Electronic Supplementary Materials

Efficient incorporation of monomeric anthracene into nanoporous silica/surfactant nanocomposite spheres using mechanochemical solid state reaction

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Experimental Procedure S1

Mechanochemical milling method:

A stainless steel vessel mounted on a centrifugal equipment (Nisshin Giken Co., Ltd., NEV-MA-8) was swung at the centrifugal rate of 40.2 rad/s for 1 h. Twenty bearing steel balls (SUJ-2) with the different diameters of 4.0 mm, 6.4 mm and 9.8 mm were used as the milling media. The medium balls move in a circular path against the inside wall of the vessel pressed against the wall by centrifugal force. When the balls compress the trapped samples, the kinetic energy transfer from the medium to the samples occurs, and the resulting compressed force was calculated by Eq. (S1).

$$F = mr\omega^2 \quad \text{(S1)}$$

The added amounts of the SNPS and Ant were calculated as follows: 50 % of the Ant occupation rate in the nanopore was estimated by the Ant molecular volume (0.43 nm^3) from CS Chem3D Pro(tm) (CabridgeSoft Corporation) and the silica nanopore volume (0.47 mL) from the nitrogen adsorption and desorption isotherms.

Solvent-extraction of SNPS:

For the TEM observation without the organic contents, the SNPS was solvent-extracted; 1.0 g (16.44 mmol) of SNPS in 0.5 mL of HCl (37.4 vol%) and 150 mL of ethanol were stirred for 5 h at 50 ^{o}C, filtered and washed 3 times with 40 mL of de-ionized water and 40 mL of ethanol, then, stored under reduced pressure for 1 day.

Characterization:

The XRD patterns were recorded by a X'Pert Pro MPD (PNAalytical Co., Ltd.) using monochromatized CuKα radiation. The infrared spectra were recorded by a FT-IR spectrometer (Perkin-Elmer Inc., Spectrum GX) with an accumulation of 128 times and resolution of 2.0 cm^{-1}. The morphologies were observed using an FE-SEM (Hitachi Co., Ltd., S-4500N). The average diameter was calculated from the mean value between the long length and short length of 50 particles. The silica framework nanostructures of the spheres were observed on a carbon-coated Cu grid using a TEM (JEOL Co., Ltd., JEM-2010F). Nitrogen adsorption and desorption isotherms were measured at 77 K by a SA3100 instrument (BECHMAN COULTER Co., Ltd.). Prior to the measurement, the samples were degassed under vacuum at 393 K for 4 h. The pore volume was calculated by the BET surface area and averaged pore size. The luminescence properties were evaluated by photoluminescence spectroscopy and microscopy. The luminescence spectra were recorded by a FluoroMax-4 spectrophotometer (Horiba Co., Ltd.) with an excitation wavelength at 365 nm and room temperature (excitation-slit/detection-slit: 2.5 nm/5.0 nm, step width: 0.5 nm, sample weight: 150 mg). The microscope images were observed using a luminescence microscope (Nikon Co., Ltd., BX-50; excitation wavelength: 330–385 nm, exposure time: 1500 ms, sensitivity: 20).

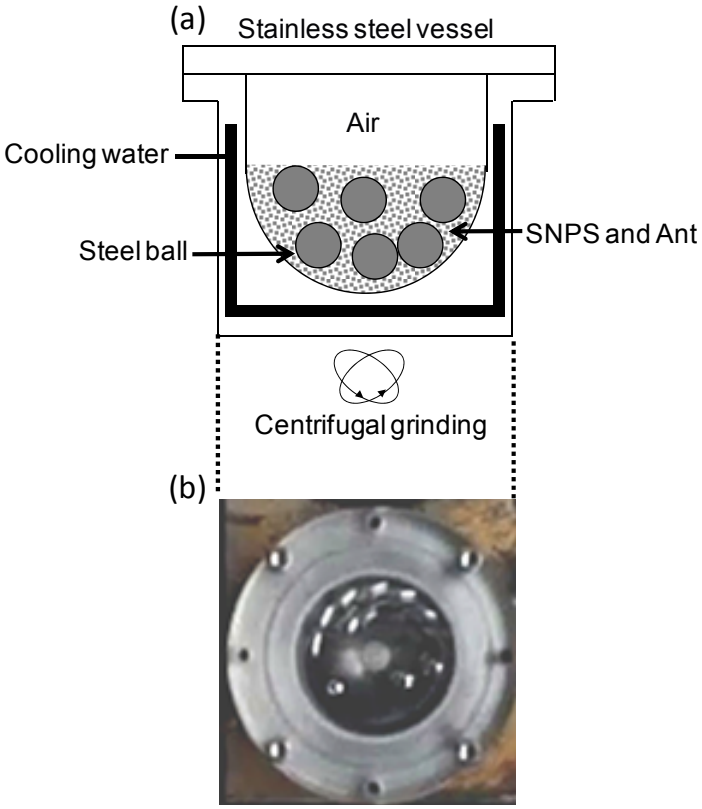

Fig. S1. (a) Set-up for the mechanochemical reaction, and (b) photograph of the top view of the equipment during the milling. The vessel made from a stainless steel rod (SUS304) with the inner volume of 70 mL was surrounded by a water jacket.

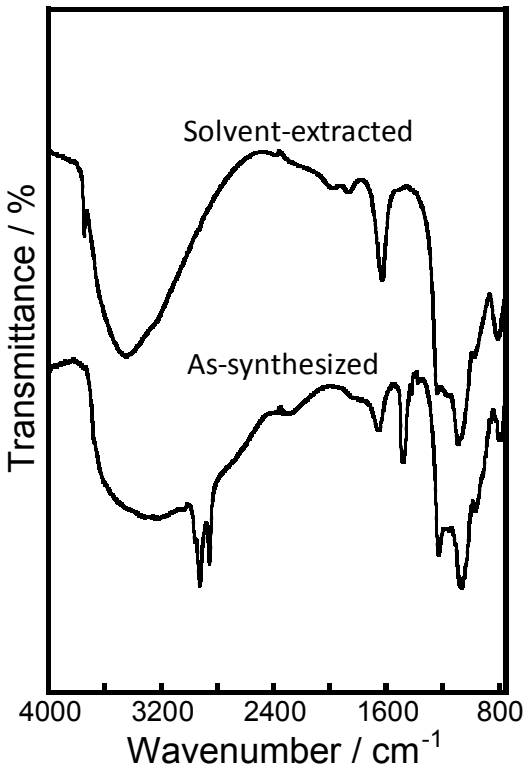

Fig. S2. FT-IR spectra of the as-synthesized and solvent-extracted SNPS nanospheres. The bands at around 1070 and 1225 cm^{-1} originated from the Si–O–Si asymmetric and symmetric stretching. The bands at around 795 and 960 cm^{-1} are assigned to the Si–OH stretching. The several bands at around 1480, 2854 and 2925 cm^{-1} assigned to the C–H stretching and bending in the CTAB molecules clearly disappeared by the solvent-extraction, indicating the complete removal of the surfactant.

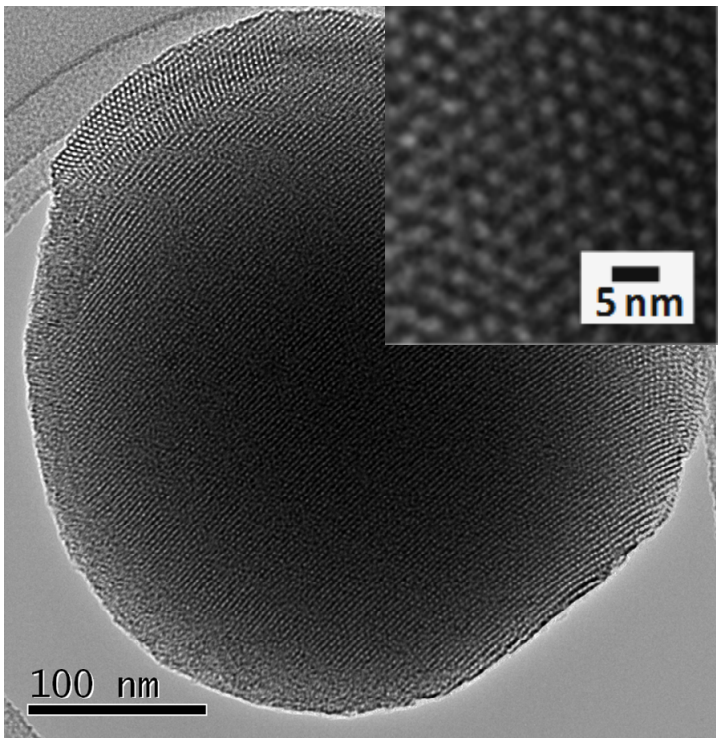

Fig. S3. TEM image (Inset: magnified image) of a solvent-extracted SNPS nanosphere. The images indicate that the cylindrical pores were homogeneously formed on the particle surfaces, the pore diameter was estimated to be 2.3−2.7 nm and the pore wall thickness was 0.6−1.0 nm.

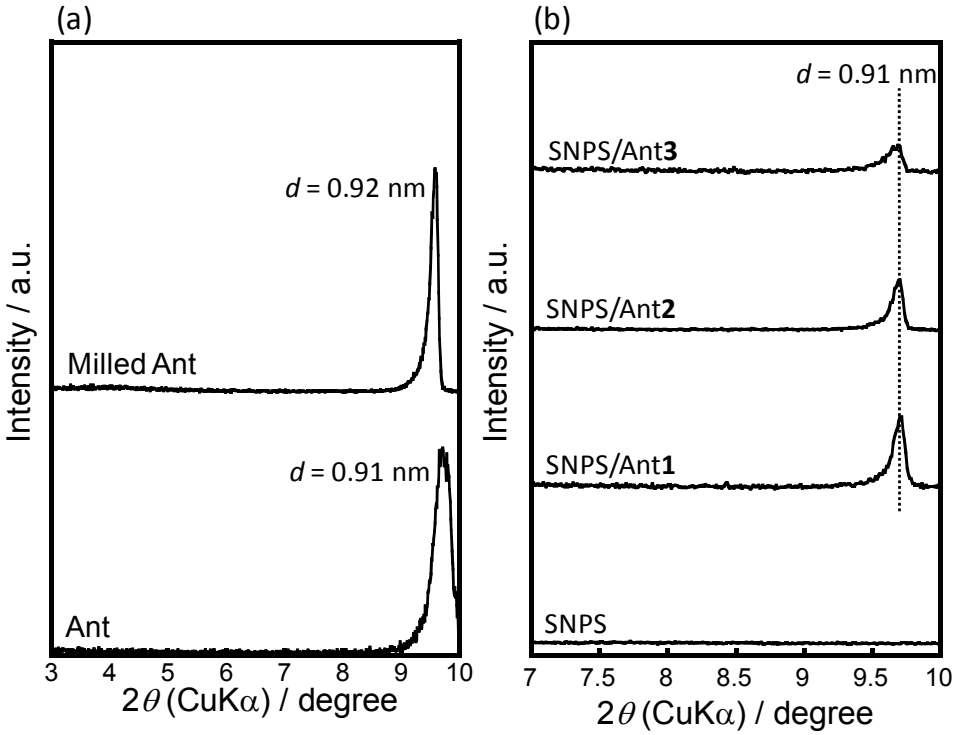

Fig. S4. XRD patterns in the higher degree regions of (a) the Ant crystal with and without the milling at a force of 174 mN, and (b) the SNPS, SNPS/Ant**1**, SNPS/Ant**2** and SNPS/Ant**3**.

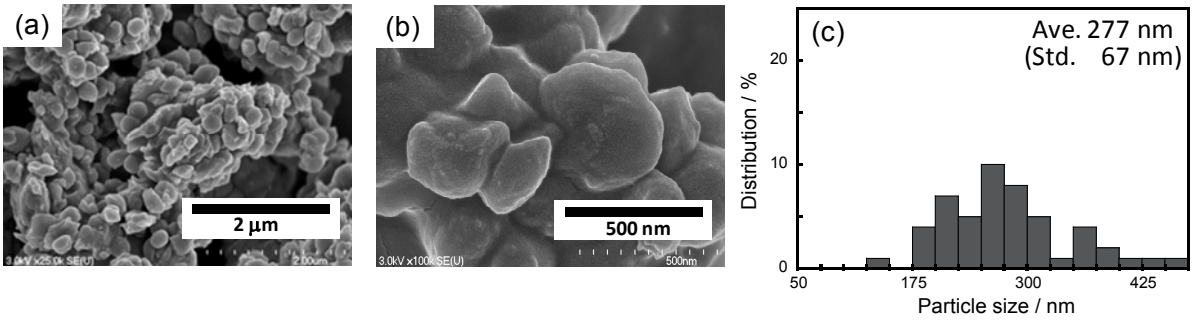

Fig. S5. FE-SEM images ((a): ×25.0 k, (b): ×100 k) of the SNPS alone milled at a force of 174 mN, and the particle size distribution.

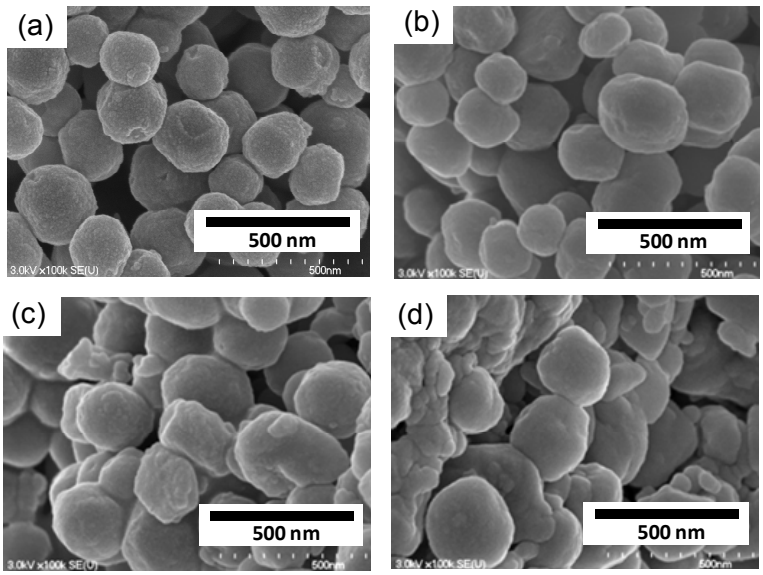

Fig. S6. FE-SEM images (×100 k) of the (a) SNPS, (b) SNPS/Ant**1**, (c) SNPS/Ant**2** and (d) SNPS/Ant**3**.

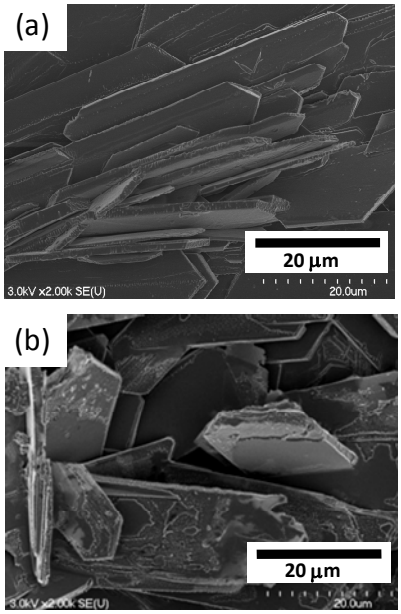

Fig. S7. FE-SEM images of the Ant crystal (a) before and after the milling at a force of 174 mN.

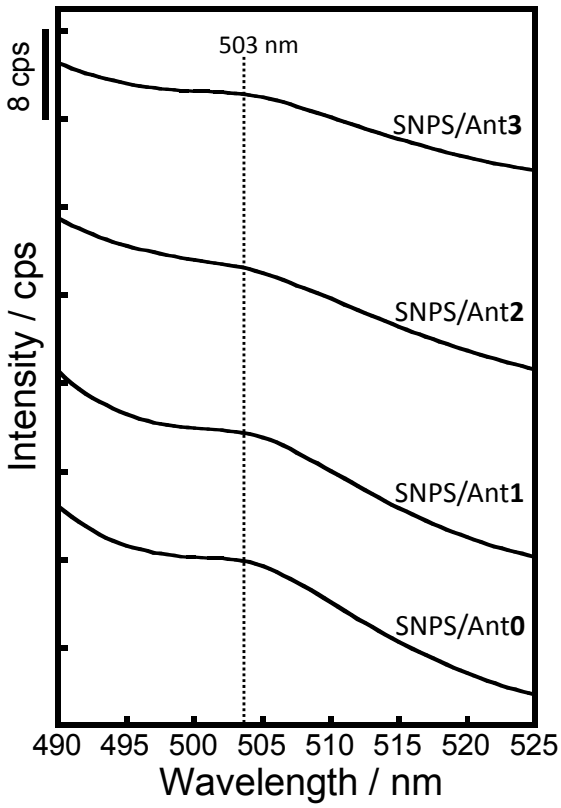

Fig. S8. Photoluminescence spectra of the SNPS/Ant**0** SNPS/Ant**1**, SNPS/Ant**2** and SNPS/Ant**3** at around the weak peak of 503 nm.