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Chemical and Electrochemical Manipulation of Mechanical Properties in Stimuli-Responsive Copper-Cross-Linked Hydrogels

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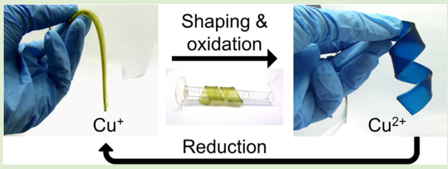
Supporting Information

ABSTRACT: Inspiration for the design of new synthetic polymers can be found in the natural world, where materials often exhibit complex properties that change depending on external stimuli. A new synthetic electroplastic elastomer hydrogel (EPEH) that undergoes changes in mechanical properties in response to both chemical and electrochemical stimuli has been prepared based on these precedents. In addition to having the capability to switch between hard and soft states, the presence of both permanent covalent and dynamic copper-based cross links also allows this stimuli-responsive material to exhibit a striking shape memory capability. The density of temporary cross links and the mechanical properties are controlled by reversible switching between the +1 and +2 oxidation states.



Stimuli-responsive materials that exhibit significant property changes when exposed to an external trigger provide new approaches to challenges in diverse areas including energy, sensing, health, chemical synthesis, construction, and electronics.[1−4] Polymers can be engineered to respond to specific stimuli including temperature, light, pH, ion concentration, chemical structure of additives, magnetic field, mechanical forces, and electricity and can respond with changes in dimension, shape, viscosity, healing, release of guest species, fluorescence, conductivity, permeability, and mechanical properties.[5−14] Moreover, as with natural materials, synthetic polymers can be designed to respond to multiple stimuli by producing either a unified response or a repertoire of stimuli-specific responses. These multiresponsive materials allow for greater flexibility in material design and a wider range of functionality and applications.[15,16]

A polymeric hydrogel is a particularly suitable medium in which to create materials that respond to environmental changes. The aqueous environment is amenable to the establishment of equilibria that can be reversibly manipulated, and the swelling/deswelling of the gels amplifies responses caused by changes in inter-/intramolecular interactions.[8−10]

We are interested in exploring the use of redox stimuli to introduce changes in mechanical properties and shape.[17] Oxidation state is a powerful tool for manipulating metal-containing materials, and a variety of responses have been shown to depend on metal oxidation state.[9,11,18−23] Copper, which exhibits redox-state preferences in coordination number, geometry, and ligand type, has been exploited in the design of responsive molecules and materials.[22,24−28]

Herein, we describe a new copper-based metallopolymer, an electroplastic elastomer hydrogel (EPEH), that is dual-responsive, undergoing both electrochemically and chemically stimulated transitions between hard and soft states (Figure 1). Analogous to the Fe^{2+}/Fe^{3+} EPEH that we reported previously, the Cu-EPEH has two cross-linking systems: a stable, covalent system that maintains the hydrogel's basic shape and a dynamic system based on the coordination of side groups to metal ions. This new copper system uses redox-specific coordination with hydrophobic pyridine groups to access higher moduli and larger differences in hard and soft moduli than those observed in the carboxylate-based iron system. Additionally, the unique redox characteristics of copper facilitate the demonstration of shape memory.

Although elegant examples of redox-responsive materials that depend on changes in metal coordination have been reported by other groups, these generally lack the secondary network and, thus, do not exhibit shape memory.[8−10] Particularly interesting and relevant examples of redox control of sol−gel transitions include the report by Tong et al. of a switchable iron/poly(acrylic acid) system,[20,21] the cobalt-based supramolecular polymer by Terech and co-workers,[29] and copper-based systems by the Rowan and Shinkai groups.[22,26] Also related is the Cu/Cu^{2+} ionoprinting methodology reported by Velev and co-workers.[27] Other mechanisms that enable redox-controlled sol−gel or interchain cross-linking transitions involve changes in hydrogen bonding,[30] disulfide/thiol equilibria,[31−33] molecular recognition,[34,35] and counterion migration.[36,37]

The basic hydrogel was prepared by simple free-radical copolymerization of commercially purchased monomers. Sodium (4-styrene sulfonate), 4-vinylpyridine, and poly-

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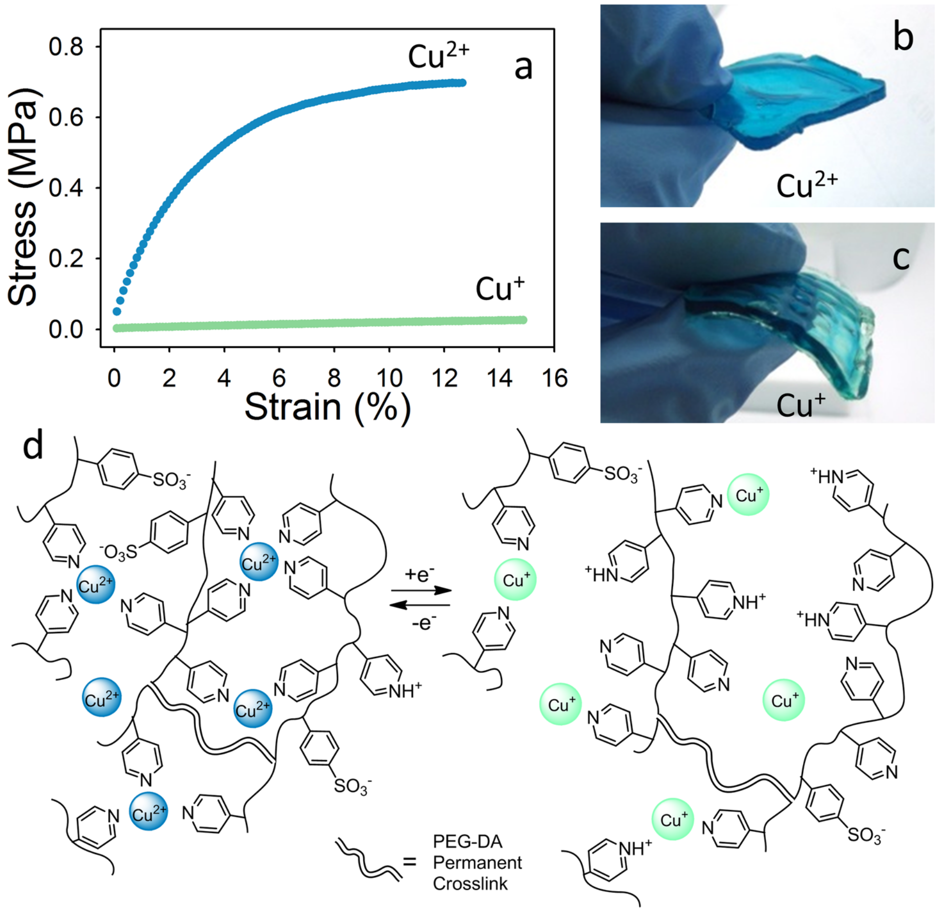

Figure 1. (a) Mechanical properties under tension of Cu^{2+}- and Cu^{+}-containing hydrogels. (b) Cu^{2+}-doped hydrogel (dark blue, stiff). (c) Cu^{+}-doped hydrogel (green-blue, soft) produced by electrochemical reduction of a Cu^{2+} hydrogel. (d) Schematic depicting changes in copper-based cross-link density.

(ethylene glycol) diacrylate (PEG-DA, M_n = 575) in a weight ratio of 16:4:1 were reacted in aqueous solution with an ammonium persulfate catalyst at 85 °C for 1.5 h to give a soft, pale yellow hydrogel. The presence of the permanent PEG-DA cross links gives the hydrogels a baseline shape defined by the reaction vessel.

The Cu^{2+} hydrogel was produced by submersion of the undoped hydrogel in a solution of 0.5 M $CuCl_2$/0.025 M urea for a period of 20−48 h. Qualitatively, the samples were bright blue in color, tougher, and stiffer than the original hydrogel. Consistent with the formation of metal-mediated cross links, the sample volume decreased with a concomitant loss of ∼19% of the water content during this process (Table S2, Supporting Information). Urea was used as a component of the metal solution to promote homogeneous doping by acting as a competitive ligand with the side-chain pyridine; use of pure $CuCl_2$ solutions gave samples with a hard shell and a soft interior because fast cross linking of the exterior inhibits ion diffusion to the interior. The mechanical properties of the Cu^{2+}-EPEH depended on the concentration of the dopant solution. The highest modulus, as determined by tensile testing, was obtained with a doping solution of 0.375 M $CuCl_2$/0.025 M urea (Figure 2 and Figure S4, Supporting Information). Both a deficiency of copper and an excess would be expected to decrease the cross-link density as too few ions should give high pyridine coordination numbers, e.g., $(py)_4Cu$, but a low number of cross-link points, whereas a high concentration of copper would be expected to give a high number of potential cross-link sites but low pyridine coordination numbers, e.g., $(py)(OH_2)CuCl_2$. Supporting this interpretation is the change in absorption frequency with increasing copper from the blue (λ_{max} = 690 nm) color associated with donor ligands to the green color (λ_{max} = 840 nm) associated with chloride ligands (Figure S8, Supporting Information).

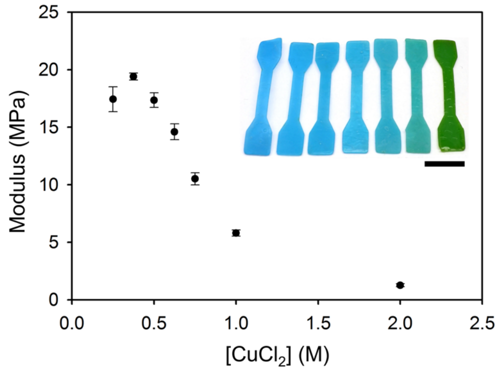

Figure 2. Dependence of mechanical stiffness on the concentration of copper in the doping solution (incl. 0.025 M urea). Inset shows dumbbell samples used for tensile testing. From left to right increasing copper concentration, scale bar 10 mm.

Both ESR and quantitative analysis of samples prepared with our standard doping concentration of 0.5 M $CuCl_2$ suggest that

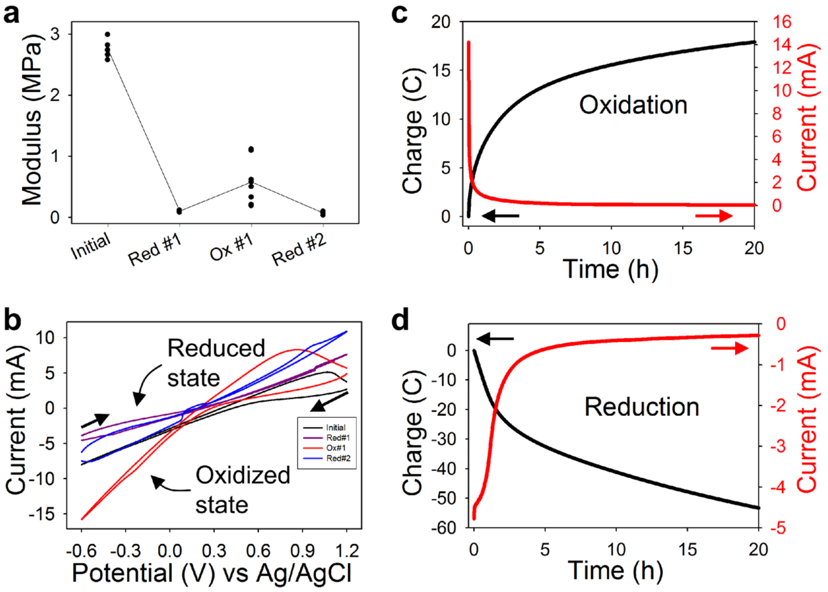

Figure 3. (a) Indentation modulus measurements of a sample at various stages of electrochemical cycling (Red = reduction, Ox = oxidation). Multiple moduli are a result of sample inhomogeneity as measured with an indentation probe. (b) Current vs potential graphs showing oxidation and reduction peaks of the copper ion. (c), (d) Chronocoulometry and chronoamperometry for the oxidation and reduction processes.

the copper coordination sphere contains both nitrogen (pyridine) and oxygen ligands (water/sulfonate). Specifically, ESR spectroscopy was consistent with four equatorial ligands, i.e., type II coordination with a 3N1O or 2N2O ligand distribution (Figures S9 and S10, Supporting Information), with possible contributions from axial ligands, most likely water in this case. Quantitative analysis of the copper in a sample at the 0.5 M $CuCl_2$ level (Table S3, Supporting Information) gave a ratio of copper to pyridine of ca. 2.5:4 which is consistent with the mixed nitrogen/oxygen coordination determined by ESR spectroscopy. Access to higher pyridine coordination numbers is likely inhibited both by the presence of sulfonate groups as well as by accessibility limitations arising from the connection of the coordinating ligands to the polymer backbone. It should be noted that although the urea codopant may also act as a ligand the relatively low concentrations and weak binding strength should minimize any contribution.

The softer Cu^+-EPEH was prepared by submersion of the hydrogel in a solution of 0.1 M CuCl/0.5 M NH_4OH in water or 0.1 M CuCl in acetonitrile for 24−48 h under nitrogen. If the sample was to be handled in air after preparation, the copper could be stabilized in the +1 state by the addition of sodium metabisulfite to the doping solution. The poor solubility of copper(I) salts precluded the use of more concentrated solutions. Qualitatively, the Cu^+-doped hydrogels were pale yellow in color, modestly stiffer, and much tougher than the undoped gel. Water content decreased by a negligible amount during this doping process (Table S2, Supporting Information), which was consistent with weak coordination between the Cu^+ ions and the pyridine ligands.

The Cu^{2+}-doped EPEHs exhibited significantly higher moduli than those observed for the iron system that we described previously.[17] Moduli obtained by indentation testing[38] ranged from 3.1 to 3.5 MPa, while those obtained using tensile measurements were as high as 10−18 MPa (for summary of mechanical data see Table S1, Supporting Information). Indentation testing of Cu^+-doped EPEHs gave much lower moduli than those of Cu^{2+}, in the 0.29−0.73 MPa range (0.15−0.16 MPa, tensile). Moduli measured for comparable iron samples were 0.06 for Fe^{2+} and 2.1 MPa for Fe^{3+} by indentation.[17] It should be noted that the indentation testing method employed, which is easier to administer to samples that were not specifically prepared for mechanical testing, produces measurements that are useful for qualitative comparisons but not as accurate in our case as those acquired by tensile testing. Schubert and co-workers[39] have reported previously that indentation tests present numerous challenges both in acquisition of accurate measurements and in the relationship of these measurements to those acquired by other methods.

The sample could be switched from the hard to soft state electrochemically (Figure 3 and Figure S1, Supporting Information). Reduction of Cu^{2+} to Cu^+ was accomplished by the application of a −0.2 V potential (vs Ag/AgCl) to the sample on a glassy carbon electrode in an electrolyte comprising 0.067 M KNO_3 in water saturated with acetonitrile (ca. 1:3). The extent of reduction could be monitored visually by the change in color from dark blue to lighter green-blue (Figure 1b,c). Indentation moduli measurements revealed a greater than 1 order of magnitude difference between the Cu^{2+}-doped state at 3.0 MPa and the reduced state at 0.11 MPa. In simple aqueous electrolyte, overreduction led to the formation of copper metal particles (Figure S6, Supporting Information). Use of a mixed acetonitrile/water solution appears to prevent this problem. Cyclic voltammograms (CVs) of the gels in the oxidized and reduced states are distinct.

The electrochemical oxidation of a freshly prepared Cu^+-gel to Cu^{2+} could be partially achieved by applying a +1.0 V potential to a Cu^+-doped hydrogel in 0.1 M CuCl (stabilized by sodium metabisulfite) in water saturated with acetonitrile. As shown in Figure 3a, the oxidation does not return the sample to the original level of stiffness, and the sample is not homogeneous. Rereduction, however, does give a hydrogel with a modulus similar to that observed after the first reduction. The electrochemical oxidation step appeared to be hindered by the formation of a hard Cu^{2+}-cross-linked shell on the hydrogel face that was in direct contact with the electrode (Figure S2, Supporting Information). We hypothesize that the Cu^{2+} shell was poorly permeable and inhibited the ion migration necessary for bulk oxidation. Also consistent with this observation was the relatively low amount of charge passed during the oxidation process.

Completely reversible switching between hard and soft states could be accomplished using chemical stimuli. Oxidation from Cu^{+} to Cu^{2+}, which was challenging electrochemically, occurs through simple exposure to ambient oxygen (Figure 4). The sample rapidly changes color and becomes stiffer. UV−vis spectra of films undergoing this oxidation process show a gradual conversion from the Cu^{+} state which absorbs only weakly in the visible to the blue absorption (λ_{max} = 690 nm) associated with the Cu^{2+} cross links (Figure S7, Supporting Information). Samples that were "shaped" prior to oxidation maintained the new shape after the transition. In contrast, samples doped with Cu^{2+} remained stable to air and retained their color, shape, and mechanical properties. The water content decreased by 12% during the air oxidation from Cu^{+} to Cu^{2+} (Table S2, Supporting Information). This decrease in water was not caused by sample drying—hydration was maintained during oxidation—but rather by the increased binding of Cu^{2+} to the polymer chains. Chemical reduction was also facile. Submersion of the stiffer Cu^{2+} samples in a solution of 0.15 M sodium metabisulfite gave a flexible, Cu^{+} hydrogel in minutes.

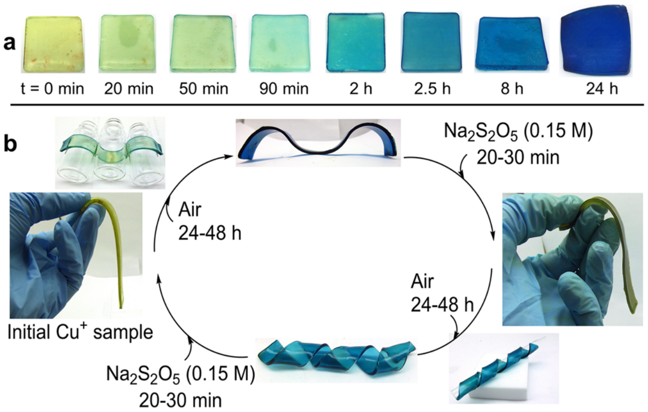

Figure 4. (a) Conversion of Cu^{+}-doped hydrogel to Cu^{2+} in air. (b) Demonstration of shape memory for copper-cross-linked hydrogels.

The copper hydrogel materials also possess shape memory characteristics. A sample prepared in the +1 oxidation state, for example, was molded to form a flat, flexible strip (Figure 4). If the sample was then formed into a shape and allowed to air oxidize, the new stiffer Cu^{2+}-EPEH held the new profile. Reduction of the sample by immersion in a solution of sodium metabisulfite regenerated the original flat, flexible form, which could be recast into a new profile and hardened by oxidation. The cycle is repeatable, although recharging of the copper ions is necessary after several cycles as the poorly bound Cu^{+} is prone to leaching. The fundamental shape of the hydrogel (2−3 mm thick rectangular prism) is determined by the original network formed with the nonreversible PEG-DA cross links. The secondary network that allows the material to hold a second shape is formed by the oxidized Cu^{2+} ions which cross link the chains by coordination with pyridine. Reduction to Cu^{+} destroys the secondary network and restores the original shape.

The creation of a stable hydrogel system that selectively coordinates more strongly to copper in the +2 oxidation state than in the +1 oxidation state has been accomplished. The material properties of hydrogels containing Cu^{2+} are significantly different from those of hydrogels containing Cu^{+}. Cu^{2+}-containing hydrogels are bright blue and fairly rigid, whereas hydrogels containing Cu^{+} are light yellow, soft, and pliable. The EPEH material can reversibly transition between these two states using chemical stimuli and unidirectionally using electrochemistry. These Cu-based EPEHs offer a multiresponsive paradigm for a self-contained, three-dimensional stimuli-responsive material that undergoes changes in mechanical properties.

■ EXPERIMENTAL METHODS

Typical Hydrogel Preparation. Sodium (4-styrene sulfonate) (SS, 1.6 g, 7.77 mmol), 4-vinylpyridine (VP, 0.41 mL, 3.80 mmol), and poly(ethylene glycol) diacrylate, (PEG-DA, M_n = 575, 100 μL, 0.194 mmol) were combined with 9 mL of deionized water and gently heated (<40 °C) until all solids were dissolved. The mixture was purged with N_2 for 1 min. Ammonium persulfate (APS, 60 mg, 2.2 mol %) was added as a radical initiator for copolymerization.

The reaction mixture was pipetted into a mold. Typical sample dimensions were 2.5 × 2.5 × 0.3 cm. For electrochemical experiments the mold for the sample was created by temporarily affixing a square glass cell using poly(dimethylsiloxane) (PDMS) adhesive to a Teflon base bearing a freshly polished glassy carbon electrode (GCE). The mold/sample combination was then heated at 85 °C for 1.5 h. After cooling to RT, the hydrogel was doped by simple submersion in aqueous 0.5 M $CuCl_2$/0.025 M urea solution. Samples were doped with 5 mL of copper solution for every 2 mL of hydrogel solution. For a typical doping solution, $CuCl_2$ (0.34 g, 2.5 mmol) and urea (0.008 g, 0.13 mmol) were combined with 5 mL of deionized water and stirred until all solids were dissolved. Both sample and solution were covered and allowed to sit overnight.

Electrochemical Measurements. Cyclic voltammetry (CV) and amperometric $i-t$ curve measurements were carried out with a CH Instruments Electrochemical workstation 430A model (Austin, TX) at room temperature using a three-electrode system, composed of a glassy carbon (GC) plate (25 × 25 mm) coated with a copper-hydrogel film of 2 mm thickness as working electrode, a Ag/AgCl reference electrode, and a platinum grid as counter electrode. The GC plate electrode was polished with 0.3 μm of Al_2O_3 paste and cleaned thoroughly in an ultrasonic water bath for 5 min. The CV and amperometric $i-t$ curves for reduction were carried out in 15 mL of electrolyte containing 0.067 M KNO_3 in water saturated with acetonitrile (ca. 1:3). Oxidation was carried out in 0.1 M CuCl (stabilized by the addition of sodium metabisulfite to the solution) in water saturated with acetonitrile. CV data were acquired at a scan rate of 100 mV/s over a voltage range of 1.2 to −0.6 V. Bulk electrolysis was performed in the same electrolyte solution for up to 30 h (reduction potential −0.2 V, oxidation potential +1.0 V). All electrochemical experiments were performed under N_2 atmosphere with careful exclusion of ambient light.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, mechanical and electrochemical measurement procedures including a schematic and photograph of the cell, ESR data, water content measurements, quantification of copper and calibration curve, and a table summarizing mechanical properties of Cu^{2+} and Cu^{+} hydrogels. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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