Electronic Supplementary Information

Chain-like nanostructures from anisotropic self-assembly of semiconducting metal oxide nanoparticles with block copolymer

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Experimental Section

Materials. Titanium isopropoxide, 2-propanol, nitric acid, and hydrochloric acid (1 mol/L) were purchased from Wako Pure Chemical Industries Ltd. Block copolymer Pluronic F127 ($PEO_{106}PPO_{70}PEO_{106}$) was obtained from Sigma–Aldrich. A tin dioxide (SnO_2) colloidal suspension (~9 nm in size, 8 wt%, and pH 10.0) was provided by Taki Chemical Co., Ltd. All chemicals were used as received without any further purification. Milli-Q water (18.2 MΩ) was used for all experiments.

Synthesis of monodisperse TiO_2 nanoparticles by peptization. TiO_2 NPs were synthesized by a modified sol–gel peptization method adapted from the literature.[1] In a typical synthesis, 12 g of titanium isopropoxide was dissolved in 130 g of 2-propanol containing 14 mL of water at room temperature under vigorous stirring. The precipitates were then isolated by filtration and washed with water many times to remove the excess 2-propanol. After washing, the precipitate was transferred into 183 mL of water; next, nitric acid with a H^+/Ti^{4+} ratio of 0.5 was added to the above mixture. The peptization process was conducted under stirring at room temperature for 3 days. The resulting product was a light-blue suspension (TiO_2: ~2wt%, pH ~1.5).

Anisotropic self-assembly of TiO_2 NPs with Pluronic F127. The pH was adjusted to 4.0 by dialysis of the as-synthesized TiO_2 dispersion (~2 wt%, pH ~1.5) against deionized water. Pluronic F127 was then added to the TiO_2 dispersion. After the Pluronic F127 was completely dissolved, the mixture was incubated at 60 °C for 1–14 days. The weight ratio of Pluronic F127 to TiO_2 was varied from 0.1–1.0.

Anisotropic self-assembly of SnO_2 NPs with Pluronic F127. The aqueous dispersion of SnO_2 NPs (8 wt%, pH 10.0) was diluted to 1 wt% (pH 8.7) with water before using. Pluronic F127 was added to the diluted SnO_2 dispersion under stirring until the F127 was completely dissolved. The pH of the SnO_2

dispersion containing F127 was adjusted to 6.0 by adding hydrochloric acid (1 mol/L). The resulting dispersion was incubated at 60 °C for 1–14 days to promote anisotropic self-assembly. The weight ratio of Pluronic F127 to SnO_2 was varied from 0.1–1.0.

Bond strength test for TiO_2 nanochains. The dispersion of TiO_2 nanochains was treated by sonication for 20 and 75 min to test the bonding intensity between neighboring TiO_2 NPs. To examine the thermal stability of the TiO_2 nanochains, the samples were dip-coated onto a silicon wafer and subsequently subjected to heat treatment at 500 and 700 °C for 8 h.

Characterization. The pH of the colloidal suspensions was measured using a pH meter (HORIBA D-52) at room temperature. Field emission scanning electron microscopy (FE-SEM) images were taken on a Hitachi S-900 instrument with an accelerating voltage of 6 kV. Samples were prepared by spin-coating of the colloidal nanochains onto silicon wafers. All the colloidal suspensions were diluted with deionized water to 10% of the initial concentration before spin-coating. The samples were dried in an oven overnight at 60 °C and then exposed to UV ozone for 30 min to remove the organic compounds before SEM observation. The SEM samples before observation were deposited by sputtering of a Pt layer for 10 s using a Hitachi E-1030 instrument. TEM images were obtained with a JEOL JEM-2800 transmission electron microscope at an accelerating voltage of 200 kV. XRD patterns were recorded on a Bruker AXS M03X-HF diffractometer with Cu Kα radiation at 40 kV and 30 mA in a 2θ range of 20–60°. Dynamic light scattering (DLS) and zeta potential measurements of the TiO_2 dispersion were performed with a Malvern Zetasizer Nano ZS90 instrument at 25 °C. The hydrodynamic diameter of the TiO_2 nanoparticles was determined by a cumulant method. Their zeta potential was calculated from the measured electrophoretic mobility using the Smoluchowski approximation.

References:

(1) K. N. P. Kumar, K. Keizer, A. J. Burggraaf, T. Okubo, H. Nagamoto and S. Mooroka, Nature 1992, **358,** 48.

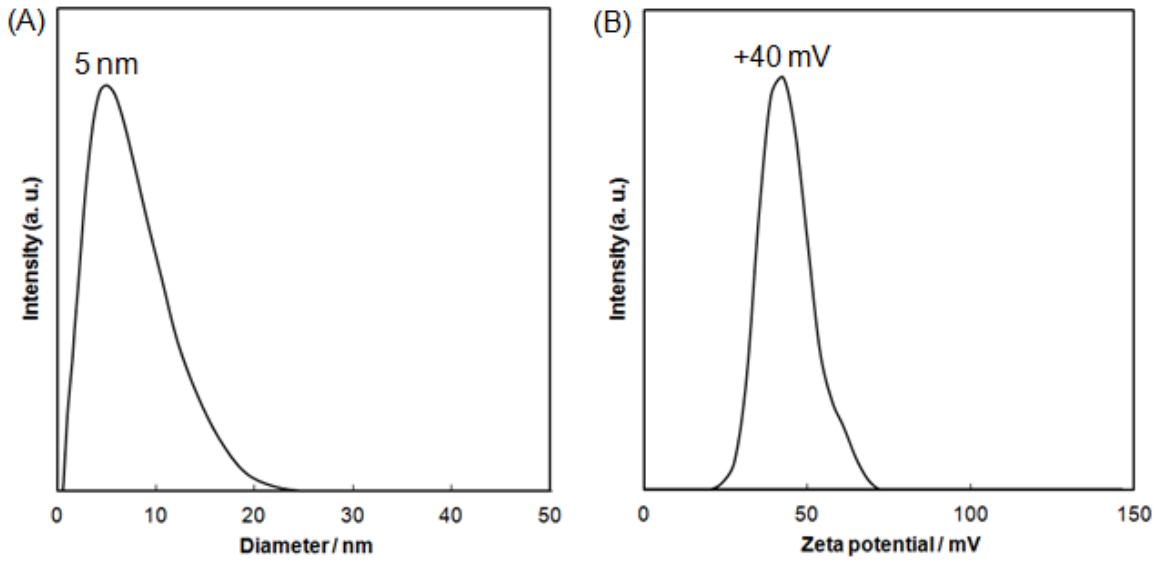

Fig. S1

DLS (A) and zeta potential (B) of as-synthesized colloidal TiO_2 nanoparticles formed by peptization method.

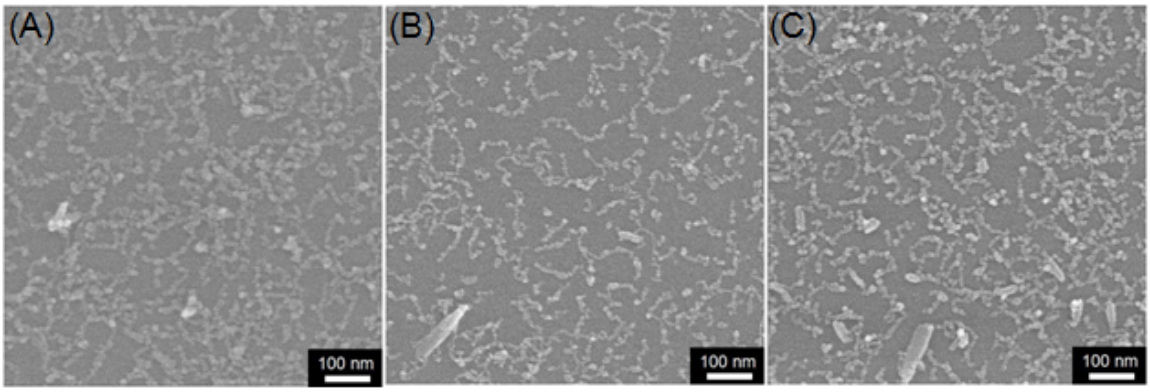

Fig. S2

SEM images of chain-like TiO_2 nanostructures prepared with various concentrations of Pluronic F127 at pH 4.0 after 7 days of incubation. Weight ratio of F127 to TiO_2 is (A) 0.1, (B) 0.25, and (C) 1.0.

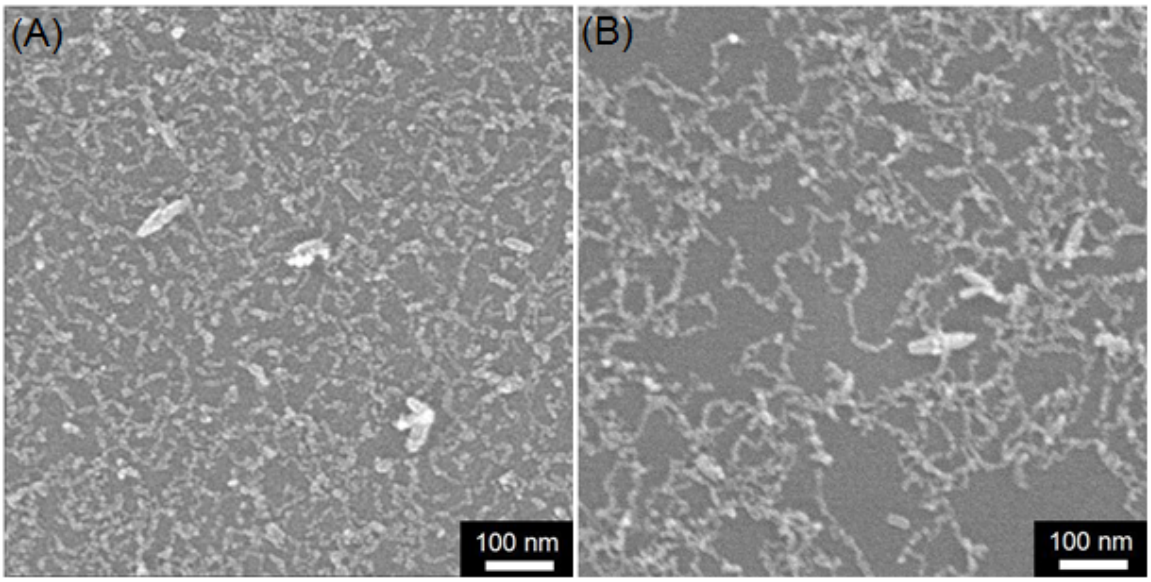

Fig. S3

SEM images of chain-like TiO_2 nanostructures prepared at pH 4.0 with incubation times of (A) 1 day and (B) 14 days. The weight ratio of F127 to TiO_2 was 0.5.

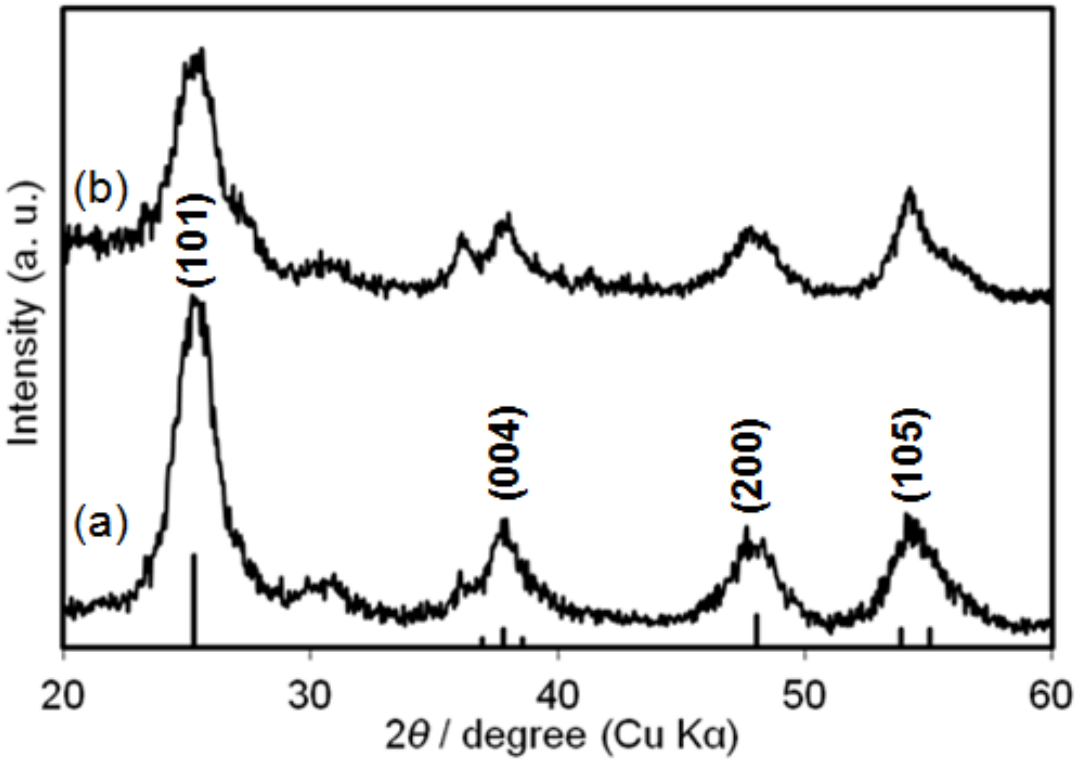

Fig. S4

XRD patterns of as-prepared (a) TiO_2 NPs and (b) TiO_2 nanochains. As a reference, the standard XRD pattern of anatase TiO_2 (JCPDS No. 21-1272) is shown as a bar diagram at the bottom. The TiO_2 nanochains were prepared at pH 4.0 with a weight ratio of F127 to TiO_2 of 0.5 after 7 days of incubation.

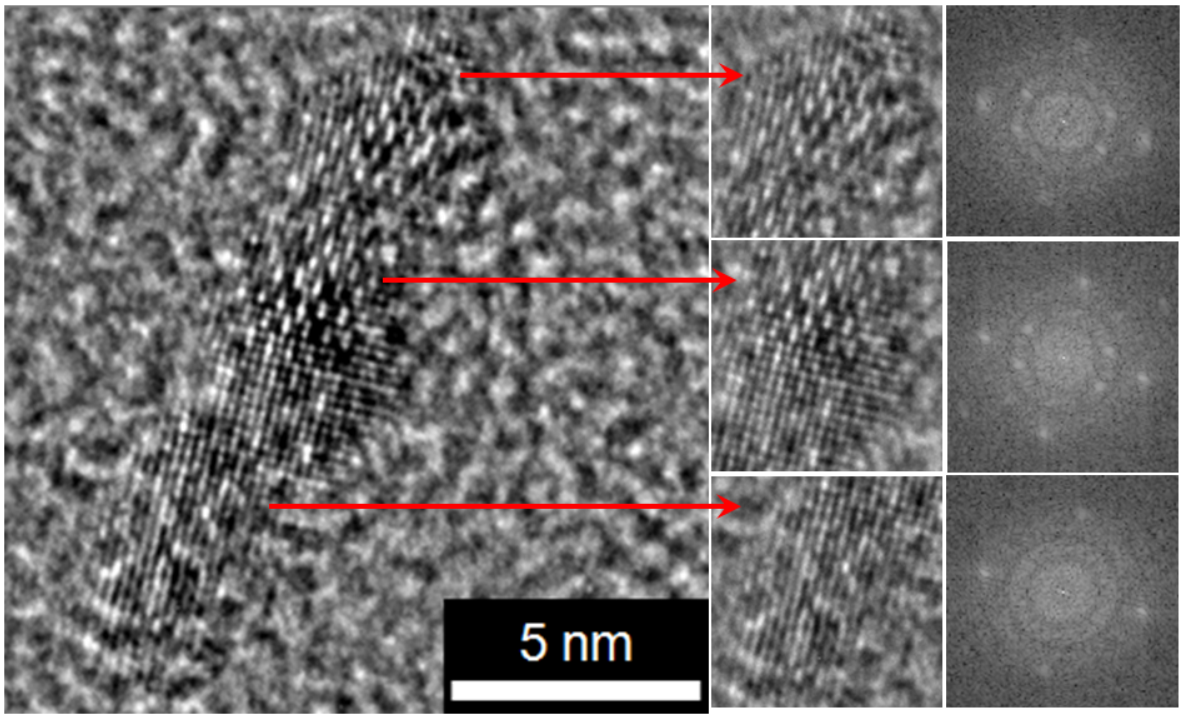

Fig. S5

HRTEM images of single as-prepared TiO_2 nanochain and corresponding FFT patterns (weight ratio: F127/TiO_2 = 0.5, pH 4.0, 7 days of incubation).

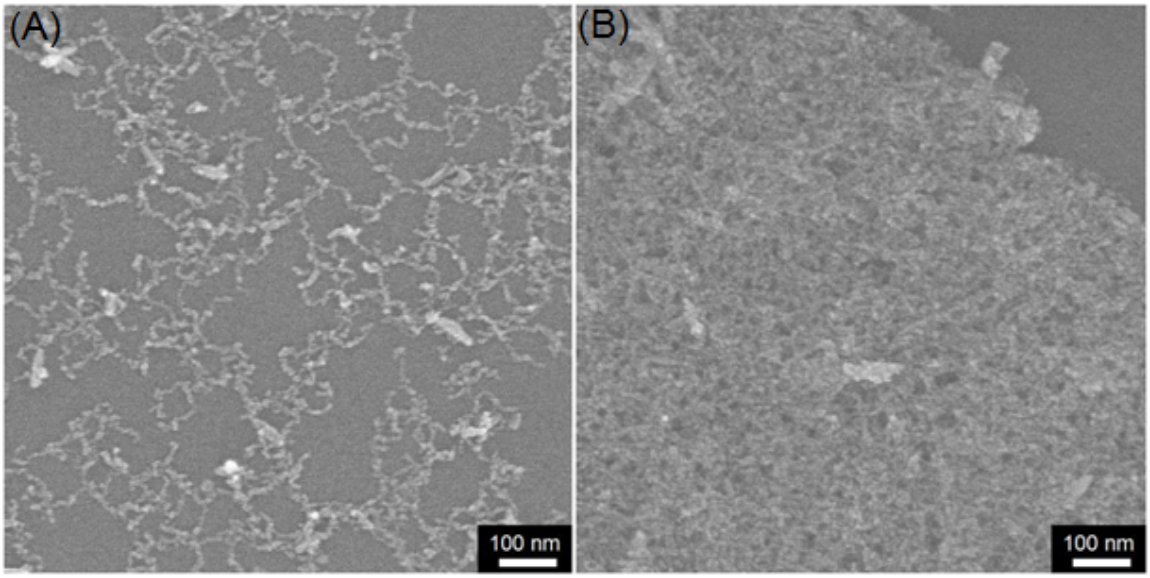

Fig. S6

SEM images of chain-like TiO_2 nanostructures (weight ratio: F127/TiO_2 = 0.5, pH 4.0, 10 days of incubation) after ultrasound treatment for time periods of (A) 20 min and (B) 75 min.

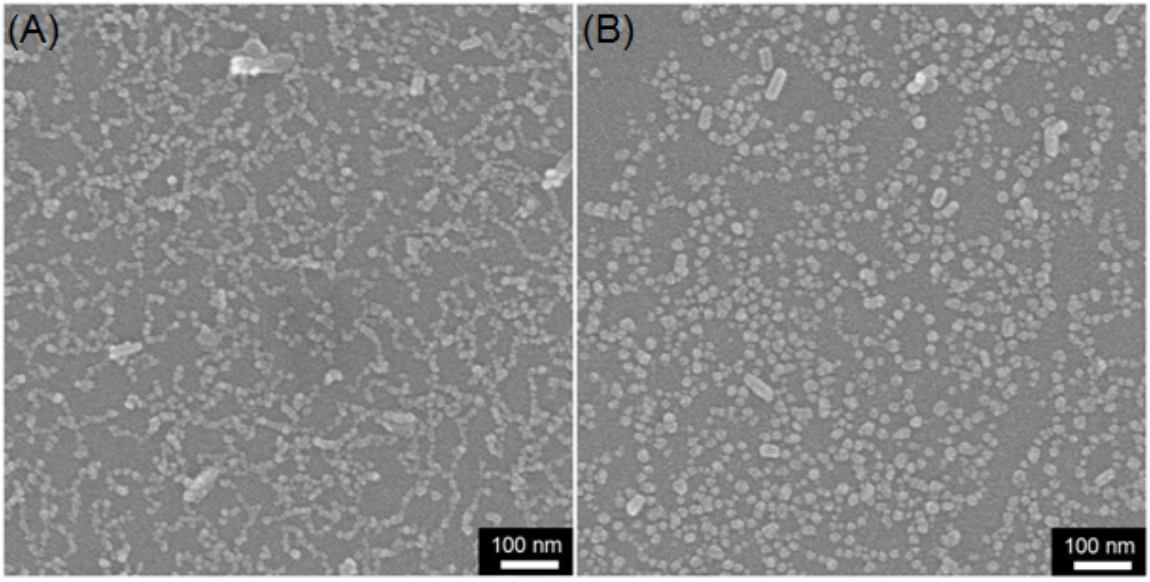

Fig. S7

SEM images of chain-like TiO_2 nanostructures (weight ratio: F127/TiO_2 = 0.5, pH 4.0, 5 days of incubation) after heat treatment at (A) 500 °C and (B) 700 °C for 8 h.

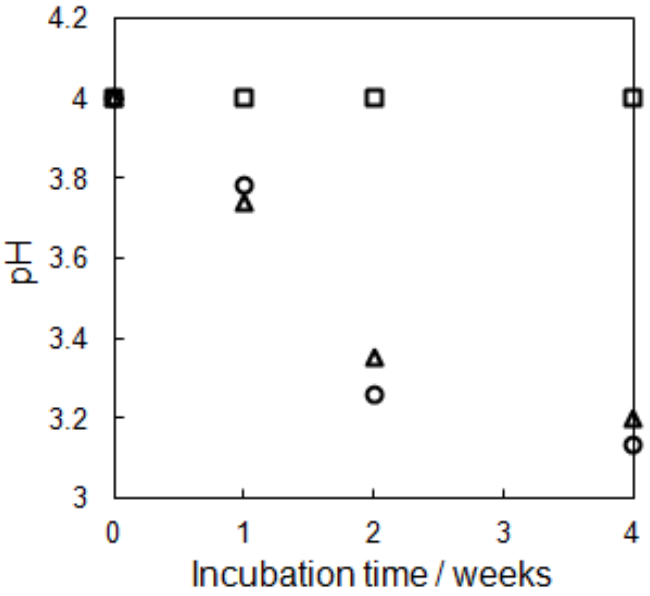

Fig. S8

Relationship between pH change of TiO_2 dispersion and incubation time. Open squares, triangles, and circles represent weight ratios of F127 to TiO_2 of 0, 0.3, and 1.0, respectively.

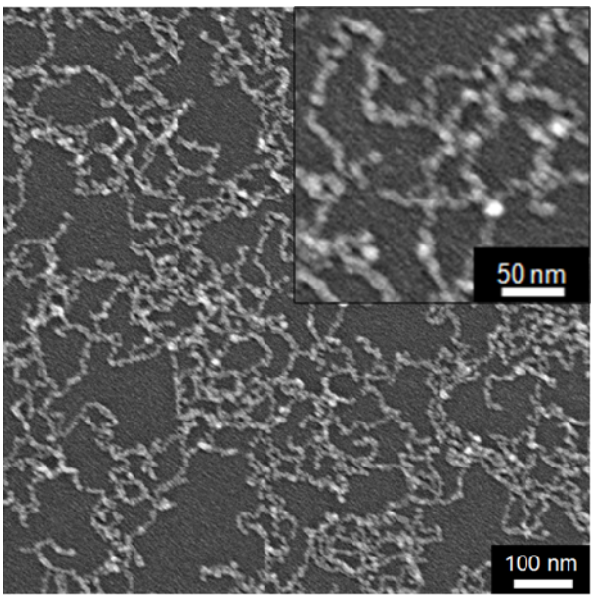

Fig. S9

SEM image of SnO_2 nanochains prepared with a weight ratio of F127 to NPs of 0.5 after 7 days of incubation. Insets show high-magnification SEM images.

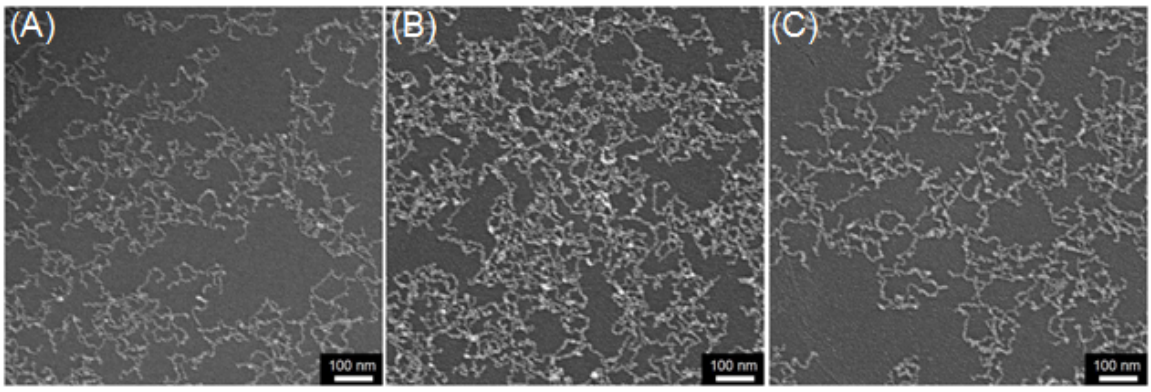

Fig. S10

SEM images of chain-like SnO_2 nanostructures prepared with various Pluronic F127 concentrations at pH 6.5 after 7 days of incubation. Weight ratio of F127 to SnO_2 is (A) 0.1, (B) 0.25, and (C) 1.0.