Electronic Supplementary Information (ESI) for

Crystallization of unidirectionally oriented fibrous calcium carbonate on thermo-responsive polymer brush matrices

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Experimental

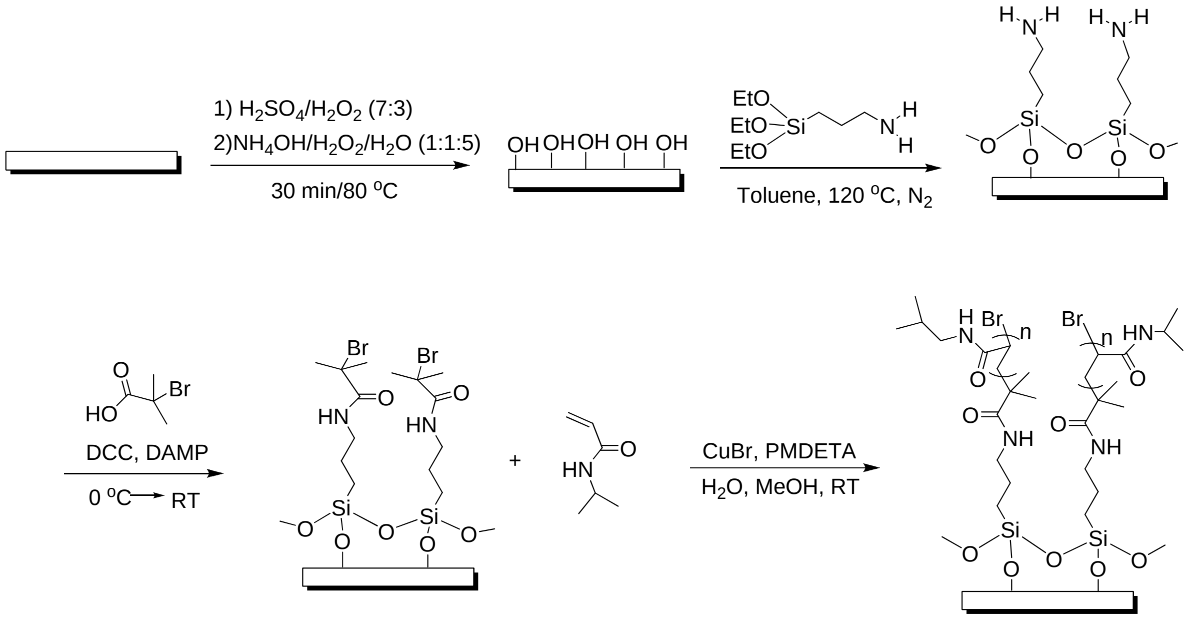
Materials. Surface-initiated ATRP was performed on commercially available glass substrates (10 mm × 10 mm size). Copper(I) bromide (CuBr, 99.9%), poly(acrylic acid) (PAA, $\bar{M}_w$: 2 x 10^3), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), and methanol (MeOH, 99.9%) were purchased from Sigma-Aldrich, Japan. (3-Aminopropyl)triethoxysilane (APS, 99%), 2-bromo-2-methylpropionic acid (98%), 4-(dimethylamino)pyridine (DMAP, 99%), *N,N′*-dicyclohexylcarbodiimide (DCC, 99%), and *N*-isopropylacrylamide (NIPAm, 97%) were purchased from Tokyo Kasei, Japan. NIPAm was purified twice by vacuum sublimation. PMDETA was vacuum-distilled prior to use. Other chemicals were used as received.

Characterization. Polarized optical micrographs were taken with Olympus BX51 polarizing optical microscope. Scanning electron microscopic (SEM) images were obtained using a Hitachi S-900S field emission (FE-) SEM and a Keyence VE-9800 SEM. Tapping-mode atomic force microscopy (AFM) measurements were conducted on Digital Instruments Nanoscope III system with standard Si cantilever. Transmission electron microscopy (TEM) observations were performed on a JEOL JEM-2010HC operated at 200 kV. The samples were used without any conductive treatments for electron microscope and analysis. Raman spectroscopy measurements were performed with a Jasco NR-1000.

Synthesis of the initiator. General schemes for the preparation of self-assembled monolayer of initiator and the surface-initiated ATRP of NIPAm are shown in Scheme S1. Glass substrates were sonicated in acetone and in deionized water for 5 min each time. Subsequently, the slides were immersed in piranha solution (H_2SO_4/H_2O_2 (7:3; v:v)) (*Caution: Piranha solution is highly corrosive and reacts violently with organic matter!*) for 30 min at 80 °C to remove any organic residues and to create silanol groups on the surfaces. The substrates were washed with a large amount of deionized water and then immersed in $H_2O_2/NH_4OH/H_2O$ (1:1:5; v:v) solution for 30 min at 80 ^oC. The substrates were rinsed extensively with water and then dried in a stream of nitrogen. Subsequently, they were rinsed in pure methanol, methanol/toluene (1:1), and pure toluene for 2 min each time. Then, the glass substrates were immediately transferred to a dry toluene solution containing 10% of APS. The functionalized glass substrates were kept at 120 ^oC for 15 h under nitrogen atmosphere.[1] The APS modified substrates were obtained after 2 min rinses in a sequence of solvents, such as pure toluene, toluene/methanol (1:1; v:v), and methanol. The dried APS modified substrates were baked for 15 min at 110 °C. To immobilize the 2-bromo-2-methylpropionic acid, the APS glass substrate treated with 1 x 10^{-1} g of 2-bromo-2-methylpropionic acid, 1 x 10^{-2} g of DMAP and 75 mg of DCC in 30 mL of dry dichloromethane at room temperature for 12 h. The self-assembled monolayer of initiator was cleaned by rinsing with plenty of dichloromethane and immediately used for the surface-initiated ATRP of NIPAm.

Surface-initiated ATRP of NIPAm. Prior to the polymerization, all solutions and flasks were thoroughly flushed with nitrogen to remove oxygen. The catalyst was synthesized in a nitrogen atmosphere by adding Cu^IBr (4 x 10^{-2} g, 3 x 10^{-2} mmol), and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) (3 x 10^{-2}

g, 2 x 10^{-1} mmol) in 3 mL of MeOH. The mixture was then sonicated for 10 min to form uniform $Cu^{I}Br$/PMDETA complex and then degassed by three freeze-pump-thaw cycles. Next, in another 100 mL round bottom flask, 2 g of NIPAm monomer, 3 x 10^{-3} g of ascorbic acid in 9.5 mL of deionized water and 1 mL of MeOH was degassed three times by freeze-pump-thaw cycles. The initiator functionalized glass substrates were placed in a sealed 100 mL round bottom flask and the monomer/complex solution (NIPAm solution and 250 μL of catalyst) was transferred into it using a syringe. The sealed flask was kept at room temperature under nitrogen atmosphere. After 5 h, substrates were removed from the polymerization solution, exhaustively rinsed with MeOH and deionized water to remove all traces of the polymerization solution, and subsequently dried in a stream of nitrogen. The water contact angle measurements are shown in Table S1. The AFM images (Fig. S1) show the measured thickness of poly(NIPAm) brush is about 150 nm.



Scheme S1 Synthesis of poly(*N*-isopropylacrylamide) by surface-initiated ATRP.

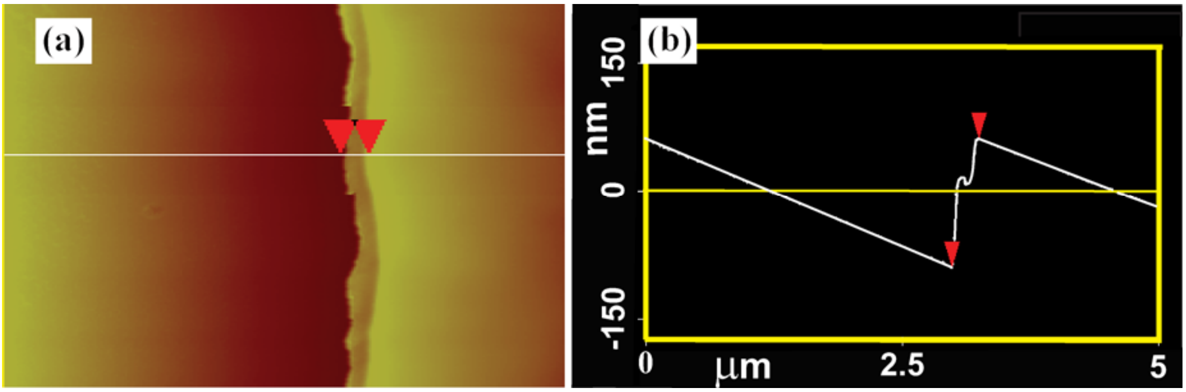


Fig. S1 A cross-sectional tapping mode AFM image of the surface-initiated poly(NIPAm) immobilized on a glass substrate: (a) height image; (b) cross-sectional profile along the line in the part (a).

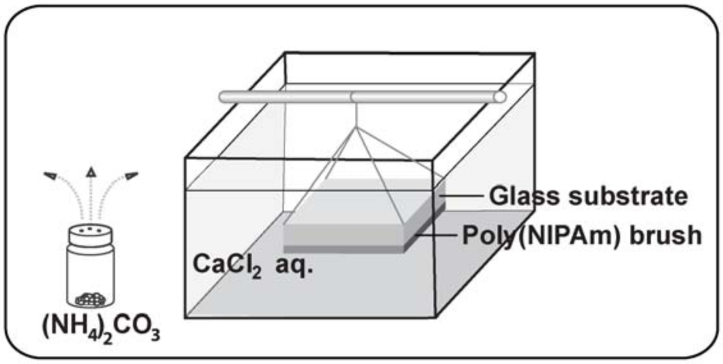


Fig. S2 Schematic representation of the experimental setup for the crystallization of $CaCO_3$ on poly(NIPAm) matrices using an ammonium carbonate diffusion method.

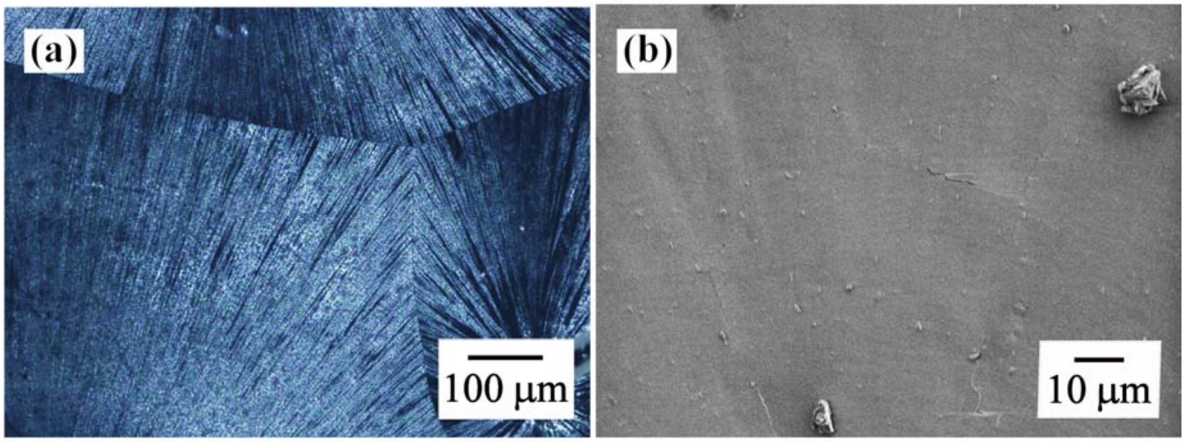


Fig. S3 Calcium carbonate crystals grown on the poly(NIPAm) brush matrix in the presence of poly(acrylic acid) (PAA) (2.5×10^{-3} wt%) at 40 ^{o}C: (a) polarized optical micrograph (POM) image; (b) scanning electron microscopy (SEM) image (top view).

Fig. S4 shows the Raman spectrum of the hybrids formed at 40 ^{o}C. The presence of a splitting in the internal υ_1 vibration (stretching vibration of CO_3^{2-}) bands of carbonate at 1090 and 1080 cm^{-1} indicates the presence of vaterite. The 750 cm^{-1} band is attributed to the internal υ_4 vibration (symmetric CO_3^{2-} deformation). The smaller frequency shifts at 303 and 270 cm^{-1} are assigned to the translational lattice vibration of CO_3^{2-}.

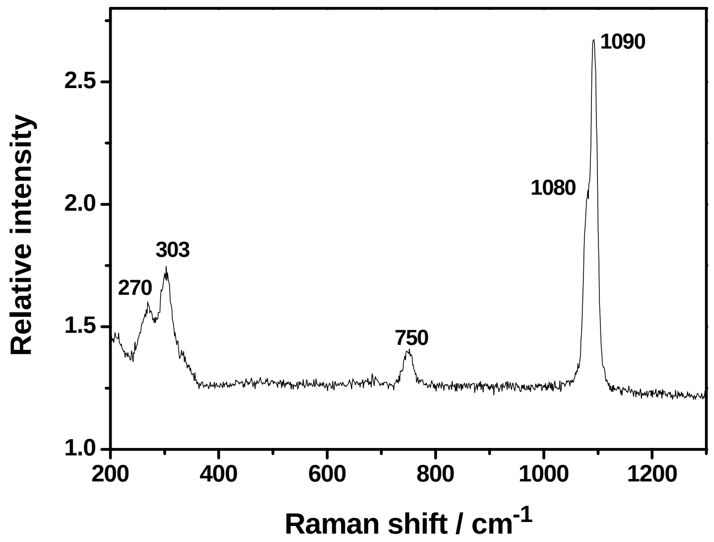


Fig. S4 Raman spectrum of the hybrids formed on the poly(NIPAm) brush at 40 ^{o}C.

Table S1 Thickness and corresponding water contact angles of the poly(NIPAm) brush used in this study

	Contact angle	
Thickness	25 °C	60 °C
150 nm	34.1°	63.3°

Reference:

1. (a) I. Haller, *J. Am. Chem. Soc.,*1978, **100**, 8050; (b) X. Kong, T. Kawai, J. Abe and T. Iyoda, *Macromolecules*, 2001, **34**, 1837.