Electroaddressing of ZnS Quantum Dots by Codeposition with Chitosan to Construct Fluorescent and Patterned Device Surface

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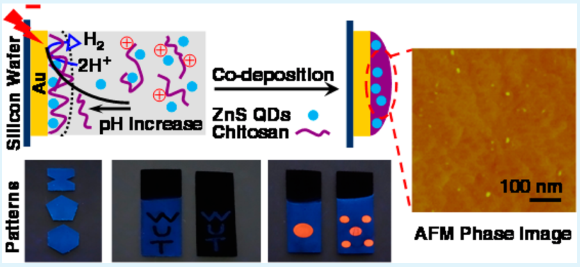

ABSTRACT: Electroaddressing is an attractive method for triggering assembly of stimuli-responsive biopolymers with exquisite spatiotemporal control, and it also offers a controllable means to concurrently assemble biological materials and nanoparticles for a diverse range of applications. Here, we demonstrate a novel method to construct fluorescent and patterned device surfaces by electroaddressing of quantum dots (QDs)/chitosan composite. First, the surfaces of ZnS QDs/chitosan composite on the electrodes are built by electrodeposition method. It is shown that the deposited surface displays clear fluorescence under UV light, and the fluorescence intensity of the surface can be controlled by electrodeposition conditions (e.g., deposition time). Furthermore, a variety of fluorescent patterns can be constructed by employing electrodes or substrates with various shapes. Specifically, taking advantage of the spatiotemporal selectivity of electroaddressing and the pH-responsive property of chitosan, we construct diverse fluorescent patterns by electroaddressing QDs/chitosan composite at the localized region. It is also found that the fluorescent patterns of QDs/chitosan composite have reproducibility. Thus, this work presents a convenient, versatile, and controllable method to construct fluorescent and patterned device surface by electroaddressing, which has promising applications in photoluminescence device, fluorescent and patterned coating, and nanocomposite biodevice.

KEYWORDS: *quantum dots, chitosan, electrodeposition, fluorescence, patterning, nanocomposite*

■ INTRODUCTION

Recently, researchers have confirmed that some stimuli-responsive polysaccharides could be enlisted to build the biodevice interface in response to device-imposed electrical stimuli, which can provide the convergent methods to couple biology with microelectronics.[1−3] Chitosan, a cationic amino-polysaccharide derived by deacetylation of naturally abundant chitin, displays many attractive properties, such as biocompatibility, biodegradability, and antibacterial bioactivity.[4−6] Specifically, owing to its pH-responsive film-forming properties, chitosan can be deposited as a stable film by employing electrical signals.[7,8] The method of electrically induced deposition of chitosan enables some biological materials (e.g., glucose oxidase and hemoglobin) to be codeposited within the chitosan films.[8,9] In addition to biological substances, it has been reported that nanoparticles (e.g., gold nanoparticles, silver nanoparticles, and carbon nanotubes) could be codeposited with chitosan.[10−12] Thus, the electrodeposition of chitosan is an attractive method for triggering assembly of biological materials and nanoparticles with precise spatial and temporal control, which deserves our further investigations on this aspect.

Quantum dots (QDs), also known as colloidal semiconductor nanocrystals, exhibit promising applications in many fields, including the preparation of fluorescence patterns,[13,14] biological detection and imaging,[15−17] and biosensors.[18] However, commonly used QDs (e.g., CdS, and CdSe) exhibit heavy-metal toxicity, which may confine their applications in biomedical field.[19,20] For this reason, efforts have been devoted toward the preparation of nontoxic QDs (e.g., ZnS QDs).[21−23] It has been confirmed by cytotoxicity tests that the nontoxicity of aqueous ZnS QDs is beneficial to the applications of in vivo imaging.[24]

Currently, only a few studies have been devoted to electrodeposition of QDs and chitosan. Sharma et al. have found that the electrodeposited chitosan/CdTe QDs could be used as a biosensor for leukemia detection.[25] Lian and coworkers have reported a molecularly imprinted chitosan/CdS QDs film prepared by the electrodepositon method for electrochemical sensor of urea.[26] Yang et al. have introduced an electrochemiluminescence aptamer biosensor constructed by electrodepositing chitosan/CdS QDs on aligned carbon nanotubes electrode.[27] It is noteworthy that above-mentioned studies on electrodeposition of QDs with chitosan have been concentrated on building biosensors. However, no research has been dedicated to the fluorescent properties and the patterning of QDs/chitosan composite on the surface. Besides, little attention has been paid to the electrodeposition of QDs/chitosan composite on various electrodes or substrates. Also, only toxic heavy-metal QDs have been used in the above studies, whereas nontoxic QDs have not been considered.

Here, we report a new method to construct fluorescent and patterned surfaces by electroaddressing of QDs/chitosan

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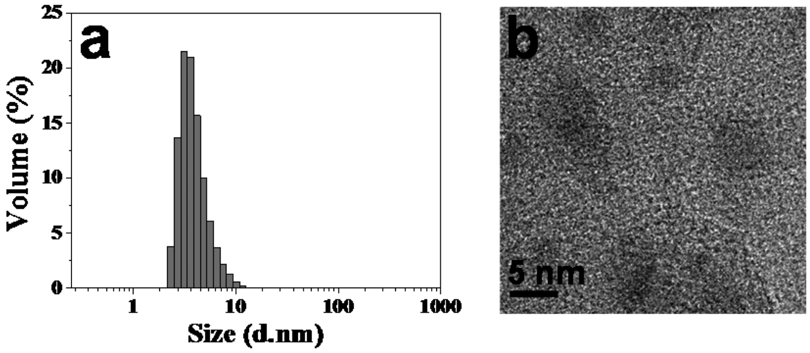


Figure 1. Size distribution of the aqueous ZnS QDs measured by DLS (a), and TEM image of the aqueous ZnS QDs (b).

composite. This method allows QDs to be assembled onto the localized region of electrodes or substrates in response to imposed electrical signals with exquisite spatial and temporal control. On the basis of this method, we can electroaddress QDs on a variety of electrodes and substrates and also fabricate the fluorescent nanocomposite coatings on metallic biomaterials or devices. Specifically, it provides a convenient, versatile, and controllable means to construct diverse fluorescent patterns on different surfaces with complicated shapes. Moreover, the electrodeposited film of organic−inorganic nanocomposite retains the pH-responsive film-forming properties of chitosan and the fluorescent property of QDs, which is particularly beneficial to construct diverse fluorescent patterns. Also, the nontoxic aqueous ZnS QDs have been used in this work, which is advantageous to its further applications in biotechnology. We expect this method may provide attractive opportunities for applications in photoluminescence and fluorescence device, nanocomposite biodevice, and patterned coating.

■ EXPERIMENTAL SECTION

Chemicals and Materials. Chitosan (90% deacetylation degree), $Zn(NO_3)_2 \cdot 6H_2O$, $Na_2S \cdot 9H_2O$, and 3-mercaptopropionic acid were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Gold-coated silicon wafer (gold electrode), silver foil, titanium alloy plate, 316L stainless steel plate, and platinum foil were purchased from commercial resources in China. All chemicals were analytical grade and were used without further purification.

Synthesis of Aqueous ZnS QDs. The aqueous ZnS QDs were prepared by following the method reported by Li and co-workers.[21] Briefly, $Zn(NO_3)_2$ was added to the distilled water containing 3-mercaptopropionic acid with stirring. The pH of the mixture was adjusted to 12 by dropping tetrapropylammonium hydroxide with continuous stirring. Then, Na_2S solution was added quickly with vigorous stirring. The above solution was heated to 90 °C and reacted for 2 h to obtain the aqueous ZnS QDs with clear blue fluorescence under 302 nm UV light.

Electrodeposition of ZnS QDs and Chitosan. Chitosan solution was prepared by dropping 1.0 M HCl to dissolve the chitosan powder, adjusting pH to 5.2 with 1.0 M NaOH, and then filtering to remove the undissolved particles. The mixture of chitosan solution and aqueous ZnS QDs were prepared by adding appropriate amount of aqueous ZnS QDs into the chitosan solution with stirring. The final mixtures for codeposition contained 1% chitosan and ZnS QDs with different concentrations (0.16 mM, 0.32 mM, and 0.80 mM). For electrodeposition, a platinum foil was used as anode, and different kinds of electrodes or substrates (e.g., gold electrode, silver foil, titanium alloy plate, and 316L stainless steel plate) were served as cathode, respectively. Before use, the gold electrodes were cleaned by submerging into piranha solution (7:3 concentrated H_2SO_4/30% H_2O_2) for 2 min and then rinsed with distilled water. Titanium alloy plates, 316L stainless steel plates, and silver foils were carefully polished before use, and then ultrasonically washed in acetone, ethanol, and distilled water for 5 min, respectively. Electrodeposition was performed using a programmable DC power supply (IT6123, TW). Both cathode and anode were partially immersed in the codeposition mixture, and a DC voltage of 2.0 V was applied. At a specific time (e.g., 150 s), the cathode was disconnected from the power supply, removed from the codeposition mixture, carefully rinsed with distilled water, and then dried at room temperature.

Electroaddressing and Patterning of QDs and Chitosan. To construct fluorescent patterns on the electrodes or substrates, we took advantage of the spatiotemporal selectivity of electroaddressing and the pH-responsive property of chitosan. First, we prepared the fluorescent patterns by employing the electrodes with various shapes. In brief, the electrodes were cut into desired shapes, carefully polished, and ultrasonically washed before use, and then electrodeposited in the codeposition mixture to obtain the patterns with various shapes.

Furthermore, we fabricated the fluorescent patterns by using the polyurethane dissolved in dimethylformamide (DMF) as the coating material. For this method, the electrodes were coated with polyurethane coating at the localized region at first and then electrodeposited in the codeposition mixture. After electrodeposition, the electrodes were immersed in DMF to dissolve the polyurethane coating and dried at room temperature. Finally, the fluorescent patterns on the electrodes were observed under 302 nm UV light.

Additionally, we fabricated the fluorescent patterns by enlisting the alcohol-soluble ink, which is mainly composed of resin (polyvinyl butyral) and solvent (ethanol) as the coating material. For this method, the electrodes were first coated with alcohol-soluble ink at the localized region, and then electrodeposited in the codeposition mixture. Next, the electrodes were washed off the coating with alcohol after electrodeposition and finally observed under 302 nm UV light after drying. Alternatively, the electrodes were electrodeposited in the codeposition mixture at first and coated with alcohol-soluble ink at the localized region after electrodeposition. Next, the electrodes were immersed in 0.1 M HCl to dissolve the region without the coating, then immersed in alcohol to dissolve the coating, and finally observed under 302 nm UV light after drying.

Characterization. The obtained ZnS QDs was dropped on the surface of a TEM grid, and then examined with a high-resolution transmission electron microscopy (HRTEM, JEM-2100F STEM/EDS, JP) after drying. The average size and size distribution of ZnS QDs were examined with a dynamic light scattering spectroscopy (DLS, Malvern Instruments, U.K.). Fluorescence of the samples was observed using a 302 nm UV lamp or a fluorescence microscope (Olympus IX71, JP). The surface morphology of the sample was investigated with atomic force microscopy (AFM, DI Nanoscope IV, U.S.A.) in tapping mode.

■ RESULTS AND DISCUSSION

Preparation of Aqueous ZnS QDs. To begin with, we prepared the aqueous ZnS QDs using an aqueous one-step method. Figure 1a shows that the size distribution of ZnS QDs

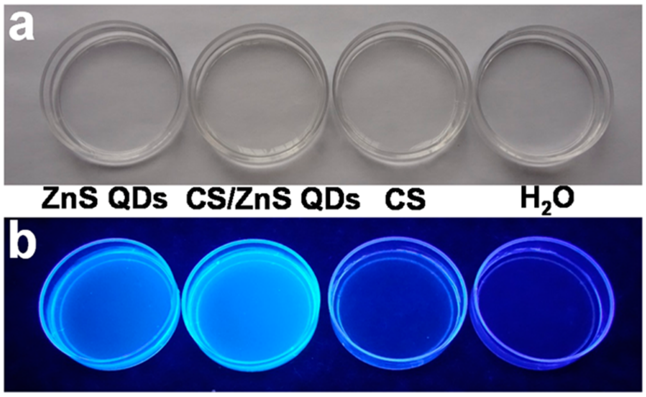


Figure 2. Photographs of aqueous ZnS QDs, mixture of chitosan solution and aqueous ZnS QDs (CS/ZnS QDs), chitosan solution (CS), and water under visible light (a), and under 302 nm UV light (b).

is monodispersed, and the average size of ZnS QDs is about 4.0 nm. A TEM image of ZnS QDs (Figure 1b) also indicates that ZnS QDs disperse well, and the size of QDs presents an average value of 4.0 nm, which is accordant with the result measured by DLS.

Images of different samples under visible light and 302 nm UV light are shown in Figure 2. All samples are colorless and transparent under visible light, and no visible difference in appearance is observed (Figure 2a). However, compared with chitosan solution and water, the aqueous ZnS QDs and CS/ZnS QDs display clear blue fluorescence under UV light (Figure 2b). These results indicate that we have prepared the aqueous ZnS QDs with clear fluorescence. Also, the mixture of ZnS QDs and chitosan remains transparent and displays clear fluorescence.

Electrodeposition of ZnS QDs and Chitosan. Scheme 1 illustrates the process of electrodeposition of ZnS QDs and chitosan. The gold electrode was partially immersed in the mixture of ZnS QDs and chitosan, and then applied a negative voltage. It is known that cathodic reactions ($H_2O \rightarrow H^+ + OH^-$; $2H^+ + 2e^- \rightarrow H_2$) result in the net consumption of H^+ (or production of OH^-) and the generation of a localized pH gradient adjacent to the cathode surface.[8,28,29] Chitosan chains close to the cathode surface can respond to the localized region of high pH and deposit as a stable film.[1] At the same time, ZnS QDs can be codeposited with chitosan and reserved in the electrodeposited film.

Figure 3 exhibits the photographs of electrodeposited gold electrodes under visible light and UV light. The chitosan-deposited electrode and no deposition electrode serve as the controls. As shown in Figure 3a, the codeposited electrode has no difference with the controls under visible light. However, Figure 3b shows that the codeposited electrode displays clear blue fluorescence under UV light, which is consistent with the fluorescence of ZnS QDs, whereas both controls show almost no fluorescence. Thus, these results indicate that ZnS QDs can be codeposited with chitosan and maintain the fluorescence after electrodeposition.

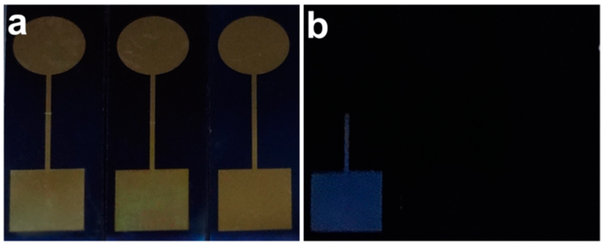


Figure 3. Photographs of electrodeposited gold electrode under visible light (a), and under 302 nm UV light (b). From left to right: electrodeposition of ZnS QDs and chitosan (2.0 V, 150 s), electrodeposition of chitosan without ZnS QDs (2.0 V, 150 s), and no deposition.

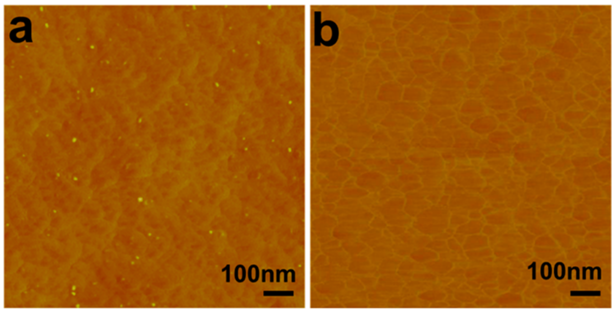


Figure 4. AFM phase images of the codeposited film (a) and the control chitosan film (b) on gold electrode (2.0 V, 150 s).

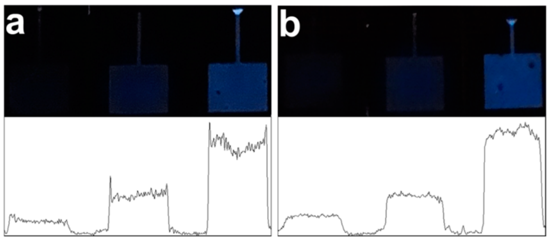
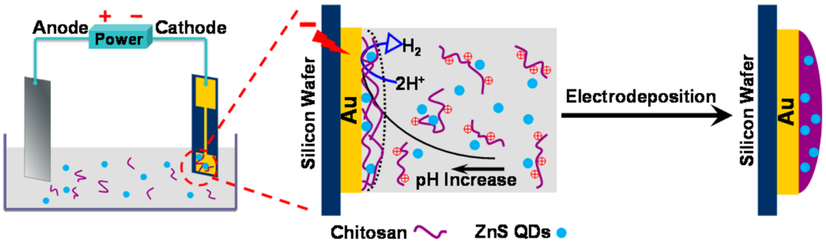


Figure 5. (a) Fluorescence images of the codeposited gold electrodes with different deposition times (from left to right: 20, 60, and 240 s) and analysis of fluorescence profiles by ImageJ software. (b) Fluorescence images of the codeposited gold electrodes with different ZnS QDs concentrations (from left to right: 0.16 mM, 0.32 mM, and 0.80 mM) and analysis of fluorescence profiles by ImageJ software.

Scheme 1. Illustration of Electrodeposition of ZnS QDs and Chitosan on Gold Electrode



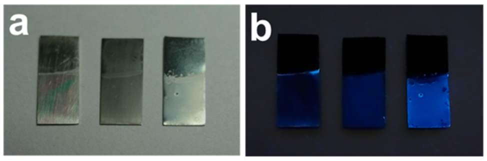


Figure 6. Photographs of the codeposited films on different kinds of substrates (from left to right: silver foil, titanium alloy plate, and 316L stainless steel plate) under visible light (a) and under 302 nm UV light (b).

Figure 4 shows the AFM phase images of the films after electrodeposition on the gold electrodes. It is known that AFM phase image is sensitive to material surface properties (e.g., stiffness, chemical composition, and viscoelasticity).[30] Thus, the large differences in surface properties of chitosan and ZnS QDs will result in a significant contrast in the AFM phase image. As shown in Figure 4a, there are some relatively bright spots in the AFM phase image of ZnS QDs/chitosan codeposited film. In contrast, no such spot is observed in the AFM phase image of the control chitosan film (Figure 4b). Therefore, these relatively bright spots in the AFM phase image are ZnS QDs, while the continuous dark domain is chitosan. These results suggest that ZnS QDs exist in the deposited film and disperse well after codeposition.

We studied the effects of electrodeposition conditions on fluorescence property of the codeposited surface, as shown in Figure 5. The image at the top in Figure 5a shows that fluorescence intensity of the surface enhances with the increase of deposition time. The fluorescence profiles that were analyzed by ImageJ software further support this result (at the bottom in Figure 5a). Further, we found that fluorescence intensity of the surface enhances with the increase of ZnS QDs concentration (Figure 5b). The above results indicate that fluorescence intensity of the codeposited surface can be changed by deposition time and concentration of ZnS QDs. Therefore, we can conveniently control the fluorescence intensity of the surface by adjusting the electrodeposition conditions.

Electroaddressing and Patterning of QDs/Chitosan Composite. In addition to gold electrode, we attempt to electrodeposit ZnS QDs/chitosan composite onto different kinds of electrodes or substrates. Figure 6a shows that the film has been generated on each substrate after electrodeposition. Moreover, the electrodeposited films all display blue fluorescence under UV light, as shown in Figure 6b. These results indicate that ZnS QDs can be codeposited on diverse substrates and retain the fluorescence, which provides a convenient and controllable means to build the fluorescent surfaces by electroaddressing of QDs. It should be noted that titanium alloy, 316L stainless steel, and silver are extensively used as metallic biomaterials. Thus, codeposition of QDs and chitosan can construct a fluorescent nanocomposite coating on metallic biomaterial or device with potential applications in biomedical field.

Figure 7 shows the fluorescent patterns of QDs/chitosan composite on titanium alloy plates prepared by different method. Figure 7a indicates that the fluorescent patterns can be generated by employing the electrodes with various shapes, indicating that electroaddressing of QDs and chitosan can provide a simple and versatile means to build the patterned device surfaces with complicated shapes. Figure 7b exhibits the fluorescent patterns prepared by using a polyurethane coating. These patterns were obtained by coating polyurethane at the localized region of the electrodes at first, and electrodepositing

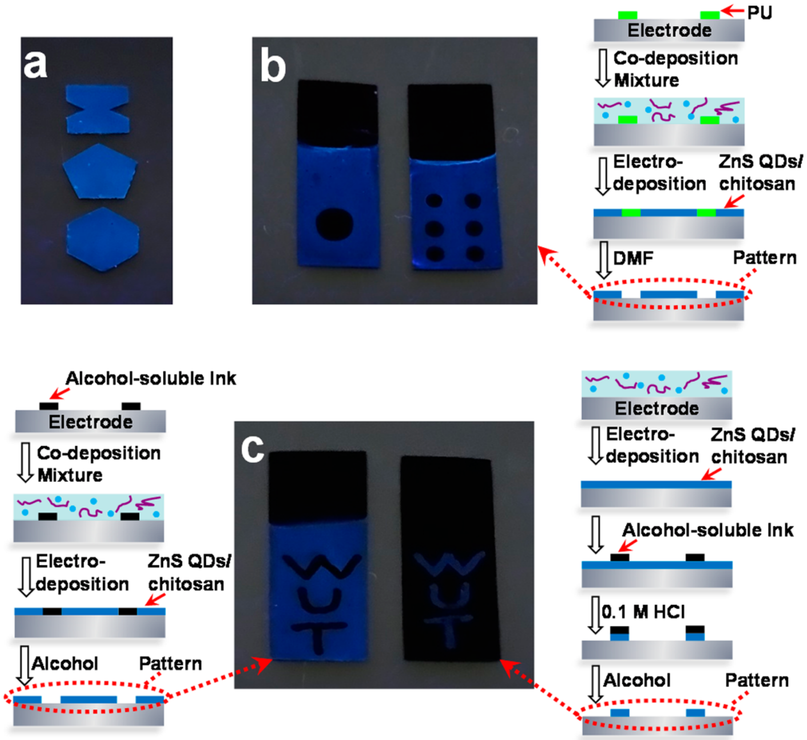


Figure 7. Fluorescent patterns of QDs/chitosan composite on titanium alloy plates. (a) Fluorescent patterns prepared by employing electrodes with various shapes. (b) Fluorescent patterns prepared with a polyurethane (PU) coating. (c) Fluorescent patterns prepared by using a coating of alcohol-soluble ink.

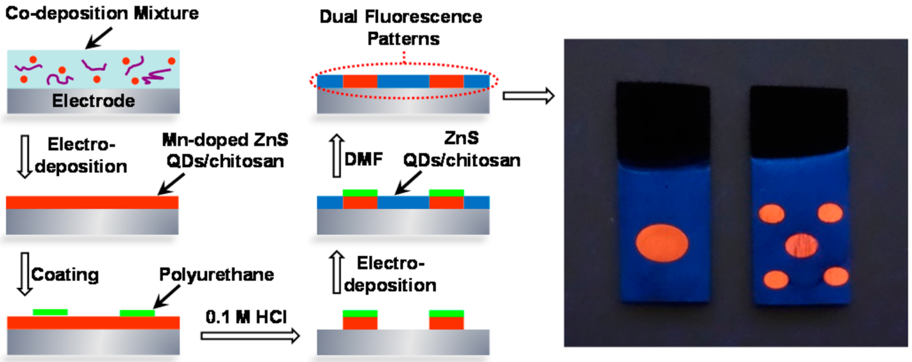


Figure 8. Dual fluorescence patterns prepared by enlisting ZnS QDs and Mn-doped ZnS QDs.

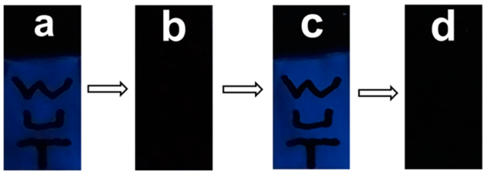


Figure 9. Photographs for reproducibility of the fluorescent pattern on titanium alloy plate. (a) Fluorescent pattern appears after electrodeposition. (b) Fluorescent pattern disappears after the electrode was immersed in 0.1 M HCl. (c) Fluorescent pattern appears again after second electrodeposition. (d) Fluorescent pattern disappears again after the electrode was immersed in 0.1 M HCl.

in the codeposition mixture, then immersing the electrodes in DMF to dissolve the polyurethane after electrodeposition. The fluorescent patterns in Figure 7c were prepared by using a coating of alcohol-soluble ink. The left pattern (a fluorescent logo of "WUT") in Figure 7c was achieved by coating alcohol-soluble ink at first, and electrodepositing in the codeposition mixture, then dissolving the coating with alcohol after electrodeposition. The right electrode in Figure 7c was first electrodeposited in the codeposition mixture, coated with alcohol-soluble ink after electrodeposition, then immersed in 0.1 M HCl to dissolve the region without the coating, and finally dissolved the coating with alcohol to obtain a fluorescent logo of "WUT" on the electrode.

Furthermore, we prepared the dual fluorescence patterns by enlisting ZnS QDs (blue fluorescence under 302 nm UV light) and Mn-doped ZnS QDs (red fluorescence under 302 nm UV light), as shown in Figure 8. First, the electrodes were electrodeposited with Mn-doped ZnS QDs and chitosan, followed by coating with polyurethane after deposition, and then immersed in 0.1 M HCl to dissolve the region without the coating. Second, the above electrodes were electrodeposited with ZnS QDs and chitosan, then immersed in DMF to wash off polyurethane coating, and finally dried to obtain the dual fluorescence patterns (at the right in Figure 8).

Besides, we investigated the reproducibility of the fluorescent pattern of ZnS QDs/chitosan composite, as shown in Figure 9. Figure 9a indicates that the electrode displays a blue fluorescent pattern after electrodeposition. This fluorescent pattern disappears after the electrode was immersed in 0.1 M HCl (Figure 9b). However, the fluorescent pattern emerges again after second electrodeposition (Figure 9c), and it disappears again after the electrode was immersed in 0.1 M HCl (Figure 9d). The results suggest that the fluorescent pattern of ZnS QDs/chitosan composite has reproducibility, which may expand its applications in technological fields.

CONCLUSIONS

We demonstrate a novel method to construct fluorescent and patterned device surfaces by electroaddressing of QDs/chitosan composite. It is shown that ZnS QDs can be codeposited with chitosan, and the deposited surface displays clear blue fluorescence under 302 nm UV light. Fluorescence intensity of the surface can be controlled by deposition conditions such as deposition time and concentration of ZnS QDs. Specifically, diverse fluorescent patterns can be constructed by electroaddressing QDs/chitosan composite at the localized region, or by employing electrodes with various shapes. It has also been found that the fluorescent patterns of QDs/chitosan composite have reproducibility. We anticipate that this convenient, versatile and controllable method for electroaddressing of QDs may have broad applications for photoluminescence devices, fluorescent and patterned coating, and nanocomposite biodevices.

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Notes

The authors declare no competing financial interest.

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