Facile synthesis and application of poly(ionic liquid)-bonded silica hybrid materials

Wentao Bi, Minglei Tian and Kyung Ho Row*

Chemicals

2,2-Azobisisobutyronitrile (AIBN) was purchased from Jun-sei Chemical Co. (Tokyo, Japan). 1-Vinylimidazole (>98%), allyl chloride (>98%), and 1-chlorohexane (>95%) were from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). (3-Chloropropyl)trimethoxysilane (97%) was from Sigma–Aldrich (St. Louis, MO, USA). The silica particles (≤7 μm) were purchased from SUNJIN Chemical Co. Ltd. and a specific surface are (BET) of 300 m^2 g^{-1}. The 15 μm C_{18} particles were purchased from Merck Chemicals Ltd. and a specific surface are (BET) of 420 m^2 g^{-1}. 1-Octanol, toluene, acetonitrile and other organic solvents were from Duksan Pure Chemicals Co., Ltd. (Ansan, Korea). Distilled water was filtered using a vacuum pump and a filter (HA-0.45, both from Millipore, USA) before use. All other solvents were of HPLC or analytical grade. All samples were filtered (MFS-25, 0.2 μm TF, Whatman, USA) before being injected into the HPLC system.

Synthesis

SilprCl: Silica was first immersed in hydrochloric acid for 24 h and then washed with deionized water and dried at 100 ^{o}C for 8h. The activated silica (5.0g) was suspended in 50.0 mL of dry toluene, after which an excess of 3-chloropropyltrimethoxysilane

(5.0mL) was added. After the suspension was refluxed for 12 h, the reaction was stopped and cooled to room temperature. The particles were washed with toluene, and methanol. SilprCl was finally dried at 60 ◦C for 10 h.

SilprPIL: ***Precipitation polymerization.*** 0.4 g SilprCl was mixed with 1.8 mL of 1-vinylimidazole, 0.4 mL of allyl chloride and 1.04 mL of 1-chlorohexane in 10.0 mL of 1-octanol. After adding 1.0 wt.% AIBN, the mixture was stirred at 80 °C for 7 h. The SilprPIL was filtered and washed with deionized water and ethanol, and dried under vacuum at 70 ^{o}C.

Emulsion polymerization. SilprCl (0.4 g), 1-vinylimidazole (1.8 mL), allyl chloride (0.4 mL), 1-chlorohexane (1.04 mL) and 1-octanol (2.0 mL) were added to a 50.0 mL flask, and the mixture was stirred for 1 h with adding 1 wt.% AIBN. Then 20.0 mL of 2 wt.% aqueous poly(vinyl alcohol) (PVA) with 0.3 g of NaCl was added. The mixture was vigorously stirred under flowing argon for 7 h at 80 ^{o}C. The mixture was cooled to room temperature, and the precipitate was filtered and washed by water and ethanol. The resulting precipitate was dried under vacuum at 70 ^{o}C.

SilprMIL and SilprNH$_2$ were synthesized according to ref. [S1].

Adsorption

10.0 mg of sorbents (C_{18}, 420 m^2 g^{-1}; SilprNH$_2$, 540 m^2 g^{-1}; SilprMIL, 130 m^2 g^{-1}; SilprPIL by precipitation polymerziation, 40 m^2 g^{-1}; SilprPIL by emulsion polymerization, 129 m^2 g^{-1}) were stirred with 1.0 mL of each standard solution in vials at room temperature until the concentration of free target compounds stopped decreasing and equilibrium adsorptions were obtained [S2]. Amounts of target compounds adsorbed on sorbents were calculated by subtraction. Repeatability was assessed over five adsorptions. Two-sided *t*-tests were used to evaluate the data obtained from independent samples. The adsorption isotherm (Fig. S1) of each target compound was measured at 15 ^{o}C, and the maximum adsorption capacity was predicted through Langmuir equation (Table S1).

$$Q = \frac{aC_E}{1 + bC_E}$$

Where, Q (mg m^{-2}) is the adsorbed amount, C_E (mg mL^{-1}) in the equation is the equilibrium concentration of the solute in the liquid phase. a and b are the parameters.

HPLC analysis and characteristic analysis

The chromatography system consisted of Waters 600s Multi solvent Delivery System, Waters 616 liquid chromatography (Waters Associates, Milford, MA, USA), a Rheodyne injector (20 μL sample loop) and a variable wavelength 2487 UV dual channel detector. Data processing was carried out with a Millenium 3.2 consisted of HP Vectra 500PC. The HPLC analysis was performed with a commercial C_{18} column (4.6×150 mm, 5.0 μm) from RStech (Daejeon, Korea). The mobile phase were methanol/water (30/70, *v/v*) for methylxanthines, acetonitrile/water/trifluoroacetic acid (16/84/0.1, *v/v/v*) for phenolic acids and methanol/water/acetic acid (78/22/0.5, *v/v/v*) for tanshinones with the flow rate of 0.5 mL min^{-1}, and the UV wavelengths were at 274 nm, 270.0 nm and 254 nm, respectively.

The carbon, hydrogen, and nitrogen contents were determined by elemental analysis that performed on an EA1112 (Italy) (Table S2). Thermogravimetric measurements were obtained on a TGA unit (SCINCO thermal gravimeter S-1000) with a heating rate of 10 °C min^{-1} under nitrogen (Fig. S2). FT-IR spectra were obtained using KBr pellets on a Vertex 80V (Bruker, Billerica, MA, USA) between 400 and 4000 cm^{-1} at a scan rate of 20 scans min^{-1} (Fig. S3). Field emission-scanning electron microscopy (FE-SEM) was conducted on an S-4200 microscope (Hitachi, Ontario, Canada). TEM images were obtained by using CM200 transmission electronic microscope (Philips, Netherlands) (Fig. S4). BET surface areas (N_2 atmosphere at -195.85 ◦C) were measured using an ASAP2020 surface area analyzer (Micromeritics, Norcross, GA, USA).

Reference

1. W. Bi, J. Zhou and K. H. Row, *Anal. Chim. Acta*, 2010, **677**, 162.
2. W. Bi, M. Tian and K. H. Row, *J. Chromatogr. A*, 2011, doi:10.1016/j.chroma.2011.08.054.

Table S1. Parameters in adsorption isotherms.

Methods	Target compounds	*a*	*b*	r^2	Maximum adsorption capacity (mg m^{-2})
Precipitation polymerization	Theobromine	0.08698	0.82352	0.98023	0.1056
	Theophylline	0.09004	0.47829	0.98702	0.1883
	Caffeine	0.12146	1.21877	0.97289	0.1000
	Protocatechuic acid	1.17382	2.7335	0.99926	0.4294
	Caffeic acid	1.81211	2.73353	0.99926	0.6629
	Ferulic acid	1.63162	4.85201	0.99264	0.3363
	Cyptotanshinone	0.78639	13.59517	0.93305	0.0578
	Tanshinone I	0.20268	11.76172	0.95837	0.0172
	Tanshinone IIA	0.20331	30.36261	0.86096	0.0067
Emulsion polymerization	Theobromine	0.08618	0.27905	0.97964	0.3088
	Theophylline	0.08895	0.4843	0.99139	0.1837
	Caffeine	0.11657	1.50866	0.95422	0.0773
	Protocatechuic acid	0.38219	3.7032	0.99499	0.1032
	Caffeic acid	0.59347	3.70323	0.99499	0.1603
	Ferulic acid	0.8161	4.22897	0.99301	0.1930
	Cyptotanshinone	0.20879	12.90195	0.93634	0.0162

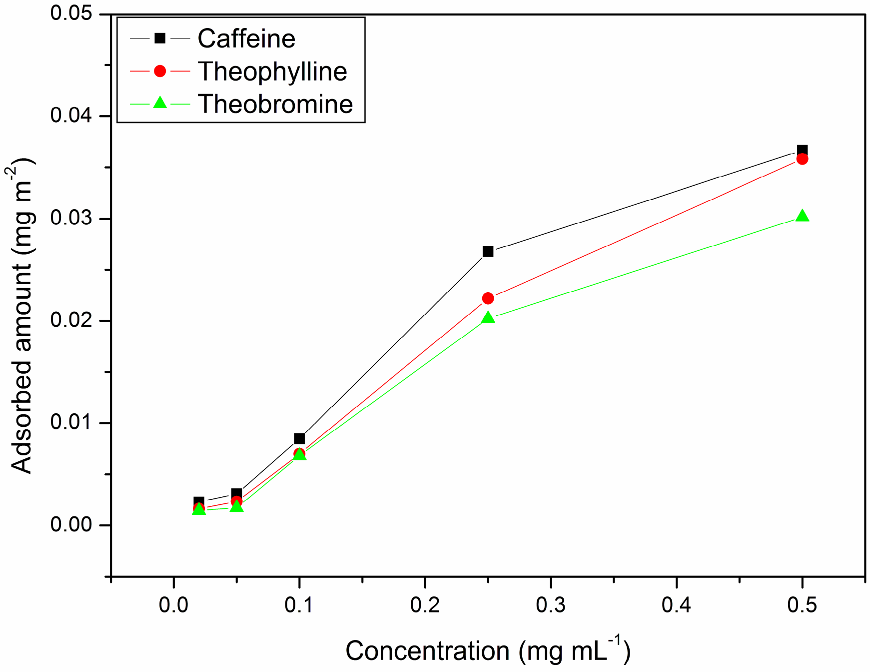
Tanshinone I	0.12091	4.99373	0.96334	0.0242
Tanshinone IIA	0.0716	8.84492	0.89441	0.0081

Table S2. Elemental analysis.

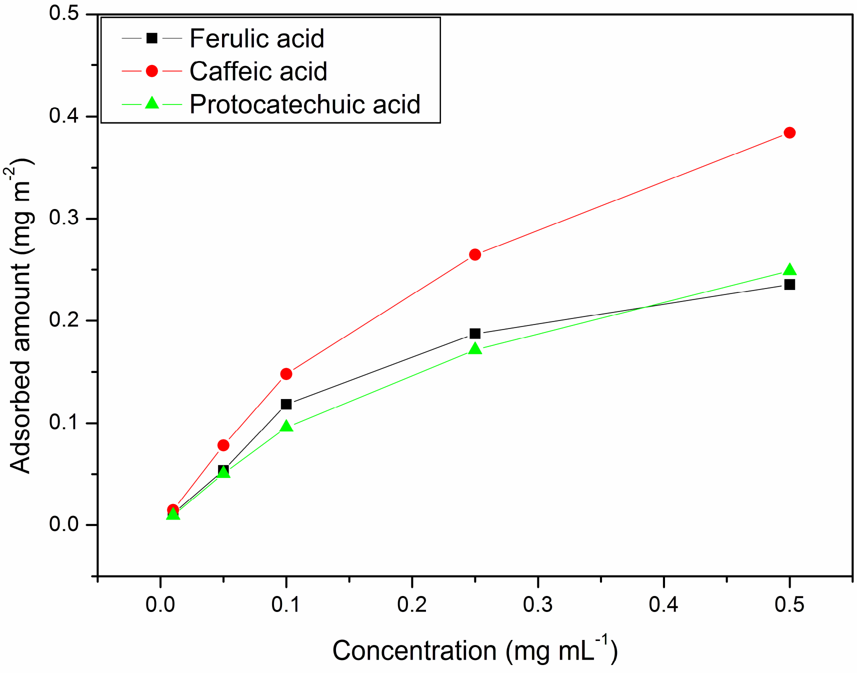
Name	C %	H %	N %	Surface coverage (μmol m^{-2})
SilprCl	5.19	1.02	-	5.12
SilprPIL (Precipitation polymerization)	16.06	2.24	5.24	8.16
SilprPIL (Emulsion Polymerization)	8.4	1.44	2.24	3.03

Ref [7]: SilprCl (μmol m^{-2}) = %C/[36*(1-%C-%H)*S]

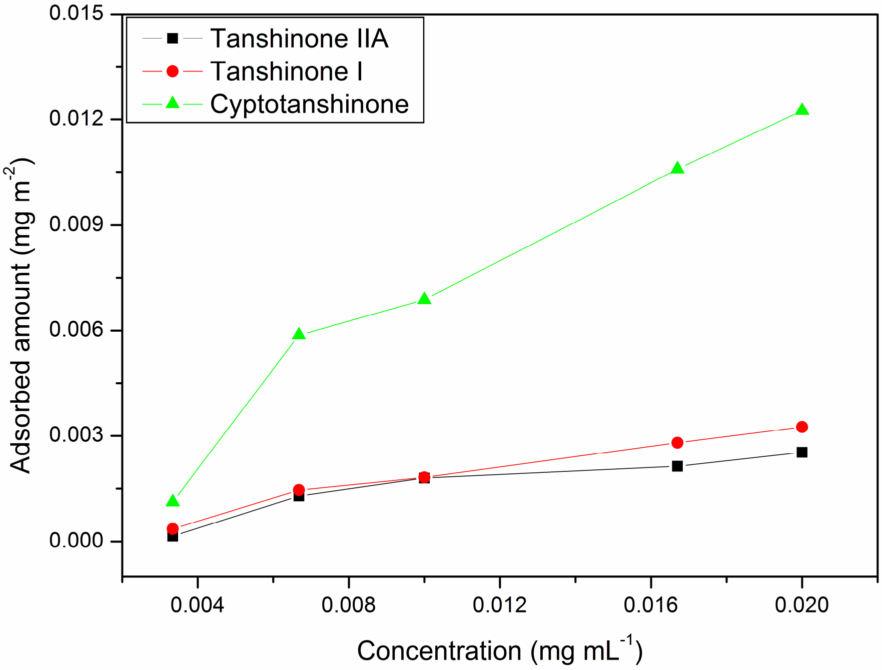
SilprPIL (μmol m^{-2}) = %N/[28*(1-%C-%H-%N)*S]


Caffeine
Theophylline
Theobromine
0.05
0.04
0.03
0.02
0.01
0.00
Adsorbed amount (mg m^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
Concentration (mg mL^{-1})

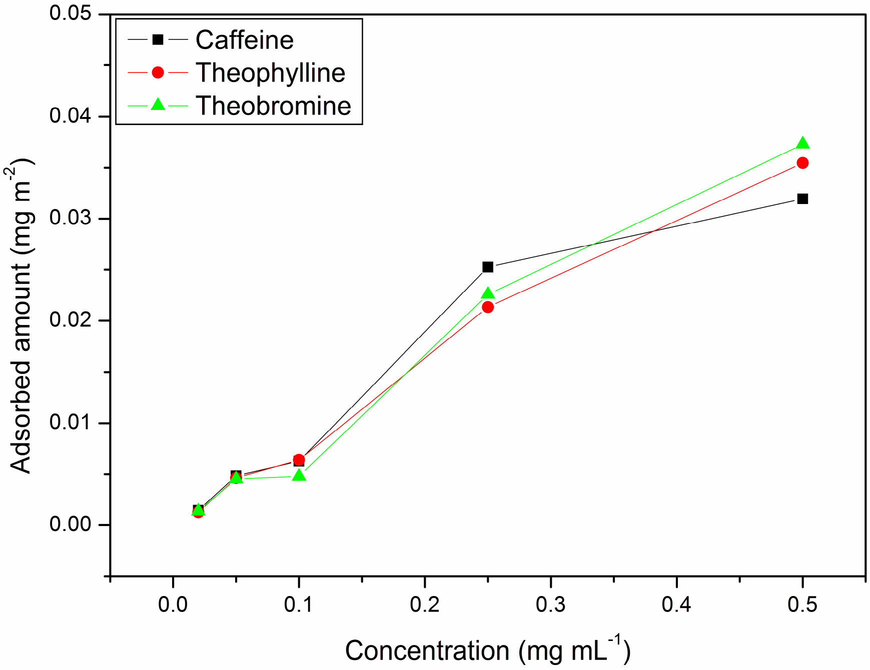
(A)


Ferulic acid
Caffeic acid
Protocatechuic acid
0.5
0.4
0.3
0.2
0.1
0.0
Adsorbed amount (mg m^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
Concentration (mg mL^{-1})

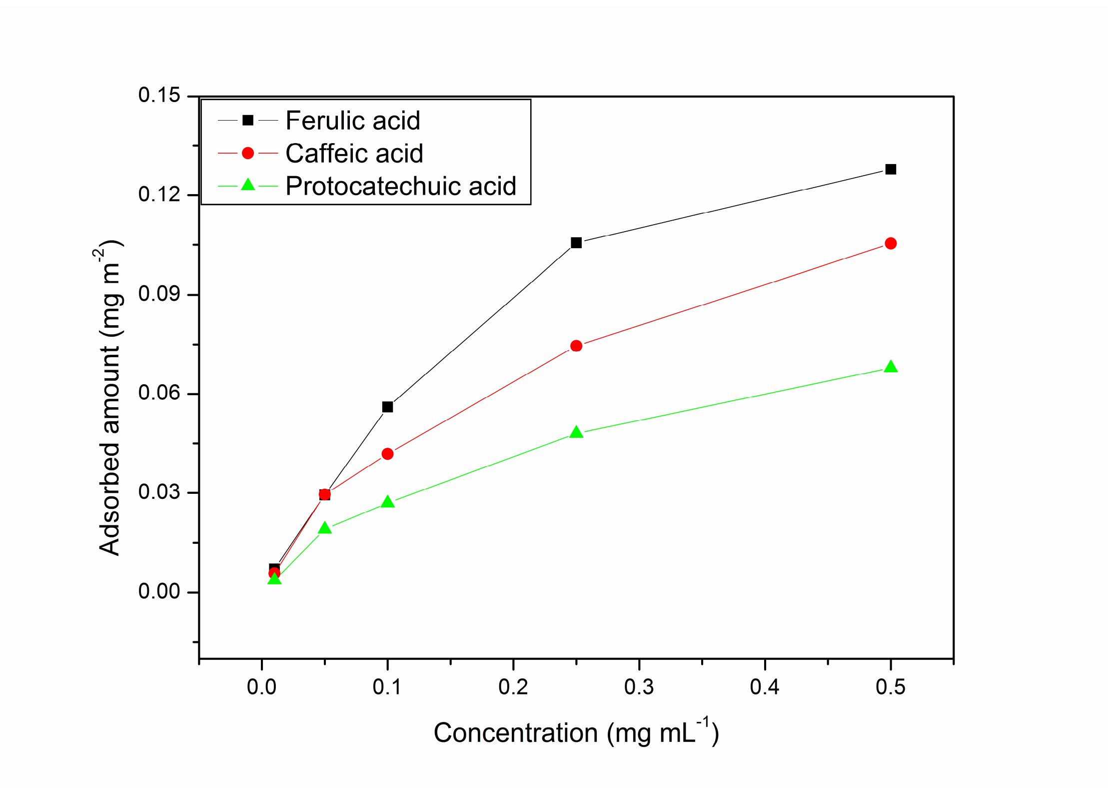
(B)


0.015
0.012
0.009
0.006
0.003
0.000
Adsorbed amount (mg m^{-2})
0.004
0.008
0.012
0.016
0.020
Concentration (mg mL^{-1})
Tanshinone IIA
Tanshinone I
Cyptotanshinone

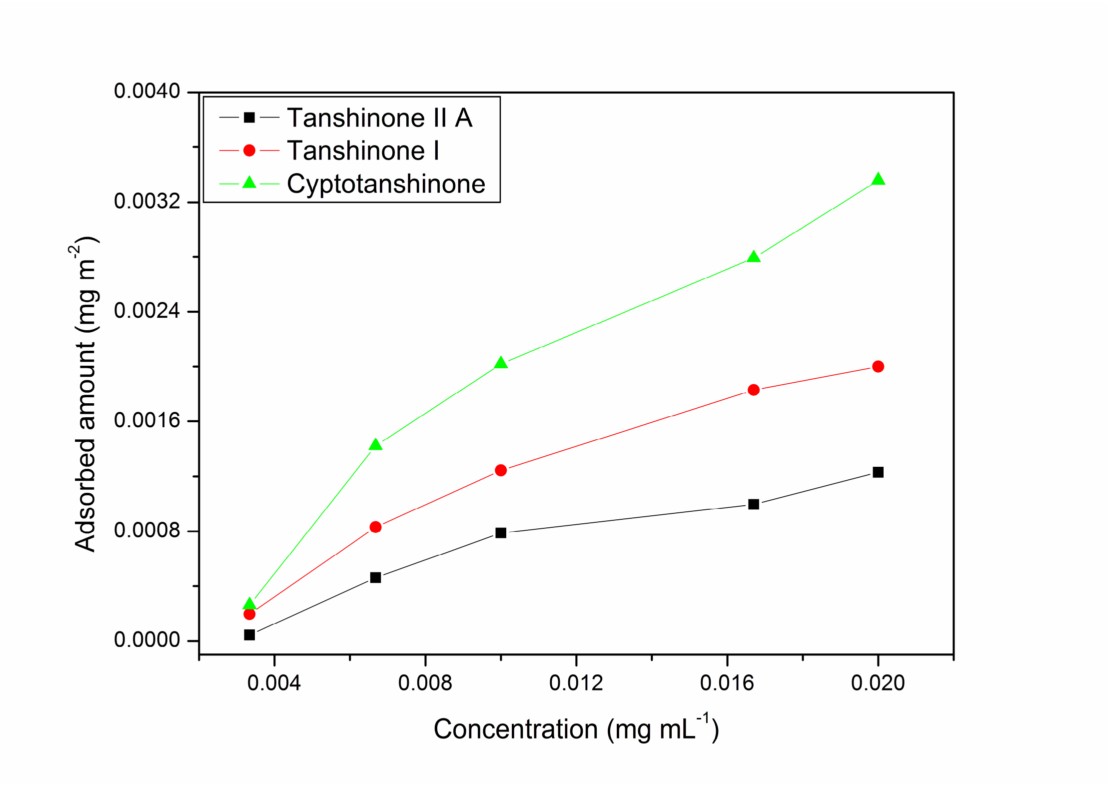
(C)


0.05
0.04
0.03
0.02
0.01
0.00
Adsorbed amount (mg m^{-2})
0.0
0.1
0.2
0.3
0.4
0.5
Concentration (mg mL^{-1})
Caffeine
Theophylline
Theobromine

(D)

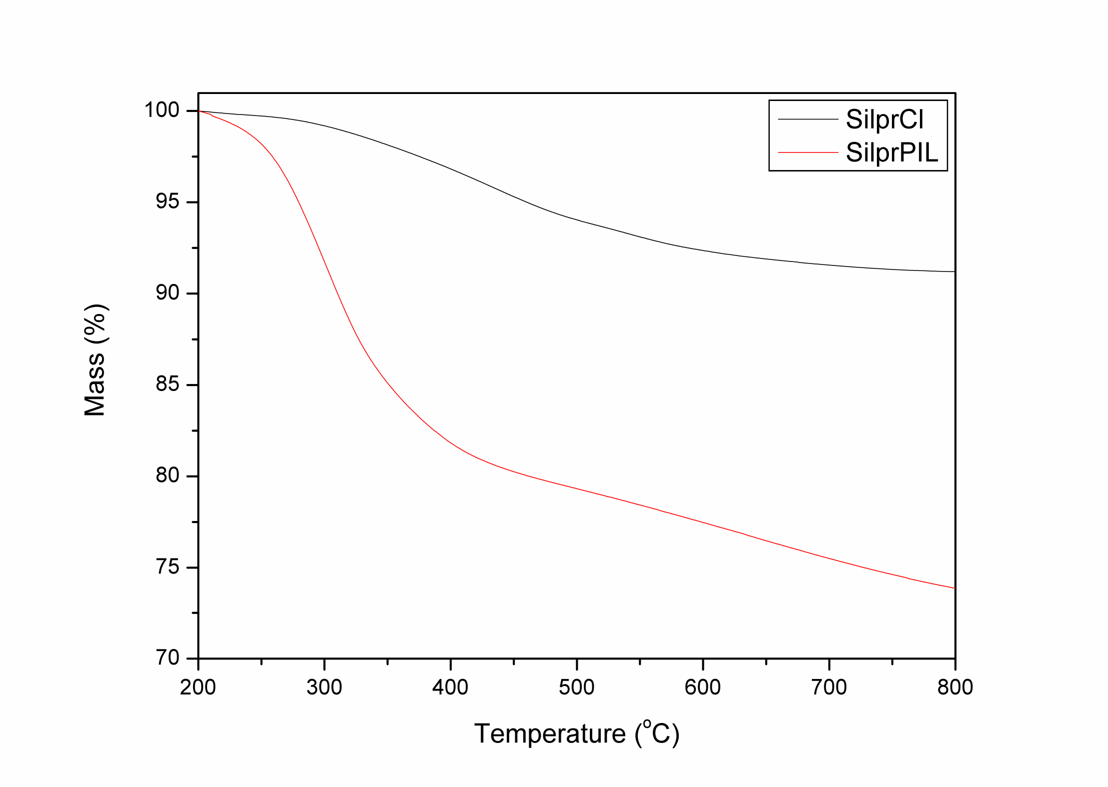


(E)

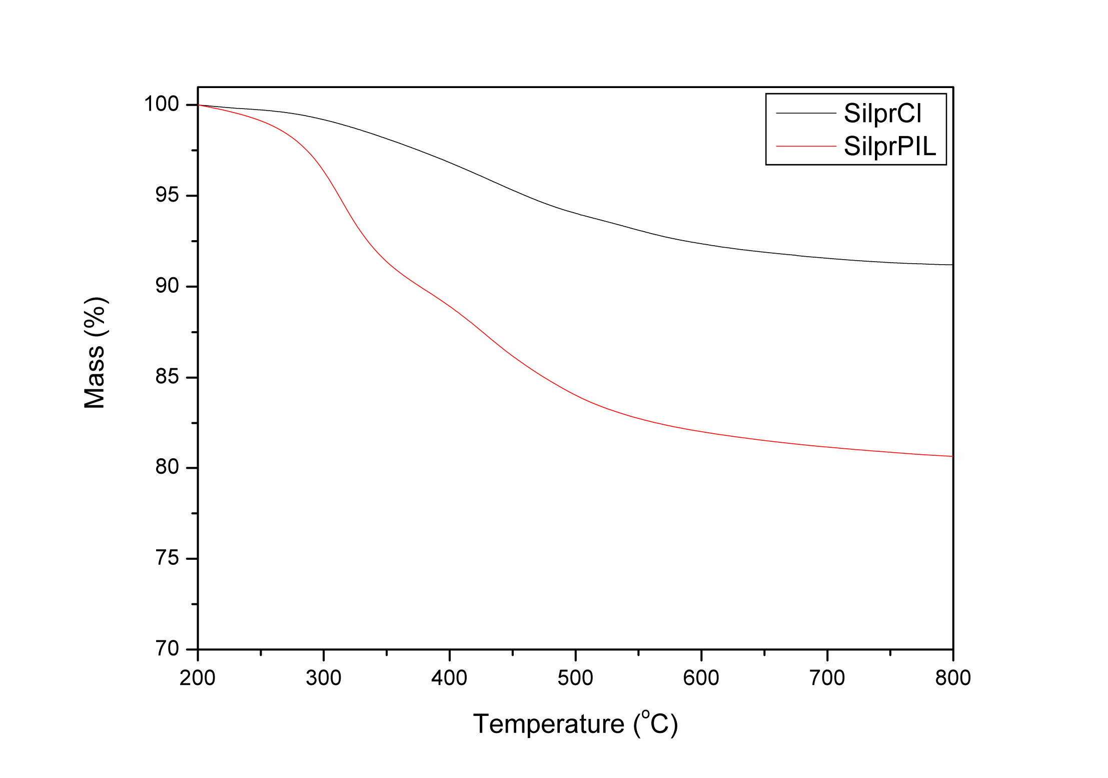


(F)

Fig. S1 Adsorption isotherms of target compounds on SilprPIL by precipitation (A-C) and emulsion (D-F) polymerization.

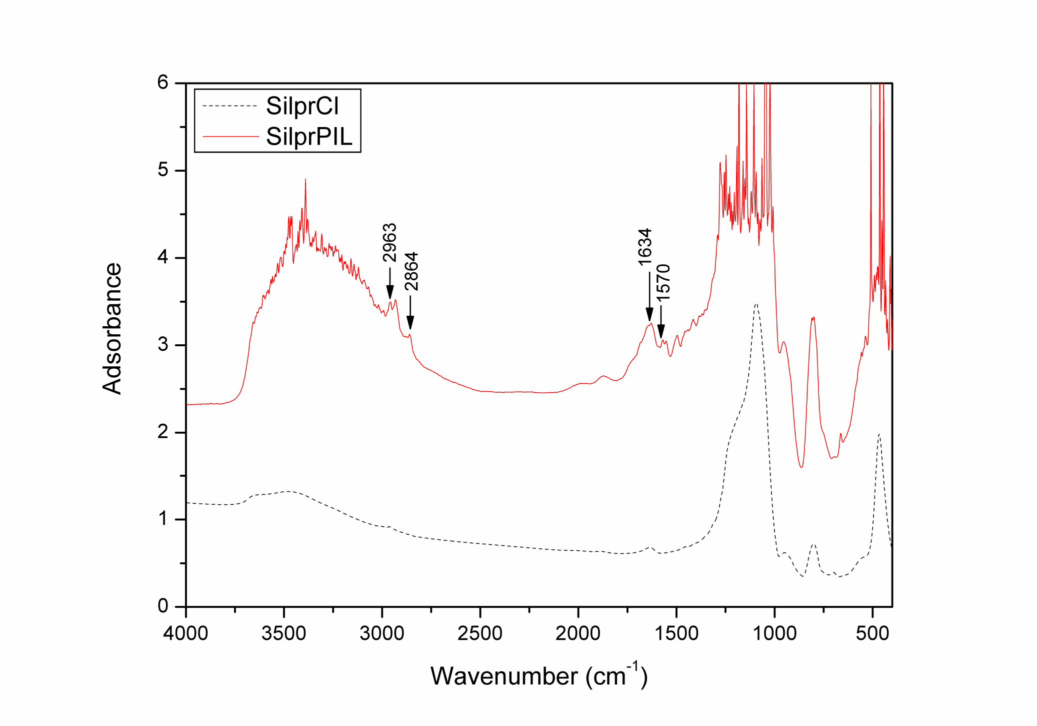


(A)

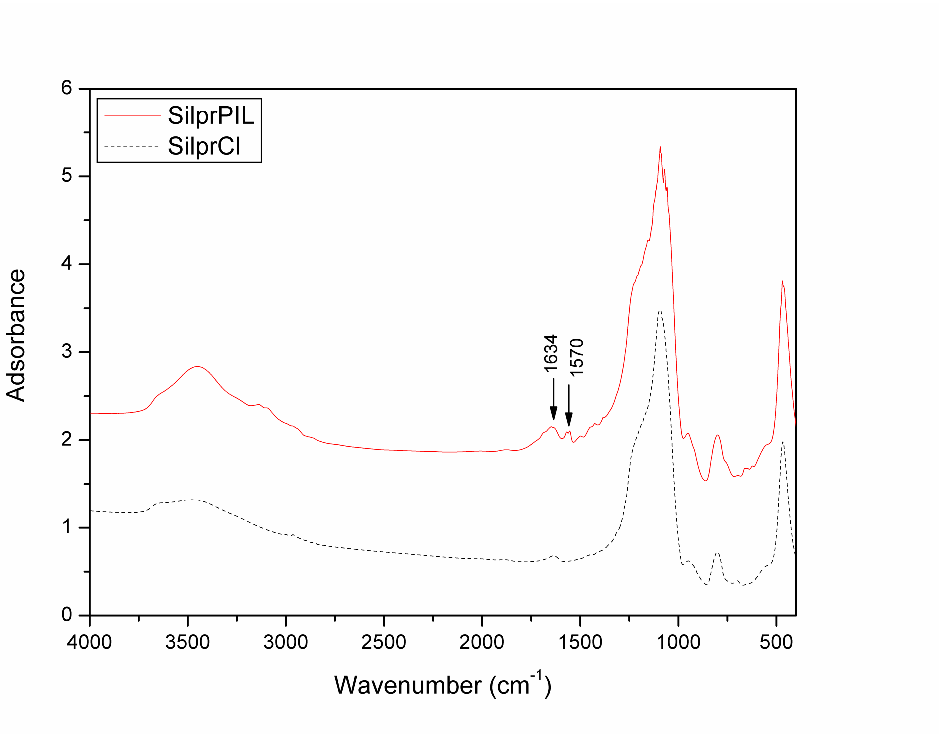


(B)

Fig. S2 Thermogravimetric curves of SilprCl and SilprPIL by precipitation (A) and emulsion (B) polymerization.



(A)



(B)

Fig. S3 FT-IR spectra of SilprCl and SilprPIL by precipitation (A) and emulsion (B) polymerization.

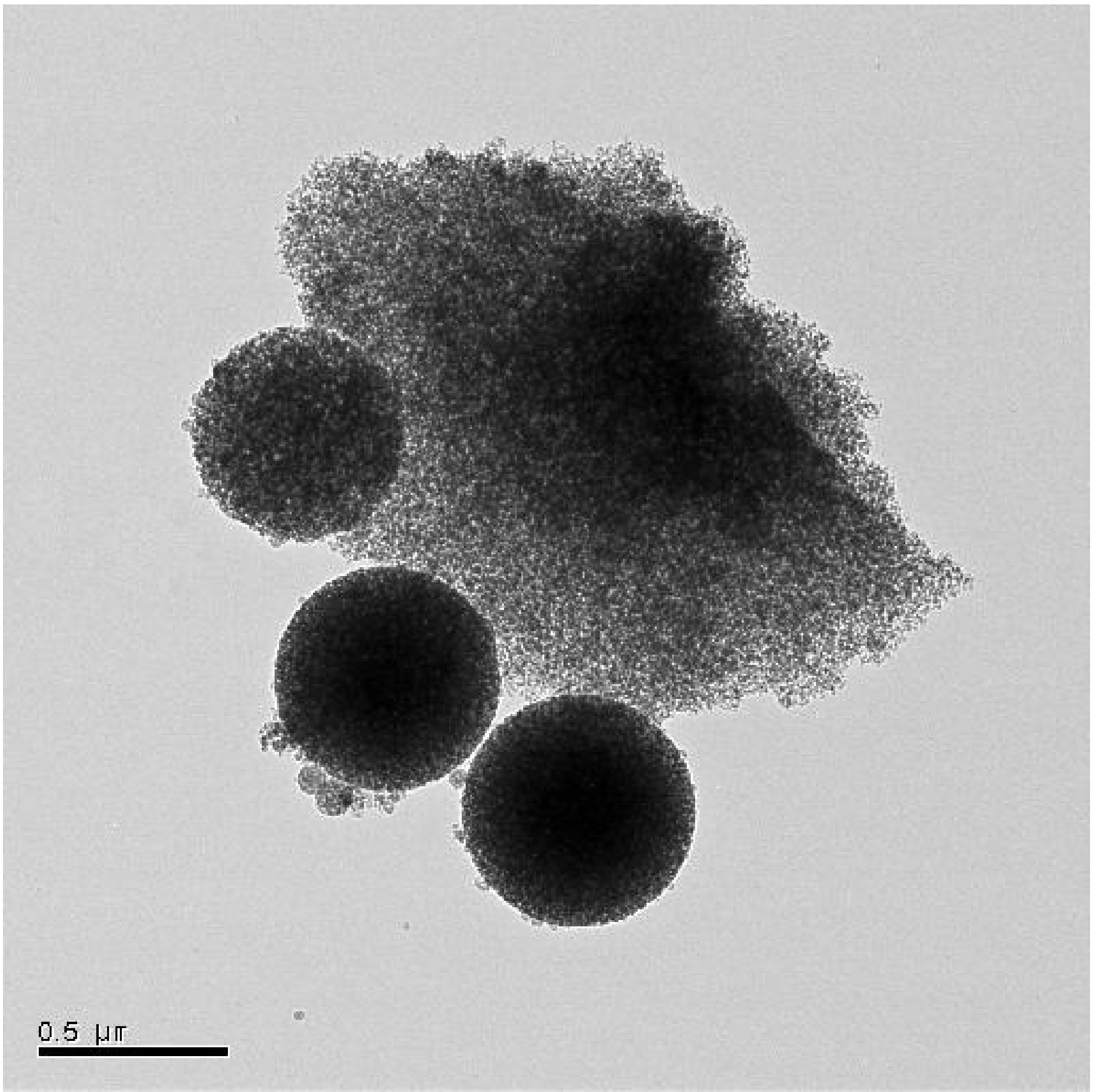


Fig. S4 TEM image of SilprPIL by emulsion polymerization.