Supporting Information

Surface modulation enhances the bulk proton conductivity of Prussian blue

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S1. Synthesis of Prussian blue samples

S1-1. Prussian blue (PB)

PB without surface modification (PB-core): $Fe(NO_3)_{3aq}$, consisting of 8 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 15 mL of ultrapure water, and $Na_4[Fe(CN)_6]_{aq}$, consisting of 5.99 mmol of $Na_4[Fe(CN)_6] \cdot 10H_2O$ and 15 mL of ultrapure water, were mixed in a 50 mL centrifuge tube. The solution was mixed for 3 min using a vibrator at 2200 rpm. To purify the PBs, the tube was centrifuged at 4000 rpm for 15 min, and the supernatant was removed. To dilute the by-product salt, an equal amount of ultrapure water was added to the tube. This purification process was performed until the concentration of NO_3^- in the supernatant was below 600 ppm. The concentration of NO_3^- was measured using an ion meter (LAQUA Twin NO3, HORIBA Advanced Techno, Co., Ltd.). After purification, the PB-core slurry dried by evaporation at 60 °C and 70 hPa to yield the PB-core powder.

PB with surface modification (PB-SM): The PB-core slurry and aqueous solution consisting of additional $Na_4[Fe(CN)_6] \cdot 10H_2O$ (see Table S1) and 10 mL of ultrapure water were stirred with a magnetic stirrer for three days at room temperature. After mixing, the PB-SM powder was obtained by drying the slurry by evaporation at 60 °C and 70 hPa.

Table S1. ____

Sample	PB-core synthesis		Surface modulation
	$Fe(NO_3)_3 \cdot 9H_2O$ (mmol)	$Na_4[Fe(CN)_6] \cdot 10H_2O$ (mmol)	$Na_4[Fe(CN)_6] \cdot 10H_2O$ (mmol)
PB-core	8.00	5.99	0
PB-SM14	8.00	5.99	1.12
PB-SM26	8.00	5.99	2.10
PB-SM52	8.00	5.99	4.20

S1-2. Manganese Prussian blue analogue (MnPBA)

MnPBA without surface modification (MnPBA-core): $MnCl_2$, consisting of 1.5 mmol of the$MnCl_2 \cdot 4H_2O$ and 3 mL of ultrapure water, and $Na_4[Fe(CN)_6]_{aq}$, consisting of 0.75 mmol of $Na_4[Fe(CN)_6] \cdot 10H_2O$ and 3 mL of ultrapure water, were mixed in a 50 mL centrifuge tube. The solution was mixed for 3 min with handshake. To purify the PBs, the tube was centrifuged at 3000 rpm for 3 min, and the supernatant was removed. To dilute the by-product salt, 40mL of ultrapure water was added to the tube. This purification process was performed twice. After purification, the MnPB-core slurry dried at 60 °C to yield the PB-core powder.

MnPBA with surface modification (MnPBA-SM26): The MnPBA-core slurry and aqueous solution consisting of 0.39 mmol $Na_4[Fe(CN)_6]\cdot 10H_2O$ and 5 mL of ultrapure water were shaken 3 hours at room temperature. After mixing, the MnPBA-SM26 powder was obtained by drying the slurry at 60 °C.

S1-3. Copper Prussian blue analogue (CuPBA)

CuPBA without surface modification (CuPBA-core): $CuSO_{4aq}$, consisting of 1.5 mmol of the $CuSO_4\cdot 5H_2O$ and 3 mL of ultrapure water, and $Na_4[Fe(CN)_6]_{aq}$, consisting of 0.75 mmol of $Na_4[Fe(CN)_6]\cdot 10H_2O$ and 3 mL of ultrapure water, were mixed in a 50 mL centrifuge tube. The solution was mixed for 3 min with handshake. To purify the PBs, the tube was centrifuged at 3000 rpm for 3 min, and the supernatant was removed. To dilute the by-product salt, 40mL of ultrapure water was added to the tube. This purification process was performed twice. After purification, the MnPB-core slurry dried at 60 °C to yield the PB-core powder.

CuPBA with surface modification (CoPBA-SM26): The CuPBA-core slurry and aqueous solution consisting of 0.39 mmol $Na_4[Fe(CN)_6]\cdot 10H_2O$ and 5 mL of ultrapure water were shaken 3 hours at room temperature. After mixing, the MnPBA-SM26 powder was obtained by drying the slurry at 60 °C.

S2. General information for experiments

Fourier transform infrared (FTIR) spectra were obtained using an FTIR spectrometer (Nicolet iS5, Thermo Fisher Scientific Inc.). The crystal structures of the samples were evaluated using powder X-ray diffraction (PXRD) (D8 Advance, Bruker Corp.) with a Cu Kα X-ray source (λ= 0.154 nm) at 40 kV and 40 mA.

The chemical compositions of the PB samples were evaluated using the following methods. First, the concentrations of sodium and iron cations were evaluated using microwave plasma atomic emission spectroscopy (MP-AES, MP-4100, Agilent Technologies Inc.) after sample decomposition with nitric acid and hydrochloric acid (Multiwave 3000, PerkinElmer Inc.). Next, the concentrations of carbon, nitrogen, and hydrogen were determined using a CHN analyser (EA-1110).

Dispersion properties of PBs in water were evaluated with preparing 1000 mg/L of aqueous solution of them dispersed by ultrasonic clear for 1 hour. Zeta potentials of PBs in water were evaluated using Zetasizer NanoZS (Malvern Panalytical Ltd.).

S3. Scanning electronic microscope image

The images of scanning electronic microscope (SEM) were observed with S-4800 (Hitachi High-Tec Corp.). Primary particle sizes of PBs were less than 10 nm.

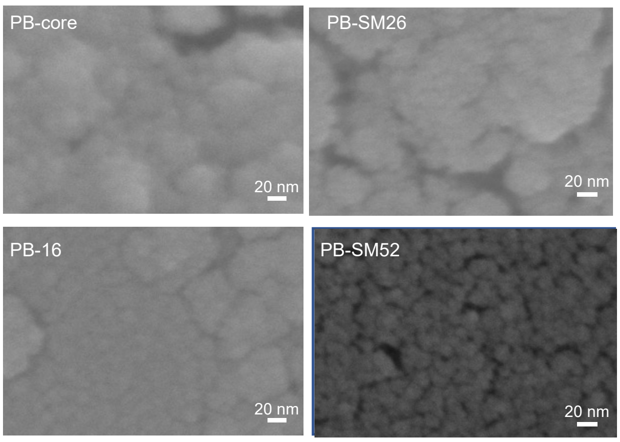

Figure S1. SEM images of PBs

S4. Dispersed particle size in water

Dispersed particle sizes of PBs in water were evaluated with dynamic light scattering (DLS) using EISZ-2000 (Ostuka electronics co. LTD.).

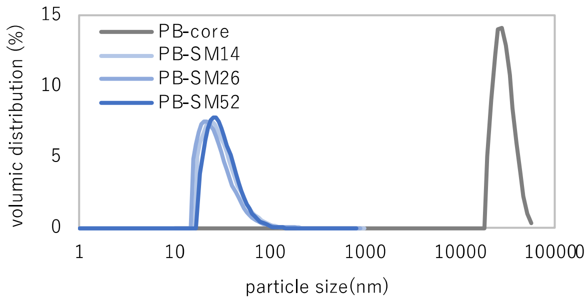

Figure S2. Volumic distribution of dispersed particle size of PBs in water

S5. Estimation of ideal amount of $Na_4[Fe(CN)_6]$ (SM_{cal})

We assumed that one $Na_4[Fe(CN)_6]$ anion was captured on one Fe^{3+} site on the surface of the PB nanoparticles. The ideal amount of $Na_4[Fe(CN)_6]$, SM_{cal} was calculated as follows:

$$SM_{cal} = SSA \times D_{site} \times M \times 100 = 23.0 \text{ (at\%)}$$

where *SSA* is the specific surface area of the PB nanoparticles, D_{site} is the Fe^{3+} site density on the surface, and *M* is the molar weight of PB. The obtained values are listed in Table S2.

Table S2. Parameters for estimation of ideal amount of $Na_4[Fe(CN)_6]$ (SM_{cal})

	Symbol	Value	Comment and reference
Avogadro constant (mol^{-1})	N_A	$6.02214076 \times 10^{23}$	NIST
Diameter of particle (m)	r	7.4×10^{-9}	See Table 1 in the main manuscript
Molar weight of PB (g/mol)	M	314	Calculated from chemical composition of PB-Core
Crystal density (g/m^3)	ρ	1.78×10^6	reference [1]
Fe^{3+} site density on the surface (mol/m^2)	D_{site}	$(4 \times \frac{1}{4} + 1)/(1.017 \times 10^{-}$	See Fig. 3(c) in the main manuscript
Specific surface area (m^2/g)	*SSA*	$3/\rho r$	Assuming a sphere shape

S6. Conductivity measurement

Conductivity measurements were performed using a precision impedance analyser (4294A, Agilent Technology) using the quasi-four-probe method in the frequency range of 40 Hz to 110 MHz. The humidity of each sample was tuned using N_2 gas and ultrapure water using a humidity controller (AHCU-2, KITZ MICRO FILTER Corp.).

S6-1. Pellet method

The sample powder was pelletized with a 7 mm pelletizer made of stainless steel. The pellets were obtained by pressing the pelletizer at 100 kg/cm^2 for 5 min. The electrodes were attached to an electron-conducting paste (TK PASTE CN-7120) at the bottom and top of the pellet.

S6-2. Mould method

Cylindrical moulds made of polactic acid (PLA) with a height of 10 mm and diameter of 12.9 mm were printed using a 3D printer. The moulds contained a rectangular groove on the top to fill the sample. Aluminium tape was attached to both sides of the groove as electrodes. The groove was filled with the sample powder and pressed with 13 mm pelletizer at 100 kg/cm^2 for 5 min.

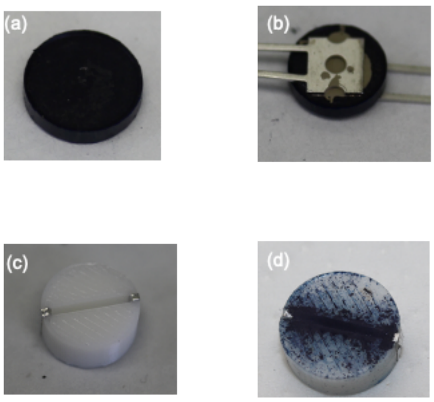

Figure S3. Pictures of (a) pellet, (b) pellet with electrode, (c) mould made of PLA, and (d) mould filled with sample powder.

S6-3. Verification of mould method accuracy

To verify the accuracy of the mould method, samples with known ion or electron conductivities were evaluated using the pellet and mould methods. The samples and their charge carriers are listed in Table S3. Graphite could not be evaluated using the pellet method because its conductivity was too high to evaluate for the pellet shape. The conductivities evaluated by the mould method were similar to those reported for the pellet method.

Table S3

Sample	Source	Carrier	Reference
PbF_2	Lead(II) fluoride (Wako chemical)	F^-	[2]
AgCl	Silver(I) chloride (Wako chemical, 99.5%)	Ag^+	[3]
Graphite	Graphite powder (Wako chemical)	e^-	[4]

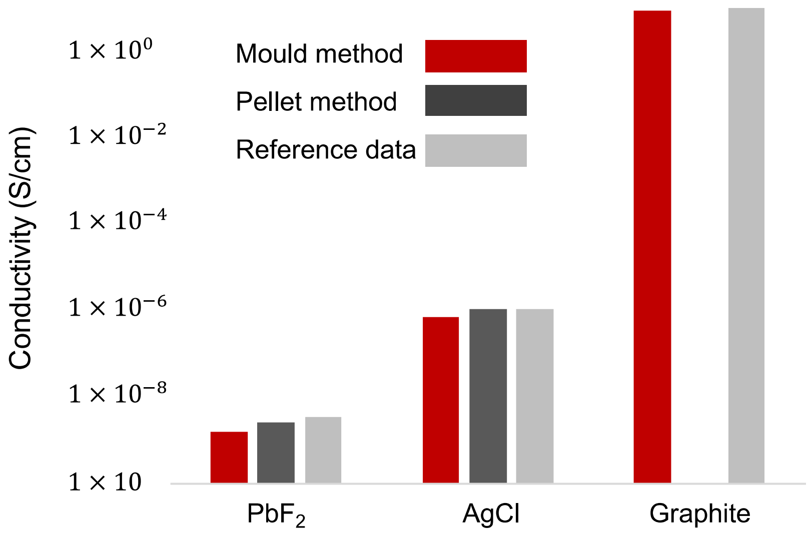

Figure S4. Conductivities of samples prepared by moulding (red bars), pellet method (dark grey bars), and value from reference (light grey bars).

S6-4 Proton conductivity of PBAs

The enhancement of bull conductivity was demonstrated with Prussian blue analogues of MnPBA and CuPBA. Both of them showed the enhancement with the surface modification as same as PB.

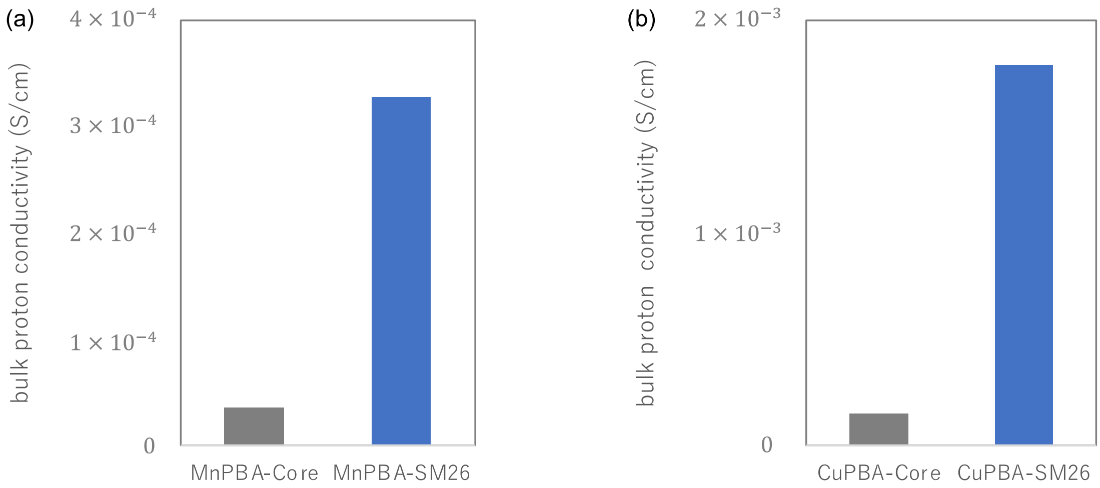

Figure S5. Proton conductivities of PBAs with and without surface modification at room temperature, 90RH% : (a) MnPBA, (b) CuPBA

S7. Water adsorption isotherm

Water adsorption isotherm of PB-SM26 at 25˚C was evaluated with constant volume method using BelsorpMAX (MicrotracBEL Corp.). The measurement was performed after vacuuming the sample at 100˚C for 23 hours.

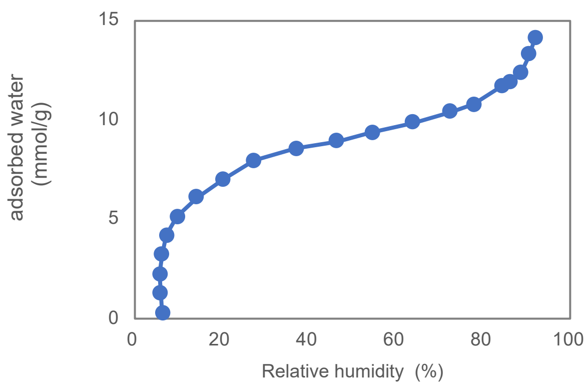

Figure S6. Water adsorption isotherm of PB-SM26 at 25˚C

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