

Electronic supplementary information (ESI) for

Preparation of dithiocarbamate polymer brush grafted nanocomposites for rapid and enhanced capture of heavy metal ions

Xin Wang,^a Shiyao Jing,^a Yingying Liu,^a Xiumin Qiu^a and Yebang Tan^{*ab}

^a *School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China.*

^b *The Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Jinan 250100, People's Republic of China.*

Synthesis of model sacrificial initiator

Propylamine (6.56 mL, 0.08 mol) and triethylamine (9.3 mL, 0.067 mol) were dissolved in 15 mL of dichloromethane. 2-bromoisobutyryl bromide (8.28 mL, 0.067 mol) was added dropwise to the reaction system in an ice bath. After the addition, the mixture was allowed to warm to ambient temperature and stirred for 10 h. The low boiling components were removed by rotary evaporation. 30 mL of ethyl acetate was added to the residue, and the mixture was washed with water (50 mL × 3 times). The organic layer was dried with anhydrous MgSO_4 . After the removal of solvent and vacuum drying, a transparent oil was obtained in 91% yield.

Synthesis of bare SiO_2 nanoparticles

SiO_2 nanoparticles were prepared by the hydrolysis of tetraethylorthosilicate (TEOS) via Stöber method. 250 mL of absolute ethanol was added into a 500 mL round-bottom flask and heated to 40 °C. 10 mL of TEOS was dripped into the system under magnetic stirring at a speed of 500 rpm. After that, 15 mL of ammonia was added into the flask. The mixture was stirred for 24 h at 40 °C. At last, the bare SiO_2 nanoparticles were obtained by centrifugal separation, exhaustive ethanol washing and vacuum drying.

Immobilization of ATRP initiator on SiO_2 nanoparticles

Firstly, amino-functionalized SiO_2 ($\text{NH}_2@ \text{SiO}_2$) nanoparticles were synthesized. 4g of SiO_2 were ultrasonically dispersed in 150 mL ethanol. After the addition of APTES (5 mL; 21.36 mmol), the dispersion was stirred for 1 h at ambient temperature and then was refluxed for 3 h at 85 °C. The $\text{NH}_2@ \text{SiO}_2$ nanoparticles were isolated by centrifugation at 11000 rpm, and were purified by ethanol washing and vacuum drying. Then, 3 g of $\text{NH}_2@ \text{SiO}_2$ and Et_3N (4 mL; 28.85 mmol) were added to 100 mL toluene. The solution of BIBB (2 mL;

16.18 mmol) in 10 mL toluene was dripped into the dispersion in an ice bath. After 10 h, the ATRP initiator immobilized SiO₂ (Br@SiO₂) was isolated by centrifugation, and was successively washed with toluene, acetone/water (v/v = 1/1) and acetone. The Br@SiO₂ nanoparticles were finally purified by vacuum drying at 35 °C.

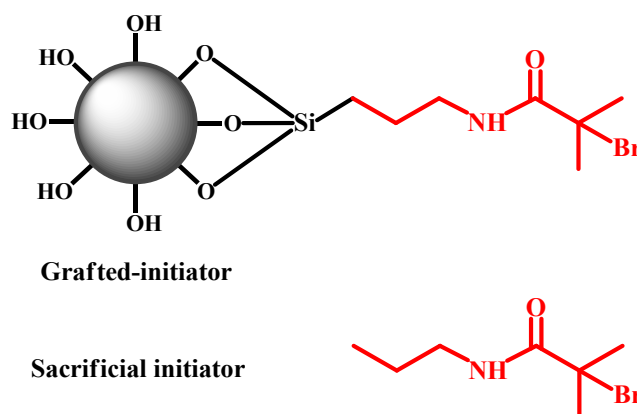


Fig. S1 The chemical structure of sacrificial initiator and grafted-initiator.

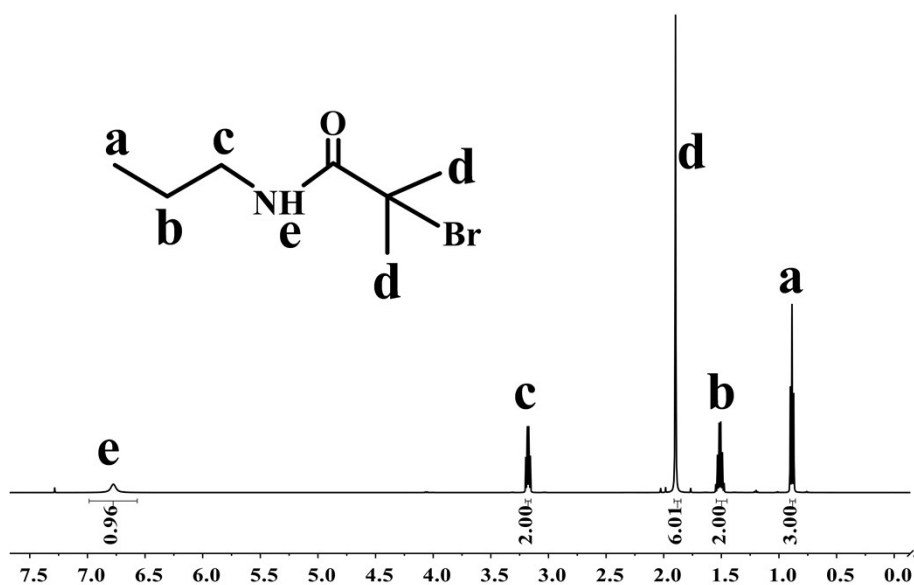


Fig. S2 The ¹H NMR spectroscopy of synthesized model sacrificial initiator in CDCl₃.

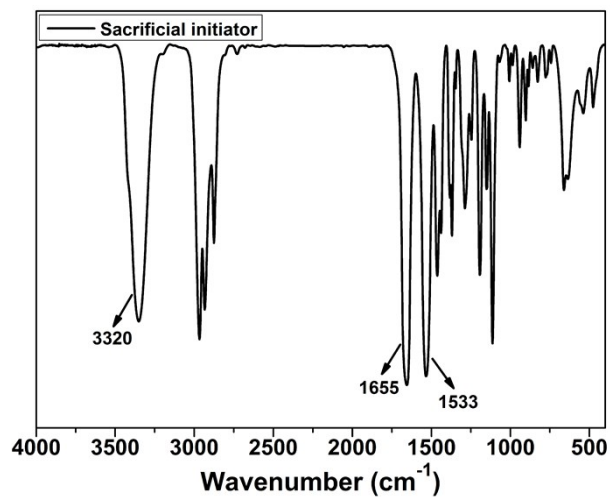


Fig. S3 The FTIR spectroscopy of synthesized model sacrificial initiator.

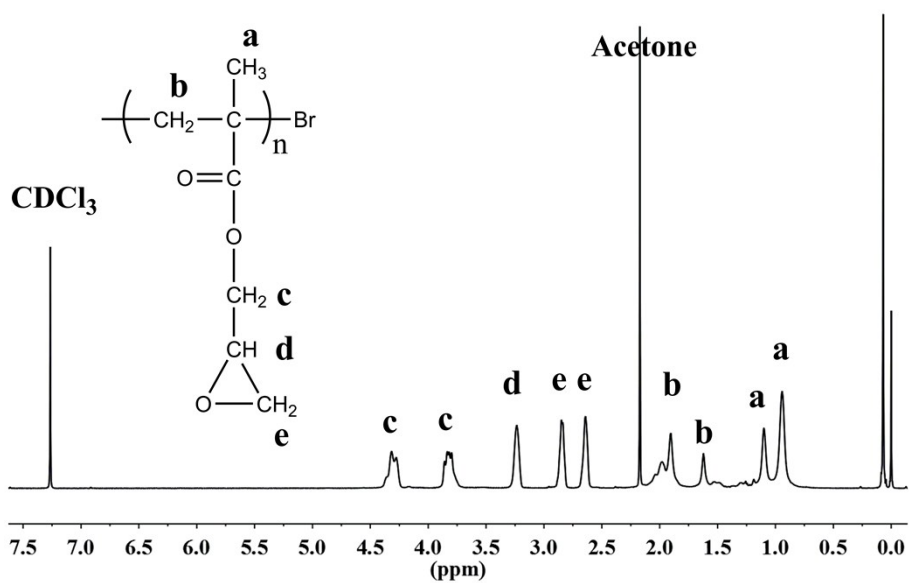


Fig. S4 ^1H NMR spectroscopy of PGMA polymer brush in CDCl_3 .

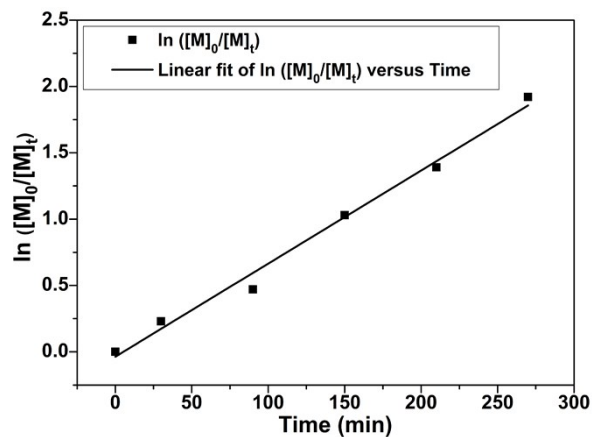


Fig. S5 Kinetic plot of SI-ATRP (polymerization condition: Molar ratio of [GMA]:[BMMA]:[CuBr]:[PMDETA] is [300]:[1]:[1]:[1]).

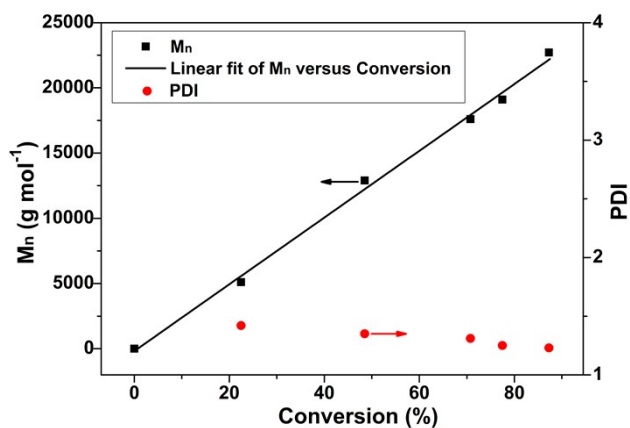


Fig. S6 The evolution of M_n and PDI with the monomer conversion (polymerization condition: Molar ratio of [GMA]:[BMMA]:[CuBr]:[PMDETA] is [300]:[1]:[1]:[1]).

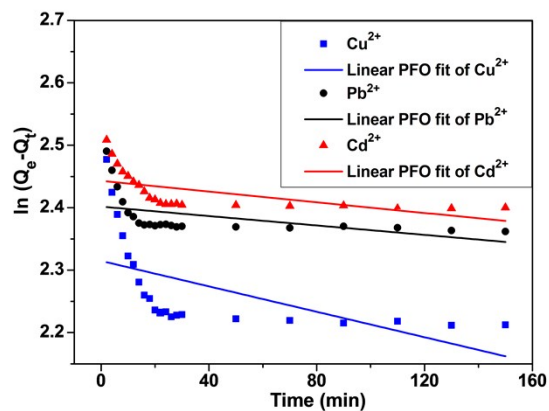


Fig. S7 Linear fitting plots for the adsorption kinetics of studied metallic ions at 298 K using PFO model.

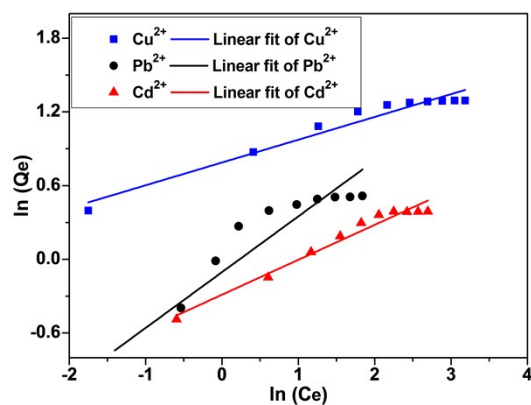


Fig. S8 Linear fitting plots for the adsorption isotherms of metallic ions at 298 K using Freundlich model.

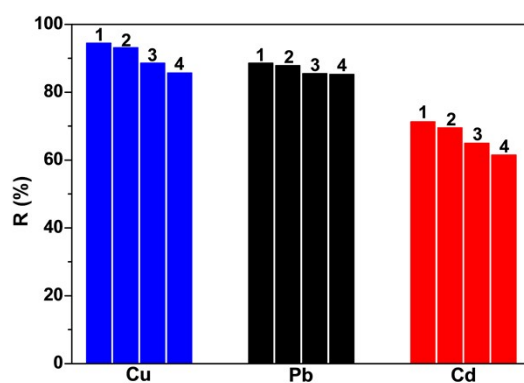


Fig. S9 Removal efficiencies of Cu^{2+} , Pb^{2+} and Cd^{2+} during 4 reuse cycles.

Table S1 CHNS elemental analysis results of synthesized nanocomposites

Sample	N (%)	C (%)	H (%)	S (%)
Bare SiO_2	—	—	0.77	—
$\text{NH}_2@ \text{SiO}_2$	0.78	3.14	0.95	—
$\text{Br}@ \text{SiO}_2$	0.58	3.82	1.20	—
$\text{PGMA}@ \text{SiO}_2$	0.12	54.21	6.40	—
$\text{NH}_2\text{-PGMA}@ \text{SiO}_2$	9.06	47.35	7.97	—
$\text{DTC-PGMA}@ \text{SiO}_2$	5.43	33.76	5.71	32.38

Table S2 Fitting parameters for the adsorption isotherms of heavy metal ions by using D-R model

Metal ion	Q_m (mmol g ⁻¹)	K (mmol ² J ⁻²)	R^2	E (kJ mmol ⁻¹)
Cu ²⁺	3.77	0.00101	0.978	22.25
Pb ²⁺	2.04	0.00141	0.975	18.83
Cd ²⁺	1.61	0.00152	0.942	18.14

Table S3 Thermodynamic parameters based on the Van't Hoff equation for the adsorption of heavy metal ions on the nanostructured DTC-PGMA@SiO₂ adsorbent.

Metal ion	T (K)	Q_m (mmol g ⁻¹)	K_L (L mmol ⁻¹)	R^2	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
Cu ²⁺	298	3.75	1.526	0.999	-13.94	25.24	131.47
	308	3.99	1.947	0.998	-15.25		
	318	4.24	2.397	0.999	-16.57		
Pb ²⁺	298	1.94	0.991	0.990	-10.33	29.51	133.69
	308	2.18	1.591	0.992	-11.67		
	318	2.37	2.511	0.991	-13.01		
Cd ²⁺	298	1.64	0.727	0.996	-9.23	9.35	62.36
	308	1.81	0.831	0.994	-9.86		
	318	2.01	0.926	0.995	-10.48		