 3 hours. The sample generated was named SDCPD-50,50. SDCPD-50,50 and SPD-50,00,50 were different samples, as SDCPD-50,50 is partly cured and SPD-50,00,50 is fully cured, though the reactant and the ratio of reactant were exactly same.

Preparation of sulfur polymer nanoparticles

500 mg of specific sulfur polymer were dissolved in 10 mL of chloroform (CHCl₃) (solvent) to generate a 50 mg mL⁻¹ polymer solution, with all insoluble part filtered out. 10 μL, 50 μL, 100 μL, and 250 μL of solution was added to 10 mL ethanol (anti-solvent) dropwise with stirring (500 rpm) at room temperature to precipitate nanoparticles. Samples were denoted as SPD-X,Y,Z-A, where A is the volume of polymer solution in microlitres. Generated nanoparticles were filtered under vacuum using a PTFE membrane (≤ 0.2 μm pore size), then, dried in the vacuum oven at room temperature overnight.

Fabrication of sulfur polymer supported membrane

50 mg sulfur polymer nanoparticles were added into 50 mL ethanol and well dispersed by sonication. When prepared mixture was a cloudy light yellow or light grey suspension, depending on sulfur polymer precursors. 20 mL resultant suspension was filtered by a PTFE membrane (≤ 0.2 μm pore size) using glass vacuum filtration, generating sulfur polymer supported membrane.

Preparation of mercury filter prototype

Sulfur polymer suspension was prepared same as mentioned above. 10 mL resultant suspension was added into a 12 mL syringe connected with a commercial syringe filter, followed by drying in the vacuum oven at room temperature overnight.

Mercury uptake

Static mercury uptake test

10 ppm HgCl₂ and 10 ppm CH₃HgCl solution were prepared by dilution of a 1000 ppm stock solution. The required mass of nanoparticles was placed into a centrifuge tube with 10 mL solution. Nanoparticles were dispersed well by sonication for 1 min. Each solution was left to agitate on a tube roller at 60 rpm for 24 h. The subsequent mixtures were separated by use of a Nylon 0.45 μm syringe filter. The filtrate was then stabilized with 1 mL HNO₃(aq), and analyzed via ICP-OES, using an Agilent 5110 ICP-OES spectrometer.

Selectivity study

10 mL Trace Metal Certified reference material (CRM) were pipetted into 14 mL glass sample vials. To each tube 10 mg of nanoparticles was added. Blank sample was prepared by adding no samples. Each solution was left to agitate on a tube roller at 60 rpm for 1 h. The subsequent mixtures were separated by use of a Nylon 0.45 μm syringe filter. The filtrate was then stabilized with 1 mL HNO₃(aq). Samples were then analyzed via inductively coupled plasma mass spectrometry (ICP-MS), using Perkin Elmer Nexion 2000 ICP-MS with a Meinhard nebuliser and cyclonic spray chamber.

Mercury removal by mercury filter prototype

10 mL Trace Metal Certified reference material (CRM) were pipetted into 12 mL syringe with a mercury filter prototype. Blank sample was prepared by adding CRM into 12 mL syringe with a syringe filter. All solutions were filtered manually within 10 second. The filtrate was then stabilized with 1 mL HNO₃(aq). Samples were then analyzed via inductively coupled plasma mass spectrometry (ICP-MS), using Perkin Elmer Nexion 2000 ICP-MS with a Meinhard nebuliser and cyclonic spray chamber.

Characterization

Dynamic Light Scattering (DLS). The size of polysulfide nanoparticles was detected by Litesizer™ 500. Nanoparticles were dispersed into ethanol by sonication, generating a nanoparticle dispersion with concentration of 0.2 mg mL⁻¹. 1.5 mL of each samples were pipetted into a 2.5 mL standard disposable cuvette, and analysed at room 25 °C temperature. All measurements were carried with a fixed backscattering angle of 175° using automated setting of a maximum of 60 runs.

Scanning electron microscopy (SEM). Morphology images of the composite were achieved using a Hitachi S-4800 cold field emission scanning electron microscope (FE-SEM). Samples were prepared by adhering nanoparticle powder to an adhesive carbon tab and subsequently sputter coating with chromium (sputter time: 25 second; current 120 mA; distance: ~100 mm; specimens rotated during coating).

Nuclear magnetic resonance (NMR). The reactions were monitor by solution NMR in deuterated chloroform, using a Bruker Advance DRX (400 MHz) spectrometer.

Gel permeation chromatography (GPC). The molecular weight of the soluble fraction of the polymers was determined by GPC using a Viscotek system comprising a GPCmax (degasser, eluent and sample delivery system), and a TDA302 detector array, using THF as eluent.

Elemental analysis (CHNS). Elemental analysis samples were submitted to the University of Liverpool, Chemistry Department Micro-Analysis service and tested by an Elementar Vario Micro Cube.

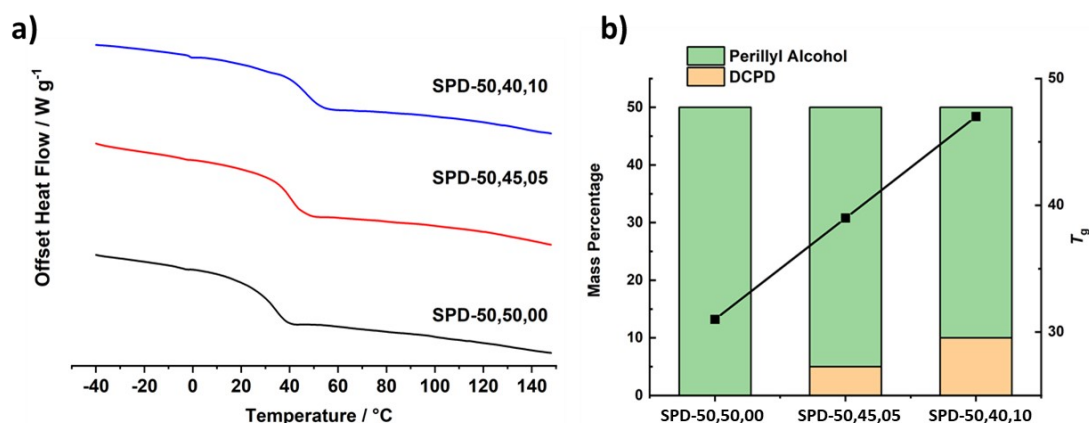


Figure S1. a) Offset DSC traces for polysulfides with varied ratio of PA to DCPD. b) T_g trending with the change of DCPD/PA ratio.

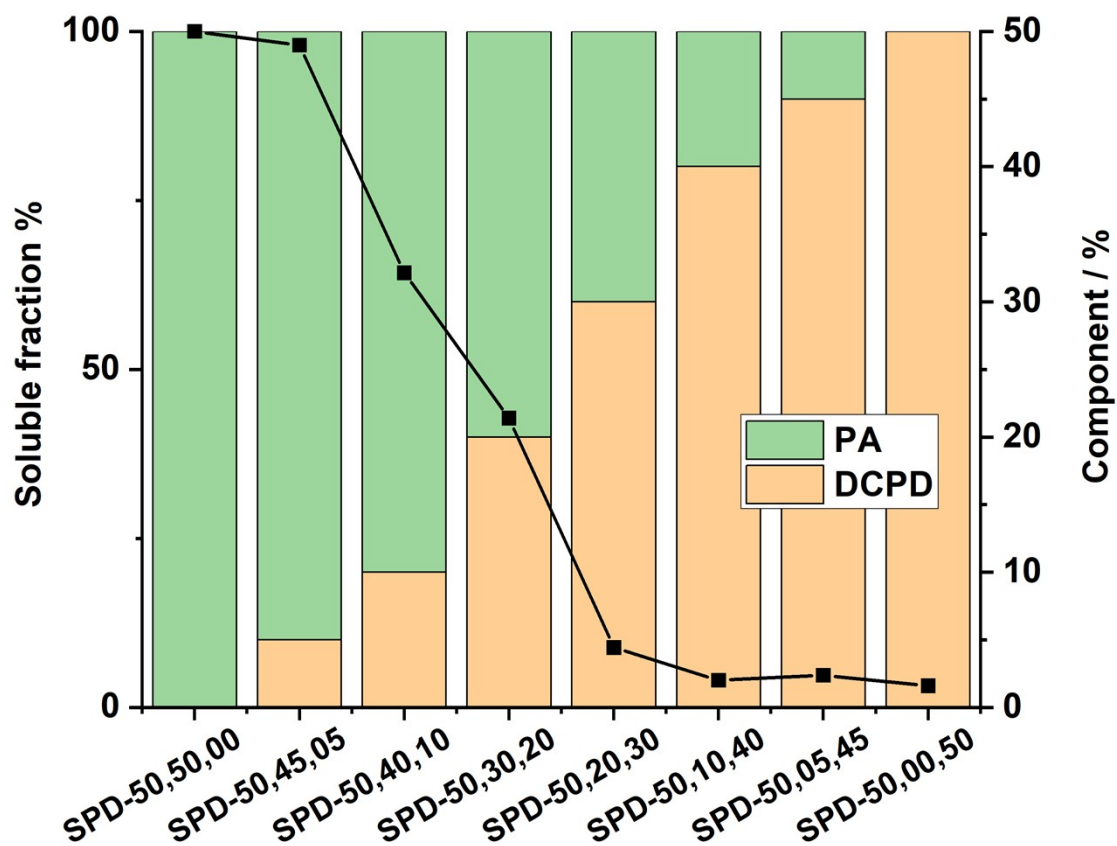


Figure S2. Solubility study (spots + line) of polysulfides. Bar chart indicated the component ratio of designed reactant of SPD-50, Y, Z.

Table S1. Solubility of representative sulfur polymers

	SDIB-50,50	SPD-50,50,00	SDCPD-50,50
Chloroform	Partly Soluble	Soluble	Soluble
Tetrahydrofuran	Partly Soluble	Soluble	Partly Soluble
Toluene	Insoluble	Soluble	Insoluble
Acetone	Insoluble	Partly Soluble	Insoluble
Ethanol	Insoluble	Insoluble	Insoluble
Hexane	Insoluble	Partly Soluble	Insoluble
Water	Insoluble	Insoluble	Insoluble

Note: 500 mg of polymer powder was placed in 10 mL solvent and agitated overnight.
Soluble = Solubility ≥ 50 mg/mL, Partly Soluble = $50 \text{ mg/mL} \geq \text{Solubility} \geq 1$ mg/mL,
Insoluble = Solubility < 1 mg/mL.

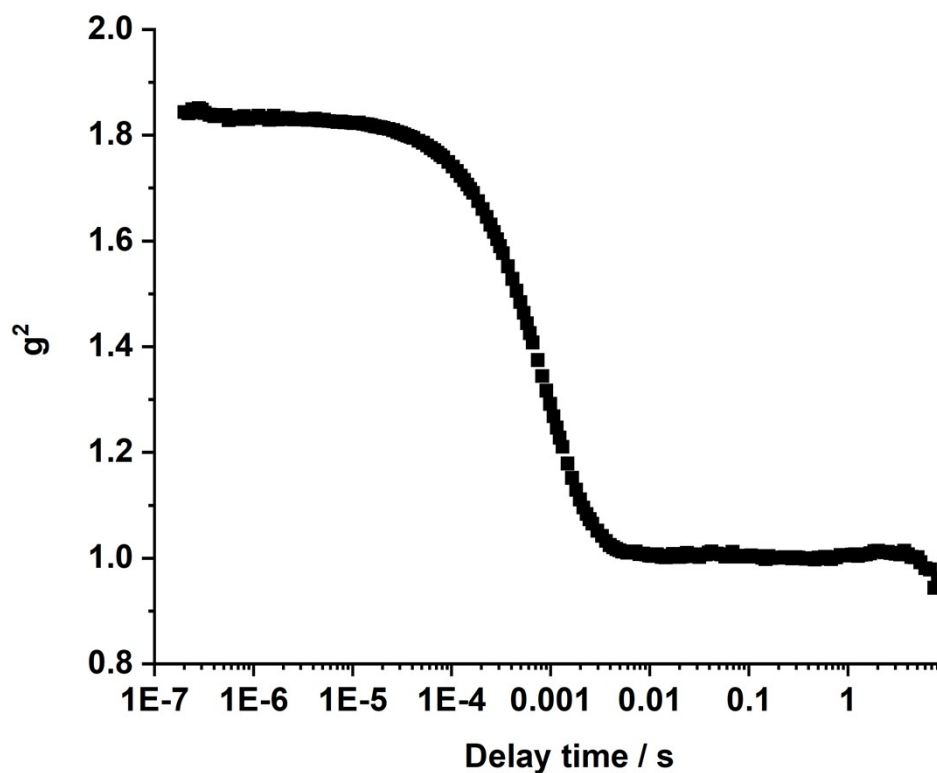


Figure S3. Correlation function of SPD-50,45,05-10

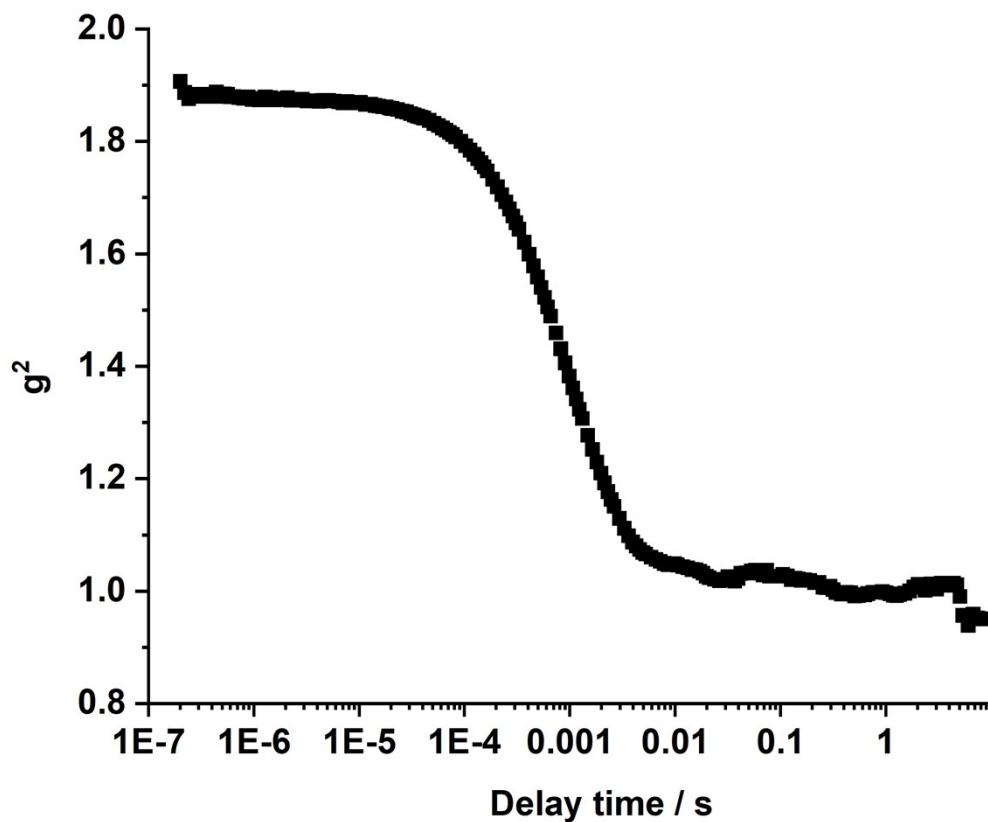


Figure S4. Correlation function of SPD-50,45,05-50

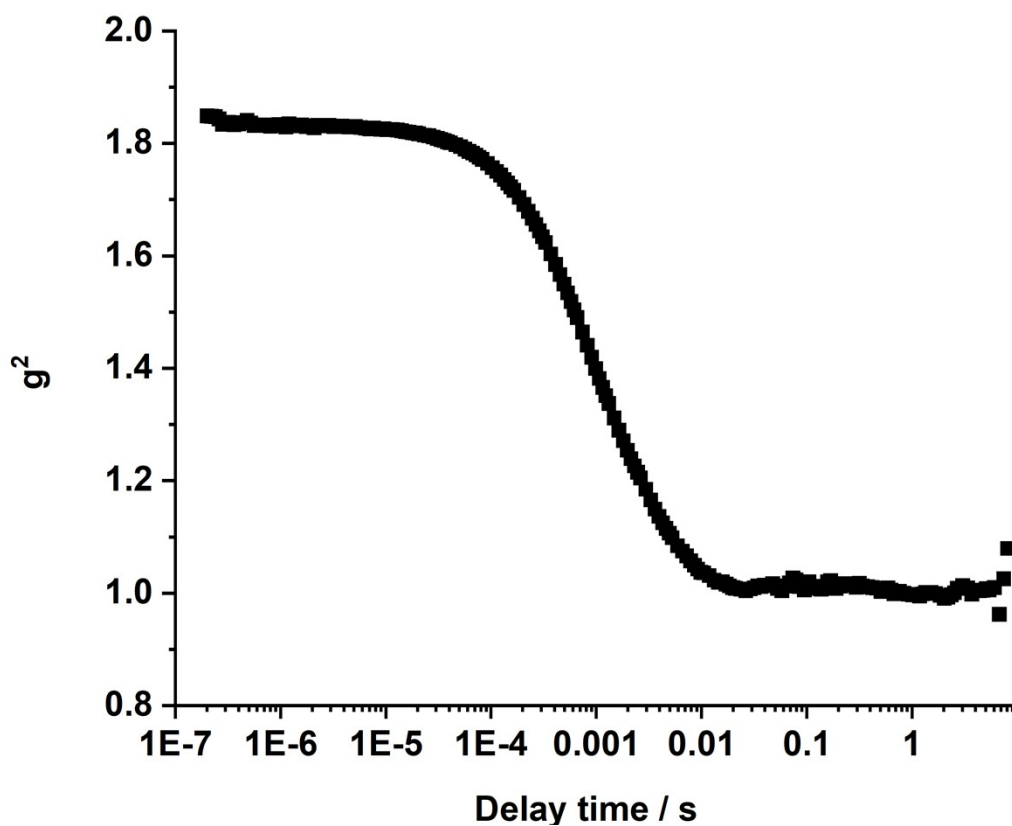


Figure S5. Correlation function of SPD-50,45,05-100

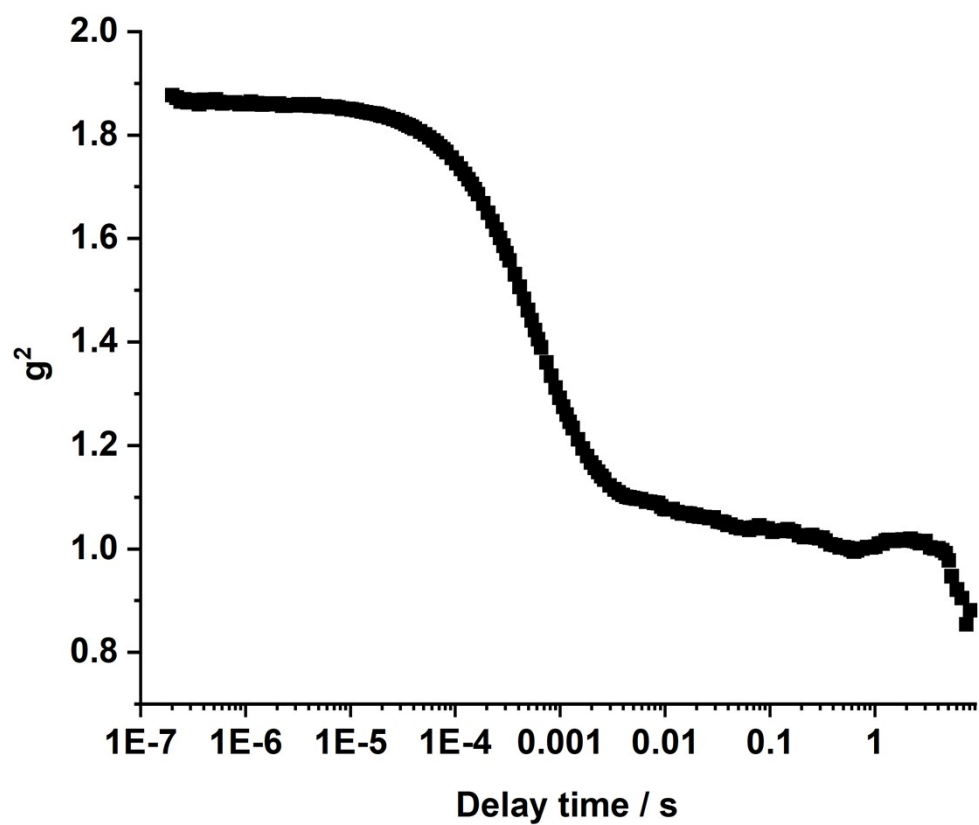


Figure S6. Correlation function of SPD-50,45,05-250

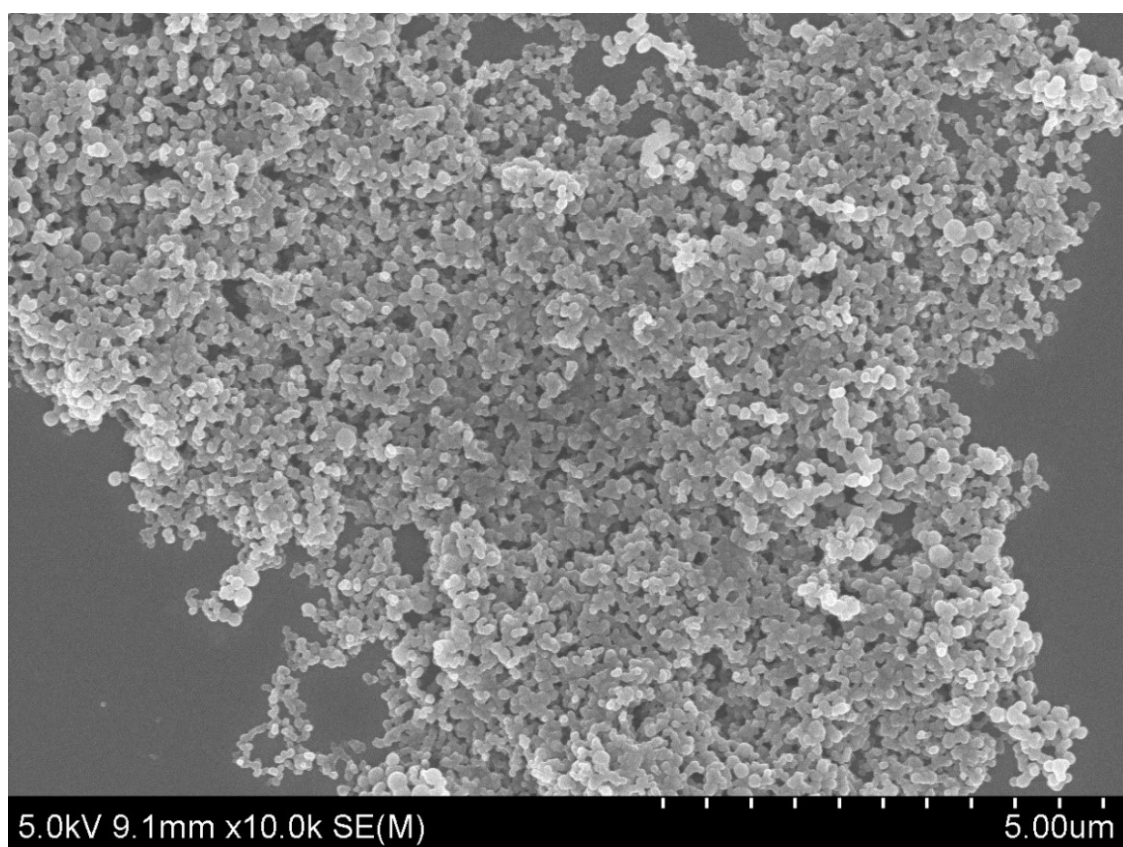


Figure S7. SEM image of SPD-50,45,05-10

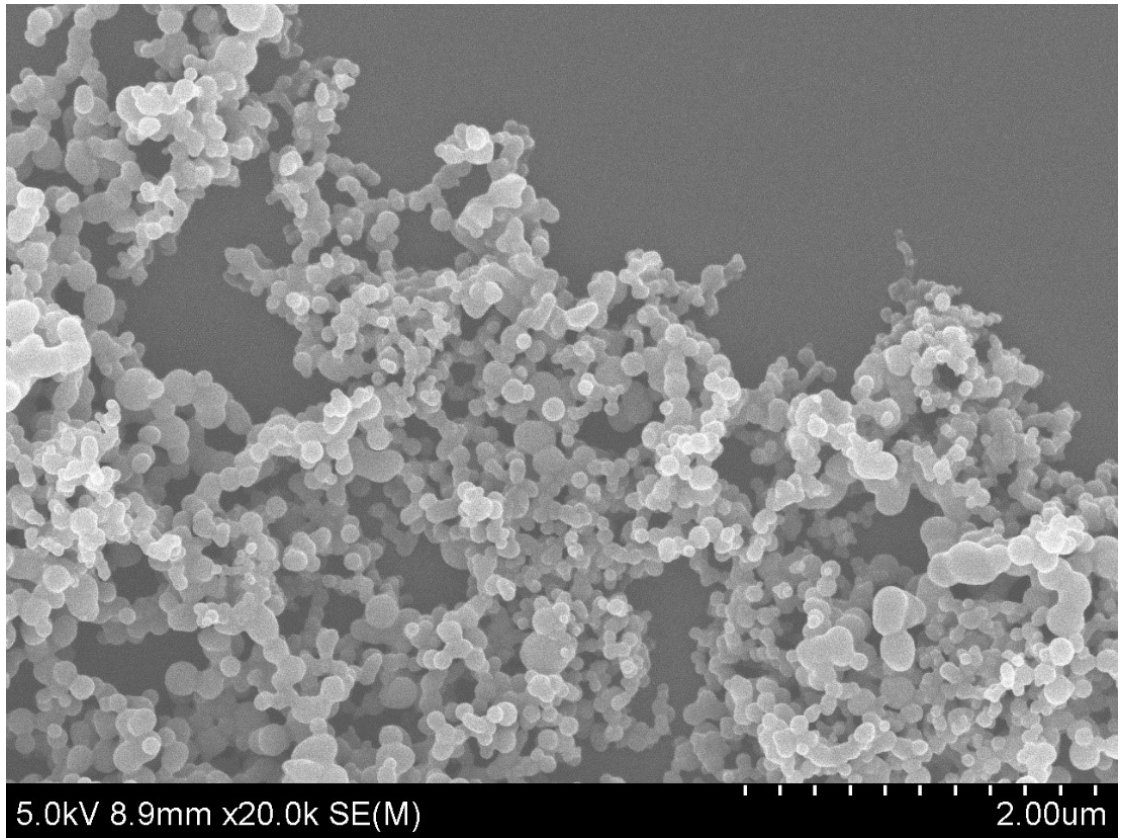


Figure S8. SEM image of SPD-50,45,05-50

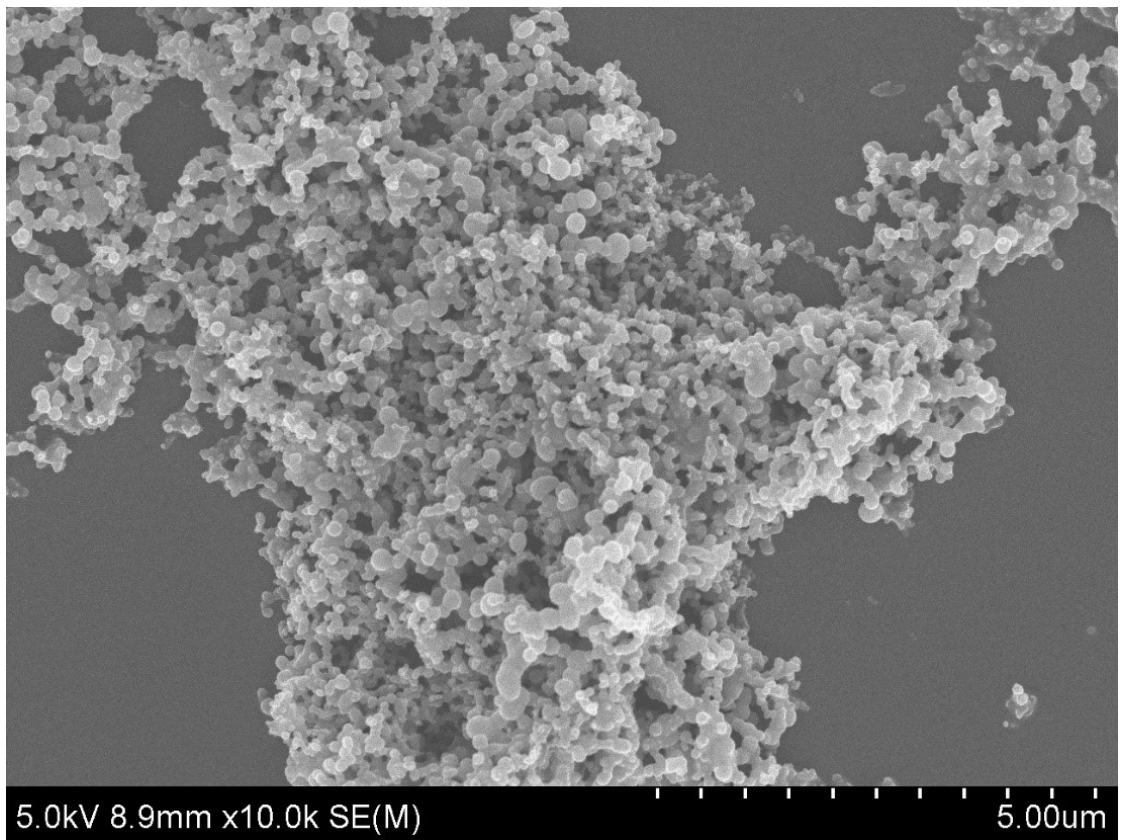


Figure S9. SEM image of SPD-50,45,05-100

Table S2. Calculated element contents and detected element contents

Sample Ref	Calc / %			Analysis / %		
	%C	%H	%S	%C	%H	%S
SPD-50,50,00	39.47	5.26	50.00	38.98	4.84	54.00
SPD-50,45,05	40.07	5.19	50.00	40.78	4.88	52.00
SPD-50,40,10	40.67	5.12	50.00	37.47	4.41	57.50
SDCPD-50,50	45.45	4.56	50.00	35.64	3.28	61.00
SPD-50,50,00-250	39.47	5.26	50.00	41.56	4.94	50.16
SPD-50,45,05-250	40.07	5.19	50.00	41.04	4.76	51.61
SPD-50,40,10-250	40.67	5.12	50.00	38.60	4.33	55.52
SDCPD-50,50-250	45.50	4.55	50.00	40.25	3.86	56.20

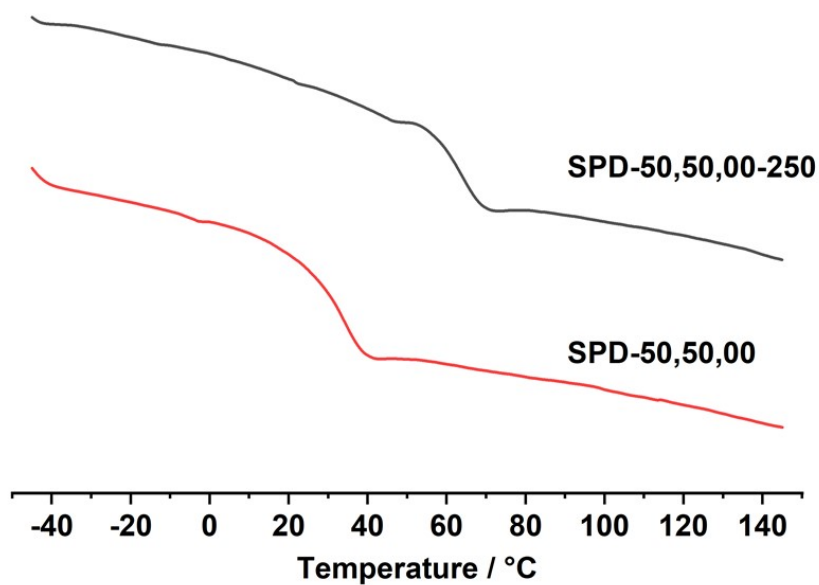


Figure S10. Offset DSC traces for polysulfide nanoparticles, SPD-50,50,00-250, and bulk polysulfide SPD-50,50,00.

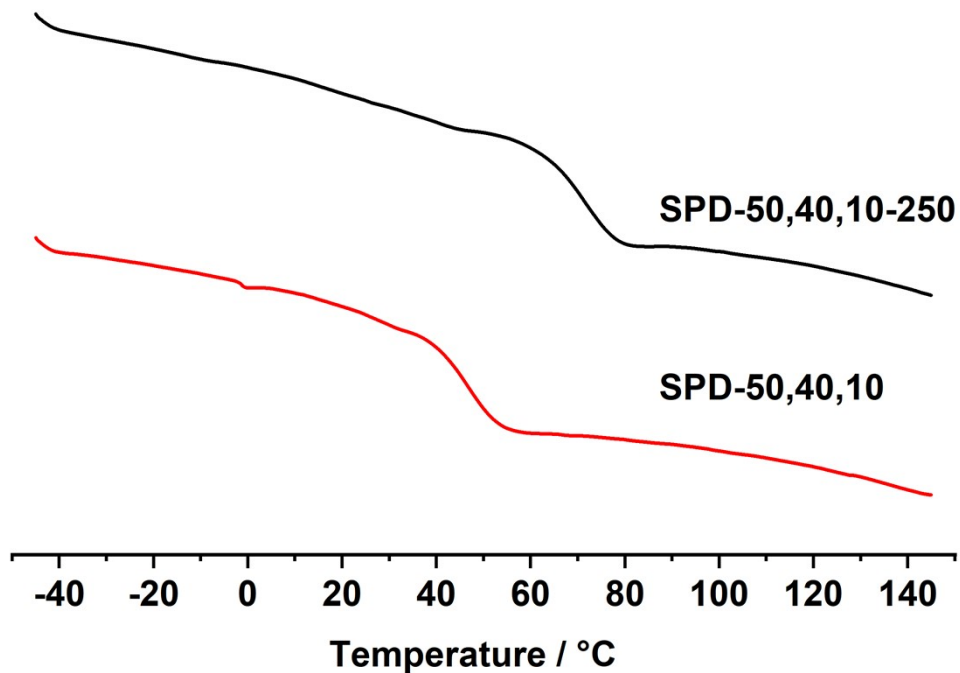


Figure S11. Offset DSC traces for polysulfide nanoparticles, SPD-50,40,10-250, and bulk polysulfide SPD-50,40,10.

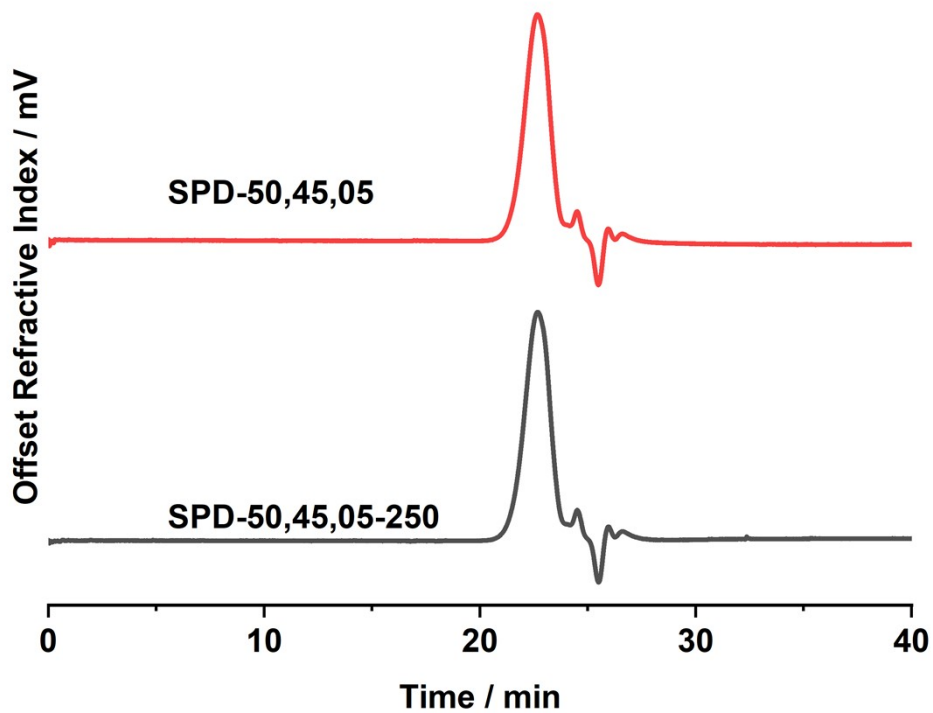


Figure S12. GPC trace for polysulfides precursors, SPD-50,45,05, and polysulfides nanoparticles, SPD-50,45,05-250.

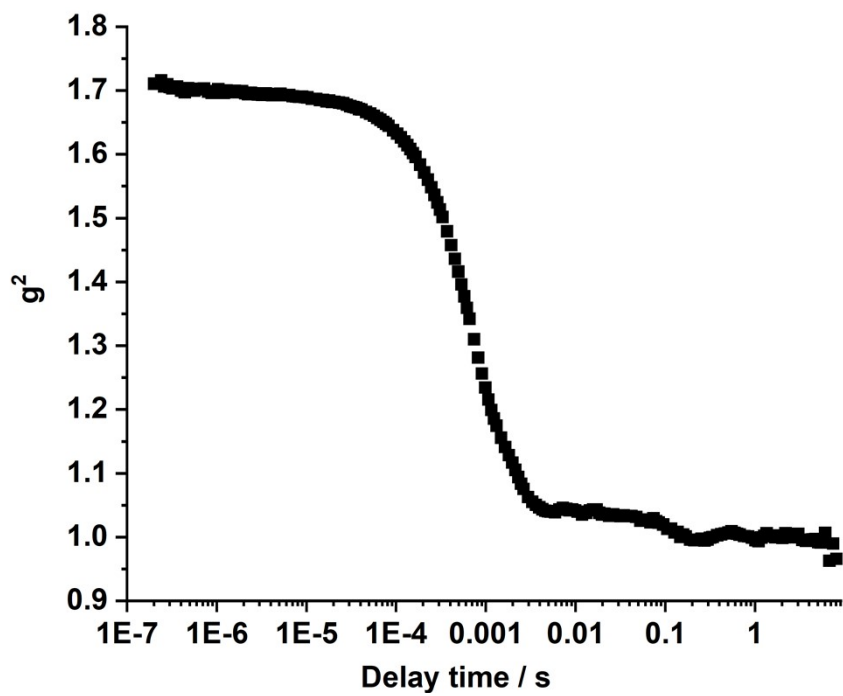


Figure S13. Correlation function of SPD-50,50,00-250

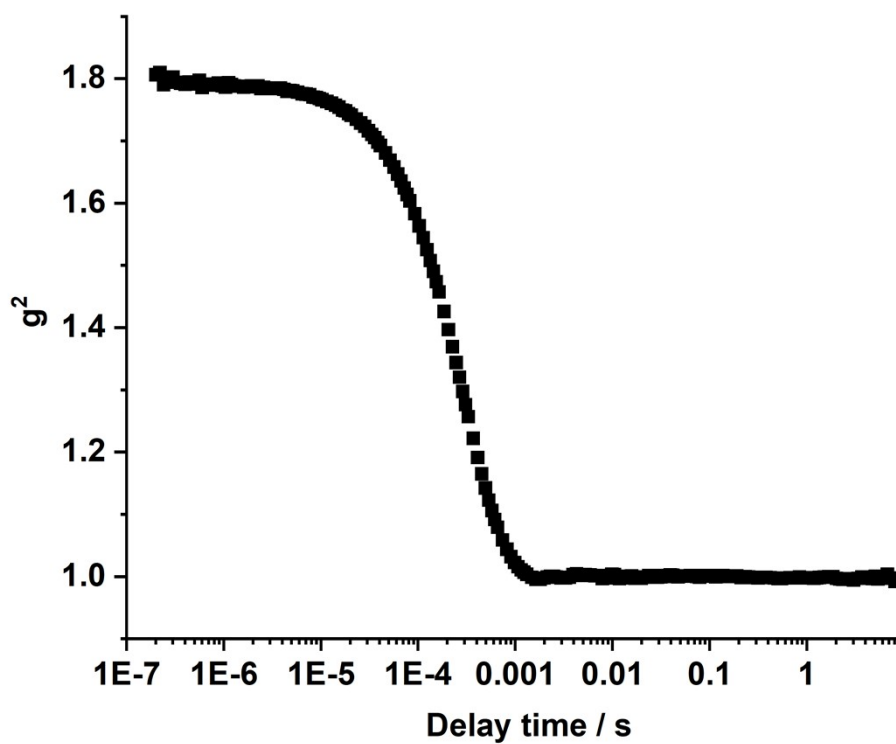


Figure S14. Correlation function of SDIB-50,50-250

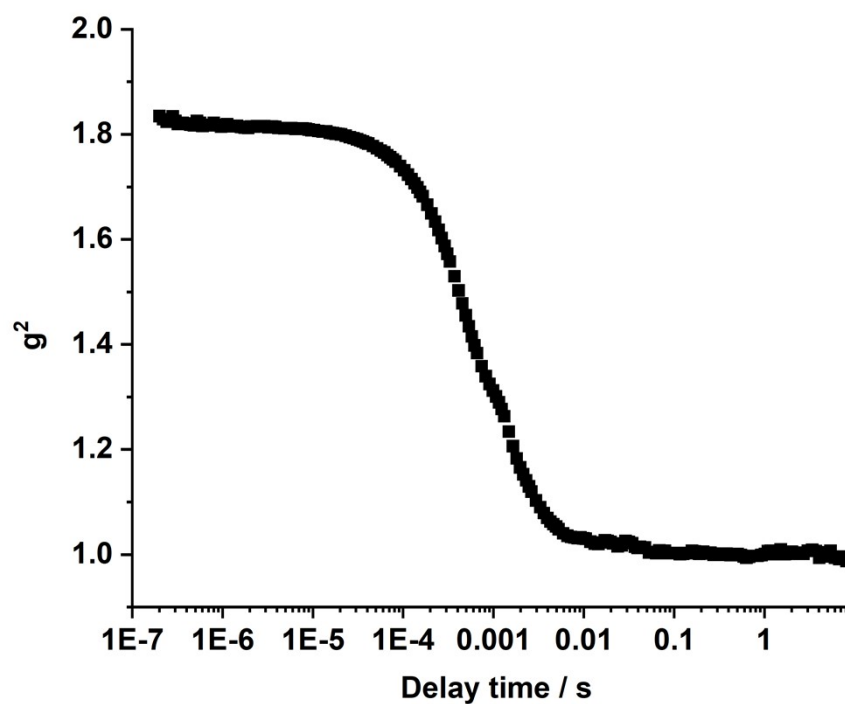


Figure S15. Correlation function of SDCPD-50,50-250

Table S3. Static mercury uptake results of polysulfide nanoparticles

	10 ppm Hg solution			10 ppm Hg solution			10 ppm CH ₃ HgCl		
	Sample weight / mg	conc. / ppm	Removed / %	Sample weight / mg	conc. / ppm	Removed / %	Sample weight / mg	conc. / ppm	Removed / %
Blank	N/A	0.05	N/A	N/A	0.05	N/A	N/A	0.02	N/A
SPD-50,50,00-250	10.5	0.08	99.25	5.4	0.07	99.34	10.7	1.51	86.73
SPD-50,45,05-250	10.1	0.04	100	5.2	0.14	98.68	10.4	1.15	89.89
SPD-50,40,10-250	9.8	0.01	100	5.2	0.17	98.40	9.9	1.61	85.85
SDCPD-50,50-250	10.3	0.01	100	5.1	0.82	96.14	9.4	20.1	82.33
Control	N/A	10.63	N/A	N/A	10.63	N/A	N/A	11.38	N/A

Table S4. Comparison of different adsorbents for Hg²⁺ uptake. Adsorbents

Adsorbents	Material type	Auxiliary materials	C ₀ (ppm)	Capacity (mg g ⁻¹)	Refs
Poly(sulfur-r-DIB)/PMMA nanofiber	Blend polymer nanofiber	Yes	600	328	1
Zn(DTC) ₂ catalyzed sulfur–limonene coated silica gel	Polymer coated silica gel	Yes	125-2000	65.25	2
SPD-50,50,00-250 nanoparticles	Polymer nanoparticles	No	10	19.5	This work
SDCPD-50,50-250 nanoparticles	Polymer nanoparticles	No	10	19.1	This work
RAC	Activated carbon	NA	16.55	12.2	3
Commercial AC	Activated carbon	NA	~10	7.8	4
Poly(S-DCPD) coated silica gel	Polymer coated silica gel	Yes	4-20	5	5
NaCl templated of Poly(S-DCPD)	Porous polymer	Yes		2.27	6
Poly(S-r-Castor)	Bulk polymer	No	107	2.01	7
Poly(S-r-Rice Bran)	Bulk polymer	No	107	1.92	7
Poly(S-r-Canola)	Bulk polymer	No	107	1.81	7
Poly(sulfur-GOB-DCPD)	Bulk polymer	No	20	1.60	8
Poly(S-perillyl alcohol)	Bulk polymer	No	2.5	0.05	9

Table S5. Selectivity test of polysulfide nanoparticles from mixed ion solution

Sample	Cr / ppb	Mn / ppb	Ni / ppb	Co / ppb	As / ppb	Se / ppb	Cd / ppb	Hg / ppb	Pb / ppb
CRM	331	1134	1215	876	248	129	434	9.70	243
SPD-50,50,00-250	333	1119	1233	886	247	126	435	-	246
SPD-50,45,05-250	330	1160	1214	881	239	121	431	-	246
SPD-50,40,10-250	328	1085	1215	884	249	124	426	-	243
SDCPD-50,50-250	342	1160	1255	907	250	129	436	-	243

Note: ‘-’ means under detectable level of ICP-MS’



Figure S16. Mercury filter prototype produced by commercial syringe filter (a Nylon 0.45 μ m syringe filter) with synthesized sulfur nanoparticles, SPD-50,25,05-250.

Table S6. Selectivity test of mercury filter prototype from mixed ion solution

Sample	Cr / ppb	Mn / ppb	Ni / ppb	Co / ppb	As / ppb	Se / ppb	Cd / ppb	Hg / ppb	Pb / ppb
Standard	294	1018	1015	751	202	79	328	7.52	227
Blank Filter	294	1011	1015	743	204	80	325	7.15	225
Hg Filter 1	284	994	953	704	199	87	326	0.72	226
Hg Filter 2	296	1004	1010	733	202	83	327	1.10	229
Hg Filter 3	297	1020	1001	733	194	81	323	0.52	229

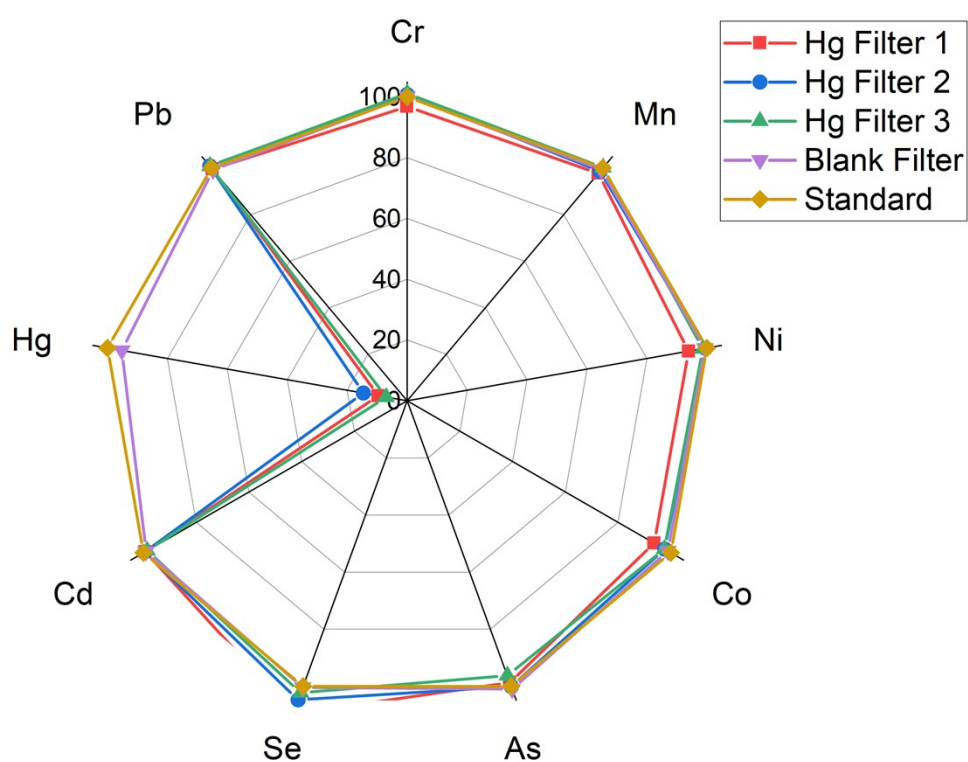


Figure S17. Selectivity test of mercury filter prototypes using mixed ion solution, simulating waste water. More than 90 % mercury was selectively removed by mercury filter prototypes.

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