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Electrodeposition of chitosan based on coordination with metal ions *in situ*-generated by electrochemical oxidation

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Abstract

Electrodeposition is an attractive technique that provides a controllable and programmable means to trigger assembly of stimuli-responsive biopolymers (*e.g.*, chitosan) for a diverse range of applications. Here, we report a new electrodeposition method of chitosan based on the coordination of chitosan to the metal ions *in situ*-generated by the simultaneous electrochemical oxidation. In particular, we typically construct a deposited hydrogel on the copper electrode through this coordinated electrodeposition method, and the obtained hydrogel is smooth, transparent and homogeneous, as well as it has stability under acidic conditions and enough strength to be readily peeled from the electrode. This coordinated electrodeposition can be conveniently employed to build coatings (on the electrodes) or hydrogel films (peeled from the electrodes) with various shapes, and it also enables nanoparticles (*e.g.*, fluorescent carbon dots) to be codeposited with chitosan. Furthermore, by enlisting the special benefits of the coordinated electrodeposition, the diverse hydrogel patterns can be constructed on the electrodes. Interestingly, this coordinated electrodeposition can be employed to directly build the complex hydrogel on the electrode to perform electrochemical detection. Therefore, it can be expected that this coordinated electrodeposition of chitosan has promising applications in biomedical device, surface coating, and metallic biomaterial.

Keywords: Electrodeposition, Chitosan, Coordination, Electrochemical oxidation, Metal ions

1. Introduction

Electrodeposition is an attractive method for triggering assembly of stimuli-responsive biopolymers (*e.g.*, chitosan) in response to imposed electrical signals with exquisite spatial and temporal control. In particular, the electrodeposition of stimuli-responsive biopolymers can be employed to construct the bio-device interface, which offer convergent methods to combine biology with microelectronics.[1] On the other hand, electrodeposition provides appealing opportunities for assembling biological components (*e.g.*, cells and proteins) and nanomaterials (*e.g.*, carbon nanotubes and quantum dots) into the deposited films by codeposition,[2-5] thus it offers a controllable and programmable means to concurrently assemble these biological components and nanomaterials for a diverse range of applications.

It is worth mentioning that chitosan was the first biopolymer to be electrodeposited, and it has been extensively used in the electrodeposition field in recent years. Chitosan, a naturally occurring polysaccharide containing amino and hydroxyl groups, has many favorable properties such as biocompatibility, biodegradability, non-toxicity and antibacterial activity,[6-10] so it is widely applied in biomedical fields such as implant material, tissue engineering, drug delivery, and cancer treatment.[11-13] The emerging researches on electrodeposition have confirmed that chitosan can be cathodically electrodeposited on diverse surfaces of electrodes or conductive substrates based on its pH-responsive film-forming properties.[14] Importantly, the chitosan electrodeposition exhibits many favorable advantages such as simple operation, programmable procedure, mild and reagentless condition, and exquisite spatiotemporal control, which enables a number of applications in biosensor, enzyme stabilization, antimicrobial coating, controlled release, and microbial fuel cell.[15-19]

With respect to electrodeposition mechanism of chitosan, Payne group has demonstrated that the electrodeposition of chitosan undergoes a cathodic neutralization mechanism.[1] Specifically, the cathodic reactions produce a localized pH gradient adjacent to the cathode surface that induces the sol-gel transition of chitosan, thus the chitosan molecules close to the cathode surface can respond to the localized high pH and deposit as a stable hydrogel coating on the cathode.[20] It should be noted that the electrochemical reactions on the cathode also generate H_2 bubbles during the electrodeposition.[21,22] These H_2 bubbles greatly affect the surface smoothness and produce defects on the deposited hydrogel,[23] which may hinder further applications of the deposited material. On the other hand, the cathodic hydrogel is stable under neutral and basic conditions, yet it is unstable and dissolves under acidic conditions. Therefore, it deserves our efforts to investigate new electrodeposition methods to fabricate deposited chitosan hydrogels with smooth surface, sufficient strength, and enough stability under acidic conditions.

In addition to above-mentioned properties, chitosan exhibits the excellent ability to coordinate to transition metal ions.[24,25] This coordination ability is associated with the presence of amino groups in chitosan, which has been applied in many fields such as water treatment, protein assembly, and catalysis.[26-28] Currently, only a few studies have considered the electrodeposition of biopolymer via coordination of the biopolymer to metal ions. Jin and co-workers have reported that the electrochemically controlled oxidation of Fe^{2+} ions to Fe^{3+} ions in the presence of alginate and protein results in the formation of an alginate-based thin-film with the entrapped protein at the electrode interface.[29] They also use this method to electrochemically build the alginate matrix cross-linked with Fe^{3+} cations to entrap lysozyme under the control of electrochemical signal.[30] It should be noted that the above studies on the electrochemically controlled deposition of biopolymer require the presence of the metal ions (*e.g.*, Fe^{2+} ions) that is additionally added into the deposition solution before electrodeposition. However, no work has been done on the electrodeposition of biopolymer via coordination with *in situ*-generated metal ions (without adding metal ions before electrodeposition). On the other hand, no attention has been paid to the electrodeposition of chitosan through coordinated method.

The purpose of this study is to develop a new electrodeposition method of chitosan through the coordination of chitosan to the metal ions *in situ*-generated by the simultaneous electrochemical oxidation. Particularly, this coordinated electrodeposition method can be enlisted to generate the deposited hydrogel with smooth and homogeneous surface, better stability under acidic conditions, and sufficient strength to be peeled from the electrode. Also, this method can be employed to concurrently assemble nanoparticles (*e.g.*, carbon dots) through codeposition with chitosan. By taking advantage of the coordinated electrodeposition, the different hydrogel patterns on the electrodes, together with the coatings (on the electrodes) and the hydrogel films (peeled from the electrodes) with various shapes can be conveniently constructed. More importantly, using this method we can directly build the complex hydrogel on the electrode, which can be sequentially applied to electrochemical detection. We anticipate that this coordinated electrodeposition of chitosan will be especially useful for applications in biomedical device, surface coating and metallic biomaterial.

2. Experimental section

2.1 Chemicals and materials

Chitosan (90% deacetylation degree), gelatin (from porcine skin), ethylenediaminetetraacetic acid disodium salt (EDTA), bovine hemoglobin, acetic acid, and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Rhodamine 6G was purchased from Sigma. Copper plate, silver plate, titanium plate, platinum foil, and other chemicals were obtained from the commercial resources in China. All chemicals were analytical grade and were not purified further before use.

2.2 Coordinated electrodeposition of chitosan

Chitosan solution (1.0% w/v) was prepared by dissolving the chitosan powder in acetic acid (0.25% v/v), and adjusting pH to 5.5, then filtering to remove the undissolved particles. For the electrodeposition, a copper plate (or a copper wire) served as the anodic electrode, and a platinum foil served as the cathodic electrode, respectively. Before use, each electrode was carefully polished, and then ultrasonically washed in acetone, ethanol and distilled water for 10 min, respectively. Next, the electrodeposition was performed using a programmable DC power supply (IT6123, TW). Both the cathode and the anode were partially-immersed into the deposition solution (1.0% w/v chitosan solution), and then a desirable DC voltage (*e.g.*, 1.5 V) was applied. After a specific time (*e.g.*, 2.5 min), the anode was disconnected from the power supply, and removed from the deposition solution, then washed with distilled water. Finally, a deposited hydrogel (named as chitosan/Cu^{2+} hydrogel) on the surface of the copper electrode was obtained.

Furthermore, we performed the electrodeposition by using a silver plate as the anode and a platinum foil as the cathode. After electrodeposition, the deposited hydrogels on the silver plate was washed by distilled water and then visually observed. In contrast, we carried out the electrodeposition by using a graphite plate (or a platinum foil) as the anode and a platinum foil as the cathode. Besides, we compared two different electrodeposition (the cathodic electrodeposition and the coordinated electrodeposition) on the copper electrode. In brief, we employed the copper plate as the cathode for the cathodic electrodeposition or as the anode for the coordinated electrodeposition respectively, and a platinum foil served as the counter electrode. After electrodeposition, the deposited hydrogels on the copper electrodes were washed and observed.

2.3 Preparation of deposited hydrogel with different patterns and shapes

By employing the coordinated electrodeposition, we fabricated different patterns of the chitosan/Cu^{2+} hydrogel on the titanium plates. Initially, the titanium plate was coated with an alcohol-soluble ink (mainly composed of polyvinyl butyral resin) at the desired region as a protective coating. After drying, the coated titanium plate was used as the cathode, and a copper plate was used as the anode. The electrodes were immersed in 0.2 M $CuSO_4$ solution for electroplating copper on the uncoated region of the titanium plate at a DC voltage of 1.0 V. After electroplating copper, the titanium plate was immersed in ethanol to dissolve the coating, and then dried at room temperature. Next, the above titanium plate was used as the anode, and a platinum foil was used as the cathode, then the electrodeposition was performed in the deposition solution (1.0% w/v chitosan solution containing Rhodamine 6G). After electrodeposition, the titanium plate was removed from the deposition solution and washed with distilled water to achieve a hydrogel pattern on the surface.

Subsequently, we produced the hydrogel coatings and the hydrogel films with various shapes by enlisting the electrodes with different shapes. In brief, the electrodes (copper plates or silver plates) were cut into the desired shapes, carefully polished and ultrasonically washed before use, then electrodeposited in the deposition solution (1.0% w/v chitosan solution), and finally achieved the coatings on the electrodes or the hydrogel films peeled from the electrodes. Moreover, the copper wires were made into different patterns (a three-dimensional spring pattern, and a "WUT" logo pattern), and then electrodeposited in the deposition solution to obtain the desired hydrogel patterns.

2.4 Codeposition of carbon dots with chitosan

For the codeposition of carbon dots, the codeposition mixture was initially prepared by mixing the aqueous carbon dots into the chitosan solution (1.0% w/v) with stirring. Then, a platinum foil was used as the cathodic electrode, and a copper plate served as the anodic electrode, respectively. Next, both the electrodes were partially-immersed into the codeposition mixture to perform the codeposition. Finally, the fluorescence of the codeposited hydrogel on the electrode was observed under 365 nm UV light.

2.5 Characterization

The surface and the cross-section morphology of the deposited hydrogel were observed by a field emission scanning electron microscope (SEM, JSM-5610LV, JEOL Ltd., JP), and the element analysis of the hydrogel was performed by the same scanning electron microscope equipped with the X-ray energy dispersive system (EDS, Phoenix, EDAX, U.S.A.). The Cu content in the chitosan/Cu^{2+} hydrogel was measured by inductively coupled plasma/atomic emission spectrometry (ICP/AES, Optima 4300DV, PerkinElmer, U.S.A.).

Electrochemical measurements were carried out with a CHI 618E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China) using a three-electrode system with chitosan/Cu^{2+} hydrogel-coated titanium plate as the working electrode, Ag/AgCl as the reference electrode, and platinum foil as the counter electrode. We used chitosan/Cu^{2+} hydrogel-coated titanium plate as the working electrode to prevent the interference of electrochemical signal of copper electrode. The chitosan/Cu^{2+} hydrogel-coated titanium plate was prepared as follows. Initially, the titanium plate was used as the cathode, and a copper plate was used as the anode. Both the electrodes were immersed in 0.2 M $CuSO_4$ solution for electroplating copper on the titanium plate at a DC voltage of 1.0 V. After electroplating copper, the above titanium plate was used as the anode, and a platinum foil was used as the cathode, then the electrodeposition was performed in the deposition solution (1.0% w/v chitosan solution) for enough time to completely consume the electroplated copper. After electrodeposition, the titanium plate was removed from the deposition solution and washed with distilled water to achieve a chitosan/Cu^{2+} hydrogel-coated electrode.

3. Results and discussion

3.1 Coordinated electrodeposition of chitosan

To begin with, a copper plate (or a copper wire) was used as the anodic electrode and a platinum foil was used as the cathodic electrode, and then the electrodeposition was performed in the chitosan solution. Figure 1a shows that there is an obvious hydrogel on the surface of the copper plate after electrodeposition. The deposited hydrogel is transparent and homogeneous, and it has a smooth surface without any bubble. Figure 1b indicates that the deposited hydrogel has sufficient strength to be readily peeled from the copper plate. In addition, the deposited hydrogel displays blue color, which accords with the typical color of Cu^{2+} ions in the aqueous solution. It is seen from Fig. 1c that a chitosan/Cu^{2+} hydrogel is generated on the copper wire after electrodeposition at the same deposition conditions. Also, the deposited hydrogel on the copper wire has blue color and smooth surface without any bubble.

We define this kind of electrodeposition method as “coordinated electrodeposition”, and a putative mechanism for this electrodeposition is illustrated in Fig. 1d. For this electrodeposition, both the anodic electrode (a copper plate) and the cathodic electrode (a platinum foil) were partially immersed in the chitosan solution, and then a DC voltage (*e.g.*, 1.5 V) was applied. During electrodeposition, the copper electrode simultaneously undergoes anodic electrochemical oxidation and then generates Cu^{2+} ions *in situ*. Subsequently, these *in situ*-generated Cu^{2+} ions can coordinate to the chitosan molecules adjacent to the copper electrode, and then a stable hydrogel based on the coordination of the chitosan molecules to the Cu^{2+} ions can be formed on the electrode surface.

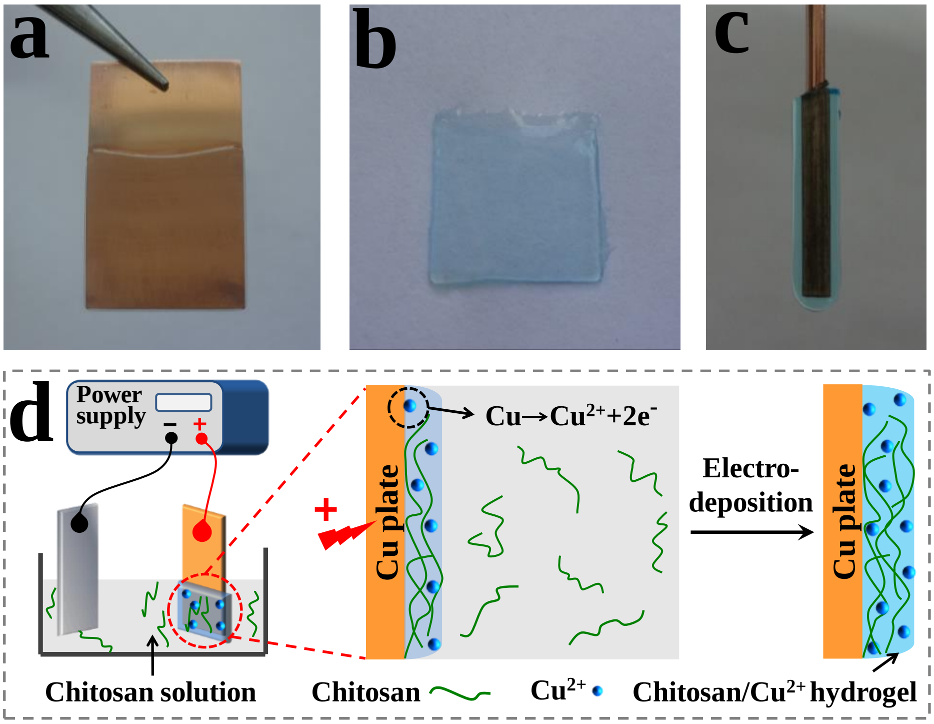

Fig. 1 (a) Photograph of the chitosan/Cu^{2+} hydrogel electrodeposited on the copper plate (about 15 mm in width). (b) Photograph of the chitosan/Cu^{2+} hydrogel peeled from the copper plate. (c) Photograph of the chitosan/Cu^{2+} hydrogel electrodeposited on the copper wire (about 2 mm in diameter). (d) Schematic illustration of the coordinated electrodeposition of chitosan on the copper electrode.

3.2 Evidences for coordinated electrodeposition mechanism

In addition to the copper plate, we used a silver plate as the anodic electrode, then the electrodes were immersed into the chitosan solution to perform the electrodeposition. In contrast, we used a graphite plate or a platinum foil as the anodic electrode to carry out the electrodeposition, respectively. As shown in Fig. 2a, a deposited hydrogel is observed on the silver plate after electrodeposition, indicating that the silver plate can also undergo the anodic electrochemical oxidation to *in situ* generate metal ions that can further coordinate to the chitosan molecules to form the deposited hydrogel. However, no hydrogel is found on the surface of the graphite plate or the platinum foil after electrodeposition at the same conditions, because they both are inert electrodes and cannot generate metal ions that could coordinate to chitosan molecules to form deposited hydrogel.

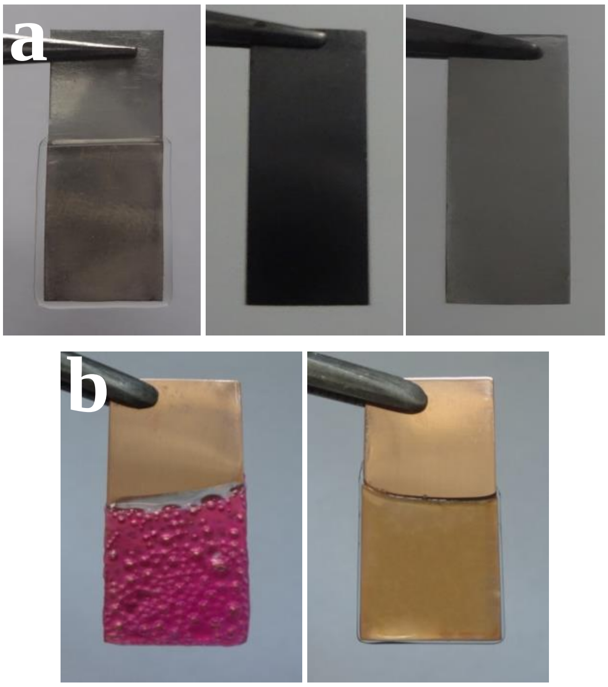

Fig. 2 (a) Photographs of the different kinds of anodic electrodes (from left to right: the silver plate, the graphite plate and the platinum foil) after electrodeposition in the chitosan solution. (b) Photographs of the copper plate after cathodic electrodeposition (left) and coordinated electrodeposition (right) in the chitosan solution containing phenolphthalein.

In contrast to the cathodic chitosan hydrogel that is electrodeposited through a neutralization mechanism, we employed the copper plate as the cathode for the cathodic electrodeposition, and as the anode for the coordinated electrodeposition, respectively. Besides, the chitosan solution containing phenolphthalein was used as the deposition solution for both electrodeposition. It is found from Fig. 2b that there is a chitosan hydrogel with red color on the surface of the copper plate after cathodic electrodeposition, because the cathodic reactions generate a localized high pH near the cathode surface which causes the color reaction with phenolphthalein. In addition, the hydrogel generated by the cathodic electrodeposition has a rough surface with a lot of bubbles due to H_2 produced by the cathodic reactions. On the other hand, the chitosan/Cu^{2+} hydrogel generated by the coordinated electrodeposition has a smooth and homogeneous surface without the color reaction to phenolphthalein, suggesting that it has significantly different mechanism with the cathodic chitosan hydrogel.

Next, we studied the dissolution difference between the cathodic chitosan hydrogel and the chitosan/Cu^{2+} hydrogel. To facilitate observation, we enlisted the deposition solution containing Rhodamine 6G to generate the hydrogels with fluorescence. The fluorescent images in Fig. 3a exhibit that the chitosan/Cu^{2+} hydrogel (electrodeposited on the copper wire) completely disappears when it was immersed in the 0.1 M EDTA solution (pH 5.5). In contrast, Fig. 3b shows that this chitosan/Cu^{2+} hydrogel remains undissolved after immersing in the buffer solution (pH 5.5) without EDTA. As expected, Fig. 3c and 3d display that the cathodic chitosan hydrogels dissolve thoroughly after immersing in either the buffer solution (pH 5.5) or the 0.1 M EDTA solution (pH 5.5), since it is formed by the neutralization mechanism and can redissolve under the acidic conditions. In comparison with the cathodic chitosan hydrogel, the chitosan/Cu^{2+} hydrogel has better stability under the acidic conditions since it is stable in the pH 5.5 buffer. On the other hand, the chitosan/Cu^{2+} hydrogel dissolves in the EDTA solution. It is well known that EDTA is a strong coordination agent that can form coordination with Cu^{2+} ions. Velev et al. have reported that Cu^{2+} ions can be removed from the ionoprinted regions of the hydrogel network when the hydrogel was immersed in EDTA solution.[31] Therefore, when incubating with EDTA solution, the Cu^{2+} ions in the chitosan/Cu^{2+} hydrogel can be removed from the hydrogel, subsequently the hydrogel lacking Cu^{2+} ions dissolves in pH 5.5 solution. Also, the above dissolution experiments support the formation mechanism of the chitosan/Cu^{2+} hydrogel.

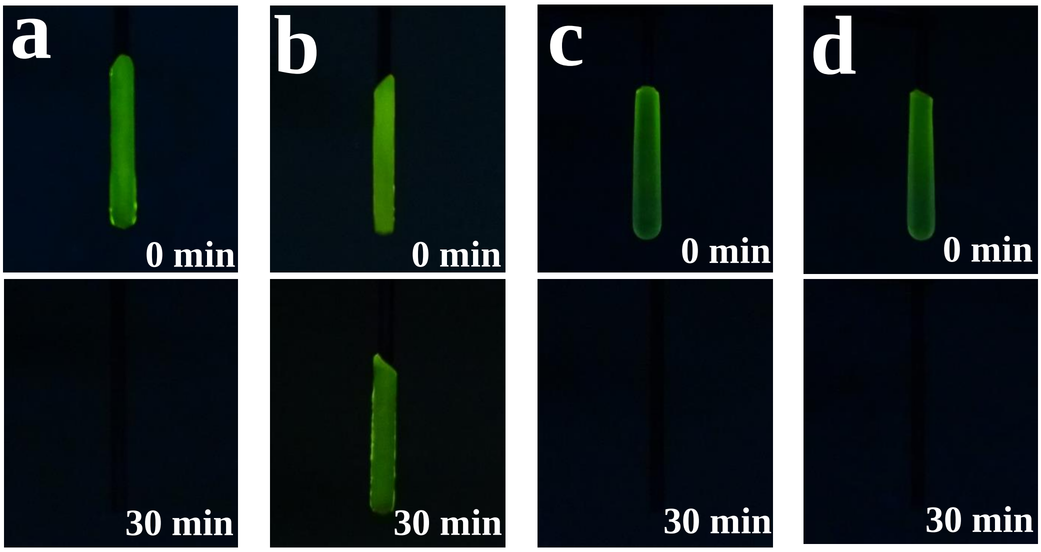

Fig. 3 (a) Fluorescent images of the chitosan/Cu^{2+} hydrogel (deposited on the copper wire) labeled by Rhodamine 6G before and after immersing in 0.1 M EDTA solution (pH 5.5). (b) Fluorescent images of the chitosan/Cu^{2+} hydrogel before and after immersing in buffer solution (pH 5.5). (c) Fluorescent images of the cathodic chitosan hydrogel before and after immersing in buffer solution (pH 5.5). (d) Fluorescent images of the cathodic chitosan hydrogel before and after immersing in 0.1 M EDTA solution (pH 5.5).

The SEM image in Fig. 4a further indicates that the surface of the chitosan/Cu^{2+} hydrogel is smooth and homogeneous. In Fig. 4b, the SEM image of the cross-section of the hydrogel shows that there is a clear border between the hydrogel and the electrode, and the thickness of the hydrogel (electrodeposition at 1.5 V for 2.5 min) is about 20 μm. In Fig. 4c, the results of the element analysis examined by EDS demonstrate that Cu exists in the hydrogel. Furthermore, the ICP/AES measurements determine that the content of Cu in the dried chitosan/Cu^{2+} hydrogel (electrodeposition at 1.5 V for 2.5 min) is about 7.0%. Consequently, the above evidences both support the proposed mechanism of the coordinated electrodeposition.

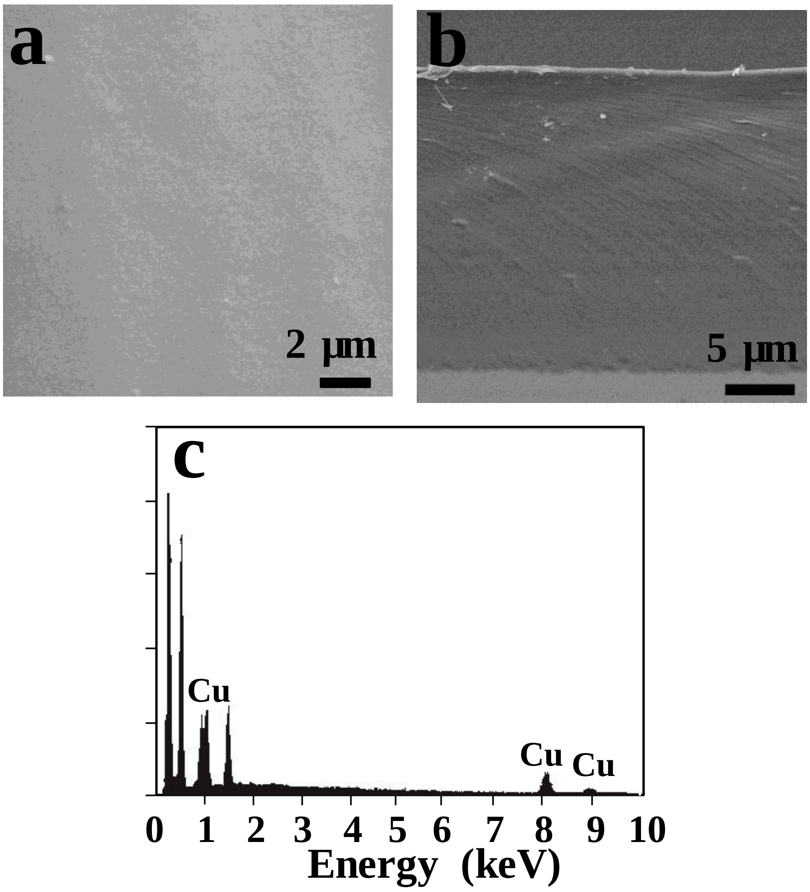

Fig. 4 (a) SEM image of the chitosan/Cu^{2+} hydrogel surface. (b) SEM image of the cross-section of the chitosan/Cu^{2+} hydrogel on the electrode. (c) EDS spectrum of the chitosan/Cu^{2+} hydrogel surface.

3.3 Fabrication of deposited hydrogel with different patterns and various shapes

Subsequently, we built various patterns of the chitosan/Cu^{2+} hydrogel on the electrodes by taking advantage of the coordinated electrodeposition. Figure 5a schematically illustrates the process for constructing patterns of the chitosan/Cu^{2+} hydrogel. In brief, we initially coated the alcohol-soluble ink on the desired region of the titanium plate as the protective coating, and electroplated copper on the uncoated region of the titanium plate in $CuSO_4$ solution, then dissolved the protective coating using ethanol, and finally performed the coordinated electrodeposition in the chitosan solution containing Rhodamine 6G. The fluorescent images in Fig. 5a displays that the patterns of the chitosan/Cu^{2+} hydrogels are only observed on the titanium plates at the regions with the electroplated copper, while no hydrogel appears at the regions without the electroplated copper. Moreover, we hierarchically assembled the hydrogel patterns containing two types of hydrogels on the titanium plates by first electrodepositing the chitosan/Cu^{2+} hydrogel at the localized region with the electroplated copper, and then electrodepositing the cathodic chitosan hydrogel, as shown in Fig. 5b. After achieving the patterns of two hydrogels, we make use of the dissolution difference of two types of hydrogels to hierarchically and selectively eliminate the hydrogel patterns. Specifically, the cathodic chitosan hydrogel disappears at first after the pattern has been immersed into the buffer solution (pH 5.5), whereas the pattern of the chitosan/Cu^{2+} hydrogel remains on the titanium plate, and then the pattern of chitosan/Cu^{2+} hydrogel disappears after it has been immersed in the EDTA solution (pH 5.5).

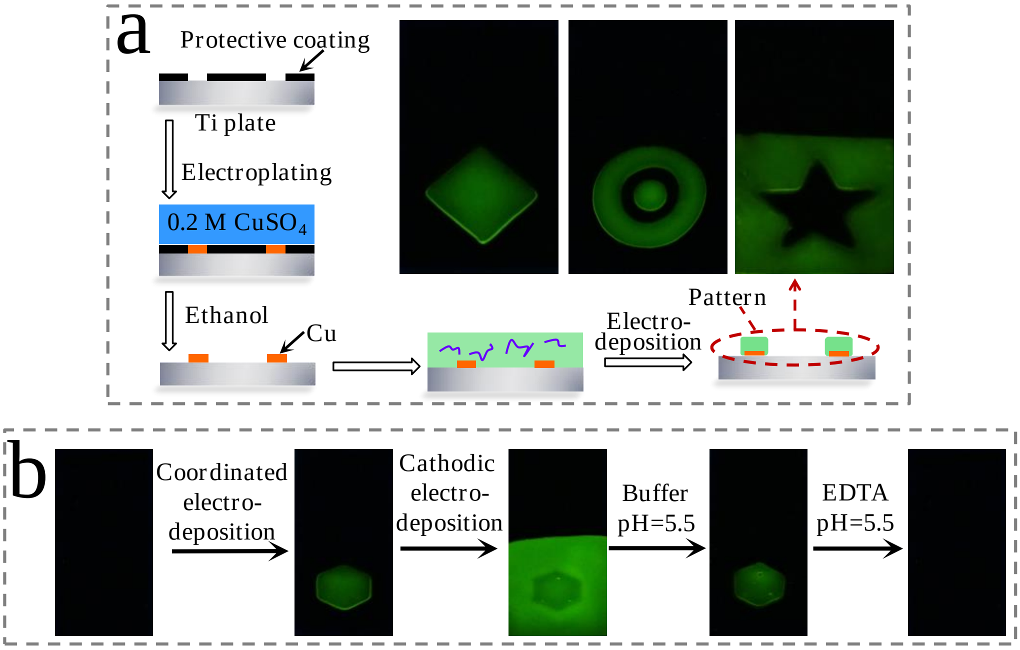

Fig. 5 (a) Fluorescent images of various patterns of the chitosan/Cu^{2+} hydrogel on the titanium (Ti) plates electroplated with copper, and schematic illustration of the patterning process. (b) Hierarchical assembly and elimination of the hydrogel patterns built by two types of hydrogels (the chitosan/Cu^{2+} hydrogel and the cathodic chitosan hydrogel).

Next, we produced the hydrogel films (peeled from the electrodes) and the hydrogel coatings (on the electrodes) with diverse shapes by employing the electrodes (copper plates or silver plates) with different shapes. It is worth mentioning that in our previous experiments the chitosan hydrogels prepared by the cathodic electrodeposition are always weak and difficult to be peeled from the electrodes for further applications. As shown in Fig. 6a, the chitosan/Cu^{2+} hydrogels with different shapes are smooth, homogeneous and transparent. Importantly, these hydrogels can be readily and completely peeled from the copper electrodes, which is extremely beneficial to their subsequent applications. In addition, Fig. 6b displays that the smooth and homogeneous coatings with different shapes can be produced on the silver plates by the coordinated electrodeposition. Moreover, the three-dimensional spring pattern, as well as the “WUT” logo pattern of the hydrogel can be conveniently created on the copper wires by employing the coordinated electrodeposition, as shown in Fig. 6c and 6d. Thus, this coordinated electrodeposition of chitosan provides a convenient, controllable and versatile means to build chitosan coatings and hydrogel films with various shapes, which have potential applications in metallic biomaterials and surface coatings.

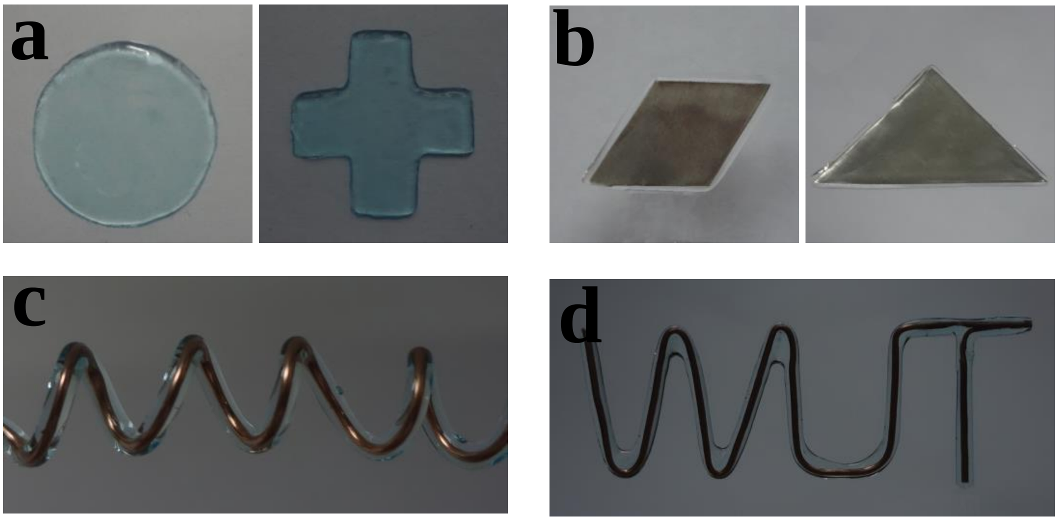

Fig. 6 (a) Photographs of the hydrogel films (peeled from the copper plates) with different shapes (left: circle; right: crisscross). (b) Photographs of the coatings (on the silver plates) with different shapes (left: rhombus; right: triangle). (c) Photograph of the three-dimensional spring pattern of the hydrogel on the copper wire. (d) Photograph of the “WUT” logo pattern of the hydrogel on the copper wire.

Carbon dots is a new type of fluorescent nanomaterial, which have drawn considerable attention due to their favorite properties such as high stability, multicolor fluorescence, non-toxicity, and biocompatibility.[32] Figure 7a schematically illustrates the process of the codeposition of carbon dots with chitosan based on coordinated electrodeposition. The photograph in Fig. 7b shows that the codeposited hydrogel on the copper plate is smooth, homogeneous and transparent. The fluorescent image of the codeposited hydrogel exhibits clear blue fluorescence under 365 nm UV light (Fig. 7c), which is consistent with the fluorescence of the original carbon dots, while the control hydrogel without codeposition of carbon dots displays no fluorescence under 365 nm UV light (Fig. 7d). These results suggest that the coordinated electrodeposition of chitosan can be employed to codeposit carbon dots, which offers a convenient means to build the fluorescent nanocomposite coatings on metallic biomaterials or biomedical devices.

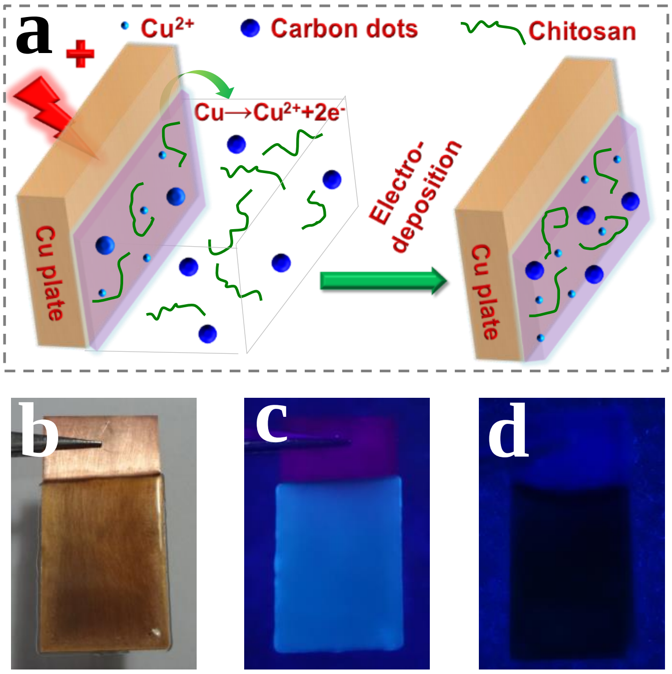

Fig. 7 (a) Schematic illustration of the codeposition of carbon dots with chitosan. (b) Photograph of the codeposited hydrogel on the copper plate. (c) Fluorescent image of the codeposited hydrogel under 365 nm UV light. (d) Fluorescent image of the control hydrogel without codeposition of carbon dots under 365 nm UV light.

3.4 Deposited hydrogel for electrochemical detection

Gu et al. have fabricated a hydrogen peroxide biosensor by using a DNA-Cu(II) complex as a elertrocatalyst for highly sensitive amperometric determination of hydrogen peroxide.[33] Cheng et al. have reported that the copper complex compounds fixing on electrodes display high selectivity to hydrogen peroxide reduction.[34] Interestingly, by enlisting the particular benefits of the coordinated electrodeposition we can straightforwardly build the chitosan/Cu^{2+} complex hydrogel on the electrode, which can be further conveniently used in electrochemical detection (*e.g.* detection of hydrogen peroxide).

As a proof-of-concept, we examined the electrochemical detection capabilities of the deposited chitosan/Cu^{2+} hydrogel for detecting H_2O_2. For this test, the chitosan/Cu^{2+} hydrogel was first deposited onto the electrode (titanium plate) through the coordinated electrodeposition, and then the hydrogel-coated titanium plate was immersed in the 0.1 M phosphate buffer solution (pH 7.4) and performed the electrochemical measurements using a three-electrode system as schematically illustrated in Fig. 8a. As shown in Fig. 8b, a peak current near -0.14 V appears in the CV curve of the chitosan/Cu^{2+} hydrogel system containing 10.0 mM H_2O_2, which is attributed to the electrochemical reaction of H_2O_2, while no such peak current is observed in the CV curve of the chitosan/Cu^{2+} hydrogel system in the absence of H_2O_2. In contrast, the CV curve of the bare electrode (titanium plate) shows no peak current either in the absence or presence of H_2O_2. These results suggest the potential capability of the chitosan/Cu^{2+} hydrogel for electrochemical detection of H_2O_2. Next, we use *i-t* measurements to examine the correlation between the current and the H_2O_2 concentration by sequentially adding H_2O_2 into the chitosan/Cu^{2+} hydrogel system to increase H_2O_2 concentration by 5.0 mM. In contrast, the *i-t* measurements of the control hydrogel (the cathodic chitosan hydrogel deposited on titanium plate) were also carried out at the same conditions. The upper *i*-*t* curve in Fig. 8b exhibits that a step change in current is observed after each addition of H_2O_2 in the chitosan/Cu^{2+} hydrogel system, indicating that there is a correlation between the current and the H_2O_2 concentration which provide potential application for H_2O_2 detection. However, the control hydrogel system shows almost no change in current after each addition of H_2O_2, suggesting no obvious correlation between the current and the H_2O_2 concentration. In Fig. 8d, the output currents display obvious response for adding H_2O_2 into the chitosan/Cu^{2+} hydrogel system, while the output currents show little change for adding NaCl, KCl and glucose into the system. These results suggest the anti-interference ability for the chitosan/Cu^{2+} hydrogel towards detecting H_2O_2. Consequently, the above results indicate that the coordinated electrodeposition method may provide a convenient and useful approach to generate electrochemical detectors and biosensors.

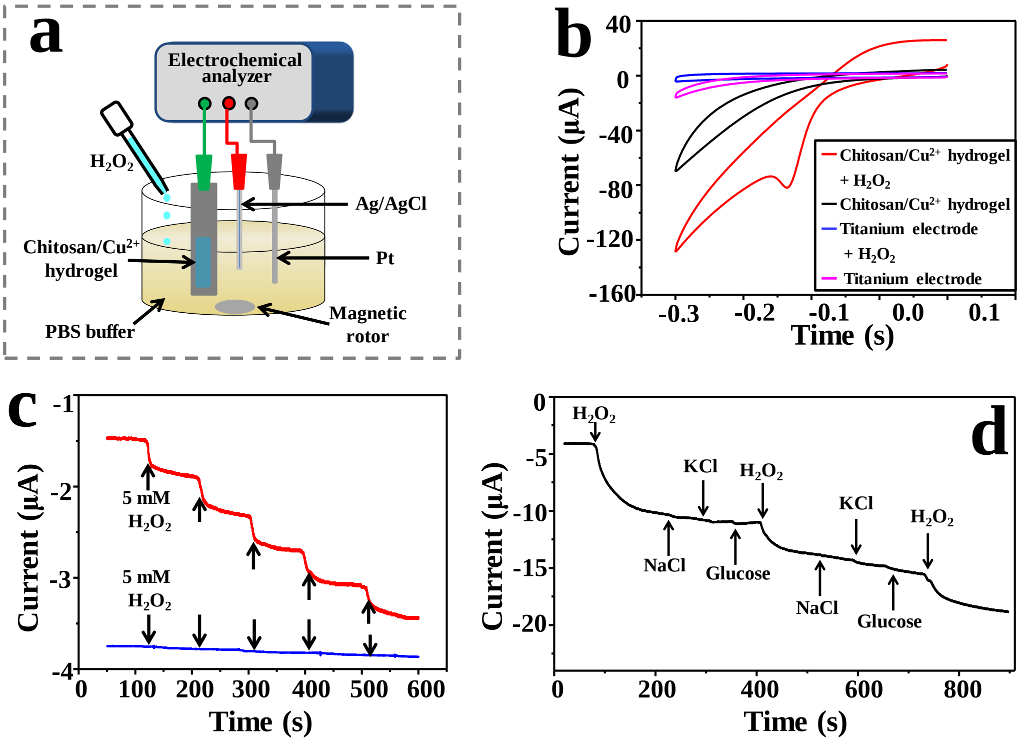

Fig. 8 (a) Schematic illustration of electrochemical measurements using a three-electrode system. (b) Cyclic voltammograms (CVs) for the chitosan/Cu^{2+} hydrogel-coated titanium plate and bare titanium plate in the absence or presence of 10.0 mM H_2O_2 (0.1 M phosphate buffer, pH 7.4). Scan rate 50 mV s^{-1}. (c) The *i-t* (current vs time) measurements for current steps upon sequential additions of 5.0 mM H_2O_2 to the system of the chitosan/Cu^{2+} hydrogel (the upper curve) and the control (cathodic chitosan hydrogel). The applied potential was -0.14 V (vs Ag/AgCl). (d) Current steps upon sequential additions of 5.0 mM H_2O_2, NaCl, KCl and glucose to the chitosan/Cu^{2+} hydrogel system. The applied potential was -0.14 V (vs Ag/AgCl).

4. Conclusions

Electrodeposition is an appealing method for initiating assembly of stimuli-responsive biopolymers in response to electrical signals with exquisite spatiotemporal control for broad applications. In this work, we present a novel electrodeposition method based on coordination of chitosan to the metal ions *in situ*-generated by the concurrent electrochemical oxidation. In particular, this coordinated electrodeposition method can be employed to produce the deposited hydrogel with smooth and homogeneous surface, better stability under acidic conditions, and adequate strength to be peeled from the electrode. Furthermore, a variety of the hydrogel patterns on the electrodes, as well as the coatings (on the electrodes) or the hydrogel films (peeled from the electrodes) with various shapes can be conveniently fabricated by taking advantage of the coordinated electrodeposition. In addition, this coordinated electrodeposition also enables fluorescent carbon dots to be codeposited with chitosan. Importantly, using the coordinated electrodeposition we can directly generate the complex hydrogel on the electrode for further electrochemical detection of H_2O_2. Consequently, this coordinated electrodeposition of chitosan provide attractive opportunities for a broad range of applications in biomedical device, surface coating and metallic biomaterial.

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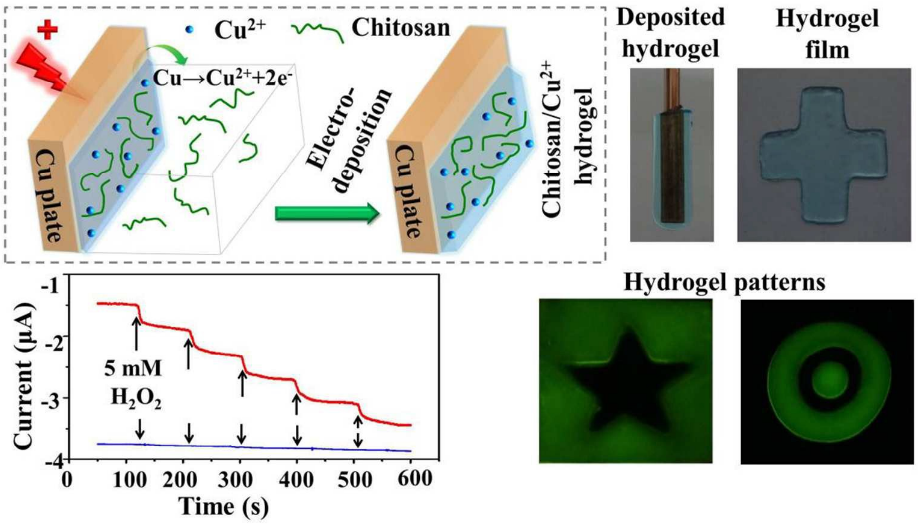
Graphical abstract



We report a new electrodeposition method of chitosan based on the coordination of chitosan to metal ions *in situ*-generated by the simultaneous electrochemical oxidation.