Supporting Information.

Atelocollagen-Templated Fabrication of Tangled Fibrous Silica

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1. General Remarks

X-ray photoelectron spectroscopy (XPS) was performed on a Shimadzu ESCA-3400. The binding energies were corrected by referencing the carbon 1s binding energy to 285 eV. Fourier transform infrared (FT-IR) spectra were conducted on a JASCO FT-IR 660 plus using the KBr disc method. Thermogravimetric analyses (TGA) were performed on a Seiko Instrumental EXSTAR 6000 with a heating rate of 10 °C min^{-1} under N_2 gas flow. Scanning electron microscopy (SEM) observation was performed on a Hitachi SU8020 FE-SEM. Relative surface area and porosity were characterized by N_2 gas (99.998% purity) adsorption/desorption isotherms using a MicrotracBEL BELSORP-mini II. Samples were dried under vacuum at 100 °C for 3 hours before measurements. The relative surface area was determined by the Brunauer-Emmet-Teller (BET) method. Circular dichroism (CD) spectra were recorded using a J820 CD spectropolarimeter (JASCO, Japan). Transmission electron microscopy (TEM) observation was performed on a JEOL JEM-2100.

2. Materials

Bovine dermis atelocollagen (AC) and succinylated atelocollagen (SC-AC) solutions (2 wt%) were purchased from KOKEN Co., Ltd. (Japan). EDA-HCl, TEOS and TiBALDH (aqueous solution, 50 % (w/v)) were from TCI (Japan). All solution samples were prepared using MilliQ water.

3. Fabrication of Collagen-templated Silica

Solutions of AC and SC-AC (0.1 wt%, 3.3 μM) were prepared by dilution of the 2 wt% solution and pH was adjusted to 6.5 by addition of NaOH and HCl. EDA-HCl (67.2 and 88.8 μmol) was added to AC and SC-AC solutions (3.3 μM, 6 mL). The final volume of the

reaction mixture was set to 7.2 ml by adding water. Then, TEOS (0.15mL, 0.67 mmol) was added and the mixture was stirred at 30 °C for 20h. SDS-PAGE analysis of the reaction mixture was performed by the Laemmli method. The mixture was centrifuged (8,000g for 5 min) and the precipitate was washed 3 times by water and 20% ethanol. The washed precipitate was freeze-dried (Christ Alpha 1-2 LD Freeze Dryer) for 20 hours. Samples were calcined under air flux in an electric muffle furnace (ADVANTEC FUW220PA) at 500 °C for 5 hours.

4. Fabrication of Collagen-templated Titania

Instead of using water-reactive titanium alkoxide as a precursor, we used the water-stable titanium(IV) bis(ammonium lactato)-dihydroxide (TiBALDH), which has been employed for biomimetic titania fabrication.[1-6] A 0.01 wt% (0.33 μM) solution of AC was prepared by dilution of the 2 wt% solution and pH was adjusted to 6.4 by addition of NaOH. To 12 mL of the 0.33 μM (0.01 wt%) solution of AC, 13.4 μmol of EDA-HCl was added. The final volume of the reaction mixture was made up to 14.4 ml with water. Then, 20 μl of TiBALDH solution (50% w/v) (42 μmol) was added and the mixture was stirred at 4 °C for 20h. The product was collected by centrifuge (8,000g for 5 min), washed by 20% ethanol, and freeze-dried for 20 hours.

5. Supporting Figure

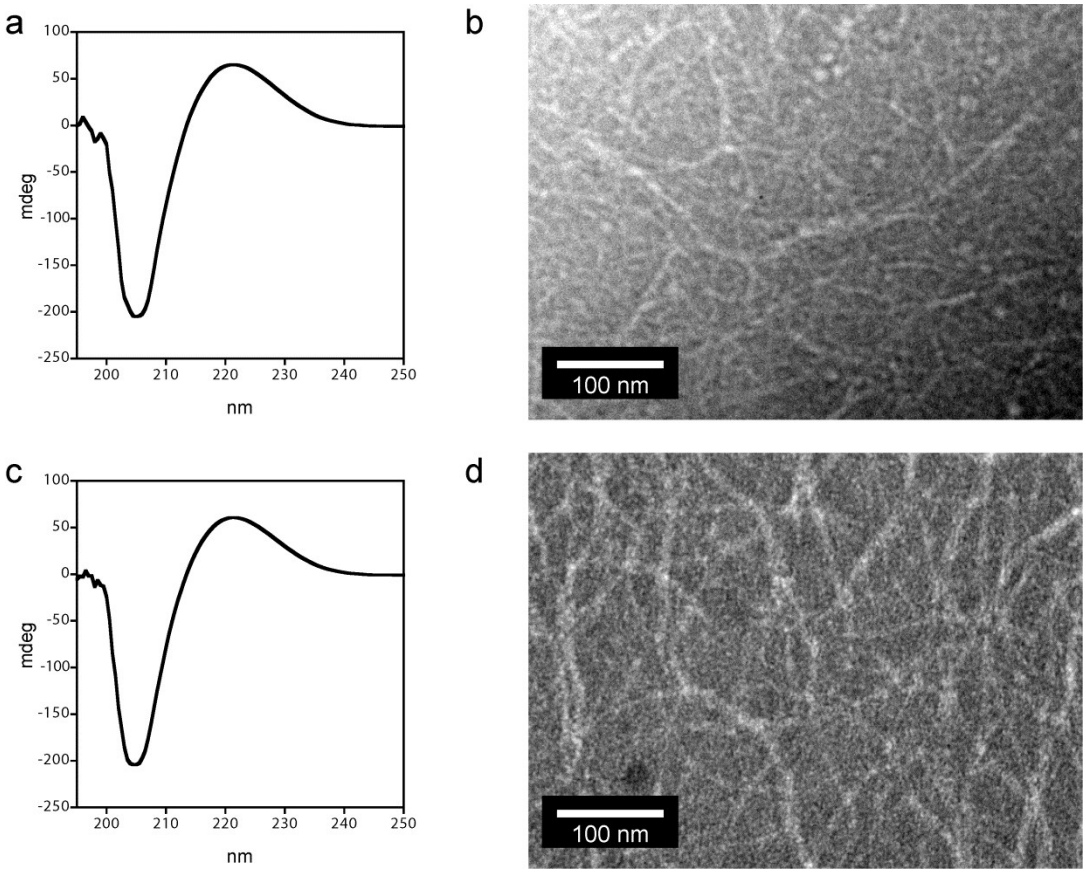

Figure S1. Structural analysis of AC and SC-AC. (a) CD spectrum of AC, (b) TEM image of AC, (c) CD spectrum of SC-AC, (d) TEM image of SC-AC. CD spectrum of AC and SC-AC solution (0.1 mg/mL) showed the peak maximum at 222 nm, derived from the triple helical structure of native collagen.[7] 2 μL of the protein solution (0.1 mg/mL) was placed on a carbon-coated grid and then stained with EM Stainer (Nisshin EM Co., Ltd.) and observed using TEM. Both AC and SC-AC showed the fibrous structure.

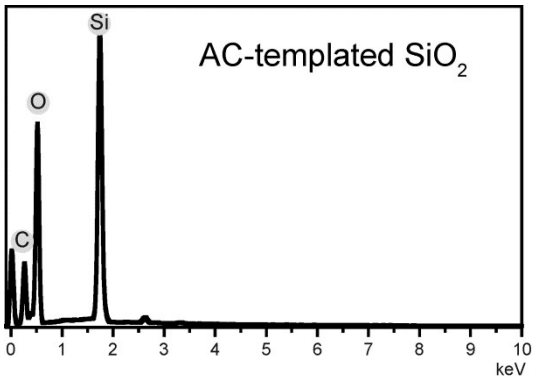

Figure S2. EDX spectrum of AC-templated silica showing silicon.

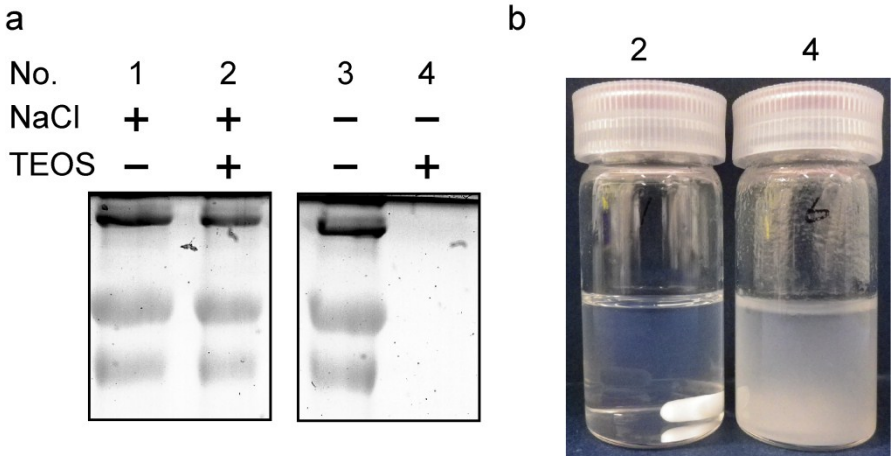

Figure S3. Effect of NaCl on SC-AC-templated silica formation. The formation of silica was investigated using SC-AC and EDA in the presence or absence of 1M NaCl. (a) SDS-PAGE analysis of the reaction mixtures. (b) A photo of the solution captured, 20 h after TEOS addition corresponding to the lane 2 and 4 of SDS-PAGE. In the presence of 1 M NaCl, SC-AC was detected after the reaction (lane 2) and the formation of silica is not observed.

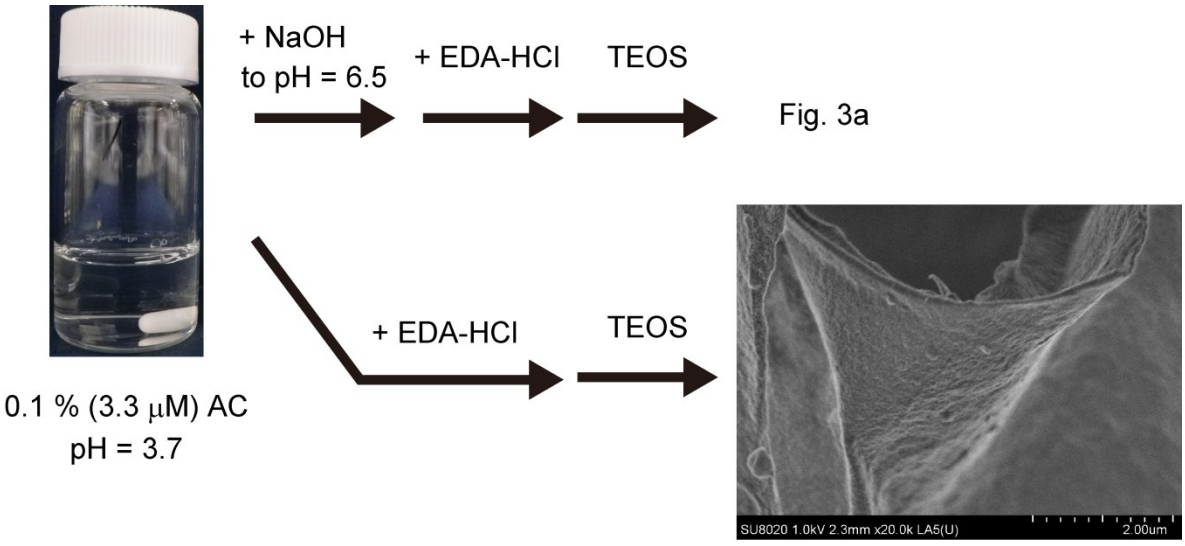

Figure S4. Effect of pH on AC-templated silica formation. The pH of of 0.1 % AC solution is 3.7. Neutralization of the AC solution by NaOH followed by the addition of EDA-HCl and TEOS lead to the formation of tangled fibrous silica (Fig. 3a). Without neutralization, silica with a sheet-like morphology is formed.

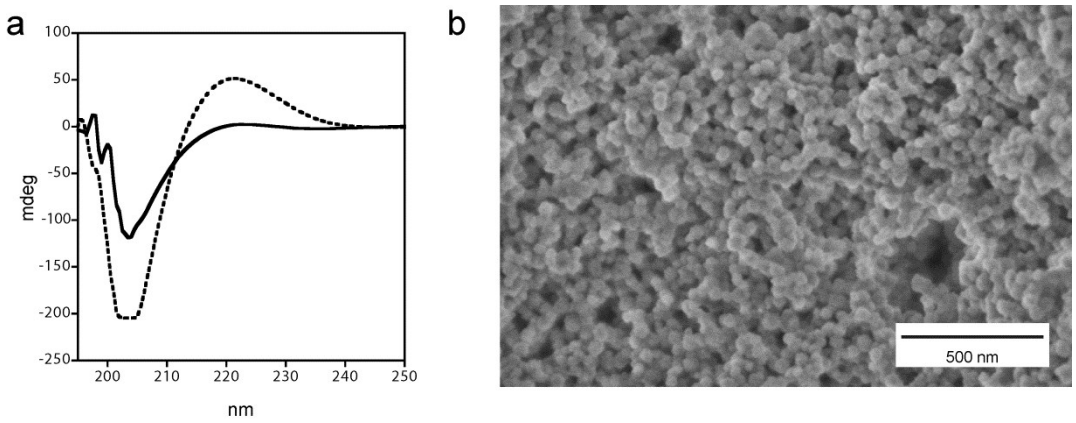

Figure S5. Heat denatured SC-AC templated silica formation. (a) CD spectrum of SC-AC before (dotted line) and after (solid line) heat denaturation (60 °C for 3 h). Heat-denatured SC-AC loses the positive peak at 222 nm. (b) SEM image of heat-denatured SC-AC templated silica.

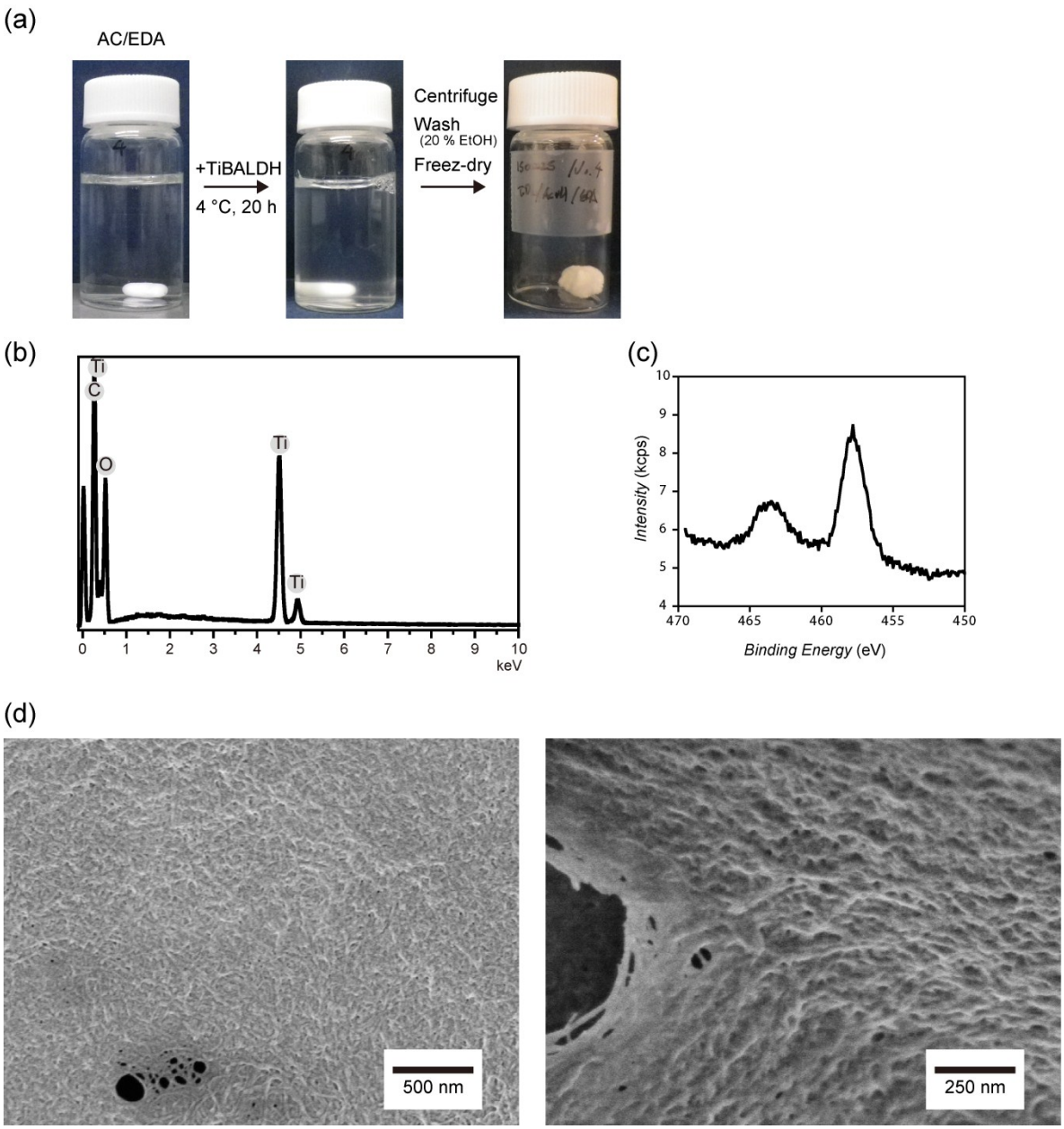

Figure S6. Fabrication and characterization of AC-templated titania. (a) Representative scheme for AC-templated titania synthesis. (b) EDX spectrum of AC-templated titania. Titanium was detected. (c) XPS spectrum of AC-templated titania. Two peaks of Ti^{4+}, $2p_{3/2}$ (459-456 eV) and $2p_{1/2}$ (264-262 eV), were detected. (d) SEM image of AC-templated titania. Fibrous structure was observed. The tangled network is denser than that of AC-templated silica, and the overall structure is a nonwoven fabric like structure.

6. References for Supplementary Information

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