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Supporting Information

Dynamic coordination of metal-alanine to control the multistimuli-responsiveness of self-powered polymer hydrogel sensors

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1. Materials

L-Alanine (Ala), N, N'-Methylene bisacrylamide (BIS) and L-Phenylglycinol (Phg) were supplied by Macklin Reagent. $Cu(NO_3)_2{\cdot}2.5H_2O$, $Zn(ClO_4)_2{\cdot}6H_2O$ and ammonium persulphate (APS) were purchased from Alfa Aesar. N,N-dimethylacrylamide (DMA), glycidyl methacrylate (GMA), 2,2'-azobis(isobutyronitrile) (AIBN) and all other metal salts ($NiCl_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Pb(NO_3)_2$ and $Cd(CH_3COO)_2$) were supplied by TCI Reagent. DMA and GMA were passed through a basic aluminum oxide column prior to use. AIBN was recrystallized twice from ethanol. All solvents were purchased from commercial sources and used as received. Deionized water (High-Q, Inc. 103S Stills) with a resistivity of > 10.0 MΩ was used throughout the preparation of hydrogels.

2. Polymer synthesis

2.1 Synthesis of the copolymer of P(DMA-co-GMA)

The copolymer of DMA and GMA was prepared by free radical polymerization. DMA (10 g, 0.1 mol), GMA (3.55 g, 0.025 mol) and AIBN (10 mg, 60 μmol) were dissolved in 17.5 mL of anisole in a 50-mL flask. The reaction mixture was degassed under vacuum and filled with nitrogen for 15 min. The flask was then sealed and placed in a pre-heated oil bath at 65 °C for 3 h. After reaction, the mixture was cooled down to room temperature. The polymer was collected after precipitation in hexane for three times and dried under vacuum for 24 h. The ^1H NMR (in $CDCl_3$) result of the P(DMA-*co*-GMA) is given in Fig. S1a. The obtained polymer has a number-average molecular weight (M_n) of 289.3 kg/mol and a dispersity ($Đ$) of 3.64 (Fig. S1b), measured by size exclusion chromatography (SEC) using polystyrene (PS) standards.

2.2 Synthesis of the Ala-modified copolymer by post-polymerization functionalization

The copolymer P(DMA-*co*-GMA) with 25 mol% of GMA units was functionalized by Ala through the ring opening reaction of epoxide moieties. Ala reacted with excess NaOH in methanol to avoid carboxylic acid reacting with epoxy. Typically, P(DMA-*co*-GMA) (5 g, 4.6 mmol in terms of GMA units) were first dissolved in 79.5 mL of methanol. Then, sodium salt of Ala methanol solution (20 wt%, 20.5 mL, 46 mmol) was added dropwise into the P(DMA-*co*-GMA) methanol solution and refluxed at 65 °C overnight to yield P(DMA-*co*-AlaHPMA). After reaction, the polymer solution was first precipitated in cold diethyl ether for three times and dried under vacuum for 24 h. The as-prepared P(DMA-*co*-AlaHPMA) was dialyzed in water to remove residual Ala sodium salt. The dialyzed polymer aqueous solution was then freeze-dried to collect the P(DMA-*co*-AlaHPMA). The ^{1}H NMR (in D_2O) result of the P(DMA-*co*-AlaHPMA) is given in Fig. S1a.

3. Preparation of hydrogels

3.1 Metal-containing P(DMA-co-AlaHPMA) supramolecular hydrogels

Typically, to prepare Cu-containing P(DMA-*co*-AlaHPMA) hydrogel with a Cu-to-Ala mole ratio of 0.5:1, 0.2 g P(DMA-*co*-AlaHPMA) was first dissolved in 1 mL water. Then, 156 μL of 20 wt% $Cu(NO_3)_2$ aqueous solution was added to the polymer solution in a vial and shook by a vortexer for 1 min. The sealed mixture was heated in boiling water and then cooled down to yield uniform hydrogels. Using the same procedure, P(DMA-*co*-AlaHPMA) hydrogels with different M:Ala ratios were prepared. Similarly, the Zn-containing P(DMA-*co*-AlaHPMA) hydrogel was prepared. For comparison, the P(DMA-*co*-AlaHPMA) hydrogel with a Ni:Ala, Co:Ala, Cd:Ala and Pb:Ala of 0.5:1 was used for rheological measurements.

3.2 Cu- and Zn-containing P(DMA-co-AlaHPMA)/PDMA IPN hydrogels

Typically, to prepare the Cu-containing P(DMA-*co*-AlaHPMA)/PDMA IPN hydrogels (Cu:Ala=1:1), 0.2 g P(DMA-*co*-AlaHPMA) was first dissolved in 1 mL water. Then, 200 μL of DMA, 2 mg of BIS and 2 mg of APS was dissolved in the P(DMA-*co*-AlaHPMA) aqueous solution. After sonication for 1 min to obtain a homogeneous mixture, 140 μL of $Cu(NO_3)_2{\cdot}2.5H_2O$ aqueous solution (40 wt%) was added to the mixture. The final mixture was degassed by purging with nitrogen gas and then reacted at 65 °C in water bath for 1 h to yield the IPN hydrogel. Using the same procedure, the Zn-containing P(DMA-*co*-AlaHPMA)/PDMA IPN hydrogel was fabricated.

4. Characterization

4.1 Size exclusion chromatography and ^{1}H NMR measurements

The SEC instrument package was supplied by Shimadzu and comprised the following setup: a Shimadzu LC-20AD pump, two series of connected columns (Shodex, K-803 and K-804) in a Shimadzu CTO-20 oven at 35 °C and a Shimadzu RID-10A refractive index detector. THF was used as the mobile phase at a flow rate of 1 $mL\cdot min^{-1}$ at 40 °C and the molecular weight was calibrated against polystyrene standards. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Ascend 400 MHz spectrometer using $CDCl_3$ and D_2O as the solvent for P(DMA-*co*-GMA) and P(DMA-*co*-AlaHPMA), respectively.

4.2 Scanning electron microscopy measurements

The Cu-element distribution in the Cu-containing hydrogel was investigated by a scanning electron microscopy (SEM) instrument (Nova NanoSEM450, FEI, USA) operation at 20 kV coupled with an energy-dispersive X-ray (EDX) spectrometer (Apollo XL, EDAX, USA).

4.3 Fourier transform infrared measurements

The Fourier transform infrared (FT-IR) spectra were measured by a Nicolet 6700 (Thermo Fisher, USA) FT-IR spectrometer. Samples were freeze-dried and cryo-milled into fine powders in liquid nitrogen using an agate mortar before compressing into KBr disc under a hydraulic press at 10,000 psi. The KBr discs were then thoroughly dried for FT-IR measurements.

4.4 Rheology measurements

Rheological measurements were conducted by a Haake Mars III rheometer. Frequency sweep (strain =1 %) spectra of the P(DMA-*co*-AlaHPMA) hydrogels with different metal-to-Ala ratios were performed on a 20 mm parallel plate and the frequency ranges from 0.01 to 10 Hz. All measurements were conducted at 25 °C. A solvent trap was used to minimize the evaporation of solvent. Continuous step strain measurements of the Cu-and Zn-containing hydrogels with an M:Ala ratio of 0.5:1 were also examined. The hydrogels were first subjected to a 500 % oscillation strain for 60 s, then to 2 % strain with a scanning frequency of 1 Hz. The temperature-sweep measurement on the Cu-containing hydrogel was carried out at the temperature range between 25 and 100 °C at a frequency of 1 Hz and a strain of 1 %.

4.5 Measurements on the electrical performance

4.5.1 Assembly of galvanic cells

To assemble galvanic cells made of supramolecular hydrogels for electrochemical measurements, the Cu- and Zn-containing hydrogels were trapped in PDMS sleeves with a Nafion film sandwiched between them. Using metal electrodes of Cu as the cathode and Zn as the anode, a Cu-Zn galvanic cell was fabricated (see Fig. 4a). Each hydrogel had a diameter of 22 mm and a height of 3.3 mm.

To assemble the Cu-Zn galvanic cells with IPN structures, the Cu- and Zn-containing P(DMA-*co*-AlaHPMA)/PDMA IPN hydrogels were directly adhered to each other without a Nafion film separated between them. The metal electrodes were also directly adhered to the hydrogels. To fabricate the IPN-structured Cu-Zn galvanic cells, the Cu-containing IPN hydrogel was first prepared in a PDMS mold. Then, the Zn-containing IPN hydrogel was cured directly on the Cu-containing IPN hydrogel in the same PDMS mold. For V-I and discharging measurements, the IPN-structured hydrogels had a diameter of 22 mm and a height of 3.3 mm. As to series-connection of galvanic cells for lighting of an LED, the Cu-/Zn-containing IPN hydrogel had a diameter of 12 mm and height of 16 mm.

To measure the moisture sensitivity of the electrical performance of the IPN-structured Cu-Zn galvanic cell, a bilayer-structured polymer hydrogel sheet was prepared using the same procedure mentioned above. After freeze-drying of the hydrogel sheet, the bilayer-structured polymer sheet (30×10.1×3.2 mm) in the absence of water was prepared. As the bilayer-structured polymer sheet was swelled under a given humidity for a certain time, the polymer sheet was immediately sandwiched between Cu (cathode) and Zn (anode) sheets to form a Cu-Zn galvanic cell for measurements on electrical performance.

4.5.2 V-I and discharging measurements

An IT8511A+ electronic load (Itech Electronic, Co. Ltd) was used to conduct the V-I and discharging measurements. The V-I measurements were taken from open circuit with a 0.1 mA steps. The electrodes had a surface area of 1.13 cm^2. A constant-current mode was chosen to measure the influence of pH (constant current density of 1 mA/cm^2) and chelating agent (constant current density of 1.5 mA/cm^2) on the voltage, while a constant-voltage mode (constant voltage of 0.77 V) was employed to investigate the influence of temperature on the current density. The influence of moisture on OCV was carried out from open circuit. The discharging behaviors of all cells were conducted at a discharging current of 1 mA and a stop voltage of 0 V. All measurements were carried out at 25 ^oC unless otherwise noted.

4.6 Mechanical tests

An MTS Criterion Model 43 material testing machine with a loading cell of 100 N was used to conduct the uniaxial tensile tests on the IPN hydrogels. The Cu-containing and Zn-containing hydrogel specimens had cylindrical shapes with a diameter 12 mm and height of 16 mm. By direct adhesion between the two types of hydrogels, a Cu-Zn galvanic cell with an IPN structure was assembled. Tensile tests were performed with a tensile speed of 50 $mm \cdot min^{-1}$.

4.7 UV-Vis and water content measurements

A Persee (China) TU-1950 UV-Vis spectrophotometer was used for the UV-Vis measurements of the Cu-containing supramolecular hydrogels upon titration with HCl. The water content in the polymer sheets discussed in Fig. 10 was calculated by measure the weight loss after freeze-drying process.

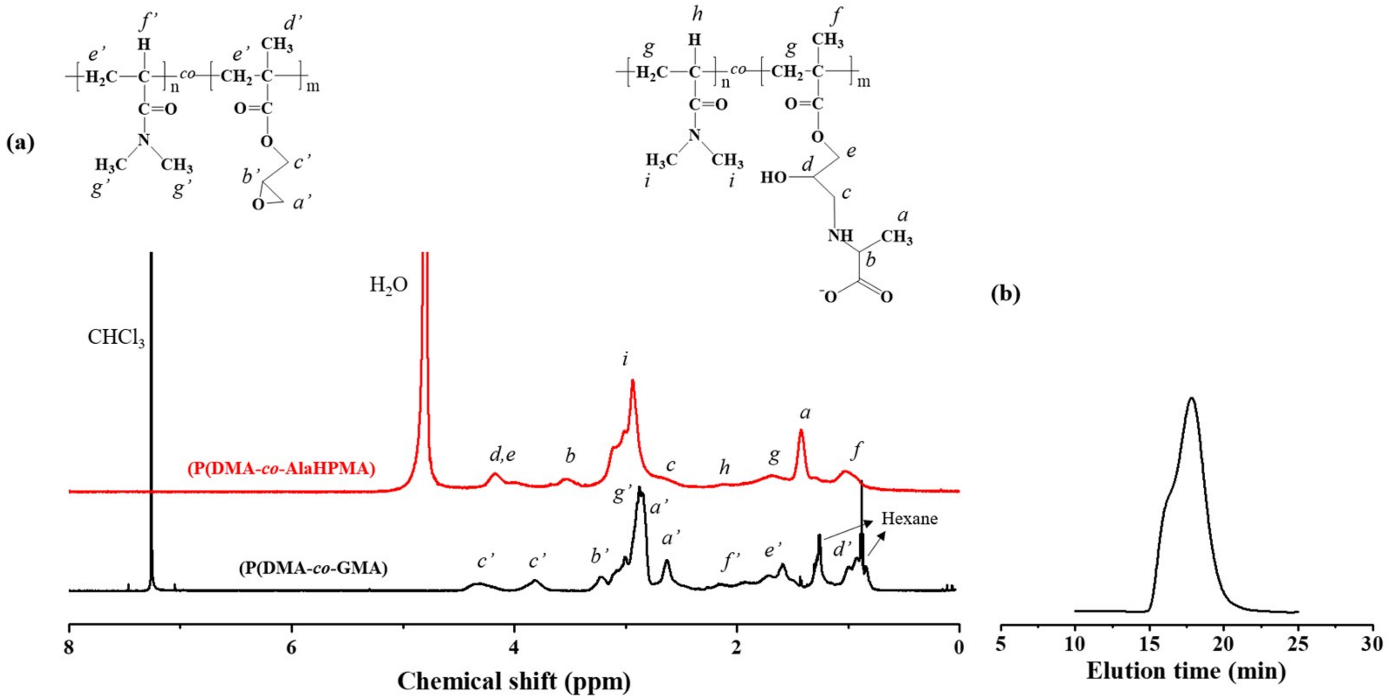

Fig. S1. (a)^{1}H NMR spectra of P(DMA-*co*-GMA) (black, bottom) and P(DMA-*co*-AlaHPMA) (red, top). The spectrum of P(DMA-*co*-AlaHPMA) was recorded in D_2O, while the spectrum of P(DMA-*co*-GMA) was recorded in $CDCl_3$. (b) The SEC elution curve of P(DMA-*co*-GMA).

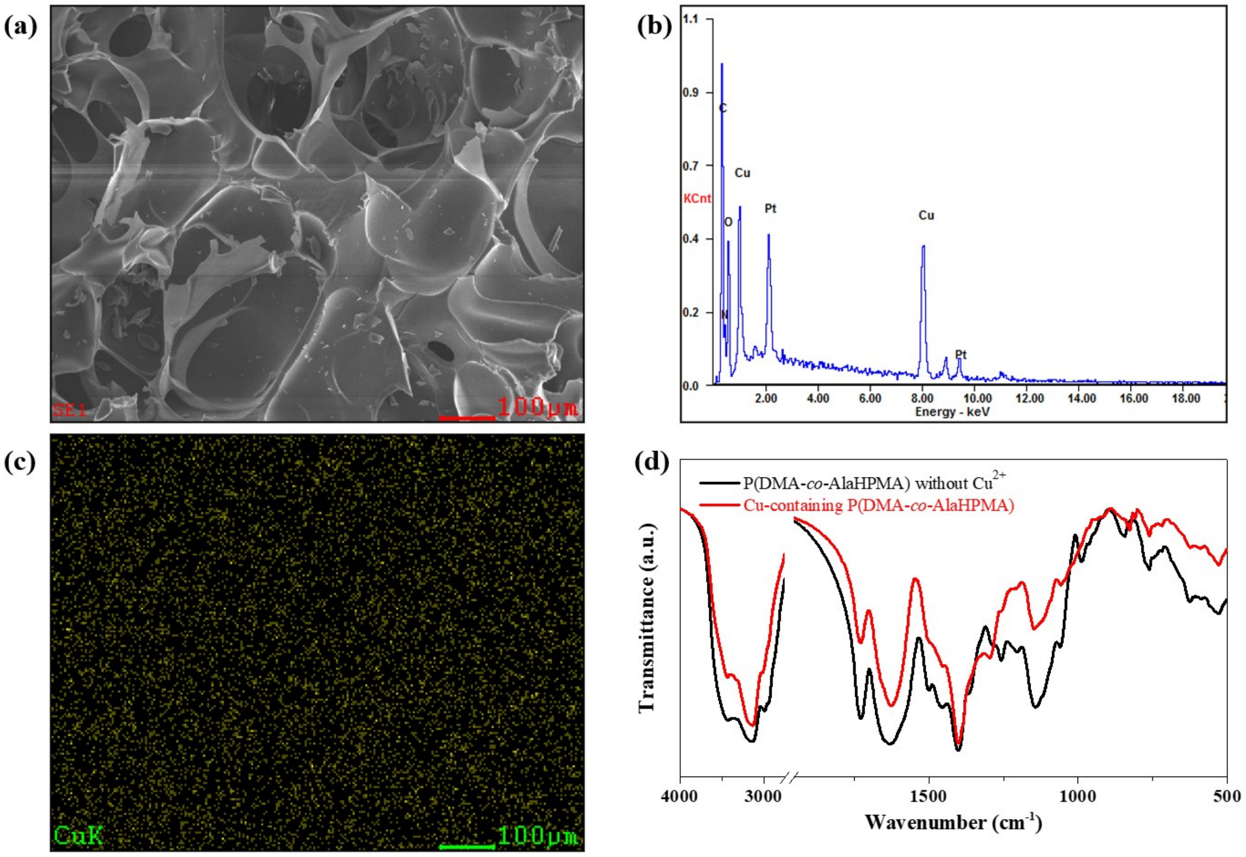

Fig. S2. (a) SEM image of the freeze-dried Cu-containing P(DMA-co-AlaHPMA) hydrogel (Cu:Ala ratio of 1:1). (b) corresponding EDX spectrum of the freeze-dried Cu-containing P(DMA-co-AlaHPMA) hydrogel. The Pt peaks originate from the cross-section coating during SEM sample preparation. (c) Cu-element mapping pattern of the freeze-dried Cu-containing P(DMA-co-AlaHPMA) hydrogel. (d) FT-IR spectra of the P(DMA-co-AlaHPMA) in the absence of Cu^{2+} ion (black curve) and in the presence of Cu^{2+} ion (red curve). Both samples were measured as dry powder.

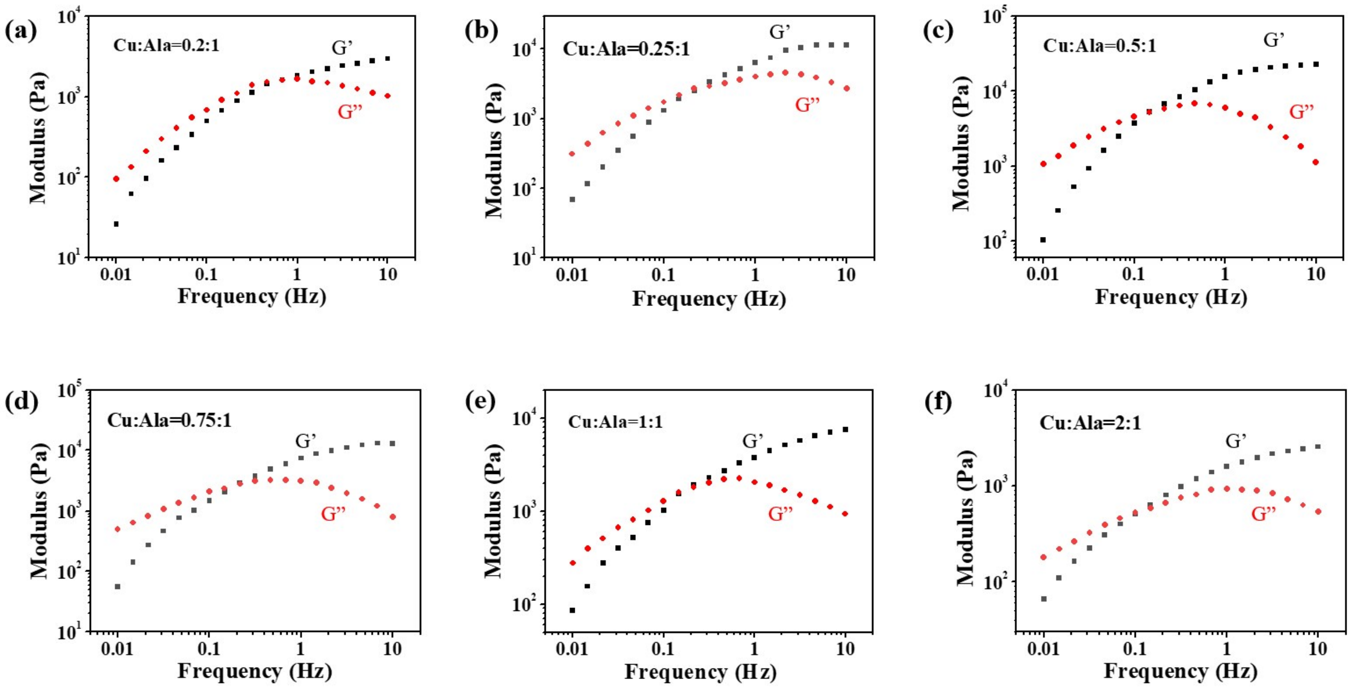

Fig. S3. Influence of Cu-to-Ala ratio on the G', G" and tan δ of Cu-containing hydrogel *versus* frequency. (a) 0.2:1; (b) 0.25:1; (c) 0.5:1; (d) 0.75:1; (e) 1:1; (f) 2:1.

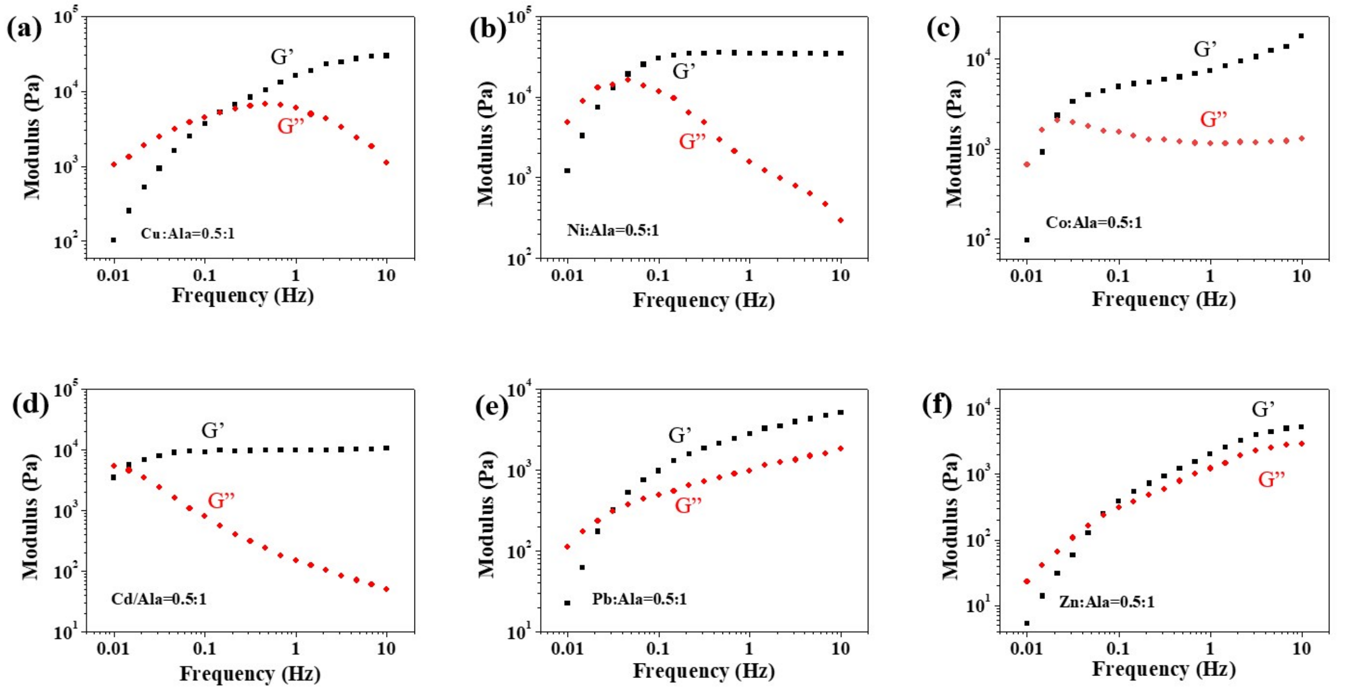

Fig. S4. Influence of different types of metal ion on the G' and G" of hydrogels cross-linked by M-Ala coordination with the metal-to-Ala mole ratio of 0.5:1.

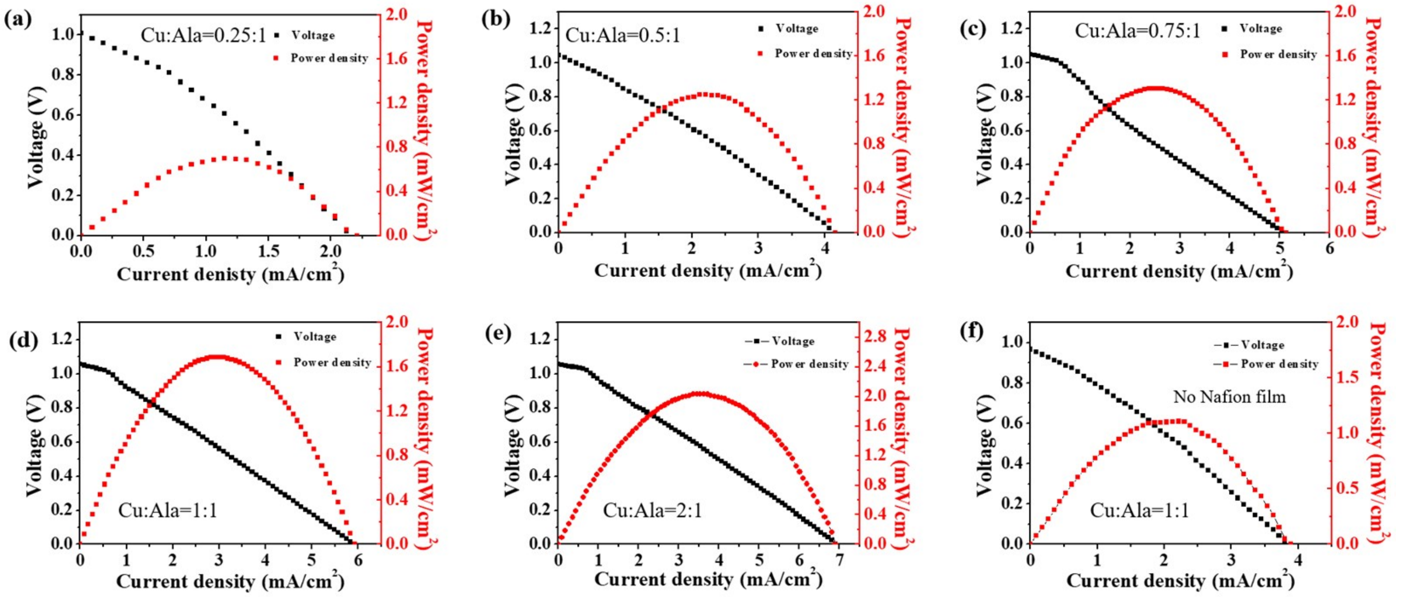

Fig. S5. (a-e) Influence of Cu:Ala ratio on the V-I performance and power density of Cu-Zn galvanic cells made of Cu-/Zn-containing supramolecular hydrogels. The Cu- and Zn-containing hydrogels were separated by Nafion films. (f) The V-I performance and power density of the Cu-Zn galvanic cell (Cu:Ala ratio of 1:1) without the using of Nafion film.

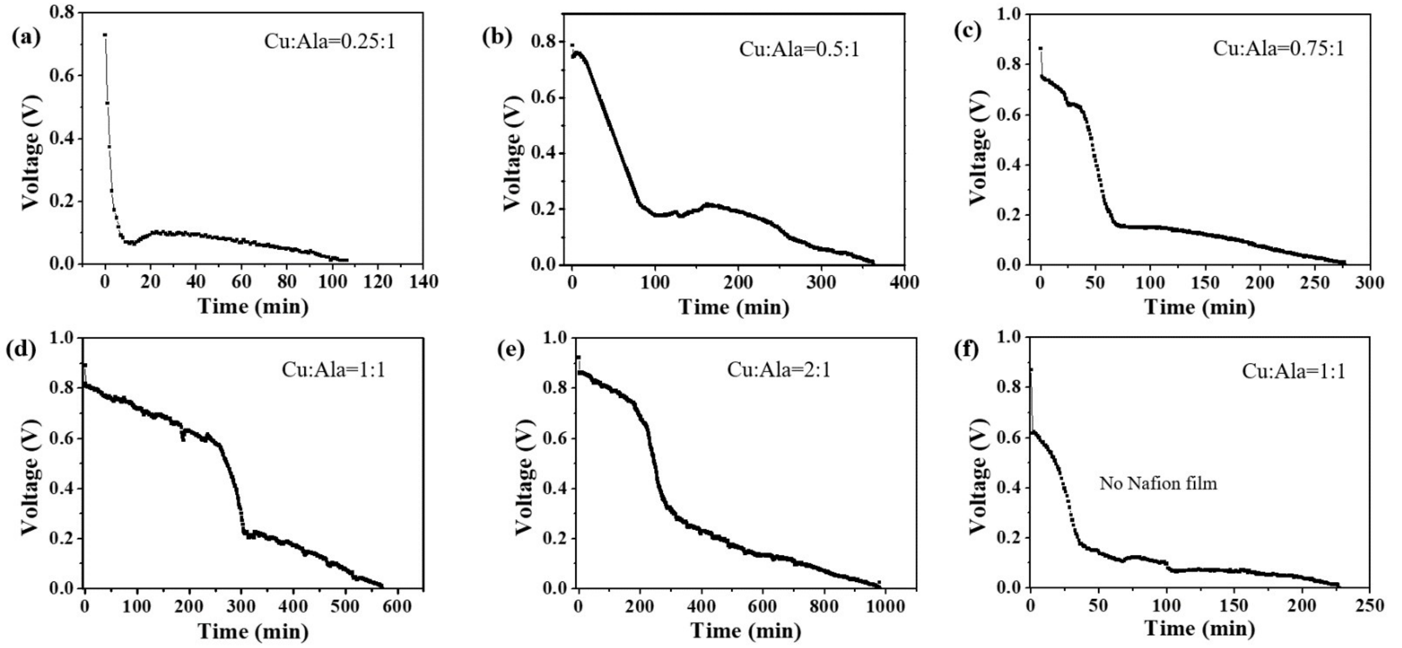

Fig. S6. (a-e) Influence of Cu:Ala ratio on the discharging curves of the Cu-Zn galvanic cells made of Cu-/Zn-containing supramolecular hydrogels. The Cu- and Zn-containing hydrogels were separated by Nafion films. (f) The discharging curve of the Cu-Zn galvanic cell (Cu:Ala ratio of 1:1) without the using of Nafion film.

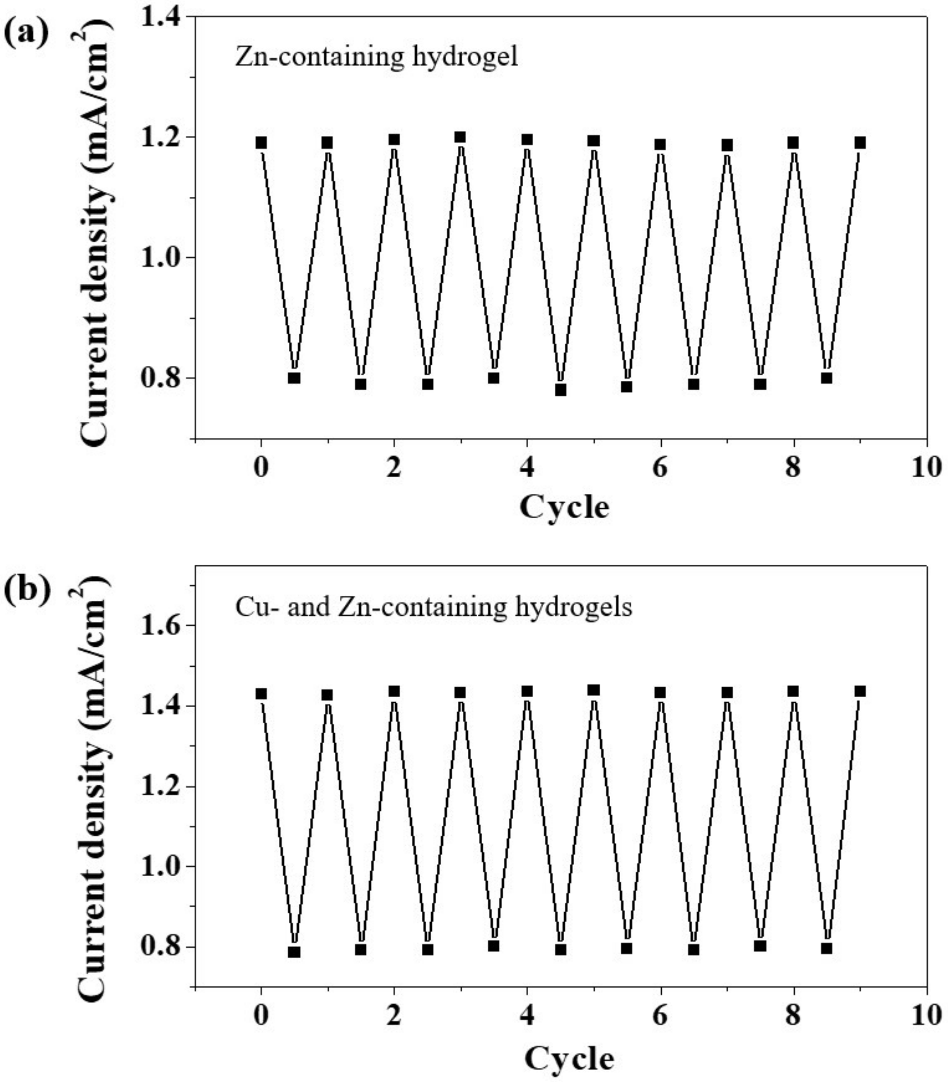

Fig. S7. Periodic change of current density of the Cu-Zn galvanic hydrogel cell by imposing heating (80 °C)/cooling cycles to the Zn-containing hydrogel (a) and both the Cu- and Zn-containing hydrogels (b). All hydrogels had an M:Ala mole ratio of 1:1.

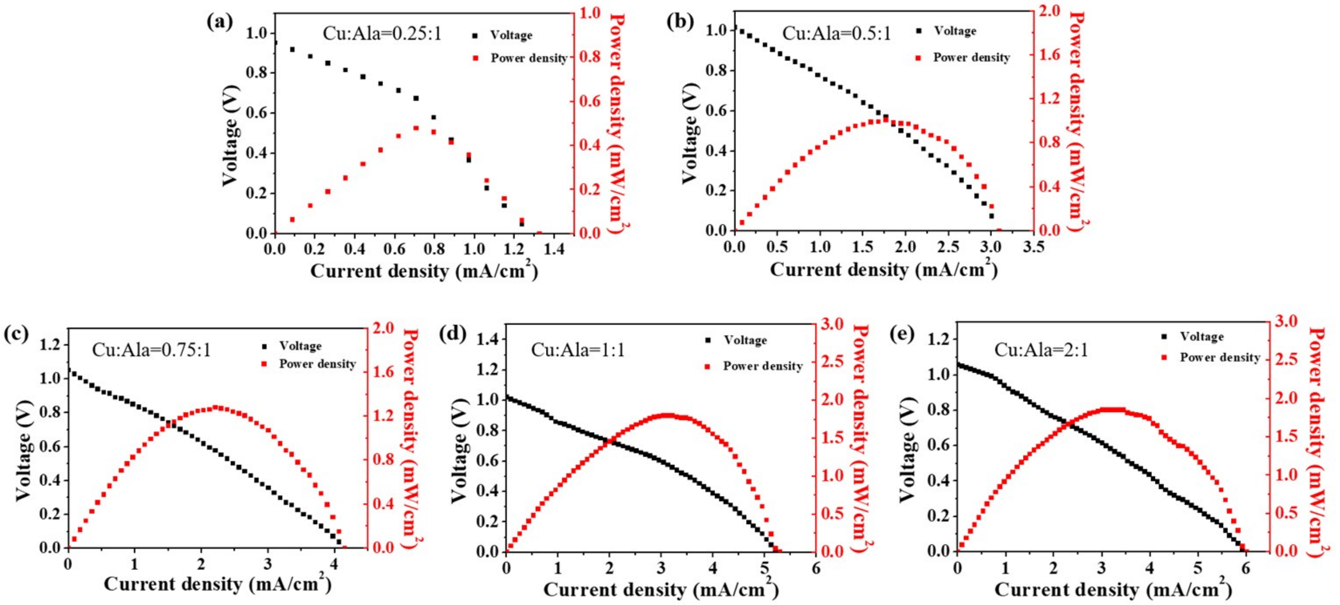

Fig. S8. Impact of Cu:Ala ratio on the V-I performance and power density of Cu-Zn galvanic cells made of Cu-/Zn-containing IPN hydrogels.

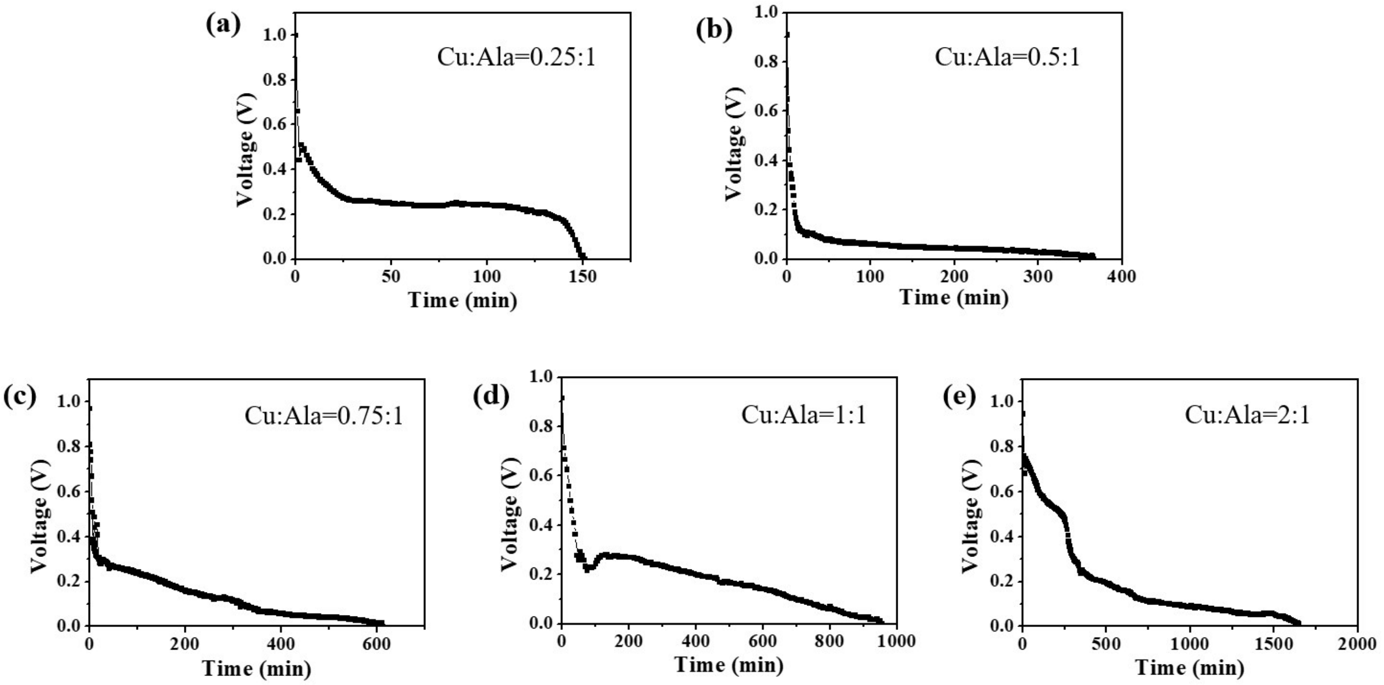

Fig. S9. Influence of Cu:Ala ratio on the discharging curves of the Cu-Zn galvanic cells made of Cu-/Zn-containing IPN hydrogels.