Supporting Information

Fe-Co Controlled Super Hygroscopic Hydrogel Toward Efficient Atmospheric Water Harvesting

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Materials and characterization

Materials. Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, AR, 98%), Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, AR, ≥ 99%), Nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, AR, 99%), Copper(II) chloride dehydrate ($CuCl_2 \cdot 2H_2O$, AR, ≥ 99%), Zinc chloride ($ZnCl_2$, AR, 98%), Ethanolamine ($NH_2CH_2CH_2OH$, AR, 99%), and Ethanol (CH_3CH_2OH, AR, ≥99.7%) were purchased from Aladdin. All chemicals were used without any further purification, and the deionized water was used for the preparation of solutions and washing.

Characterization. The surface microstructures of the hydrogels were characterized by field-emission scanning electron microscopy (FE-SEM, Nova 400 Nano-SEM), the size and crystal structure was detected by a transmission electron microscopy (TEM, Talos F200S, 200 KV). The in-situ photo absorption spectra were detected by a UV-Vis spectrophotometer (UV-3600, Shimadzu). The surface composition and chemical states analysis was measured with an X-ray photoelectron spectroscopy (XPS, ESCALab250). Thermogravimetric analysis (TGA) was carried out on a thermal instrument (TGA2) in the atmosphere of air.

Video S1. The video record of moisture harvesting by Co hydrogel at 80% RH. The exposed area of the hydrogel is 25 cm^2, and the weight of the dehydrated hydrogel is about 0.1 g. The video shows an apparent color transition from blue to pink, and liquid water accumulated on the surface of hydrogel can be observed.

The calculation of the energy required to generate 3.5 L of water (the minimum amount an adult need per day). We put 3.0 g of dehydrated Fe-Co hydrogel on a dish

(150 cm^2) for the moisture capture at night (~75% RH), the mass of absorbed moisture is measured to be 4.51 g. Later, we put the hydrous hydrogel into the atmospheric water generator, all the adsorbed water can be released under simulated sunlight with 100 mW cm^{-2} for 40 min. The total volume of collected water is about 3.6 mL. The required energy for one sorption/desorption cycle is:

$$E = \frac{100\ mW\ cm^{-2} \times 150\ cm^2 \times 40\ min}{3.0\ g}$$

Thus, more than 3.5 L water can be collected by consuming energy of 1.2×10^4 kJ g^{-1}at the same conditions, which meets the water intake for an adult per day. Following the above sorption/desorption cycles (8 h sorption and 40 min desorption), it is estimated that 3.0 kg dehydrated hydrogel can produce enough drinking water to meet daily needs for adults, and the freshwater yield of over 3.6 L per day per kilogram of the hydrogel used. Significantly, we can also choose the sorption and desorption time of the hydrogel to optimize maximum freshwater yield per day.

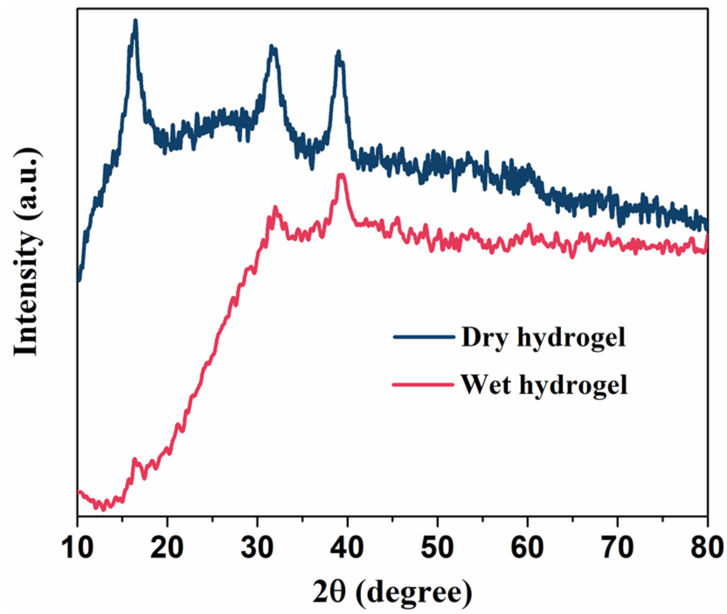

Figure S1. X-ray diffraction plots of the Fe-Co hydrogel in dry and wet state, demonstrating the both states are low crystallinity. The peak situated at 16.33° was disappeared for the hydrogel at wet sate, demonstrating the moisture sorption break the hydrogel's structure.

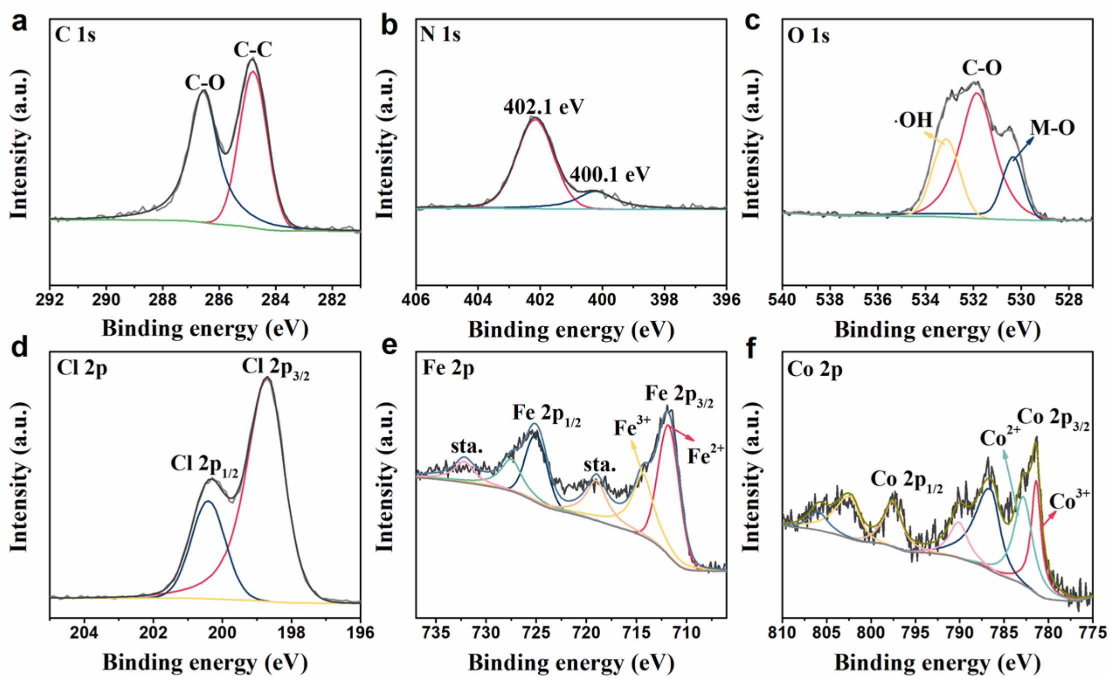

Figure S2. XPS of the Fe-Co hydrogel. The high resolution spectra of (a) C 1s, (b) N 1s, (c) O 1s, (d) Cl 2p, (e) Fe 2p, (f) Co 2p. The C 1s peak at 284.8 eV is attributed to the absorbed carbon element from air. The peak at higher binding energy indicates the C-O species, which can be assigned to the species of ethanolamine.[1] The N 1s data implies two peaks at 420.1 eV and 400.1 eV, which can be coordinated with ligand due to its lone pair electron. The O 1s spectra shows the metal-oxygen bond at the 530.2 eV, the peak at 531.2 eV displays the C-O, and the peak at 533.2 eV demonstrates the absorbed water from air. The Cl 2p plots shows the Cl^- exists in the hydrogel. For the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks, the lower energy (711.3 eV and 724.9 eV) and higher energy (714.2 eV and 727.8 eV) was assigned to the Fe^{2+} and Fe^{3+}. The Co 2p spectra suggest the peaks at 781.4 eV and 782.7 eV are ascribed to the Co^{3+} and Co^{2+}.

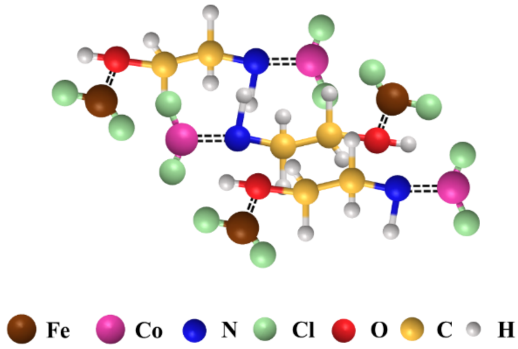

Figure S3. The molecular structure of our designed Fe-Co hydrogel. The Fe or Co ions can be effectively coordinated with the amino or hydroxyl of ethanolamine, that is, the coordination interaction between the metal empty electron orbit and the lone electron pairs of nitrogen or oxygen atom. This coordination interaction causes the information of active water sorption sites (Fe-Co sites), which endows the hydrogel with a high affinity for moisture.

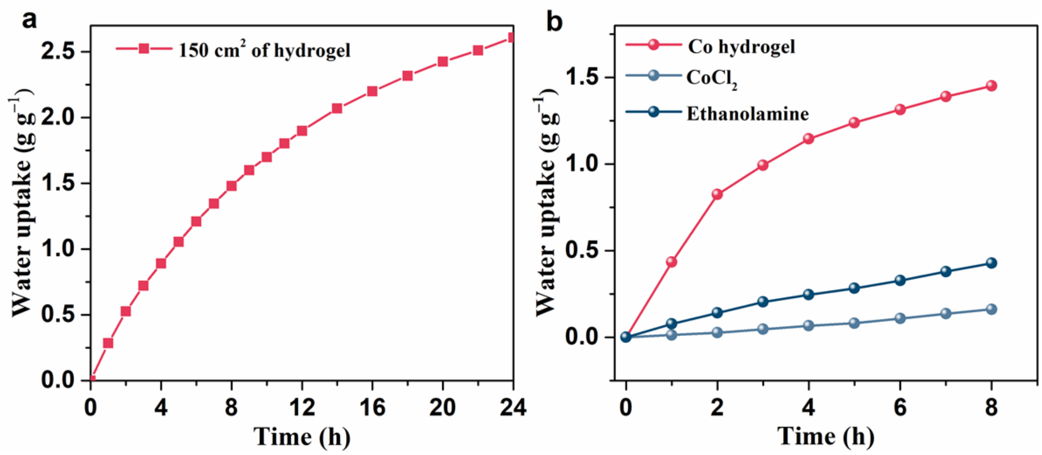

Figure S4. The moisture capture ability of Co hydrogel. (a) Weight changes for 150 cm^2 Co hydrogel at room temperature and 90% RH within 24 h. (b) Moisture harvesting rate of Co hydrogel, $CoCl_2$, and ethanolamine under room temperature and humidity. The sorption rate of Co hydrogel is superior to the pure $CoCl_2$ and ethanolamine, demonstrating the successful coordination of metal ions with ethanolamine ligand, leading to the formation of sorption sites that can bond enormous moisture.

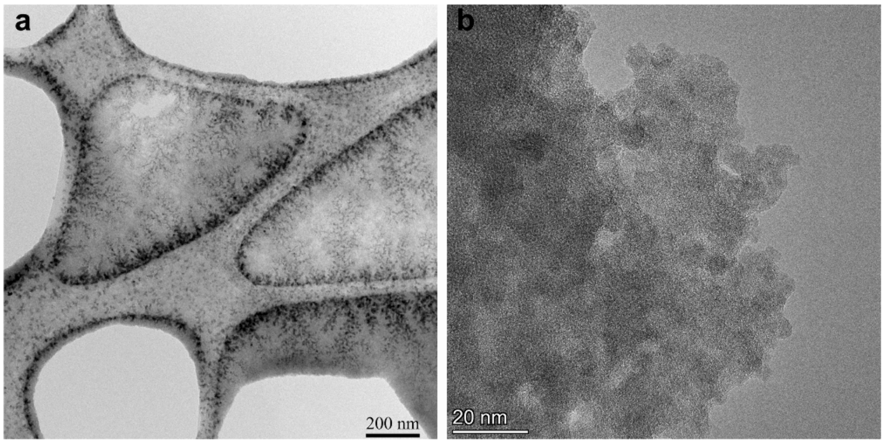

Figure S5. TEM images of Co hydrogel. (a) The TEM image of the hydrogel shows nanoparticles morphology in microstructure. (b) The high-resolution TEM image of the hydrogel displays the diameter of the nanoparticles is ~5 nm and a low crystallinity.

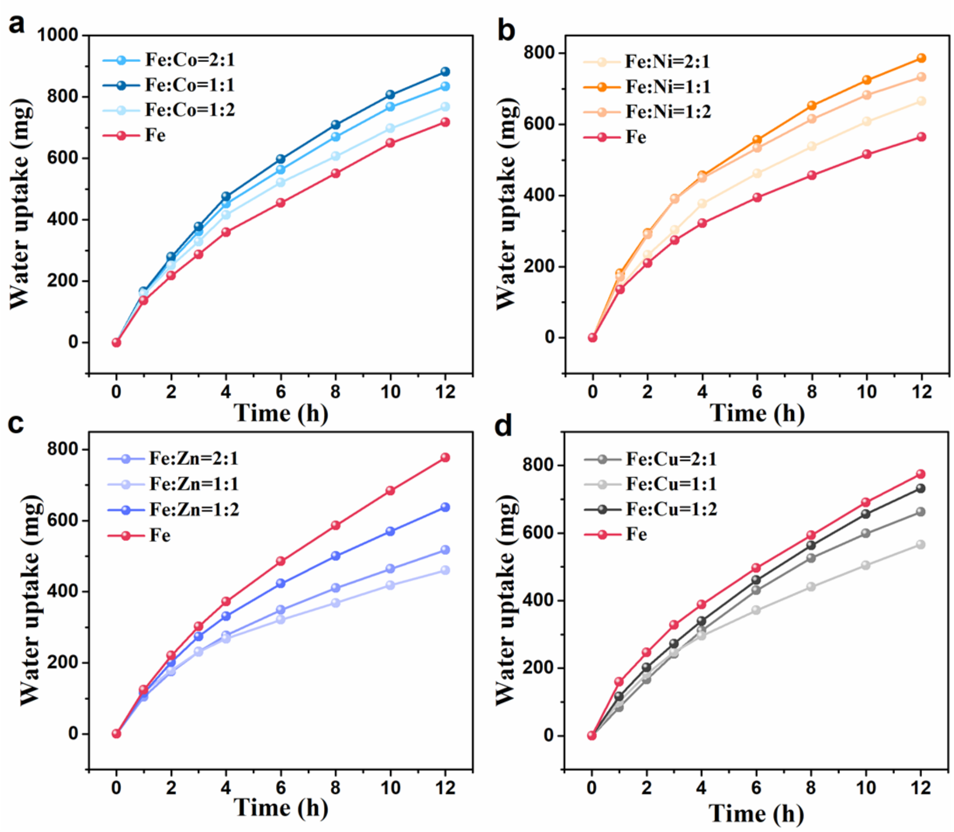

Figure S6. The water uptake ability of bimetal hydrogels with different proportions under room temperature and humidity. The Fe-Co and Fe-Ni hydrogel present an enhanced moisture capture ability comparing with Fe hydrogel due to the synergistic effect of Fe and Co (Ni) ions. While the Fe-Cu and Fe-Zn hydrogel present a poorer moisture capture ability comparing with Fe hydrogel.

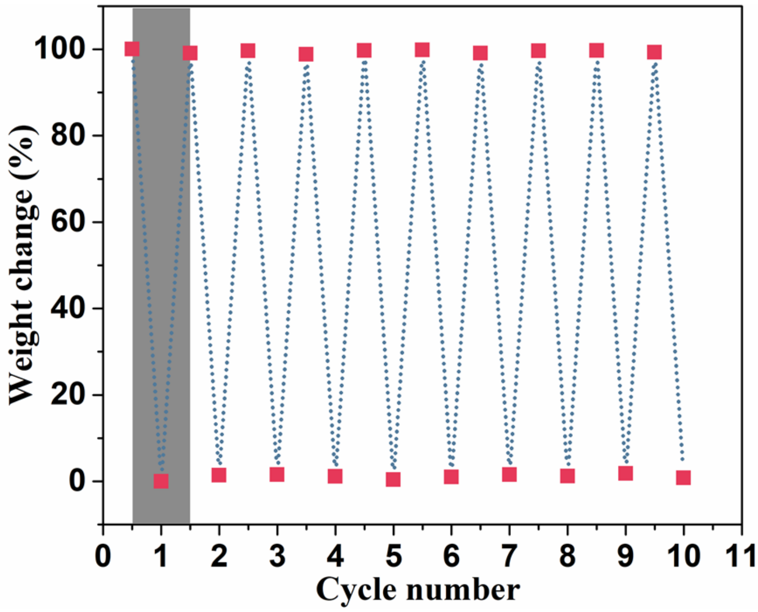

Figure S7. Weight changes during each sorption-desorption cycle of Fe-Co hydrogel.

Notes: weight change is calculated based on the mass of water in hydrogel after first adsorption.

$$weight\ change = \frac{mass\ of\ water\ in\ current\ cycle}{mass\ of\ absorbed\ in\ first\ cycle}$$

and

$$weight\ change = \frac{mass\ of\ residual\ water\ in\ current\ cycle}{mass\ of\ absorbed\ in\ first\ cycle}$$

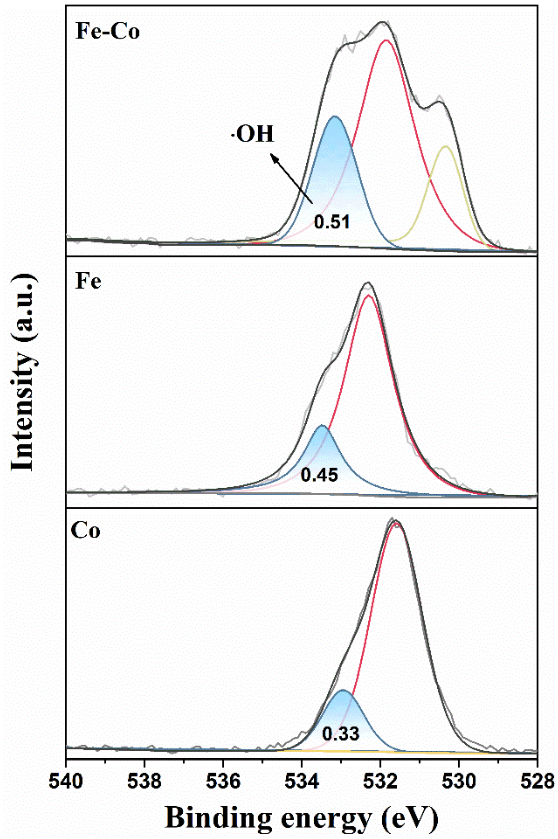

Figure S8. The O 1s spectra of Fe-Co, Fe, and Co hydrogel. The surface oxygen is related to the OH groups, water molecules on the surface of the hydrogel.[2] The Fe-Co hydrogel has a larger ratio of the surface oxygen, illustrating a higher ability to harvest moisture from air.

Evaluation of the heat of the hydrogel.

The heat of sorption of the hydrogel was obtained by first measuring the sorption isotherms at different temperatures (Figure S4a). Then, the corresponding equilibrium pressures P at different temperatures T were obtained and the lnP vs. $1/T$ diagram was plotted (Figure S4b). According to the Clausius-Clapeyron equation, we can get the heat of sorption ΔH_{sorp}, whose value is the slope of the curve of lnP vs. $1/T$ multiplied by gas constant R:

$$ln\frac{P_1}{P_2}=-\frac{\Delta H_{sorp}}{R}\cdot(\frac{1}{T_1}-\frac{1}{T_2})$$

The obtained values of ΔH_{sorp} varying with water uptake is shown in Figure S4c. Significantly, the hydrogel requires relatively higher heat of sorption at the initial sorption time (low water content), then decreases remarkably as the water content increase.

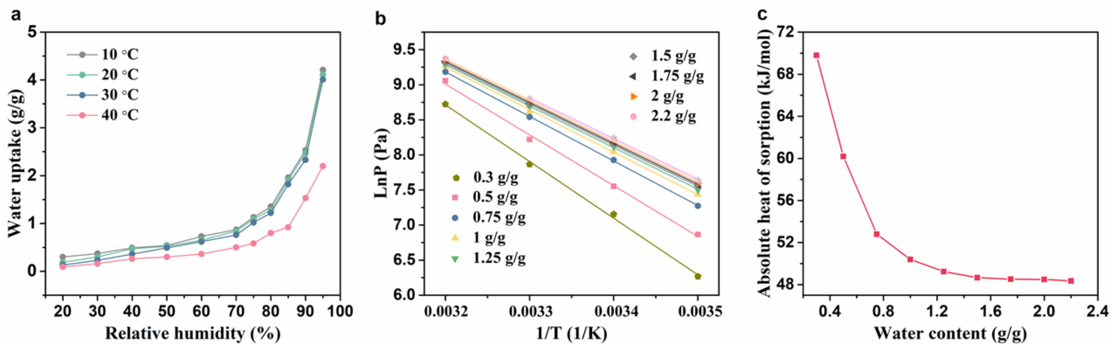

Figure S9. (a) Isotherm curves of Co hydrogel at 10 °C, 20 °C, 30 °C, and 40 °C. (b) ln(P) vs. 1/T curves. (c) Heat of sorption of the hydrogel at different water contents.

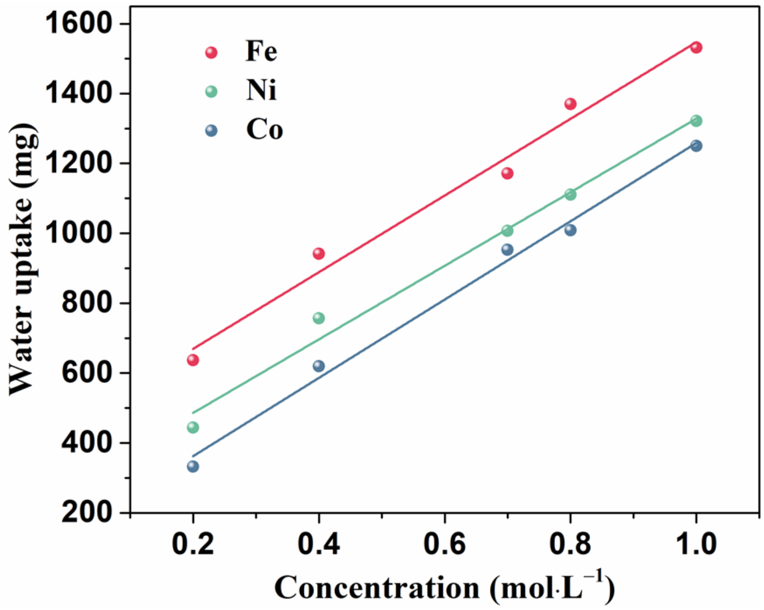

Figure S10. Moisture harvesting with different concentrations of metal in the Fe, Ni, and Co hydrogel. It can be observed that the moisture capture ability is positively related to the metal concentrations in the hydrogel, suggesting the metal ions distributed in the single-metal hydrogel act as the water holder to capture moisture from air.

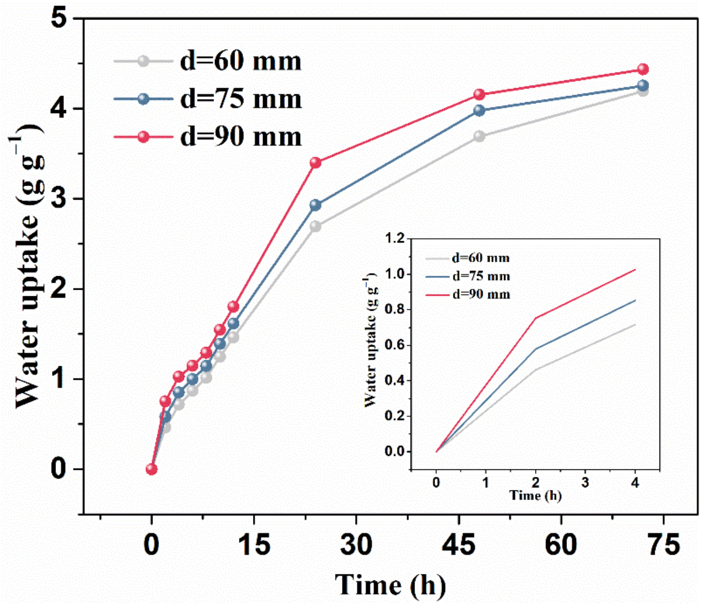

Figure S11. Water harvesting of Fe-Co hydrogel coated uniformly on dishes with different surface area at 90% RH (d is the diameter of exposed hydrogel). The inset picture illustrates the hydrogel capture moisture from air at a fast rate during early period. Then, the hydrogels gradually reach a same saturation water value.

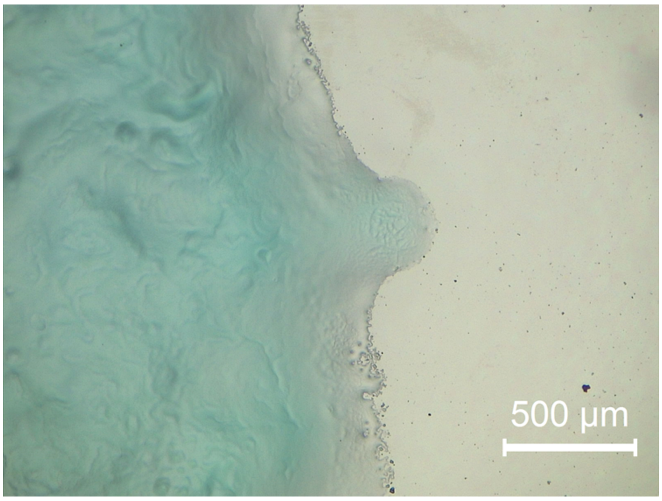

Figure S12. The optical microscope images of the hydrogel after moisture capture. There is an apparent phenomenon that the hydrogel's surface is unsmooth after moisture sorption, resulting in the appearance of some holes (pores) on the hydrogel surface.

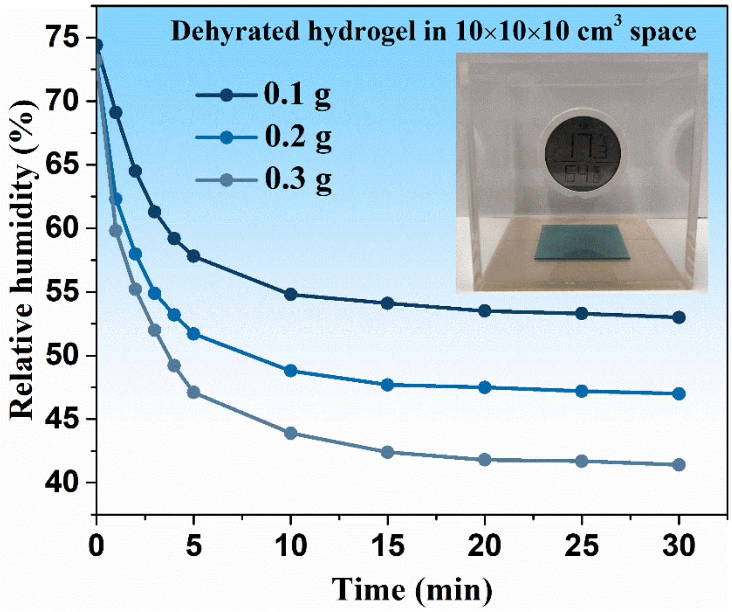

Figure S13. Relative humidity changes in a 10×10×10 cm^3 enclosed space by various weights of the Co hydrogel. The relative humidity (RH) inside the confined space significantly decreased because of the super-hygroscopic property of the hydrogel. 0.3 g of hydrated hydrogel can induce a 32.4 % RH drop in 20 min.

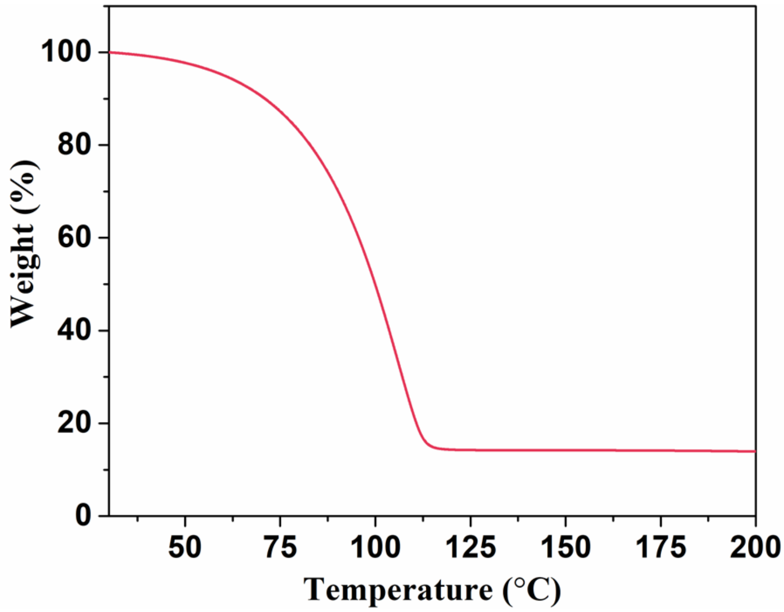

Figure S14. TGA curve of Fe-Co hydrogel, where the temperature is increased from room temperature to 200 °C at a rate of 2 °C min^{-1}.

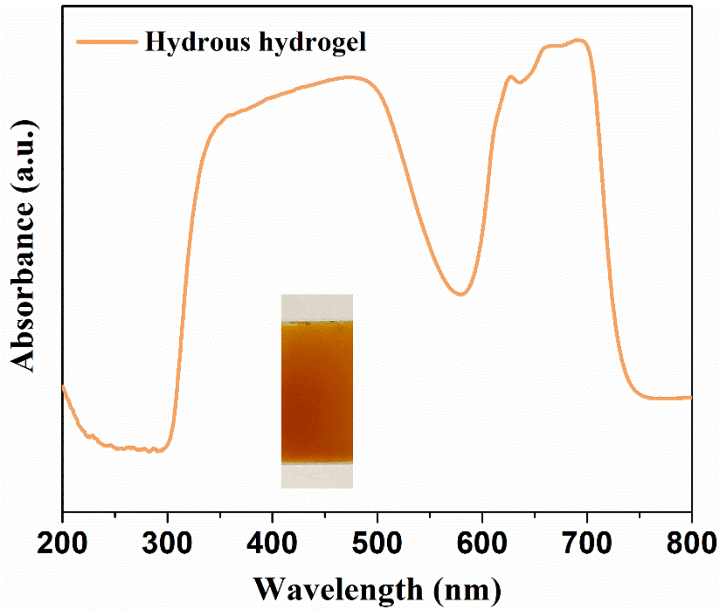

Figure S15. The light absorption of the Fe-Co hydrogel in hydrous sate. A thin layer hydrogel was coated on a glass sheet and exposed into ambient air for about 20 min moisture sorption, an extraordinary light absorption ability can be observed.

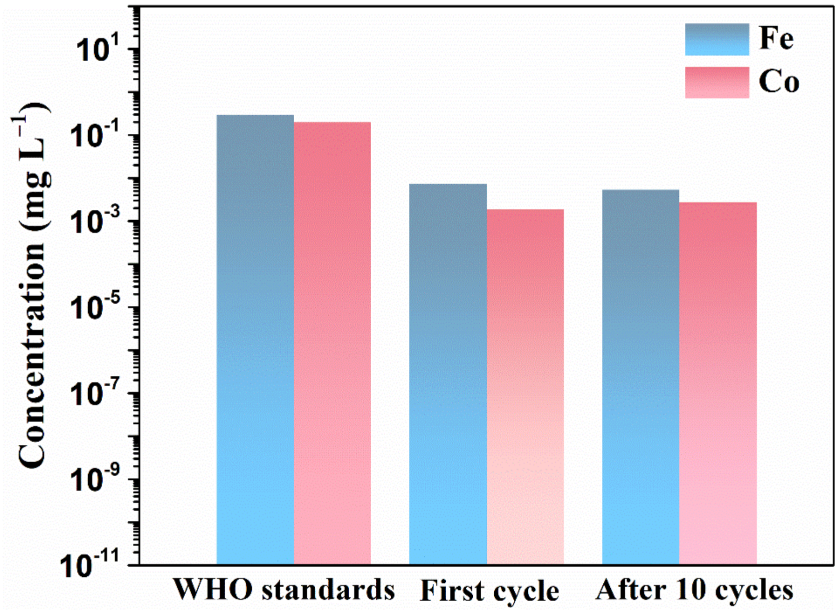

Figure S16. Comparative bar chart of the metal concentrations of collected water from the AWG device with WHO's drinking water standards after 10 sorption-desorption cycles. Even after 10 cycles, the concentrations of Fe and Co ions are 5.5 and 2.8 ppb, which are typically below the WHO standards (300 and 20 ppb), indicating the collected water has a potential application for drinking.

Table S1. The different metal-based hydrogels.

Metal salts	Ligand	Metal-based hydrogels
$FeCl_3{\cdot}6H_2O$	Ethanolamine	Fe hydrogel
$NiCl_2{\cdot}6H_2O$	Ethanolamine	Ni hydrogel
$CoCl_2{\cdot}6H_2O$	Ethanolamine	Co hydrogel
$ZnCl_2$	Ethanolamine	Zn hydrogel
$CuCl_2{\cdot}2H_2O$	Ethanolamine	Cu hydrogel
$FeCl_3{\cdot}6H_2O$ + $NiCl_2{\cdot}6H_2O$	Ethanolamine	Fe-Ni hydrogel
$FeCl_3{\cdot}6H_2O$ + $CoCl_2{\cdot}6H_2O$	Ethanolamine	Fe-Co hydrogel
$FeCl_3{\cdot}6H_2O$ + $ZnCl_2$	Ethanolamine	Fe-Zn hydrogel
$FeCl_3{\cdot}6H_2O$ + $CuCl_2{\cdot}2H_2O$	Ethanolamine	Fe-Cu hydrogel

Table S2. The moisture sorption capacity of Fe, Co, and Fe-Co hydrogel under various RH and 25 °C.

RH (%)	Fe ($g\ g^{-1}$)	Co ($g\ g^{-1}$)	Fe-Co ($g\ g^{-1}$)
40	0.70	0.49	0.90
50	0.80	0.54	1.02
60	1.0	0.73	1.29
70	1.13	0.87	1.48
75	1.40	1.13	1.76
80	1.65	1.35	2.01
85	2.42	1.96	2.91
90	3.17	2.53	3.62
95	4.68	4.21	5.22

Table S3. Comparison between elemental analysis results of water collected from atmospheric water generator and the WHO's guidelines for drinking quality.

Ions/elements	Determined values (mg/L)	WHO standards (mg/L)
Fluoride, F^-	0.3668	1.5
Chloride, Cl^-	49.1616	250
Nitrate, NO_3^-	0.5650	50
Sulfate, SO_4^{2-}	0.1222	250
Iron, Fe	0.007578	0.3
Cobalt, Co	0.001890	0.02

References

1 R. Li, Y. Shi, M. Wu, S. Hong and P. Wang, *Nano Energy*, 2020, **67,** 104255.

2 Y. Luo, R. Chen, W. Peng, G. Tang and X. Gao, *Appl. Surf. Sci.*, 2017, **416,** 911-917.