Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Porous Charged Polymer Nanosheets Formed Via Microplastic Removal from Frozen Ice for Virus Filtration and Detection

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EXPERIMENTAL SECTION

Materials

Aniline (>99.5%), APS >98.0%, and chloroform (>99.8%) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl 36%) was obtained from Alfa Aesar. PS particles with diameters of 450, 220, 120, and 60 nm were purchased from Spherotech. Heat-inactivated SARS-CoV-2 was purchased from ATCC. The Monarch Total RNA Miniprep Kit and Luna SARS-CoV-2 RT-qPCR Multiplex Assay Kit were obtained from New England Biolabs. Hydrophilic PTFE membranes with 1.0 μm-sized pores and 0.1 μm-sized pores were purchased from Millipore. Aqueous solution of 100 nm-sized silica particles (10 mg mL^{-1}) were purchased from NanoXact. The water used in all the experiments was purified using a Millipore system. All chemicals were used as received.

Removal of Microplastics in a Frozen State Through Ice-Assisted Synthesis of PANI Nanosheets

Directional freezing of the PS particle-containing aqueous solution at -20 °C resulted in the accumulation of PS particles on the ice surface. Aniline (0.25 M) in 1 M HCl solution and 0.25 M of APS in 1 M HCl solution were prepared and dropped on the particle-concentrated ice surface, and 10 min of chemical oxidative polymerization at 0 °C was allowed to develop green-colored PANI films on the surfaces of the PS particles. Using predetermined substrates, the PANI/PS films were detached from the ice surface via the stamping method. PS particles in the PANI/PS films were selectively washed off with chloroform. The removal efficiency of PS particles through this process was calculated based on the characteristic peak of PS at 279 nm in the UV-visible spectra (Shimadzu UV-2600). This yielded porous PANI nanosheets whose pore sizes could be adjusted by controlling the size of the PS particles.

Structural Characterizations of Porous PANI Nanosheets

SEM (Philips XL-30 FEG) experiments were performed on the porous PANI nanosheets after transferring them onto Si wafers. TEM (JEOL JEM-2200FS, 200 kV) experiments equipped with EELS were performed by stamping PANI nanosheets with gold TEM grids. FTIR (Two IR spectrometer, PerkinElmer) spectra were obtained using KBr pellet method. The Brunauer–Emmet–Teller (BET) specific surface area of the porous PANI nanosheets was estimated through the measurements of nitrogen adsorption and desorption isotherms using autosorb iQ (Quantachrome) at 77 K.

Virus Filtration

For the virus filtration experiments, porous PANI membranes were prepared using 100 nm-sized PS particles and transferred onto a commercially available hydrophilic PTFE membrane with an average pore size of 1 μm via the stamping method. SARS-CoV-2 filtration was conducted at room temperature using a stirred cell (Advantec UHP-25K) with an effective membrane area of 4.9 cm^2. After virus filtration, RNA extraction and purification were performed using a Monarch Total RNA Miniprep Kit. To quantify the amount of viruses in the RNA-extracted solution, real-time quantitative reverse transcription PCR (Roche LightCycler 96 instrument) was carried out using the Luna SARS-CoV-2RT-qPCR Multiplex Assay Kit. From the threshold cycle values of different concentrations of purified SARS-CoV-2 N gene (from 200 to 2×106 copies), the standard curve was prepared and used for the quantitative measurement of extracted viral RNAs before and after membrane filtration. To assess the flux value, the volume of water permeated across the filtration membrane was measured during filtration at a given effective filtration area.

Electrophoretic Capturing of Charged Targets

Electrophoretic sifting or gluing of 100 nm-sized silica particles onto porous PANI membranes was performed. For this purpose, porous PANI membranes with different pore sizes were transferred onto an Si wafer with low-resistivity for use as a working electrode. Stainless steel was used as the reference electrode and an aqueous solution of 100 nm-sized silica particles as electrolyte. An electric field of 6 Vcm^{-1} (potential of 3V) was applied to the working electrode using a potentiostat (VersaSTAT3, AMETEK Inc.). The surface morphology of the porous PANI membranes was examined using an SEM (Philips XL-30 FEG).

Computational Methods

A model of the electric field distribution on porous PANI membranes was developed in COMSOL Multiphysics 6 software using an electrostatic module. Periodic porous films with pore diameters of 400 and 200 nm were created to represent two different porous PANI membranes. By assigning the median geometry to water, the electric potential was calculated under an applied electric field of 6 Vcm^{-1}.

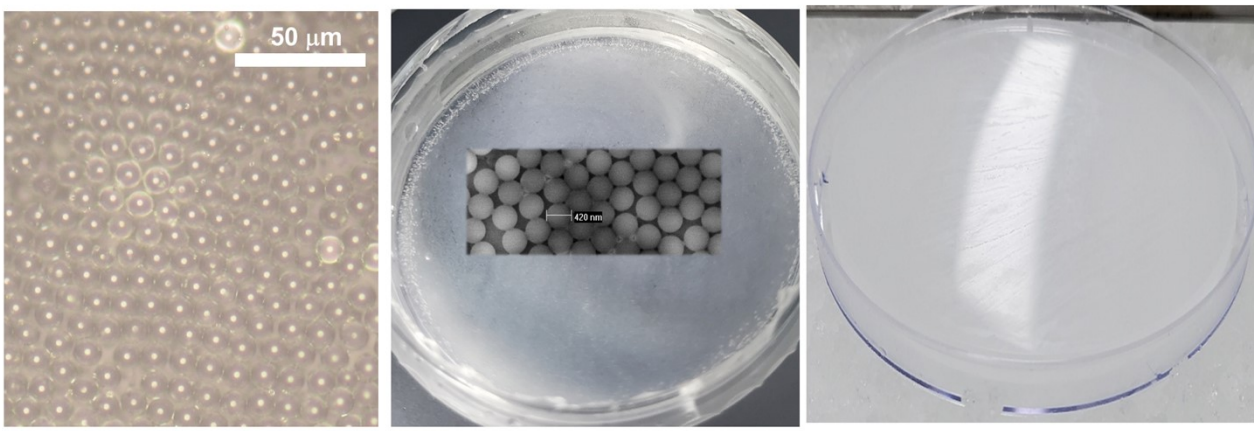

Fig. S1 Representative optical/digital micrographs showing the PS-accumulated ice surfaces with various sizes, compared with pure ice surface, obtained by the directional freezing. Note that the blue color came from the structural color of 400 nm-sized PS particles because undyed particles were used.

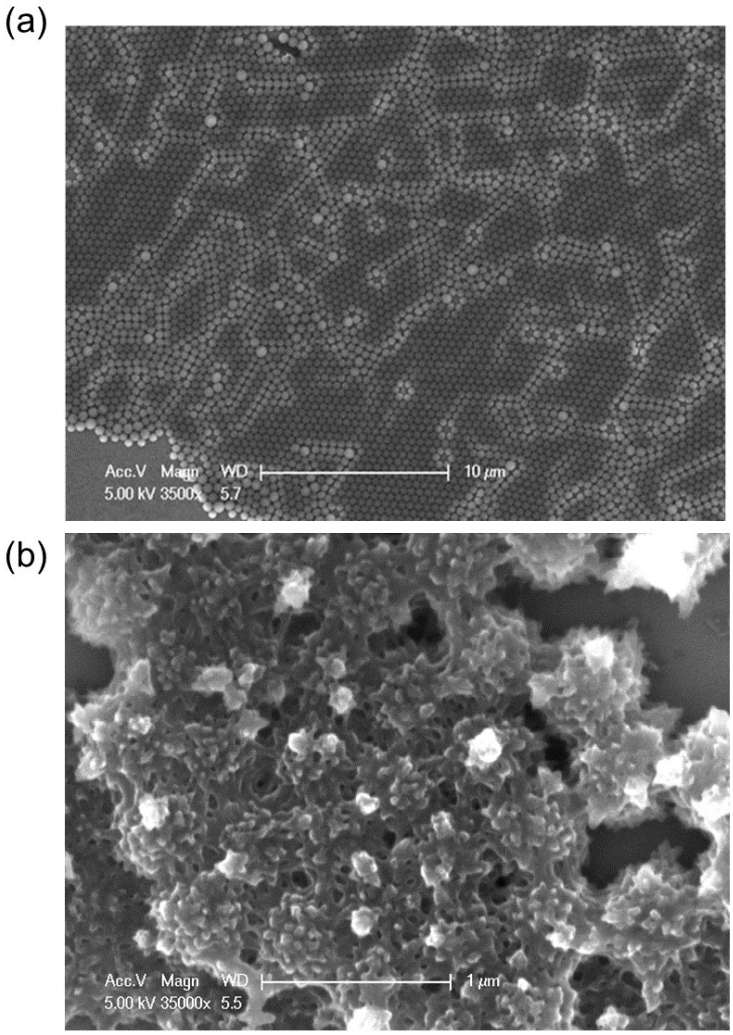

Fig. S2 SEM images of (a) PS opal templates on an Si/SiO_2 wafer and (b) aggregated PANI-coated PS particles after 10 min of chemical oxidative polymerization at 0 °C.

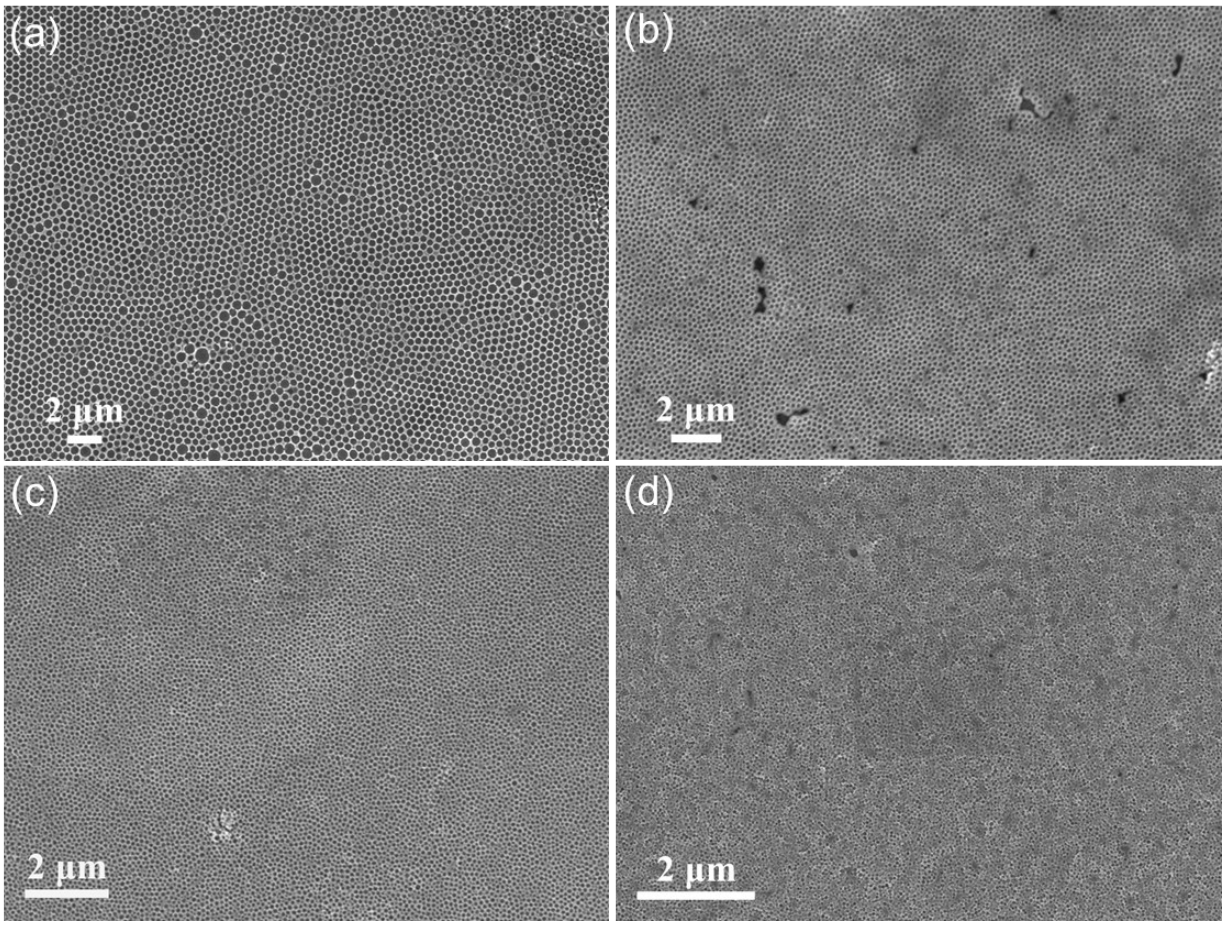

Fig. S3 Low magnitude SEM images showing the large-area porous PANI nanosheets with different pore sizes of (a) 400 nm, (b) 200 nm, (c) 100 nm, and (d) 50 nm.

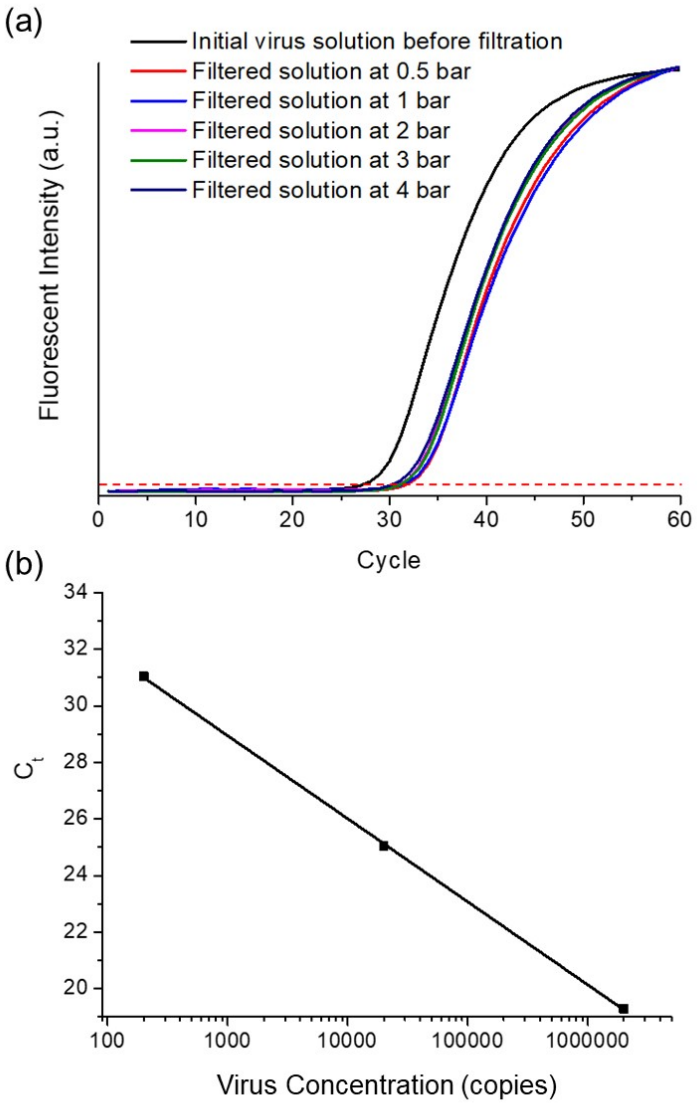

Fig. S4 (a) The real-time quantitative PCR curves of virus solutions before and after membrane filtration at different pressures. (b) The PCR standard curve for detection of SARS-CoV-2 N1 gene.

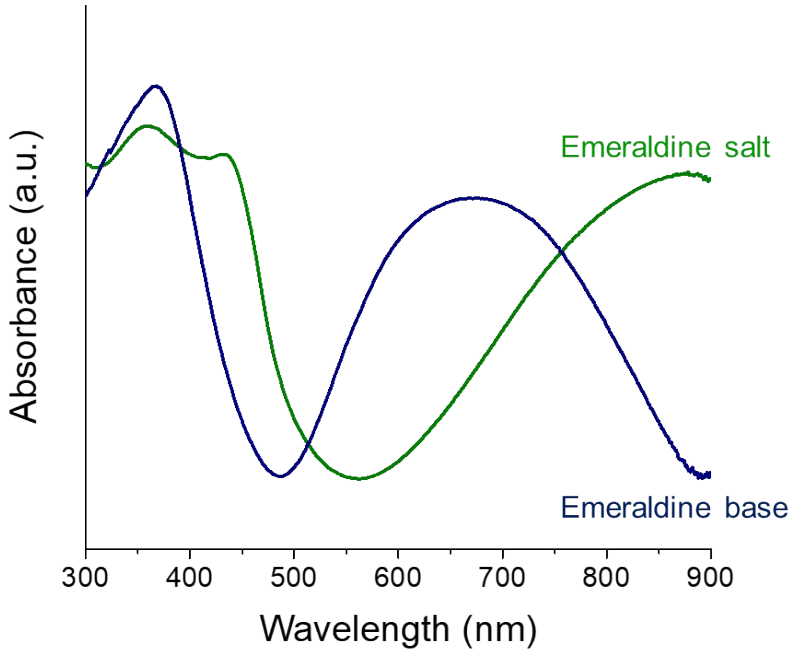

Fig. S5 UV-visible spectra of PANIs in emeraldine salt and emeraldine base states.

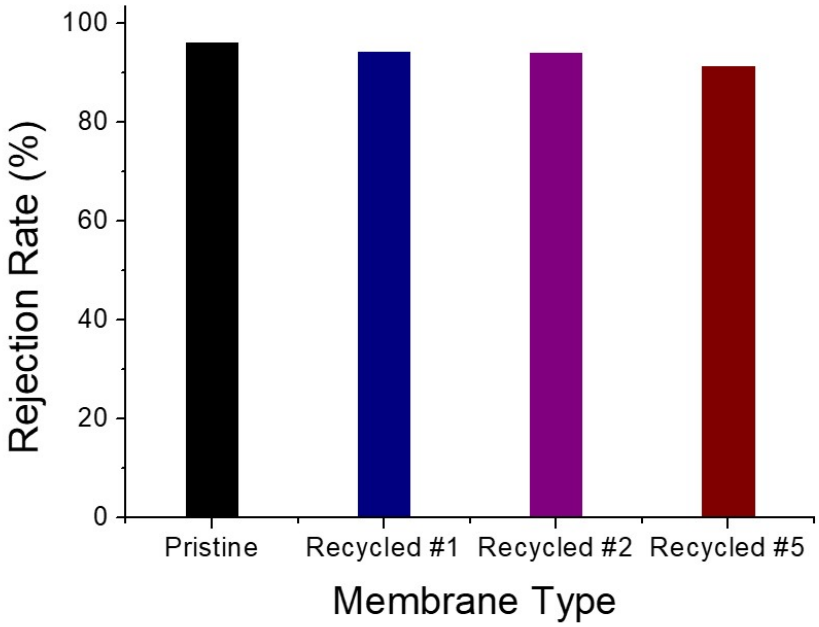

Fig. S6 Rejection rates of the recycled *p*PN-100 for SARS-CoV-2 at 0.5 bar.