Electronic Supplementary Information (ESI)

A hydrophobic adsorbent based on hierarchical porous polymers derived from morphologies of a biomineral

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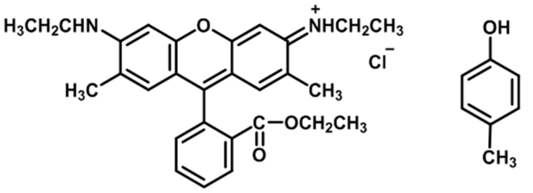
Experimental section

Materials. All the reagents except 2,2'-azobis-(isobutyronitrile) (AIBN, Wako, 99.0%), styrene (Kanto, 99.0%), and methyl methacrylate (Kanto, 99.0%) were used as purchased without purification. AIBN was recrystallized from the methanol solution in a refrigerator at 4 ˚C. The vinyl monomers, such as St and MMA, were distilled to remove the polymerization inhibitors. The spines of a sea urchin (*Echinometra mathaei*) were treated with 5 % of sodium hypochlorite solution (NaClO, Kanto) under room temperature for 24 h to remove the incorporated biological macromolecules. Then, the heat treatment was performed on the NaClO-treated samples at 450 ˚C for 4 h. The biomineral samples after these treatments were used for the polymerization, as reported in our previous works.[11]

Polymerization of the vinyl monomers. The biomineral samples after the treatments were immersed in 1 cm^3 of neat monomer liquid such as St and MMA containing 6 mg of AIBN at room temperature for 1 day. The samples with incorporation of the monomers and radical initiator were set in a glass vessel (20 cm^3) with leaning against the wall. The monomer liquid, namely 0.1 cm^3, was added into the vessel to prevent the evaporation of the monomers from the sample. Then, the sample was maintained at 70 ˚C for 48 h to perform the polymerization. The AIBN concentrations and polymerization temperature are referred to a previous work about the polymerization in a metal organic framework.[16*b*] The composites of the $CaCO_3$/PSt and $CaCO_3$/PMMA were obtained. The original $CaCO_3$ was dissolved by 0.2 mol dm^{-3} of hydrochloric acid (HCl) with immersion of the composite for 1 day. The replicated PSt and PMMA architecture were obtained after drying.

Measurements. The morphologies were observed by a field-emission scanning electron microscopy (FESEM, Hitachi S-4700 or JEOL JSM-7600F) operated at an accelerating voltage of 3.0 kV and a field-emission transmitted electron microscopy (FETEM, FEI tecnai G2 F20) operated at an accelerating voltage of 200 kV. The characterization of the resultant PSt and PMMA was performed by FT-IR (Jasco FT/IR-4200ST). The content of the polymer in the composites was estimated by thermogravimetric (TG) analysis (Seiko TG/DTA7200) under air condition. The thermal properties were measured by DSC (Rigaku Thermo plus 2) at a heating rate of 5 K min^{-1}.

Adsorption properties. The adsorption properties were studied by using the aqueous solutions of rhodamine 6G (Junsei, 85 %) and *p*-cresol (Kanto, 99 %) (Scheme S1). The PSt hierarchical structure and reprecipitated one were used as the adsorbates. The adsorption experiments were performed in 1 cm^3 of the rhodamine 6G and *p*-cresol aqueous solutions with addition of 10 mg of the adsorbates. The concentration of these organic molecules were measured by UV-Vis absorption spectroscopy (Jasco, V-670). The initial concentrations of these organic molecules (C_0) were set at 0.05, 0.25, 0.5, 0.75, and 1.0 wt% for rhodamine 6G and at 0.1, 0.2, 0.5, 1.0, and 1.5 wt% for *p*-cresol. Since the concentration of the aqueous solutions was not changed after 24 h, the concentration after 2 days was adopted as the concentration at the adsorption equilibrium (C_e). The reprecipitated PSt was used as the reference for the adsorption experiment (Fig. S5 in the ESI). The precipitates were obtained by addition of 30 cm^3 methanol as a poor solvent to 5 cm^3 of toluene solution containing 3 wt% of a commercial PSt (Aldrich, M_W=35000).



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Scheme S1. Molecular structures of rhodamine 6G (**1**) and *p*-cresol (**2**).

FT-IR spectra of the PSt samples

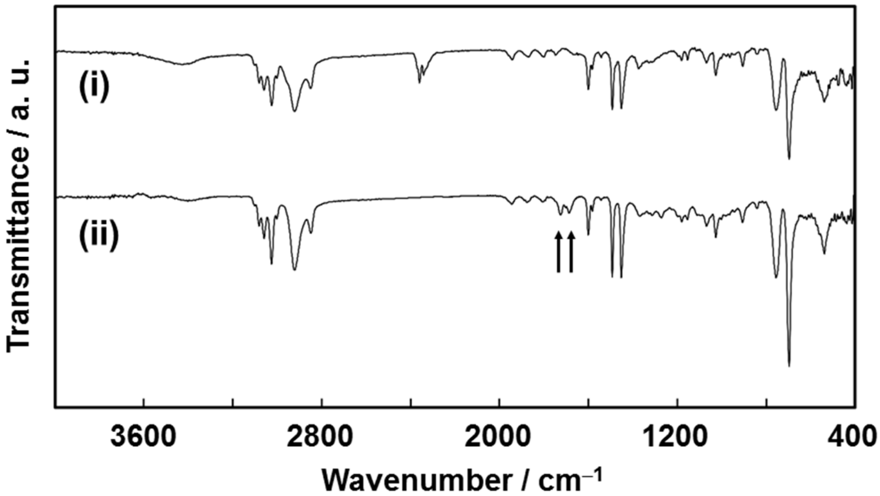

Fig. S1. FT-IR spectra of a commercial PSt reagent (i) and the hierarchical PSt architecture (ii).

A commercial PSt (Aldrich, M_W=35000) was used as the reference. All the absorption bands of the PSt hierarchical architecture except two absorption peaks, denoted by the arrows, were consistent with those of the commercial one. The two peaks around 1700 cm^{-1} correspond to the stretching vibration of C=C groups of the remaining St monomer or stretching vibration of C=O groups of the remaining carbonate ions.

PSt content in the $CaCO_3$/PSt composites

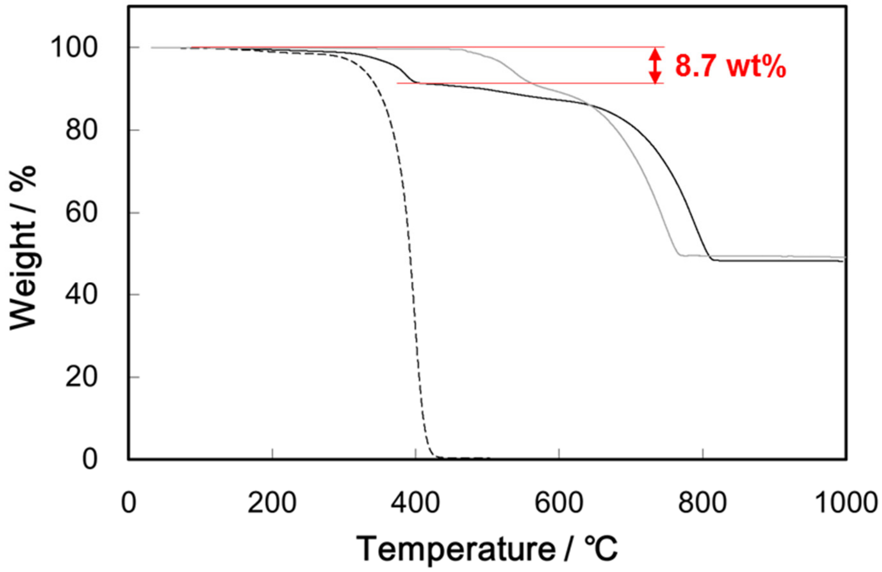

Fig. S2. TG curves of the $CaCO_3$/PSt composites (solid line), bulk-polymerized PSt (dashed line), and the original $CaCO_3$ with NaClO treatment and subsequent heat treatment at 450 ˚C for 4 h (gray solid line).

The weight loss around 400 ˚C is caused by combustion of PSt. Therefore, the PSt content in the composite is estimated to be 8.7 wt%. The weight loss was observed at the temperature lower than 600 ˚C on the original $CaCO_3$ with NaClO treatment and subsequent heat treatment at 450 ˚C for 4 h. Therefore, the weight loss at the temperature lower than 600 ˚C is ascribed to the remaining biological macromolecules. The weight loss at the temperature higher than 600 ˚C is ascribed to the decomposition of $CaCO_3$.

FETEM and EDX analyses of the resultant PSt hierarchical architecture

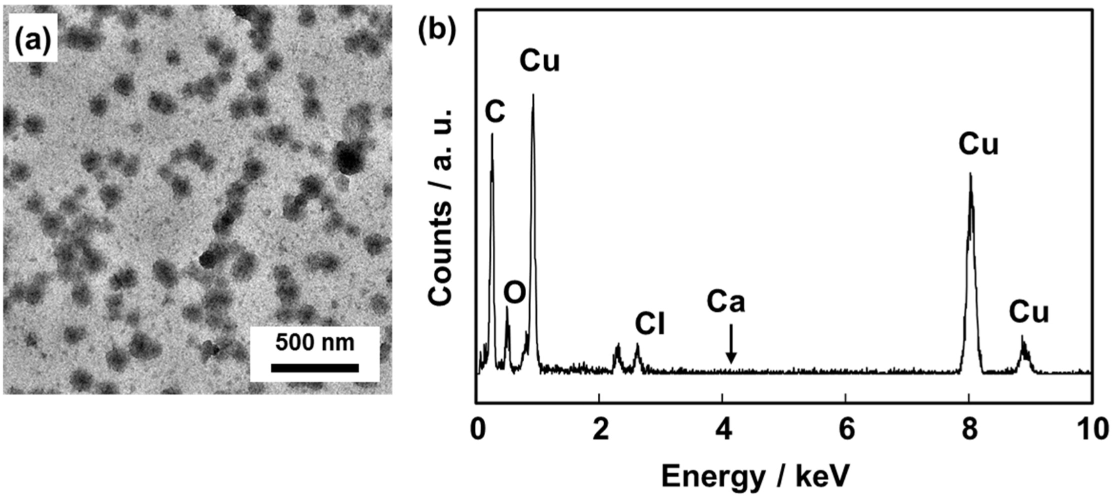

Fig. S3.FTEM image of the PSt nanoparticles (a) and EDX spectrum on the FETEM observation (b).

The PSt hierarchical architecture was dispersed in water with sonication. The PSt nanoparticles were observed on the FETEM image (Fig. S3a). The peak of calcium species was not detected on the EDX spectrum (Fig. S3b). The result supported the removal of the original $CaCO_3$ in the PSt hierarchical architecture.

PMMA hierarchical architectures

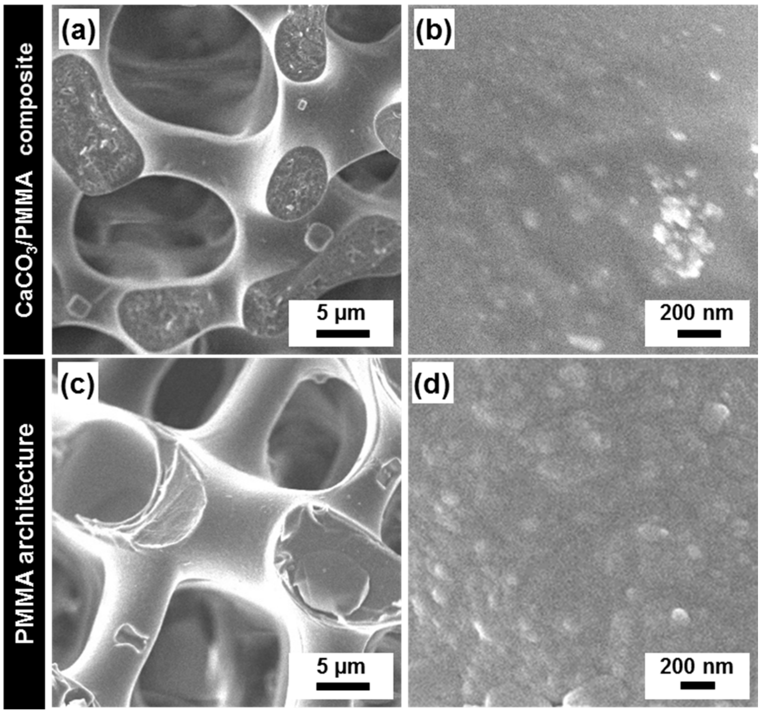

Fig. S4. FESEM images of the $CaCO_3$/PMMA composites (a,b) and replicated PMMA (c,d).

The micrometer-scale sponge morphology was preserved after the incorporation and polymerization of MMA (Fig. S4a). The grain boundary of the $CaCO_3$ nanocrystals was not clearly observed on the magnified image of the composites (Fig. S4b). The results indicate that PMMA was formed not in the pores of the micrometer-scale sponge but in the nanoscale interspace of the unit crystals. The replicated PMMA showed the similar hierarchical architecture as that of the original one (Fig. S4c,d).

Reprecipitated PSt as the reference sample

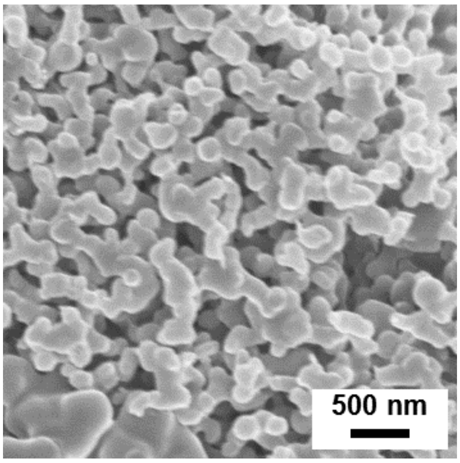

Fig. S5. FESEM images of the reprecipitated PSt sample.

The preparation methods were described in P. S2–S3. The reprecipitated PSt showed the connected nanoparticles around 200 nm in size.

Adsorption properties of the resultant PSt and its references

Table S1. Adsorption properties of rhodamine 6G on the PSt samples.

PSt samples	C_0 / wt%	0.05	0.25	0.5	0.75	1
Hierarchical	C_e / wt%	0.0377	0.195	0.349	0.444	0.608
	W / mg g^{-1}	10.3	40.3	123	253	324
Reprecipitated	C_e / wt%	0.0484	0.239	0.484	0.707	0.948
	W / mg g^{-1}	1.58	11.1	15.8	40.3	42.5
Commercial	C_e / wt%	0.0385	0.156	0.337	0.416	0.477
	W / mg g^{-1}	10.6	83.6	148	300	459

A typical hydrophobic adsorbent (Amberlite XAD-2000) was adopted as the commercial PSt. The adsorption isotherm in Fig. 3b was prepared by these C_e and W. The data in the colored cells were mentioned in the main text.

Table S2. Adsorption properties of *p*-cresol on the PSt samples.

PSt Samples						
Hierarchical	C_0 / wt%	0.101	0.190	0.556	1.11	1.59
	C_e / wt%	0.0961	0.180	0.518	0.943*	1.26
	W / mg g^{-1}	19.9	29.4	33.5	64.1*	109
Reprecipitated	C_0 / wt%	0.101	0.184	0.556	1.11	1.66
	C_e / wt%	0.094	0.181	0.534	1.08	1.62
	W / mg g^{-1}	6.65	2.22	17.2	23.7	26.4
Commercial	C_0 / wt%	0.101	0.184	0.556	1.11	2.02
	C_e / wt%	0.0653	0.129	0.373	0.838*	1.64
	W / mg g^{-1}	37.2	50.2	182	238*	338

The adsorption isotherm in Fig. 3d was prepared by these C_e and W. The data in the colored cells were mentioned in the main text.

Table S3. Adsorption properties of *m*-cresol on the porous PSt in a previous report.[22a]

Sample	C_0 / wt%	0.51	0.76	1.03	1.54	2.04
Porous PSt	C_e / wt%	0.392	0.575	0.719	0.978*	1.298
	W / mg g^{-1}	26.0	40.2	68.4	126*	164

Ichinose *et al.* reported preparation of the porous PSt by flash-freezing process and its application to hydrophobic adsorbent.[22a] The data were used as the reference. In the previous paper, *m*-cresol was used as the adsorbate. We assumed that the adsorption properties were not influenced by the isomeric forms.

Based on the Tables S2 and S3, the number of the cresol molecules on 1 nm^2 of the PSt samples (n_c) in the main text was calculated by the following equation (eq. S1):

$$n_c = \frac{F_W S_{PSt}}{W N_A} \quad \text{… (eq. S1)}$$

where F_W is formula weight of cresol and N_A is Avogadro constant.

The data marked with ‘*’ in Tables S2 and S3 were used for the calculation of n_c in the each PSt sample.

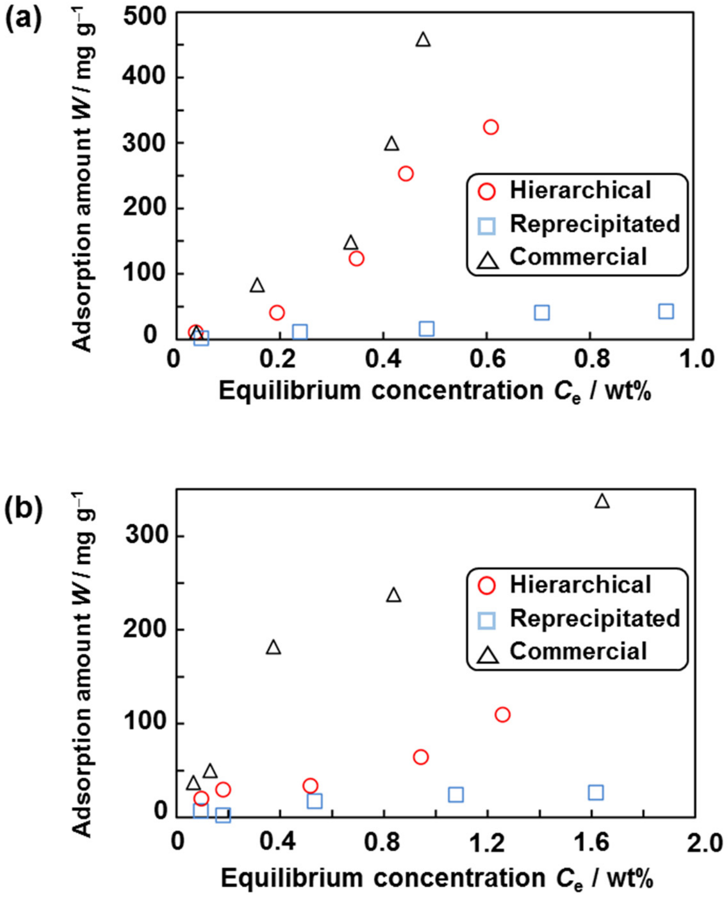

Fig. S6. The adsorption isotherms of rhobamine 6G (a) and *p*-cresol (b) on the PSt hierarchical architecture, reprecipitated PSt, and commercial PSt. The isotherms of the PSt hierarchical architecture and reprecipitated PSt are the same as those in the Fig. 3b,d in the main text.

The adsorption amounts of the resultant PSt sponge were less than those of the commercial sample. The commercial sample has the higher specific surface area and different polymer structure including a cross-linker. In a recent report, the adsorption amount of the pure porous PSt, prepared by a new phase separation technique, were less than that of the commercial sample. It is not so easy to prepare pure PSt adsorbents exhibiting the higher adsorption properties rather than the commercial sample.