

Supporting Information

Effect of Nanosizing on Sodium Cobalt(II)

Hexacyanoferrate(II) Nanoparticles in Nanofibers for Enhanced Ammonium Adsorption Capacity

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Experimental Methods

Materials

EVOH copolymer (Soarnol V2504RB) was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Dulbecco phosphate-buffered saline (PBS) was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Sodium ferrocyanide decahydrate, cobalt(II) nitrate hexahydrate, and ammonium chloride were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan).

Synthesis of Nano-NaCoHCF

Micro-NaCoHCF was synthesized according to a previously reported method. Sodium ferrocyanide decahydrate and cobalt(II) nitrate hexahydrate were dissolved separately in ultrapure water to prepare 0.4 mol/L solutions. These solutions were mixed in a beaker and stirred at 25 °C for 15 min to obtain a slurry. Slurry was then washed five times via centrifugation, and the supernatant was replaced with fresh water. Finally slurry was lyophilized overnight to obtain NaCoHCF powder.

Nano-NaCoHCF were synthesized using a Y-shaped microchannel with an inner diameter of 500 μm (NT Science MFDTC-YC3W16PK). Aqueous solutions of 0.4 mol/L sodium ferrocyanide decahydrate and cobalt(II) nitrate hexahydrate were delivered from syringe pumps (CETONI NEM-B101-03A), and the solutions were mixed within the Y-shaped microchannel. Silicon tubes and Y-shaped microchannels of inner diameters 500 μm were used. Flow rates were set at 5, 10, and 20 mL/min. Resulting particle dispersion was collected, washed using the aforementioned method, and freeze-dried overnight to obtain the nanoparticles.

Particle size measurement using dynamic light scattering

Synthesized NaCoHCF powder was dispersed in distilled water at a concentration of 1 mg/dL and the particle size was measured using a dynamic light scattering (DLS) analyzer (Otsuka Electronics ELSZ-2000ZS). The measurements were conducted at 25 °C. The average particle size and polydispersity index (PDI) were calculated using the cumulant method.

Fabrication of EVOH/NaCoHCF nanofibers by electrospinning

Polymer solution was prepared by dissolving 4 wt.% EVOH in HFIP. Synthesized nano-NaCoHCF was added to the EVOH solution at a concentration of 50 wt.% relative to the polymer and dispersed using ultrasonic agitation. Resulting solution containing dispersed NaCoHCF was electrospun under the following conditions: applied voltage 25 kV, flow rate 1.0 mL/h, needle size 18G, and distance between the needle and collector 15 cm. Nanofibers were electrospun onto aluminum foil and collected as nanofiber sheets.

SEM observation

Powder and nanofiber samples were mounted on a sample stage using carbon tape. After coating the sample surface with platinum, observations were made using scanning electron microscopy (SEM, Hitachi SU8230).

TEM observation

For TEM observations, a microgrid was placed inside the electrospinning machine, allowing nanofibers to be directly electrospun onto a microgrid. Obtained samples were observed using transmission electron microscopy (TEM, JEOL JEM-2100F2).

Ammonium adsorption test

Ammonium chloride solution was prepared by dissolving the salt in PBS at a concentration of 1.0 g/L. EVOH/NaCoHCF nanofibers (50 mg) were added to the solution and incubated in a 37 °C oven with continuous rotation using a rotator to ensure thorough mixing. At predetermined time intervals, 1 mL of the supernatant was collected and diluted ten-fold in the PBS. Ammonium concentration of the diluted solution was measured using an ammonium analyzer (Toko Kagaku TiN-9001). Then, ammonium concentration in the original solution was calculated by multiplying the measured concentration by ten.

TG/DTA analysis

Five mg each of Nano-NaCoHCF powder, Micro-NaCoHCF powder, EVOH/nano-NaCoHCF nanofibers, and EVOH/micro-NaCoHCF were measured, then change in mass was measured by TG/DTA (Seiko Instruments TG/DTA6200) when the temperature was increased from room temperature to 550°C. Temperature increase rate was set at 10°C/min and the reaction was left at 550°C for 10 minutes to allow the reaction to proceed completely. NaCoHCF content of EVOH/nano-NaCoHCF nanofibers and EVOH/micro-NaCoHCF nanofibers was calculated from their respective remaining mass using the following formula (1).

$$\text{Content of NaCoHCF in the nanofibers} = W_{\text{nanofibers}} \times 100 / W_{\text{NaCoHCF}} \quad (1)$$

where $W_{\text{nanofibers}}$ is residual weight of each EVOH/NaCoHCF nanofibers at 550°C, and W_{NaCoHCF} is residual weight of NaCoHCF powder at 550°C.

Results

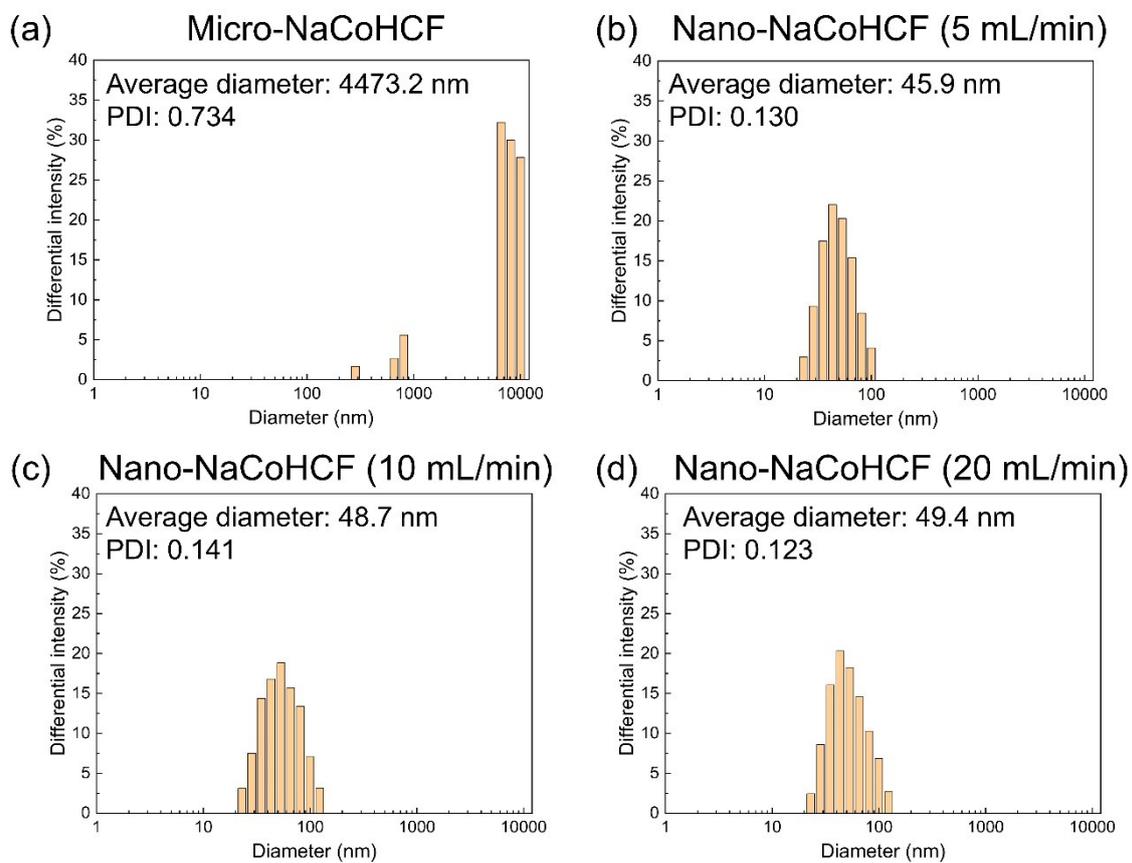


Figure S1: Intensity-weighted size distributions of (a) micro-NaCoHCF, (b) nano-NaCoHCF (flow rate: 5 mL/min), (c) nano-NaCoHCF (10 mL/min), and (d) nano-NaCoHCF (20 mL/min) particles measured using dynamic light scattering (DLS). The average particle diameter and polydispersity index (PDI) were calculated using the cumulant method.

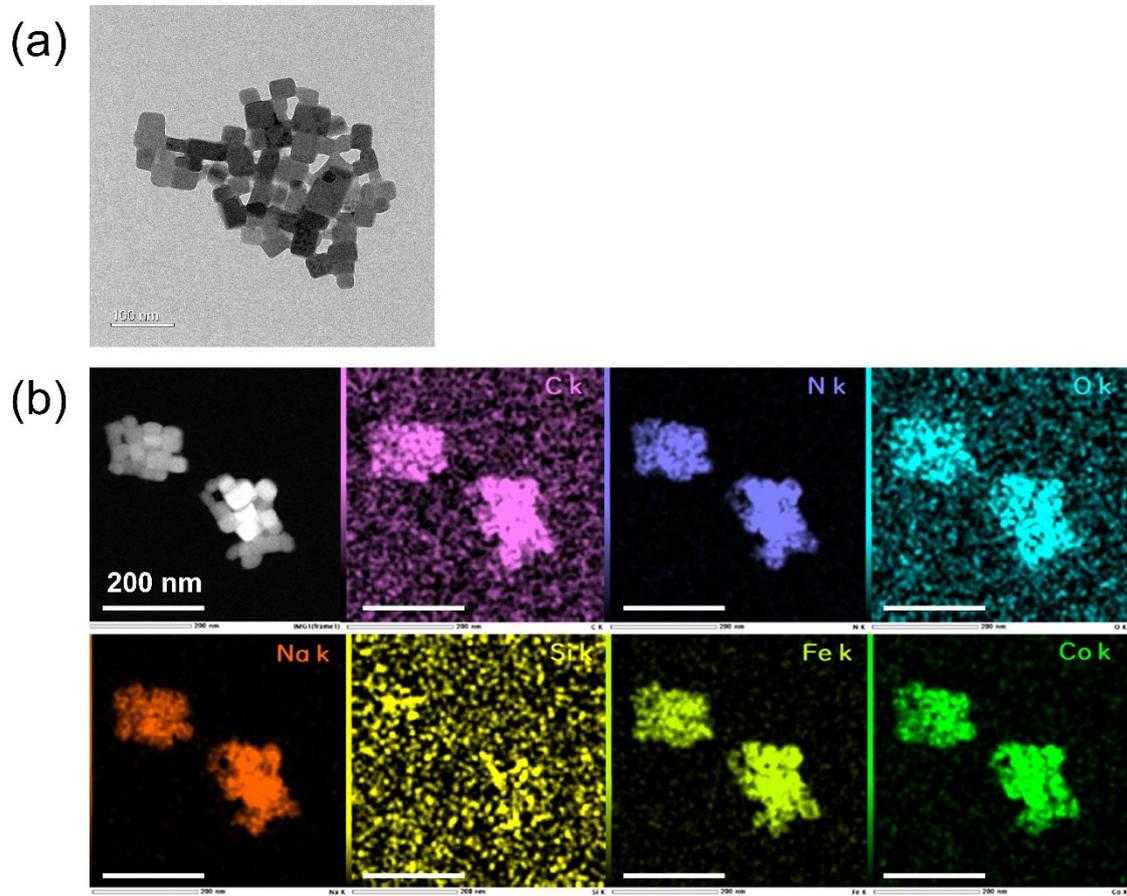


Figure S2: (a) TEM image of the nano-NaCoHCF particles. (b) Image of EDX mapping image of for the nano-NaCoHCF particles.

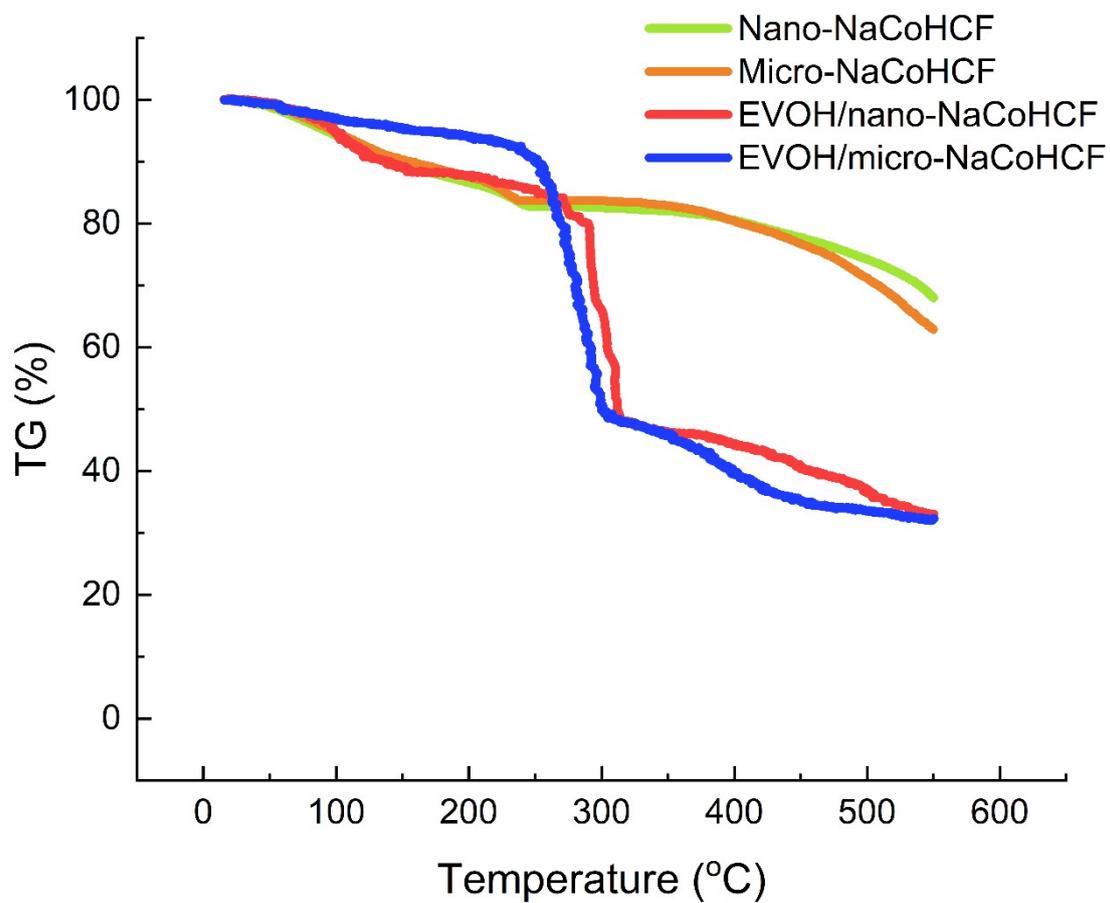


Figure S3: TG/DTA curves of Nano-NaCoHCF particles, Micro-NaCoHCF particles, EVOH/nano-NaCoHCF nanofibers, and EVOH/micro-NaCoHCF nanofibers.