



Effect of metal ion type on the movement of hydrogel actuator based on catechol-metal ion coordination chemistry



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ABSTRACT

Catechol-containing hydrogels were ionprinted with various metal ions (copper, zinc, aluminum, and titanium) to investigate the effect of the metal ion type on the movements of hydrogel actuators based on the coordination chemistry found in mussel adhesive proteins. The movement of the ionprinted hydrogels was characterized by monitoring the bending curvature at the site of ionprinting and compared with previously published results for iron ions. The rate of curvature change (R') was highly dependent on the strength of catechol-metal ion interaction, which varied in the following order: $Ti^{4+} > Fe^{3+} \approx Al^{3+} \approx Cu^{2+} > Zn^{2+}$. The extremely fast rate of actuation for Ti^{4+} ions was due to its ability to displace borate protecting group, which eliminated the need for pH change to initiate hydrogel movement. The maximum degree of bending curvature (R_{max}) followed the order of $Ti^{4+} > Fe^{3+} > Al^{3+} \approx Cu^{2+} \approx Zn^{2+}$, and is dependent on the stoichiometry of the catechol-metal ion complex (i.e., bis- vs. tris-complex) as well as the strength of the interaction. Depending on the metal and the applied voltage, hydrogels exhibited a wide range of R' (0.1 – $2.5 \text{ mm}^{-1} \text{ s}^{-1}$) and R_{max} (0.1 – 0.5 mm^{-1}) values. When a single piece of hydrogel was ionprinted with different metal ions, different sections of the hydrogel actuated independently at different rates and to different bending curvatures. Additionally, these actuators can be reprogrammed to transform into different three-dimensional shapes and the movement of the hydrogel can be initiated on demand. These are unique features not observed in other hydrogel-based actuators.

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1. Introduction

Hydrogel actuators that can change their shape and physical properties in response to environmental stimuli (e.g., temperature, pH, electricity) are currently being explored as soft robotic components [1–3], biosensors [4], artificial muscle tissues [5], and controlled drug delivery applications [6]. However, existing hydrogel actuators are limited by slow actuation, ability to adopt limited shape transformation, or require complicated fabrication techniques to transform into complex three-dimensional structures

Abbreviations: EDTA, ethylenediaminetetraacetic acid; Ti^{4+} ion, titanium(IV) ion; Fe^{3+} ion, iron(III) ion; Al^{3+} ion, aluminum(III) ion; Cu^{2+} ion, copper(II) ion; Zn^{2+} ion, zinc(II) ion; DMA, dopamine methacrylamide; DMPA, 2,2-dimethoxy-2-phenylacetophenone; DOPA, 3,4-dihydroxyphenylalanine; HEA, *N*-hydroxyethyl acrylamide; MBAA, *N,N'*-methylene-bisacrylamide; pHEA, poly(*N*-hydroxyethyl acrylamide); R' , rate of change in the bending curvature; R_0 , initial bending curvature; R_{max} , maximum bending curvature; ICP-OES, inductively coupled plasma optical emission spectroscopy; FTIR, Fourier transform infrared.

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[7,8]. Specifically, hydrogels that can form predictable and complex structures through sequential actuation have been difficult to engineer.

Mussels secrete proteinaceous fluids that harden to form an adhesive plaque and byssal thread complex that enables these organisms to anchor themselves to surfaces in wet, saline, and turbulent environments [9,10]. These proteins contain a large abundance of 3,4-dihydroxyphenylalanine (DOPA) residues, which form strong complexes with iron(III) (Fe^{3+}) ions [11,12]. Catechol- Fe^{3+} ion coordination bond is significantly more stable when compared to polymeric acid- or amino acid-based ligands [13,14]. Breaking and reformation of strong catechol- Fe^{3+} ion complexes is responsible for the energy dissipative properties of the byssal thread coating [15,16]. This complexation chemistry has been exploited in creating self-healing hydrogels [17–19], pH-responsive drug carrier [20], and mechanically reinforced polymeric fibers [21,22].

Our lab recently employed catechol- Fe^{3+} ion complex chemistry to create a novel pH-responsive hydrogel actuator [23]. Hydrogels with network-bound catechol were ionprinted with Fe^{3+} ion through electrochemical oxidation of an iron electrode in contact with the hydrogel surface. When the pH was increased, catechol

Table 1
Log stability constant of mono-, bis-, and triscatecholate–metal ion complexes.

| Metal | Mono | Bis | Tris | Reference |
|------------------|------|-----|------|-----------|
| Cu ²⁺ | 15 | 27 | | [11] |
| Zn ²⁺ | 13 | 27 | | [28] |
| Fe ³⁺ | 18 | 33 | 41 | [11] |
| Ti ⁴⁺ | | 25 | 62 | [26] |

formed intermolecular coordination bonds with increased stoichiometry (i.e., triscatecholate-Fe³⁺ complex), which resulted in local network shrinkage. The formation of a sever crosslinking density gradient resulted in sharp hydrogel bending at the ionoprinting site. Depending on the catechol and Fe³⁺ ion content, pH, and hydrogel thickness, the rate and extent of hydrogel actuation can be modulated [23,24].

In addition to Fe³⁺ ion, catechol also forms strong complexes with other metal ions, including copper (Cu²⁺), zinc (Zn²⁺), and titanium (Ti⁴⁺) [17,25]. Depending on the pH and metal ion type, catechol forms complexes with different stability and estimated bond strengths (Table 1). For example, catechol-Ti⁴⁺ ion tris-complex is 10²⁰ times more stable as compared to that of catechol and Fe³⁺ ion [11,26]. The strength of catechol-Ti bond was also estimated to be at least 24% higher when compared to those formed between catechol and other metal ions (i.e., Fe, Zn, etc.) [27].

We hypothesize that the strength of catechol–metal ion interaction can be used to further tune the movement of catechol-modified actuator. To this end, we investigated the effect of metal ion type on the movement of catechol-modified hydrogel actuator. Hydrogels were formed by photo-initiated polymerization of dopamine methacrylamide (DMA) and ionoprinted with various metal ions (copper, zinc, aluminum, and titanium) and the effect of the type of metal ion on the rate and extent of actuation was examined. Additionally, the ability for hydrogels ionoprinted with different metal ions to actuate sequentially was explored.

2. Materials and methods

2.1. Materials

N-hydroxyethyl acrylamide (HEA) and ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma–Aldrich (St. Louis, MO). *N,N'*-methylene-bisacrylamide (MBAA) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were obtained from Acros Organics (Geel, Belgium). Sodium borate, sodium hydroxide, dimethyl sulfoxide (DMSO) and 12 M hydrochloric acid were purchased from Fisher Scientific (Pittsburg, PA). Copper (99.9%, 6.35-mm diameter), zinc (99.9985%, 7-mm diameter), aluminum (99.95%, 6.35-mm diameter), and titanium (99.7%, 6.4-mm diameter) rods and platinum foil (99.9%, 0.025 mm thick) were purchased from Alfa Aesar (Ward Hill, MA). DMA was synthesized using previously published protocol [29].

2.2. Hydrogel preparation

Catechol-containing hydrogels were prepared using previously published protocol [23,24]. Briefly, a precursor solution containing 2.5 M of HEA, 12 mol% DMA, 0.5 mol% MBAA, and 0.04 mol% DMPA were dissolved in a DMSO and deionized water mixture (33 v/v % DMSO) and degassed by back-filling with nitrogen three times. The solution was added to a mold consisting of two pieces of glass separated by a 1-mm thick spacer. Photoirradiation was performed on both sides of the mold for a total of 20 min using a UV crosslinking chamber (XL-1000, Spectronics Corporation, Westbury, NY) located in a N₂-filled glove box. Hydrogels were soaked in 6 mM HCl while frequently changing the dialysate for three days to remove

unreacted monomers before testing. After purification, the thickness of the hydrogel was measured to be 1.3 mm.

2.3. Ionoprinting and initiating actuation

Hydrogels were incubated in 0.1 M sodium borate solution containing 0.1 M NaCl and 50 mM NaOH for at least 30 min. Borate acts as a temporary protecting group for catechol, which is necessary to concentrate the metal ion near the ionoprinting site to generate sufficient crosslinking density differential for hydrogel actuation [23]. Metal ions were patterned into the hydrogel network by placing it in contact with an metal rod (anode) and aluminum foil (cathode) and applying a desired electrical potential (5–20 V) using a DC regulated power supply (CSI3003X, Circuit Specialists, Inc., Mesa, AZ) for 10 s. For ionoprinting using aluminum and titanium electrodes, platinum foil was used as the cathode. To initiate actuation, the hydrogel was first submerged in pH 3.5 0.1 M NaCl solution for 2 min to remove borate protecting group and then transferred to a pH 9.5 0.1 M NaCl solution. Hydrogels ionoprinted with titanium actuate without the removal of borate and these samples were directly placed in the pH9.5 0.1 M NaCl solution immediately after ionoprinting. The bending curvature around the ionoprinting site was tracked over time by digital photography to determine the initial curvature (R_0), the rate of change in the curvature (R') as measured by the slope of the fitted line for data during the initial time points, and the maximum curvature (R_{max}) as determined by the average value after a maximum bending curvature was reached [24].

2.4. Characterization of the ionoprinted hydrogels

To determine the formation of catechol–metal ion complex, ionoprinted samples were dried under vacuum and characterize using Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum One spectrometer). To quantify the amount of metal ion incorporated into the hydrogel, ionoprinted samples were soaked in 10 mL of 0.1 M EDTA (pH 4.0) for 2 weeks to extract the deposited ions [23]. The EDTA solutions were evaluated for metal content using inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer Optima 7000DV), which utilizes a cross-flow nebulizer with the following parameters: plasma 15 mL/min; auxiliary 0.2 mL/min; nebulizer 0.80 mL/min; RF power 1350 W; pump speed 1.5 ml/min. Calibration standards were made from Instrument Calibration Standard 3 (Perkin Elmer). Initial calibration verification was made from the Interference Check Standard (Perkin Elmer). 3 samples per treatment were collected and each sample was analyzed 3 times using ICP-OES.

2.5. Statistical analysis

Statistical analysis was performed using JMP Pro 10 software. One-way analysis of variance (ANOVA) with Tukey HSD analysis and student t-test were performed for comparing means of multiple and two groups, respectively, using a *p*-value of 0.05.

3. Results and discussion

Catechol-functionalized hydrogels were formed by photo-initiated polymerization of DMA with a neutral monomer, HEA. FTIR spectra (Fig. 1) of the hydrogel confirmed the characteristic features of polyHEA (3260 and 1059 cm⁻¹ for alcohol, 2931 and 2860 cm⁻¹ for aliphatic –CH₂–, 1629 and 1530 cm⁻¹ for amide) and those of catechol (1430 and 600 cm⁻¹) [30,31]. When samples were ionoprinted using various metallic electrodes, a new peak between 1485 and 1497 cm⁻¹ was observed (arrows in Fig. 1), which

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