

Supporting Information

Dispersion of Al₂O₃ Nanoparticles with Mussel-Inspired Amphiphilic Copolymers in Organic Solvents and Formation of Hierarchic Porous Films by the Breath Figure Technique

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• Chemicals

Dopamine hydrochloride, methacrylate anhydride, and Al₂O₃ NPs (gamma phase, <50 nm) were purchased from Aldrich. Benzene, tetrahydrofuran, and dimethylsulfoxide (DMSO) were purchased from Wako. Azobisisobutyronitrile (AIBN) was purchased from Aldrich and was purified by recrystallization in MeOH before use.

• Characterization Equipment

TG and FT-IR analyses were performed on a TG analyzer TG8120 (Rigaku) and a FT/IR-6100TY spectrometer (JASCO), respectively. The DLS measurements were recorded on an FDLS-3000 spectrometer (Otsuka Electronics). The film structure and NP shape were observed by using S-5200 and H-7650 microscopes (Hitachi).

• Experimental Method

• Synthesis of Catecholic Amphiphilic Copolymer

N-(3,4-Dihydroxyphenethyl)methacrylamide (DMA) was prepared from dopamine hydrochloride and methacrylate anhydride. A solution of sodium bicarbonate and sodium borate was used to protect the dihydroxybenzene moiety, as previously reported.¹ The DMA was recrystallized in ethyl acetate and dried under vacuum, to yield the monomer as a light brown powder (78.9%). ¹H NMR (Bruker 400 MHz, MeOD) δ_{H} 6.71-6.67 (m, 2H, C₆H₂(OH)₂-), 6.56-6.54 (m, 1H, C₆H₂(OH)₂-), 5.65 (s, 1H, -C(=O)-C(-CH₃)=CH_H), 5.35 (s, 1H, -C(=O)-C(-CH₃)=CH_H), 3.42-3.34 (m, 2H, C₆H₃(OH)₂-CH₂-CH₂(NH)-C(=O)), 2.71-2.67 (t, 2H, C₆H₃(OH)₂-CH₂-CH₂(NH)-), 1.93 (s, 3H, -C(=O)-C(-CH₃)=CH₂) ppm. Each peak was identified by comparison with the literature data.¹

The amphiphilic copolymers which contained the catechol group were synthesized from DMA, and *N*-dodecylacrylamide (DAA) by free-radical polymerization. DAA (1.73 g), DMA (0.41 g), and AIBN (29.7 mg) were dissolved in benzene/DMSO (10:0.5) in a three-necked round-bottomed flask equipped with a thermometer, a nitrogen inlet, and a reflux funnel. The reaction mixture was degassed by three freeze-evacuate-thaw cycles, and the flask was filled with dry nitrogen. The mixture was heated at 72 °C for 5 h. The polymer was purified by reprecipitation in a large volume of acetonitrile. The white powder was collected by centrifugation and dried under vacuum.

1. Haeshin Lee, Bruce P. Lee, Phillip B. Messersmith, *Nature*, **2007**, 448, 338-341

• Preparation of Surface-Coated Al₂O₃ NPs

The Al₂O₃ NPs were stabilized for dispersion in organic solvent by using the amphiphilic copolymer polymer 1. The Al₂O₃ NPs (150 mg; average diameter ~289.8 nm in water) were added to chloroform (5 mL). The dispersion was ultrasonicated for 5 min and then a 10 g/L chloroform solution of the amphiphilic copolymer (5 mL) was added dropwise to the dispersion. The mixture was ultrasonicated for 1 min and then stirred overnight. The excess amphiphilic copolymer was removed by centrifugation in chloroform/acetone (1:1 v/v) three times. The solid was dried in vacuo and then re-dispersed in chloroform. The solution was allowed to stand overnight, and the supernatant was collected.

• Preparation of Honeycomb-Patterned Porous Al₂O₃ NP Films

Honeycomb-patterned porous films containing Al₂O₃ NPs were prepared on a glass substrate. A chloroform solution of the amphiphilic copolymer (1.67 g/L) containing the surface-coated Al₂O₃ NPs (12.5 g/L) was cast on a glass substrate under a flow of humid air at a flow rate of 1.0 L/min. The weight ratio of the surface-coated Al₂O₃ NPs to the amphiphilic copolymer was 7.5:1.

• Evaluation of Nano-Sized Pores

Sizes of nano-sized pores were estimated from cross-sectional TEM images by using an image software (Image J). Fig. S1 plots frequency as a function of cross-sectional area of nano-sized pores. The histogram suggested that the hierarchic porous structure ranging from few to several hundreds nm² are formed.

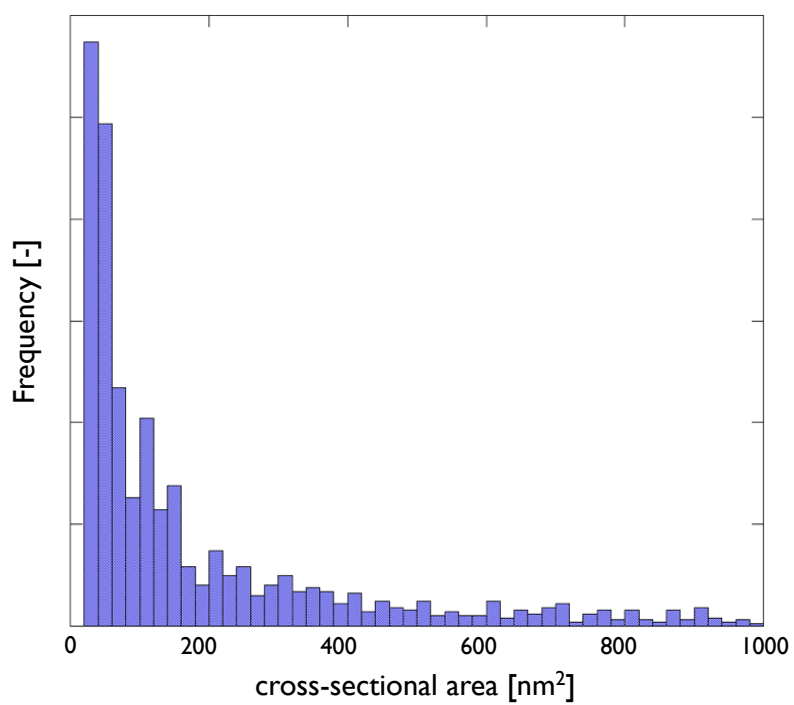


Fig. S1, Histogram of size of nano-sized pores formed in the frame of films.