

Electronic Supporting Information

Materials and reagents

Water was distilled and deionized with a Milli-Q filtering system, other reagents are commercial available and were used without further purification.

Preparation of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powder

Target materials were prepared according to the previously reported procedure [S. S. Kaye, J. R. Long, *J. Am. Chem. Soc.* 2005, **127**, 6506]. A solution of $\text{K}_3[\text{Co}(\text{CN})_6]$ (10 mmol in 100 mL of deionized H_2O) was added dropwise to a stirred solution of CuCl_2 (10 mmol in 100 mL of deionized H_2O) at ambient temperature to yield a sky-blue precipitate immediately. The precipitate was then centrifugated and dried in air, yielding blackish green powders. The powdered sample was characterized by PXRD and EDX measurements and the results are shown in Fig.S1 and Fig. S8. The PXRD profile is in agreement with that in the reference [S. S. Kaye, J. R. Long, *J. Am. Chem. Soc.* 2005, **127**, 6506]. EDX mapping images disclosed that the molar ratio of C/N is close to the theoretical value 1:1 and the molar ration of Cu/Co is roughly close to the theoretical value 1.5.

Growth of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ film

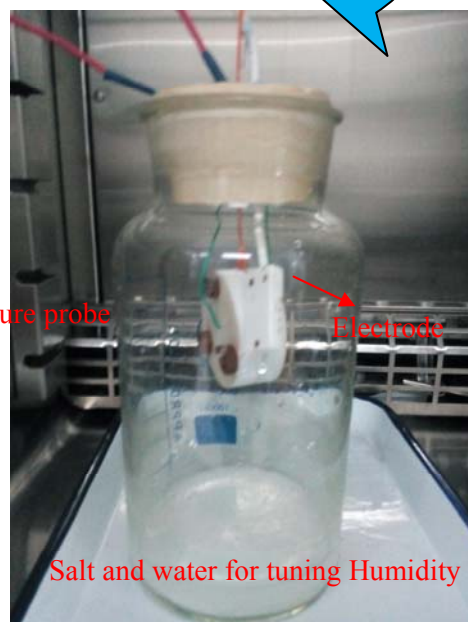
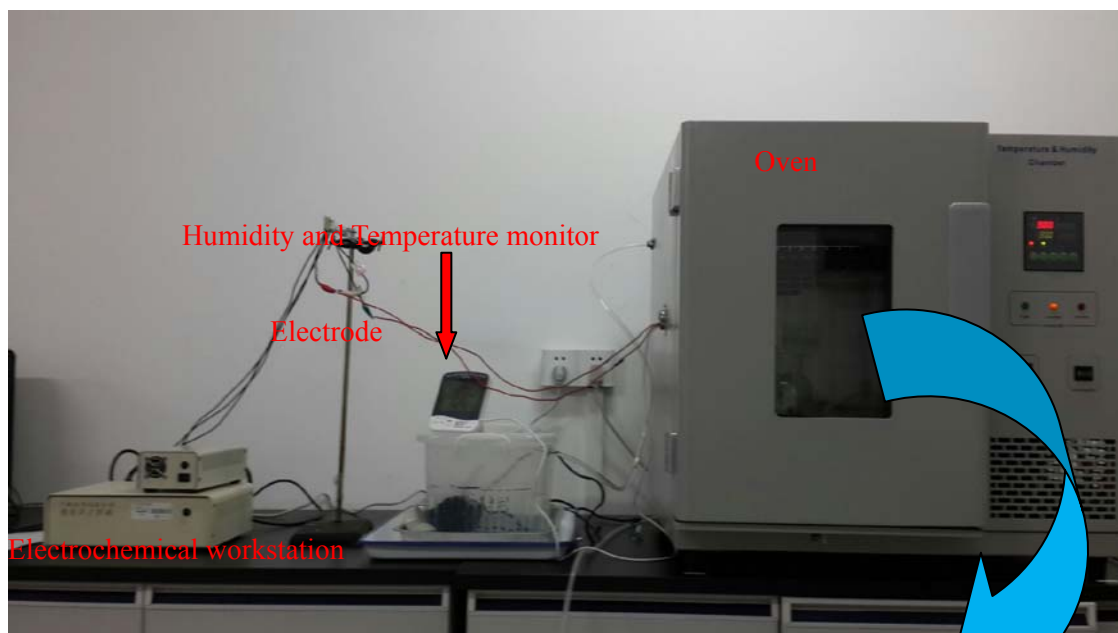
Porous α -alumina support disks with ca. 16 mm in diameter and ca. 1 mm in thickness were prepared by the press and sintering method. Prior to use, both sides of the disk were polished with SiC sandpaper (800 and 2000 mesh) to obtain the smooth surface, and then followed by ultrasonic treatment in deionized water several times until the water clear and dried at 100 °C (373 K). To fabricate the $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ film, the layer-by-layer self-assembly method was used. Solution A is made from the $\text{K}_3[\text{Co}(\text{CN})_6]$ (0.01 mol·L⁻¹) with HCl (0.1 mol·L⁻¹), solution B is made from CuCl_2 (0.01 mol·L⁻¹) with HCl (0.1 mol·L⁻¹). The pretreated substrate was consecutively dipped into solution A, pure water, solution B, and pure water. The dipping process in solutions A and B remains for 1 min, and the washed

process using pure water remain for 30 s. The four steps of preparation that the substrate was dipped into solution A, pure water, solution B, and pure water are denoted as a fabricate cycle (or self-assembly cycle), and such a cycle leads to the adsorption of a single PBA layer on the substrate. The films reported in this paper were fabricated using the above-mentioned self-assembly method for 60 cycles, and washed by water and then dried in the air.

For the growth of PBA film on the ITO and the flexible non-woven fabrics substrates, the layer-by-layer self-assembly process is similar to that used for growth of PBA film on α -alumina support disk. It is noteworthy that the ITO and the flexible non-woven fabrics substrates were not modified besides cleared by water.

Proton conductivity measurements of film and powdered pellet samples

The proton conduction measurements were carried out using a conventional three-electrode method with a CHI 660D electrochemical workstation and the reference electrode has been shortened with auxiliary electrode, the cable connected the copper plate electrodes with the electrochemical workstation is ca. 1.2 m. The copper plate electrode is 13 mm in diameter. The frequency of the applied alternating current (ac) field ranges from 100 Hz to 2 MHz with 5 mV of signal amplitude. The DC offset is zero. The powdered pellet of sample or the film on the α -Al₂O₃ support was sandwiched between two copper plate electrodes, which is suspended in a wild-mouth bottle with a rubber stopper and water solution of salt on the bottom, such a bottle was placed in an oven. The humidity was tuned by the concentration of salt and monitored using a humidity probe (see picture below).



The powdered pellet of sample was prepared by grinding the polycrystalline sample into a homogeneous powder with a mortar and pestle. Then added to a standard 13 mm diameter, sandwiched between two stainless steel disks and pressed under 8 MPa static pressures for 1 min. The powdered pellet is 1.94 mm in thickness. Measurements were carried out over the temperature range of 10-25 °C under 100% RH. The conductivity of pellet sample was measured at 303 K under selected relative humidity.

The powdered pellet sample impedances of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ were also

investigated in the temperature range of 293-383 K and under the N₂ atmosphere using a Concept 80 system (Novocontrol, Germany). The frequency spans from 1 Hz to 10⁷ Hz. The DC offset is zero.

The corresponding Z'' vs Z' plots were obtained at selected temperatures and the resistance value was calculated by fitting semicircles in the Z'' vs Z' plots. The conductivity at selected temperatures was calculated using the following equation,

$$\sigma = L/RS$$

Where L and S are the thickness (cm) and cross-sectional area (cm²) of the pellet respectively, and R, which was extracted directly from the impedance plots, is the bulk resistance of the sample and σ is the conductivity (S·cm⁻¹).

The activation energy for proton conductivity was calculated using the equation below

$$\sigma T = A \exp(E_a/k_B T)$$

Where σ is the proton conductivity, A is the pre-exponential factor, k_B is the Boltzmann constant and E_a represents the proton transfer activation energy.

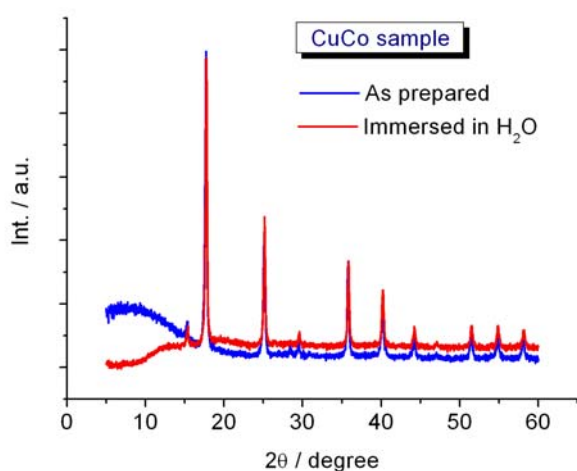


Figure S1 Powder x-ray diffraction patterns of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ (blue line: as-prepared sample; red line: the as-prepared sample immersed in water for two months).

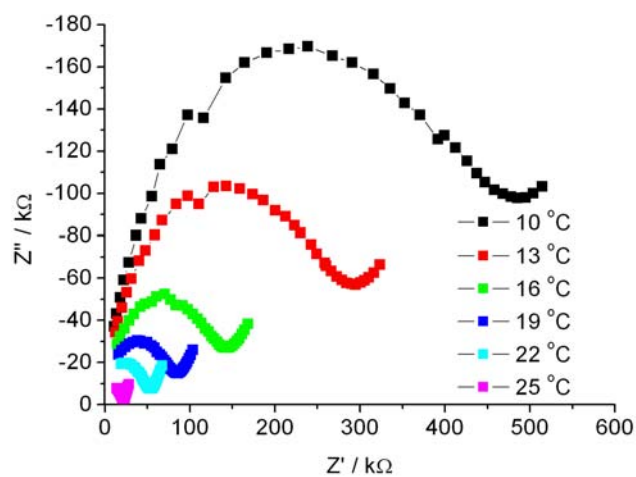


Figure S2 Z'' vs Z' plots of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powdered sample at selected temperatures under 100% RH.

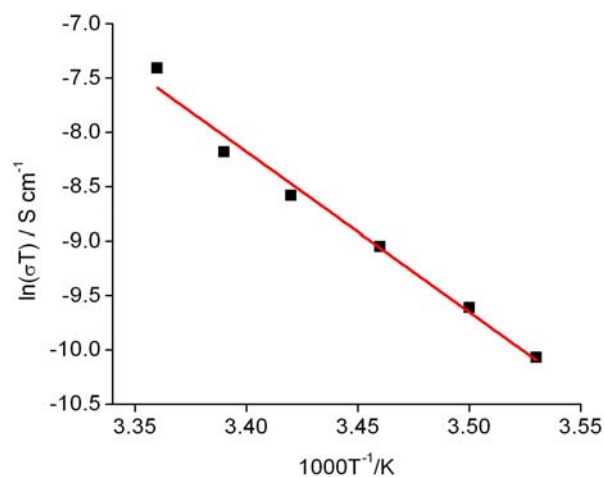


Figure S3 Arrhenius-type plot of the proton conductivity of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powdered sample under 100% RH.

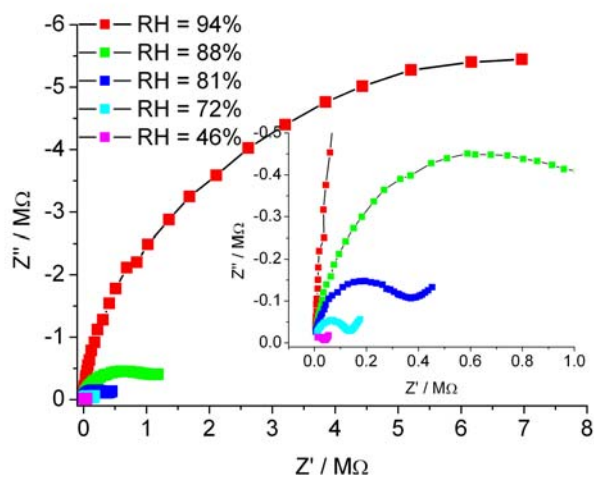


Figure S4 Z'' vs Z' plots of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powdered sample at 303 K and under the selected relative humidity.

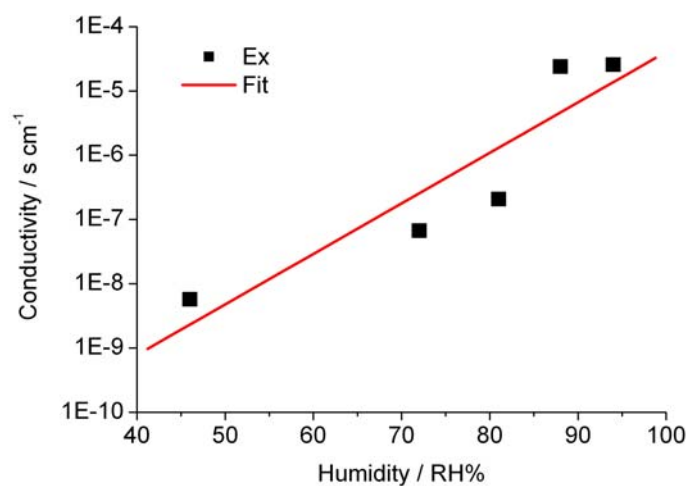


Figure S5 Plots of the proton conductivity of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powdered sample at 303 K and under the selected relative humidity (RH = 46, 72, 81, 88 and 94%).

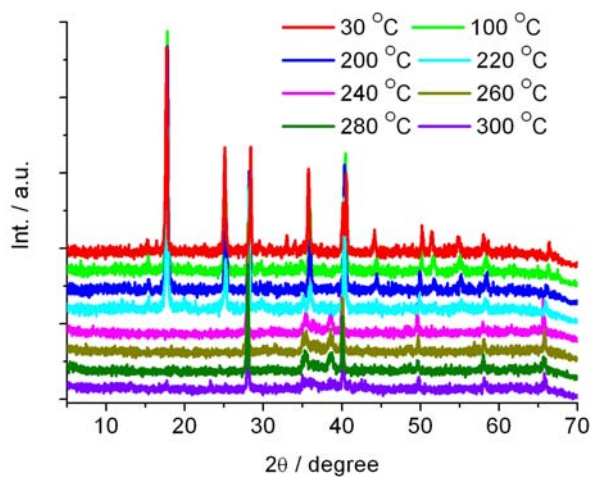


Figure S6 Temperature dependent PXRD patterns of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powdered sample, which show the framework is stable below 300 °C.

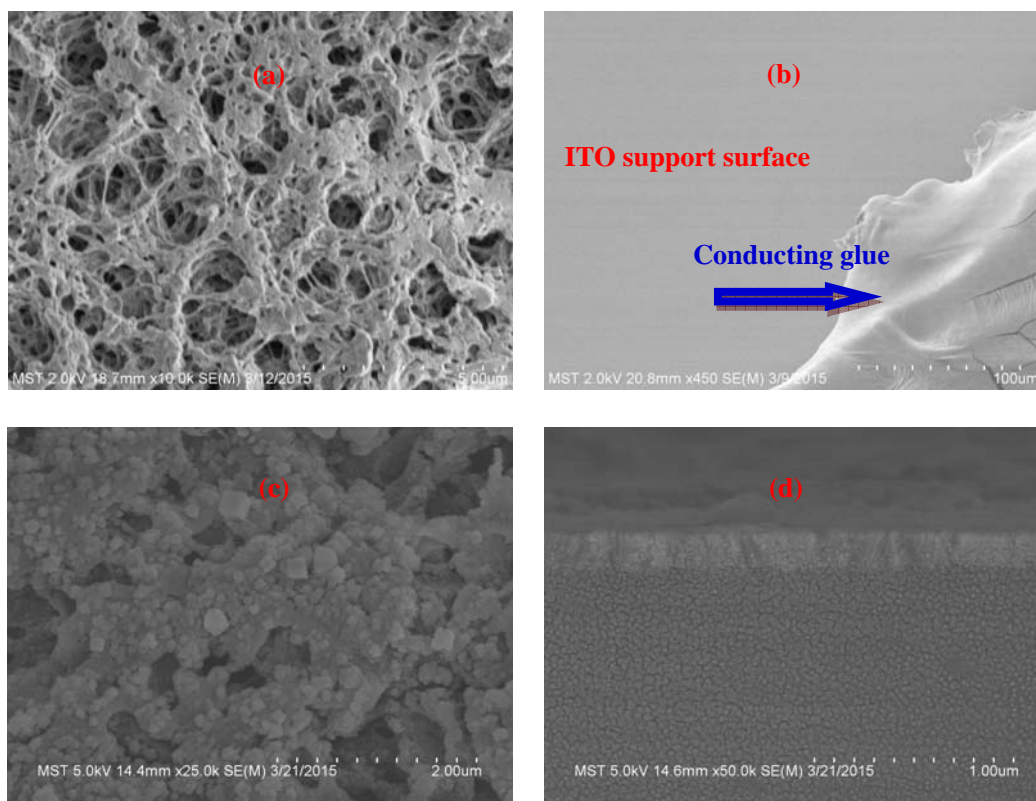


Figure S7 SEM images of (a) flexible non-woven fabrics (PVDF) and (b) ITO where it is conducting glue for attached gold wire as electrode at the right bottom of the picture. (c, d) the cross sections of flexible non-woven fabrics and ITO films, respectively. It is mentioned that no clear cross section was observed for flexible non-woven fabrics film owing to the support is too thin.

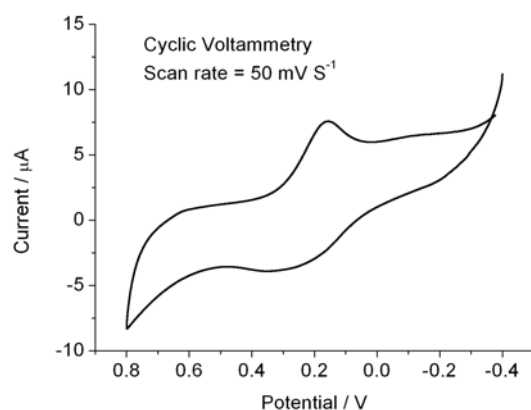


Figure S8 Cyclic voltammetric measurement was made on a EG&G potentiostat/galvanostat model 273 analyzer in a one-compartment cell under air atmosphere at 25 °C. The Phosphate Buffer solution (0.06 mol L⁻¹ of KH₂PO₄, 0.04 mol L⁻¹ of K₂HPO₄ and 0.1 mol L⁻¹ of KCl) was used as supporting electrolyte. A Pt disk was used as a working electrode, and a Pt plate was used as a counter electrode. Ag/AgCl wire was used as the reference electrode. The Cu₃[Co(CN)₆]₂·nH₂O was modified on the Pt disk electrode. The potential scan was performed in the region from -0,4 to +0.8 V with a rate of 50 mV s⁻¹.

Project 1

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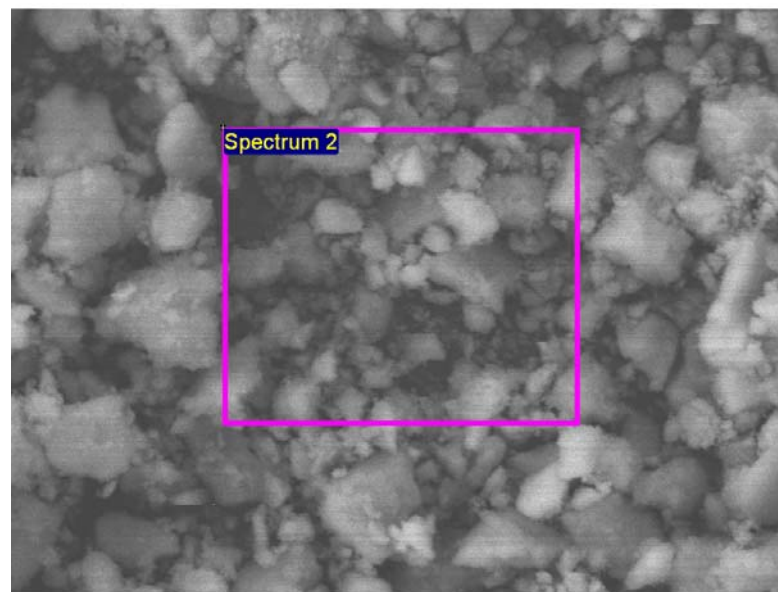
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Processing option : All elements analyzed (Normalised)
Number of iterations = 5

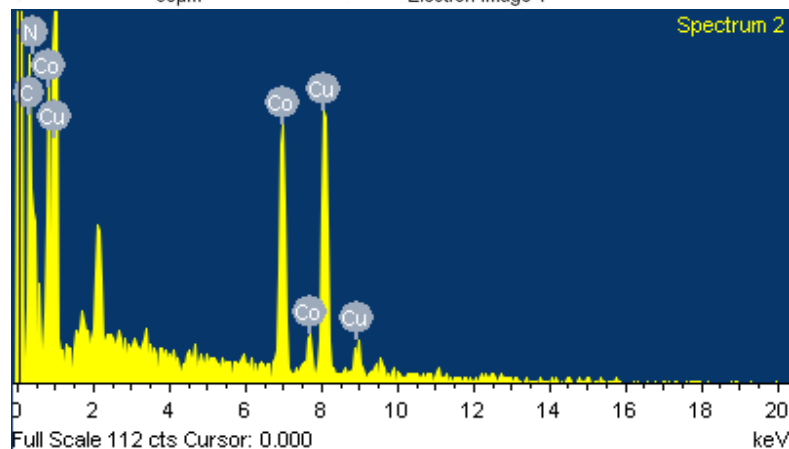
Standard :

C CaCO₃ 1-Jun-1999 12:00 AM
N Not defined 1-Jun-1999 12:00 AM
Co Co 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	29.26	45.88
N K	31.34	42.13
Co K	13.55	4.33
Cu K	25.85	7.66
Totals	100.00	



50µm Electron Image 1



Comment:

EMAX

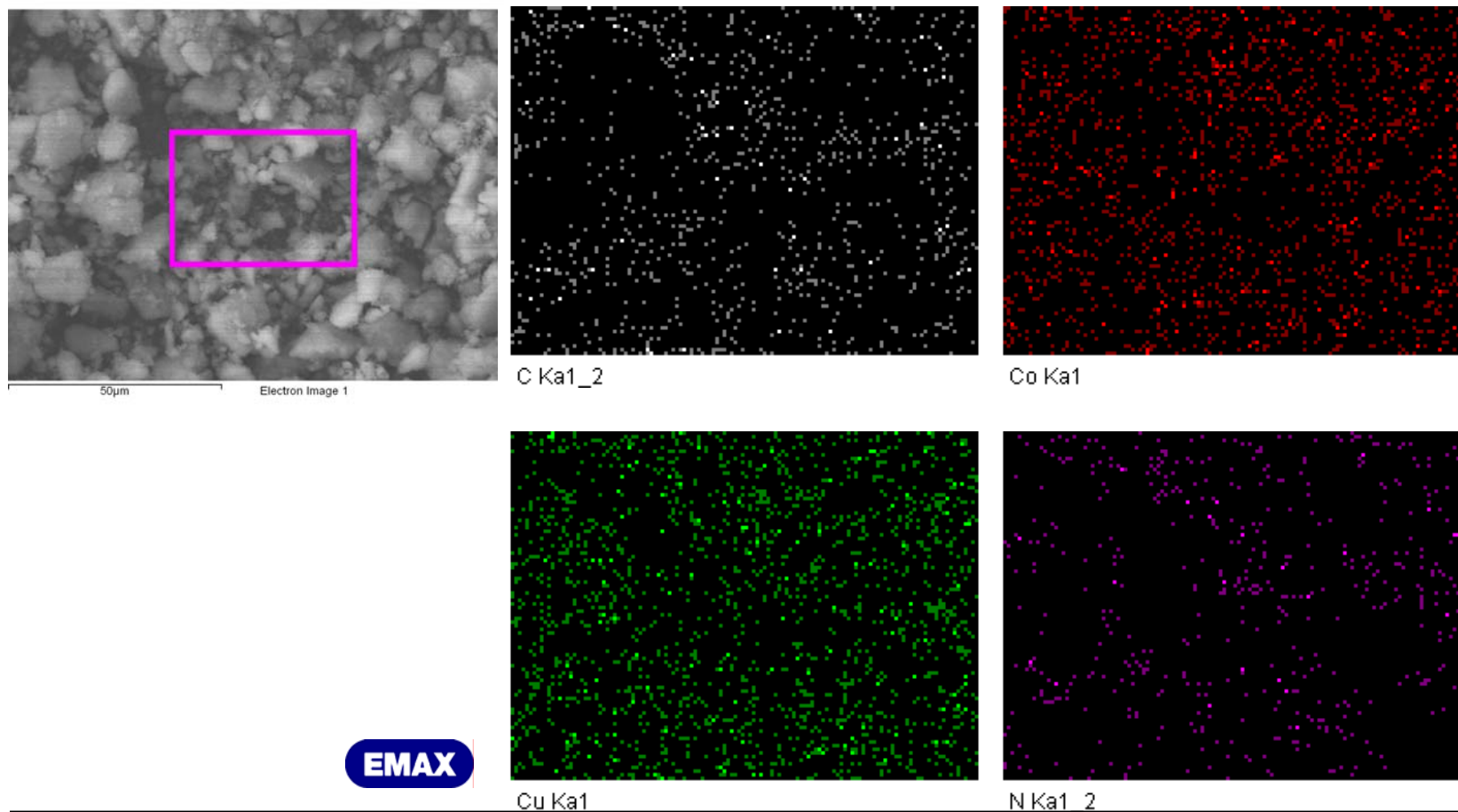


Figure S9 Elemental mapping images measured by EDX, which disclosed that $\text{Cu/Co} = 1.769 \approx 1.5$, $\text{C/N} = 1.089 \approx 1/1$ in the crystal of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powdered sample