Journal of Materials Chemistry B

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsB

Electrodeposition of carbon dots/chitosan composite produced by a simple *in situ* method and electrically controlled release of carbon dots

Yifeng Wang,*[a] Xia Wang,[a] Zenghua Geng,[a] Yanfei Xiong,[b] Wencheng Wu[a] and Yanjun Chen*[a]

[a] *School of Material Science and Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China*

[b] *Department of Biological Science and Technology, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China*

**Corresponding author at: School of Material Science and Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China*

E-mail addresses: yifengwang@whut.edu.cn; yanjunchen@whut.edu.cn

Fax: +86 2787651779

Abstract

Carbon dots (CDs), a new type of fluorescent nanomaterial, have drawn considerable attention due to their attractive applications in biolabeling, bioimaging and fluorescent probes. Here, a CDs/chitosan composite that can be straightforward used for further electrodeposition and electrically controlled release of CDs, was produced by a simple and novel *in situ* method based on one-step microwave treatment of chitosan solution. We choose the chitosan solution as the only reactant for producing the CDs/chitosan composite, because chitosan can not only be served as the precursor for preparing CDs, but also be frequently used for electrodeposition. Importantly, the prepared CDs/chitosan composite is not only endowed with the multicolor fluorescence features coming from CDs, but also reserves pH-responsive film-forming properties of chitosan. On the basis of these favorable properties, we can straightforward employ the CDs/chitosan composite to construct fluorescent coatings, as well as a variety of multicolor-fluorescent patterns on different electrodes or substrates through electrodeposition technique. More interestingly, the release of CDs in the electrodeposited coatings or patterns can be controlled by electrical signals. Consequently, this CDs/chitosan composite with straightforward applications in electrodeposition and electrically controlled release of CDs has promising uses in photoluminescent coatings, fluorescent patterns, fluorescent labeling, and controlled release.

Keywords: Carbon dots, Chitosan, Electrodeposition, Controlled release, *In situ* method

1. Introduction

Fluorescent carbon dots (CDs), a new type of carbon nanomaterial first prepared in 2004,[1] are attracting more and more attention nowadays because of their potential applications in cell labeling, bioimaging, drug carriers, fluorescent probes, and catalysts.[2-4] It is worth mentioning that CDs exhibit appealing properties such as highly stable and multicolor fluorescence, non-toxicity, and biocompatibility.[5, 6] To date, a variety of approaches have been developed to prepare CDs, including ultrasonic treatment, laser irradiation, pyrolysis and so forth.[6-8] Particularly, microwave synthesis method has attracted growing attention owing to its special advantages, such as simple and "green" process, low cost, and high efficiency.[9, 10]

Chitosan, an amino-polysaccharide derived by deacetylation of naturally abundant chitin, exhibits a number of favorable properties such as biocompatibility, biodegradability, non-toxicity and antimicrobial activity, so it has been widely used in biomedical fields.[11-14] Chitosan has film-forming properties, which provides chitosan with broad applications including wound healing and biosensors.[15, 16] Moreover, chitosan has pH-responsive properties, and it can dissolve at low pH but turns insoluble at high pH. The soluble-to-insoluble transition of chitosan occurs in the pH range of 6 to 7, which offers attractive opportunities for biological applications.[17] On the basis of its pH-responsive and film-forming properties, chitosan is able to electrodeposit on diverse surfaces of electrodes or conductive substrates to form coatings or patterns with precise spatial and temporal control, which allows a range of uses in surface patterns, energy storage materials and biosensors.[18-20] The electrodeposition of chitosan enables some biological materials (*e.g.*, glucose oxidase and hemoglobin) or nanoparticles (*e.g.*, silver nanoparticles and carbon nanotubes) to be codeposited with chitosan.[21-24] More interestingly, Shi et al. have reported that the release of antibiotics codeposited with chitosan on the titanium plate is controlled by an anodic signal imposed to the titanium plate.[25]

It should be noted that chitosan can be used as the precursor or source for preparing CDs. Chowdhury et al. have demonstrated a simple strategy to prepare fluorescent CDs from chitosan gel.[26] Xiao and co-workers have reported a microwave-assisted approach to fabricate carbon nitride dots with fluorescence quantum yield of 6.4% from chitosan.[27] On the other hand, several studies have been devoted to the composite materials of CDs and chitosan. Tan et al. have employed chitosan as a type of passivation ligand to enhance the fluorescence quantum yields of CDs.[28] Huang et al. have developed a sensitive and reliable dopamine biosensor based on carbon dots and chitosan composite film.[29] As mentioned above, although several researchers have reported on preparing CDs by using chitosan as the precursor, they have not paid attention to CDs and chitosan composite as well as their combined properties for further applications (*e.g.*, electrodeposition). Besides, only a few studies have been published on the CDs/chitosan composites that are generated by blending method. However, no research has been dedicated to construct a CDs/chitosan composite using one-step *in situ* method. More importantly, no work has been done on electrodeposition and electrically controlled release of carbon dots.

In this work, we produce a CDs/chitosan composite that can be straightforward used for further electrodeposition and electrically controlled release of CDs using a simple and novel *in situ* method based on one-step microwave treatment of chitosan solution. Compared with other traditional methods, chitosan aqueous solution is chosen as the only reactant for producing the CDs/chitosan composite, since chitosan can not only be served as the precursor for preparing CDs and surface passivation agent of carbon dots, but also be usually used for electrodeposition. Importantly, the obtained CDs/chitosan composite not only has attractive properties (*e.g.*, multicolor fluorescence) that belong to CDs, but also retains the favorable properties (*e.g.*, pH-responsive and film-forming properties) of chitosan. Furthermore, this work has mainly investigated further applications of the CDs/chitosan composite in electrodeposition and electrically controlled release of carbon dots. Taking advantage of the combined properties, the CDs/chitosan composite can be straightforward used for constructing multicolor-fluorescent coatings, as well as various fluorescent patterns on different electrodes or substrates through electrodeposition technique. More interestingly, the CDs electrodeposited on the electrodes or substrates can be released under the control of the electrical signals. We anticipate that this CDs/chitosan composite may have promising applications in photoluminescent coatings and patterns, fluorescent labeling, and controlled release.

2. Experimental section

2.1 Chemicals and materials

Chitosan (90% deacetylation degree), quinine sulfate, H_2O_2 were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Gold-coated silicon wafer (gold electrode), 316L stainless steel plate, titanium (Ti) plate and platinum (Pt) foil were purchased from commercial resources in China. All chemicals were analytical grade and without further purification before use.

2.2 Preparation of CDs/chitosan composite

The CDs/chitosan composite was prepared by an *in situ* method based on one-step microwave treatment of chitosan solution. After a number of comparison experiments, the suitable amount of reactants and the reasonable reaction conditions were used in the following preparation procedure. First, chitosan solution (3% w/v) was prepared by dispersing 3.0 g chitosan powder in 100 mL distilled water, dropping 1.0 M HCl to dissolve the chitosan under stirring, and adjusting pH to 5.3 with 1.0 M NaOH. Subsequently, 20 mL chitosan solution was heated in a domestic microwave oven (700 W, Midea EG7KCW3-NA, China), reacted for a specific time (*e.g.*, 250 s), and then cooled to room temperature. Finally, the CDs/chitosan composite was obtained by adding 40 mL distilled water to the microwave products with vigorous stirring, and centrifuging at 10000 rpm for 10 min to remove the deposit.

The CDs/chitosan composite films were produced by casting method as follows. Initially, the CDs/chitosan composite was cast into a clean plastic dish, and then removed the bubbles by ultrasonic treatment for 10 min, finally dried at 40°C for 24 h. The obtained CDs/chitosan composite films displayed clear blue fluorescence under 365 nm UV light.

2.3 Electrodeposition of CDs/chitosan composite

The electrodeposition mixture was prepared by adjusting the pH of CDs/chitosan composite to 5.5, and then adding H_2O_2 (2% v/v) under stirring. For electrodeposition, a Pt foil was served as anode, and different electrodes or conductive substrates (*e.g.*, gold electrode, 316L stainless steel plate or Ti plate) were used as cathode respectively. Prior to use, the gold electrodes were washed with piranha solution (7:3 concentrated H_2SO_4:30% H_2O_2) for 2 min, and then rinsed with distilled water. 316L stainless steel plates and Ti plates were carefully polished, 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 the cathode and the anode were partially-immersed in the electrodeposition mixture, and a current of 4.0 A/m^2 was applied. After specific time (*e.g.*, 120 s), the cathode was disconnected with the power supply, and removed from the electrodeposition mixture, then carefully washed with distilled water and finally dried at room temperature.

To fabricate fluorescent patterns of CDs/chitosan composite on the electrodes or substrates, we made use of the fluorescent features of carbon dots, and the spatial selectivity of electrodeposition technique. First, we obtained the fluorescent patterns by using the electrodes or substrates with different shapes. In short, the electrodes or substrates were cut into desired shapes, carefully polished and ultrasonically washed before use, then immersed and electrodeposited in the electrodeposition mixture to obtain the fluorescent patterns of CDs/chitosan composite with different shapes, and finally observed by fluorescence microscope.

Furthermore, we constructed the fluorescent patterns of CDs/chitosan composite by enlisting gelatin dissolved in distilled water as the coating material. The electrodes were first coated with the gelatin solution at the desired region, and promptly put into 4^{o}C refrigerator for 10 min to obtain the gelatin gel on the surfaces, then electrodeposited in the electrodeposition mixture. After electrodeposition, the electrodes were carefully washed in 45^{o}C distilled water to remove the gelatin, and dried at room temperature. Finally, the fluorescent patterns of CDs/chitosan composite on the electrodes were observed under 365 nm UV light.

2.4 Electrically controlled release of CDs

For this experiment, the electrode (*e.g.*, Ti plate) electrodeposited with CDs/chitosan composite was served as anode, and a platinum foil was used as cathode. Both the cathode and the anode were immersed in NaCl solution (0.9%, w/v), and a DC voltage (5.0 V) was applied. After specific time (*e.g.*, 90 min), the anode was disconnected with the DC power supply, and removed from the NaCl solution, then washed with distilled water and finally observed under 365 nm UV light. Besides, the final NaCl solution was measured by UV-vis spectrophotometer. On the other hand, the control electrode (electrodeposited with CDs/chitosan composite) was immersed in NaCl solution (0.9%, w/v) without applying DC voltage. After specific time, the control electrode and the NaCl solution were also examined using the same method. In addition, the electrically controlled release of CDs from the electrodeposited patterns was observed by above method.

2.5 Characterization

The CDs/chitosan composite was dropped on the surface of a TEM grid, and examined with a high-resolution transmission electron microscopy (HRTEM, JEM-2100F STEM/EDS, JP) after drying. Fluorescence of the sample was observed using a 365 nm UV lamp or a fluorescence microscope. UV-vis absorption spectra of the samples were performed with UV-vis spectrophotometer (UV-2550, SHIMADZU, JP). The photoluminescence spectra of the samples were examined using spectrofluorometer (RF-5301PC, SHIMADZU, JP).

3. Results and discussion

3.1 Preparation of CDs/chitosan composite

Figure 1a illustrates the preparation process of the CDs/chitosan composite through a simple *in situ* method based on one-step microwave treatment of chitosan aqueous solution. This method has many benefits such as easy operation, environment-friendly process, no need of organic solvent, and simplified post-treatment. Initially, the chitosan solution (3% w/v) is heated in a microwave oven and reacted for a desired time (*e.g.*, 250 s) to obtain the microwave products with brown color. Next, the microwave products are dispersed in distilled water and then centrifuged to obtain the CDs/chitosan composite. In contrast, Hou et al. have employed various organic compounds such as carbohydrates as carbon sources to prepare CDs by a microwave-assisted approach, and proposed a mechanism for the formation of CDs.[30] During the microwave treatment, a homogeneous solution might undergo thermal carbonization of the precursors that led to nucleation, and the color of the obtained powders changed from yellow to dark brown with the increase of microwave irradiation time. In the case of our method, as shown in Fig. 1a, the CDs/chitosan composite dispersion presents brown color under visible light, suggesting that carbonization of chitosan took place during the microwave treatment of chitosan solution. Moreover, the CDs/chitosan composite dispersion is transparent and homogeneous, indicating that the obtained CDs disperse well in aqueous solution. On the other hand, the CDs/chitosan composite exhibits clear blue fluorescence under the excitation of 365 nm UV light (in Fig. 1a).

TEM images of the CDs/chitosan composite in Fig. 1b show that CDs disperse well in the composite, and the size of CDs presents an average value about 7 nm. Also, Chandra and coworkers have prepared fluorescent carbon nanoparticles by microwave irradiation of sucrose with phosphoric acid, and TEM images show their average particle sizes range from 3 to 10 nm.[9]

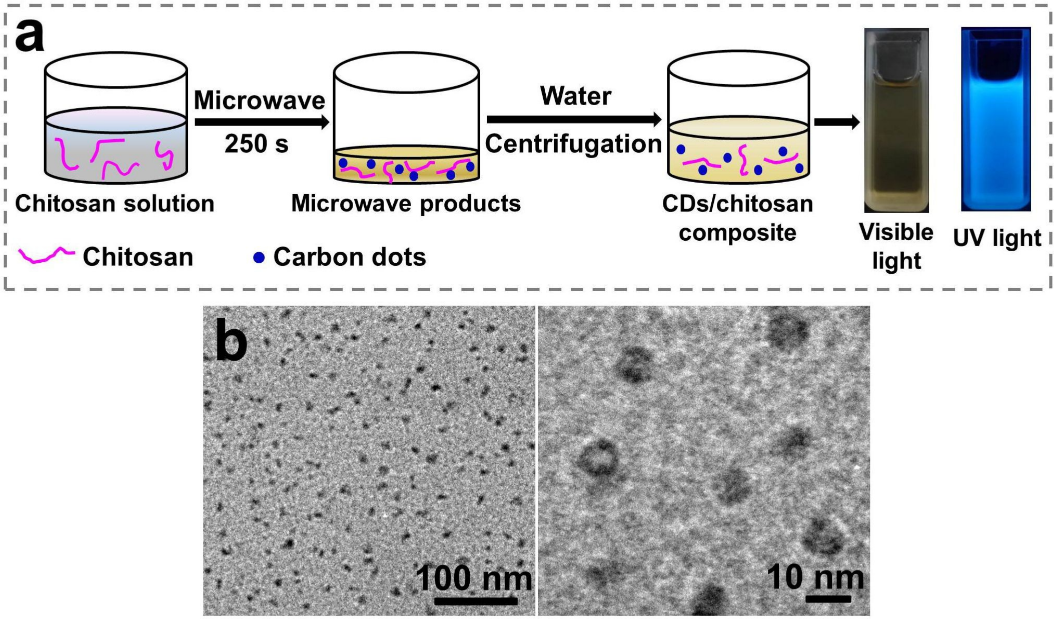


Fig. 1 Schematic illustration of preparation of CDs/chitosan composite and photographs of CDs/chitosan composite under visible light and 365 nm UV light (a), and TEM images of CDs/chitosan composite (b).

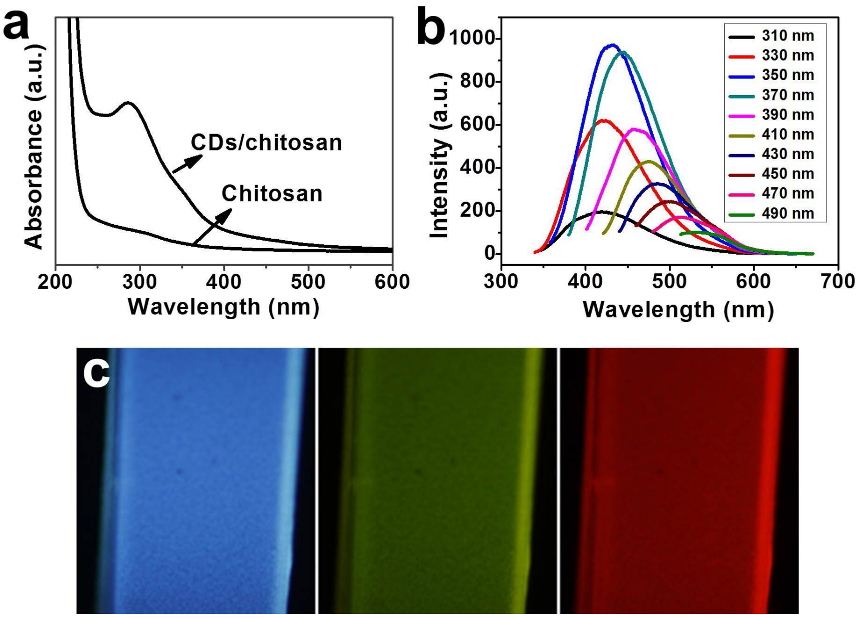


Fig. 2 UV-vis absorption spectra of CDs/chitosan composite and control chitosan (a), photoluminescence spectra of CDs/chitosan composite under different excitation wavelengths (b), and fluorescence microscopy images of CDs/chitosan composite film under the excitation of UV light, blue light and green light (c).

In Fig. 2a, UV-vis spectrum of the CDs/chitosan composite presents a new broad absorption peak from 250 to 440 nm compared with that of the control chitosan, which is attribute to the absorption of CDs in the composite. Besides, the UV-vis spectrum of the CDs/chitosan composite displays a maximum absorption value around 290 nm. Yang et al. have synthesized fluorescent carbon nanoparticles by hydrothermal carbonization of chitosan that show a similar UV-vis absorption peak centered at 288 nm.[31] It is found from photoluminescence spectra (Fig. 2b) that the emission peaks of the CDs/chitosan composite progressively shift from 420 to 540 nm when the excitation wavelength gradually increases from 310 to 490 nm, which suggest a typical excitation-dependent photoluminescence (or multicolor fluorescence) features of CDs. In addition, when the excitation wavelength is 350 nm, the CDs/chitosan composite displays the strongest emission peak at 435 nm corresponding to blue light. In contrast, Yang et al. have also reported the excitation-dependent photoluminescence of the carbon nanoparticles prepared by hydrothermal carbonization of chitosan.[31] Furthermore, the quantum yield of the CDs/chitosan composite was tested by using quinine sulfate as a standard as previously described,[32] and the result indicates that the CDs/chitosan composite has relatively high fluorescent quantum yield (29.2%). Therefore, the above results both demonstrate that we have prepared CDs by one-step microwave treatment of chitosan solution.

In order to directly observe the multicolor fluorescence of carbon dots/chitosan composite, we produced CDs/chitosan composite films by casting method, and then the composite films were cut into small strips and examined under fluorescence microscope. As shown in Fig. 2c, the CDs/chitosan film displays clear blue fluorescence under the excitation of UV light, green fluorescence under the excitation of blue light, and red fluorescence under the excitation of green light, respectively. Thus, these results prove that the CDs/chitosan composite can not only reserve the favorable film-forming properties of chitosan, but also be endowed with attractive multicolor-fluorescent features of CDs.

3.2 Electrodeposition of CDs/chitosan composite

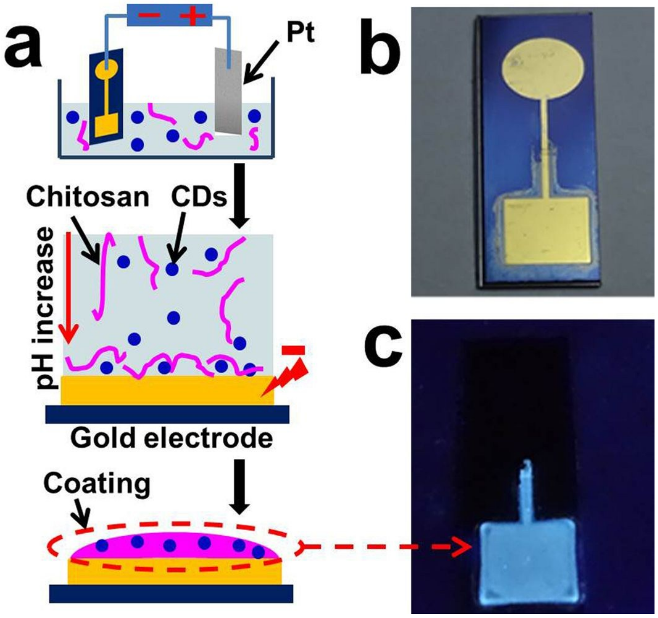


Fig. 3 Schematic illustration of electrodeposition of CDs/chitosan composite on gold electrode (a), and photographs of electrodeposited CDs/chitosan composite under visible light (b) and 365 nm UV light (c).

Subsequently, we constructed the CDs/chitosan composite coatings on the electrodes by electrodeposition technique. For electrodeposition, a Pt foil was served as anode and a gold electrode was used as cathode, and then the electrodeposition was performed using a power supply for a specific time to obtain the deposited coating on the gold electrode. As illustrated in Fig. 3a, cathodic reactions can generate a localized pH gradient adjacent to the cathode surface, and chitosan molecules near the cathode surface are able to respond to the localized high pH and deposit as a stable hydrogel coating on the surface.[21, 33] At the same time, CDs can be codeposited with chitosan and retained in the electrodeposited coating. Figure 3b shows that the electrodeposited coating on the gold electrode is transparent under visible light. However, the electrodeposited coating displays clear blue fluorescence under 365 nm UV light (Fig. 3c). The above results indicate that the CDs/chitosan composite can be electrodeposited on conductive electrode or substrate to fabricate surface coating, and the CDs in the electrodeposited coating can reserve their fluorescence features after electrodeposition.

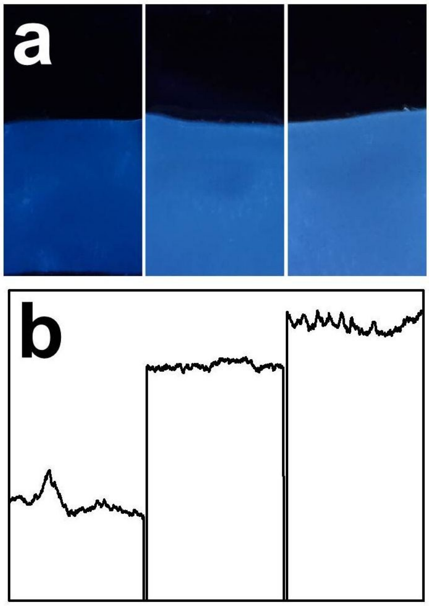


Fig. 4 Fluorescence images of the CDs/chitosan composite coatings on Ti plates with different electrodeposition voltages (from left to right: 2, 3, and 4 V) (a), and analysis of fluorescence profiles by Image J software (b).

In addition to gold electrode, we attempted to electrodeposit the CDs/chitosan composite on other substrates (*e.g.*, Ti plate) and studied the effects of electrodeposition condition (*e.g.*, voltage) on fluorescence property of the electrodeposited coatings. It is well known that titanium is widely used in biomedical field, especially as hard tissue replacements and cardiovascular applications, because of their desirable properties, such as relatively low modulus, good fatigue strength, corrosion resistance, and biocompatibility. However, titanium cannot meet all of the clinical requirements, so the surface modification on titanium is often performed to improve its biological, chemical, and mechanical properties.[34] The images in Fig. 4a display that the CDs/chitosan composite can also be electrodeposited on Ti plate to generate fluorescent coating. Importantly, it is found that the fluorescence intensity of the coating enhances with the increase of electrodeposition voltage, and the corresponding fluorescence profiles in Fig. 4b analyzed by Image J software further support this result. Therefore, we can readily control the fluorescence intensity of the CDs/chitosan composite coating by adjusting the electrodeposition voltage.

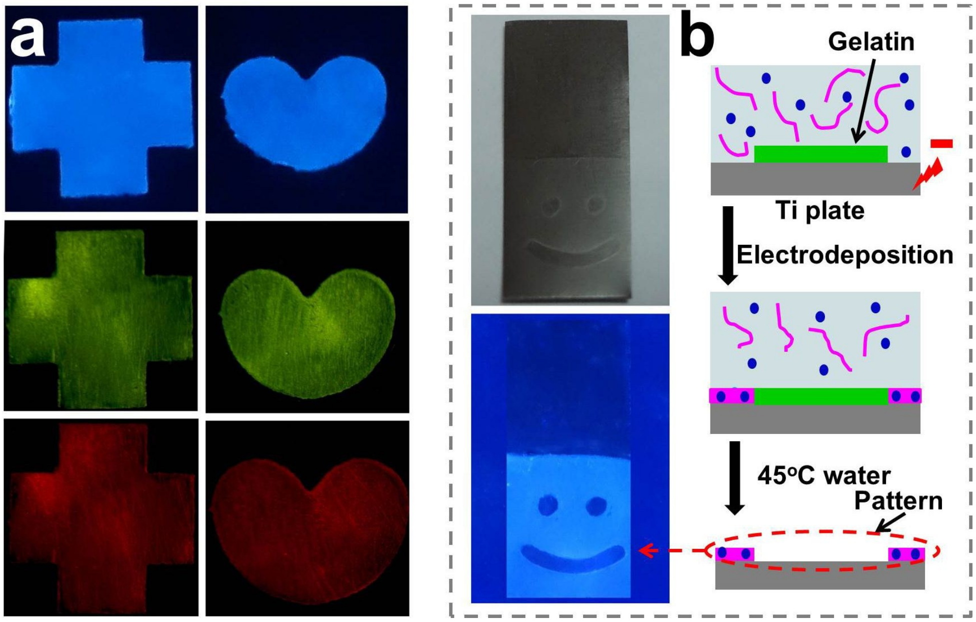


Fig. 5 Images of electrodeposited CDs/chitosan patterns prepared by employing 316L stainless steel plate with desired shapes under 365 nm UV light, blue light and green light (a), and images of electrodeposited CDs/chitosan patterns on Ti plate prepared by using gelatin coating under visible light (top) and 365 nm UV light (bottom), and its schematic illustration (b).

Taking advantage of the spatial selectivity of electrodeposition technique and the multicolor-fluorescence of CDs, we conveniently generated diverse fluorescent patterns by employing 316L stainless steel plate with desired shapes (*e.g.*, crisscross shape and heart shape). Figure 5a shows that the fluorescent patterns of CDs/chitosan display blue fluorescence under the excitation of 365 nm UV light, green fluorescence under the excitation of blue light, and red fluorescence under the excitation of green light, respectively. Additionally, we created the fluorescent patterns by using gelatin as the coating material to cover the desired region of Ti plate. Gelatin, a biopolymer derived from collagen, is receiving great attention due to its desirable properties such as biocompatibility, biodegradability and no toxicity, so gelatin has many biomedical applications such as tissue engineering and drug delivery. It has been reported that gelatin dissolves readily in hot water, and when the gelatin solution is cooled below room temperature it can turn into gel.[35, 36] In this method, the Ti plates were first coated with gelatin solution and put into a refrigerator to form gelatin gel. Next, the Ti plates were electrodeposited in the electrodeposition mixture, and then immersed into 45^{o}C distilled water to dissolve the gelatin gel. Finally, the fluorescent patterns of CDs/chitosan composite on the Ti plates were observed under 365 nm UV light, as shown in Fig. 5b.

The above results illustrate that the CDs/chitosan composite can be deposited on different electrodes or substrates through electrodeposition technique, and particularly can be employed to construct fluorescent patterns with various shapes. Also, these results further demonstrate that the CDs/chitosan composite not only retains the pH-responsive film-forming properties of chitosan, but also can be endowed with the multicolor fluorescence of CDs. Consequently, this CDs/chitosan composite produced by the simple *in situ* method may offer attractive applications in surface coatings, fluorescent patterns, and fluorescent labeling.

3.3 Electrically controlled release of CDs

Next, we performed the experiments to evaluate the electrically controlled release of the electrodeposited CDs. In the experiments, the Ti plate electrodeposited with the CDs/chitosan composite coating was used as anode and immersed in 0.9% NaCl solution, and then a DC voltage (5.0 V) was applied. Figure 6a shows that the fluorescence intensity of the CDs/chitosan composite coating gradually weakens after applying the DC voltage, and finally disappears in 90-minute experiment, indicating that the CDs can be released from the Ti plate under the control of the electrical signals. However, Fig. 6b displays that the fluorescence intensity of the control CDs/chitosan coating without applying the DC voltage has almost no change in 90-minute experiment, suggesting that electrical signals is essential for the release of carbon dots. Figure 6c illustrates the process for this electrically controlled release of CDs from the Ti plate. Anodic electrochemical reactions can generate a localized pH decrease on the surface of the anode, so that the chitosan electrodeposited on the Ti plate is able to dissolve. At the same time, CDs can be released with chitosan dissolution and disperse in NaCl solution. In addition, Fig. 6d shows that the fluorescence intensity of the CDs pattern on the Ti plate decreases after applying the DC voltage, and disappears gradually in 90-minute experiment, indicating that the CDs pattern generated by electrodeposition can also be removed under the control of the electrical signals.

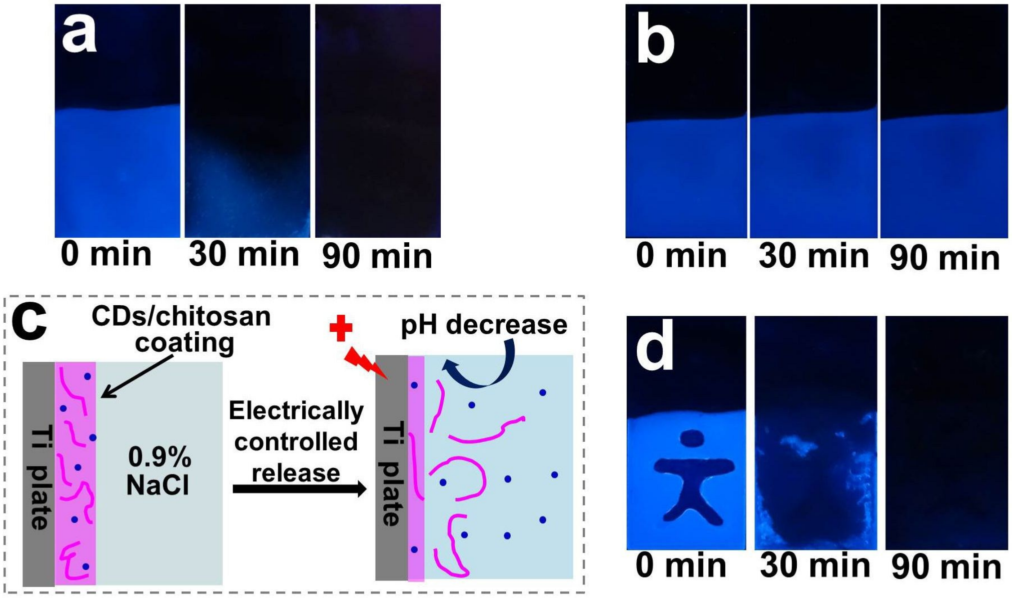


Fig. 6 (a) Fluorescence images of the CDs/chitosan composite coating (on Ti plate) in 0.9% NaCl solution after applying DC voltage for different time (from left to right: 0, 30, and 90 min). (b) Fluorescence images of the control CDs/chitosan composite coating (on Ti plate) in 0.9% NaCl solution without applying DC voltage for different time (from left to right: 0, 30, and 90 min). (c) Schematic illustration of controlled release of CDs under the control of electrical signals. (d) Fluorescent pattern of the CDs/chitosan composite (on Ti plate) in 0.9% NaCl solution after applying DC voltage for different time (from left to right: 0, 30, and 90 min).

Furthermore, UV-vis absorption spectra of the NaCl solution after applying DC voltage, the NaCl solution without applying DC voltage, and control 0.9% NaCl solution were measured respectively. As shown in Fig. 7a, the UV-vis spectrum of the NaCl solution after applying DC voltage shows a broad absorption from 240 to 440 nm compared with that of the control NaCl solution, which is attribute to the absorption of the released CDs in the NaCl solution. However, the UV-vis spectrum of NaCl solution without applying DC voltage exhibits little difference with that of the control NaCl solution. These results further support that the electrodeposited CDs can be released under the control of electrical signals. Besides, the electrical release profiles of CDs in 0.9% NaCl solution at different time were detected by UV-vis spectrophotometer at 350 nm. It is found from Fig. 7b that the CDs on the Ti plate release continuously when the DC voltage was applied, and almost all the CDs release in 90-minute experiment. Therefore, it can be expected that this electrically controlled release of CDs have potential applications in controlled release, fluorescent labeling, and bio-detection.

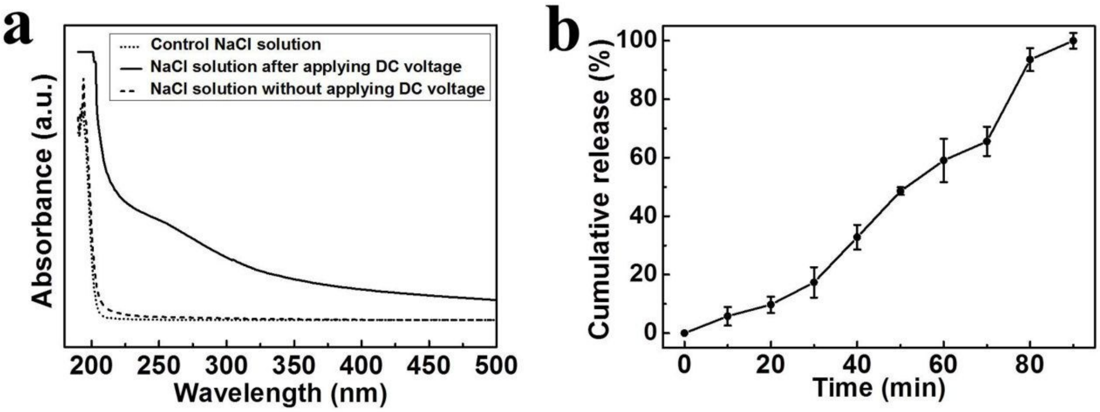


Fig. 7 (a) UV-vis absorption spectra of the NaCl solution with Ti plate (deposited with CDs/chitosan composite coatings) after applying DC voltage for 90 min, the NaCl solution with Ti plate (deposited with CDs/chitosan composite coatings) without applying DC voltage for 90 min, and control 0.9% NaCl solution. (b) Electrical release profiles of CDs on Ti plate in 0.9% NaCl solution at different time.

4. Conclusions

We present a simple and novel *in situ* method based on microwave treatment of chitosan solution to construct fluorescent CDs/chitosan composite that can be straightforward used for further electrodeposition and electrically controlled release of CDs. Importantly, this CDs/chitosan composite not only displays excitation-dependent photoluminescence (or multicolor fluorescence) features that come from CDs, but also retains pH-responsive film-forming properties of chitosan. This CDs/chitosan composite can be electrodeposited on different electrodes or substrates (*e.g.*, gold electrode, Ti plate, and 316L stainless steel plate) to construct fluorescent coatings, as well as a variety of fluorescent patterns. Moreover, the CDs in the electrodeposited coatings or patterns can be released under the control of electrical signals. Thus, this CDs/chitosan composite provide promising applications in photoluminescent coatings, fluorescent patterns, fluorescent labeling, and controlled release.

Acknowledgements

This work was supported by the Fundamental Research Funds for the Central Universities (WUT: 2015-zy-008), the Natural Science Foundation of Hubei Province of China (2014CFB256), the Scientific Foundation for the Returned Overseas Chinese Scholars from State Education Ministry (No. 47), and the ESI Academic Development Program (WUT, 2015, 2016).

References

1 X. Y. Xu, R. Ray, Y. L. Gu, H. J. Ploehn, L. Gearheart, K. Raker and W. A. Scrivens, *J. Am. Chem. Soc.*, 2004, **126**, 12736-12737.

2 M. Zheng, S. Liu, J. Li, D. Qu, H. F. Zhao, X. G. Guan, X. L. Hu, Z. G. Xie, X. B. Jing and Z. C. Sun, *Adv. Mater.*, 2014, **26**, 3554-3560.

3 Y. B. Song, S. J. Zhu, S. Y. Xiang, X. H. Zhao, J. H. Zhang, H. Zhang, Y. Fu and B. Yang, *Nanoscale*, 2014, **6**, 4676-4682.

4 H. T. Li, R. H. Liu, W. Q. Kong, J. Liu, Y. Liu, L. Zhou, X. Zhang, S. T. Lee and Z. H. Kang, *Nanoscale*, 2014, **6**, 867-873.

5 H. Q. Tao, K. Yang, Z. Ma, J. M. Wan, Y. J. Zhang, Z. H. Kang and Z. Liu, *Small*, 2012, **8**, 281-290.

6 H. T. Li, X. D. He, Y. Liu, H. Huang, S. Y. Lian, S. T. Lee and Z. H. Kang, *Carbon*, 2011, **49**, 605-609.

7 Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. F. Wang, P. J. G. Luo, H. Yang, M. E. Kose, B. L. Chen, L. M. Veca and S. Y. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756-7757.

8 L. L. Zhu, Y. J. Yin, C. F. Wang and S. Chen, *J. Mater. Chem. C*, 2013, **1**, 4925-4932.

9 S. Chandra, P. Das, S. Bag, D. Laha and P. Pramanik, *Nanoscale*, 2011, **3**, 1533-1540.

10 X. H. Wang, K. G. Qu, B. L. Xu, J. S. Ren and X. G. Qu, *J. Mater. Chem.*, 2011, **21**, 2445-2450.

11 R. R. Costa, A. I. Neto, I. Calgeris, C. R. Correia, A. C. M Pinho, J. Fonseca, E. T. Oner and J. F. Mano, *J. Mater. Chem. B*, 2013, **1**, 2367-2374.

12 P. B. Malafaya, G. A. Silva and R. L. Reis, *Adv. Drug Delivery Rev.,* 2007, **59**, 207-233.

13 F. Croisier, P. Sibret, C. C. Dupont-Gillain, M. J. Genet, C. Detrembleur and C. Jerome, *J. Mater. Chem. B,* 2015, **3**, 3508-3517.

14 P. Avetta, R. Nistico, M. G. Faga, D. D'Angelo, E. A. Boot, R. Lamberti, S. Martorana, P. Calza, D. Fabbri and G. Magnacca, *J. Mater. Chem. B,* 2014, **2**, 5287-5294.

15 Z. P. Xu, L. Y. Shi, M. Y. Yang, H. P. Zhang and L. J. Zhu, *J. Mater. Chem. B,* 2015, **3**, 3634-3642.

16 C. S. Shan, H. F. Yang, D. X. Han, Q. X. Zhang, A. Ivaska and L. Niu, *Biosens. Bioelectron.*, 2010, **25**, 1070-1074.

17 Y. Liu, E. Kim, R. Ghodssi, G. W. Rubloff, J. N. Culver, W. E. Bentley and G. F. Payne, *Biofabrication*, 2010, **2**, 022002.

18 Y. F. Wang, Z. H. Geng, M. M. Guo, Y. J. Chen, X. C. Guo and X. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 15510-15515.

19 S. Hassan, M. Suzuki and A. Abd El-Moneim, *Journal of Power Sources*, 2014, **246**, 68-73.

20 Y. F. Wang, Y. Liu, Y. Cheng, E. Kim, G. W. Rubloff, W. E. Bentley and G. F. Payne, *Adv. Mater.*, 2011, **23**, 5817-5821.

21 G. F. Payne and S. R. Raghavan, *Soft Matter*, 2007, **3**, 521-527.

22 Y. Li, X. Pang, R.F. Epand and I. Zhitomirsky, *Mater. Lett.*, 2011, **65**, 1463-1465.

23 B. Z. Liu, Y. H. Deng, X. B. Hu, Z. Q. Gao and C. Sun, *Electrochimica Acta*, 2012, **76**, 410-415.

24 X. L. Luo, J. J. Xu, J. L. Wang and H. Y. Chen, *Chem. Commun.*, 2005, **16**, 2169-2171.

25 X. W. Shi, H. P. Wu, Y. Y. Li, X. P. Wei, and Y. M. Du, *J. Biomed. Mater. Res. Part A*, 2013, **101A**, 1373-1378.

26 D. Chowdhury, N. Gogoi and G. Majumdar, *RSC Adv.*, 2012, **2**, 12156-12159.

27 D. L. Xiao, D. H. Yuan, H. He and J. R. Lu, *Luminescence*, 2013, **28**, 612-615.

28 M. Q. Tan, L. X. Zhang, R. Tang, X. J. Song, Y. M. Li, H. Wu, Y. F. Wang, G. J. Lv, W. F. Liu and X. Ma, *Talanta,* 2013, **115**, 950-956.

29 Q. T. Huang, S. R. Hu, H. Q. Zhang, J. H. Chen, Y. S. He, F. M. Li, W. Weng, J. C. Ni, X. X. Bao and Y. Lin, *Analyst*, 2013, **138**, 5417-5423.

30 J. Hou, J. Yan, Q. Zhao, Y. Li, H. Ding and L. Ding, *Nanoscale*, 2013, **5**, 9558-9561.

31 Y. H. Yang, J. H. Cui, M. T. Zheng, C. F. Hu, S. Z. Tan, Y. Xiao, Q. Yang and Y. L. Liu, *Chem. Commun.*, 2012, **48**, 380-382.

32 Q. H. Liang, W. J. Ma, Y. Shi, Z. Li and X. M. Yang, *Carbon*, 2013, **60**, 421-428.

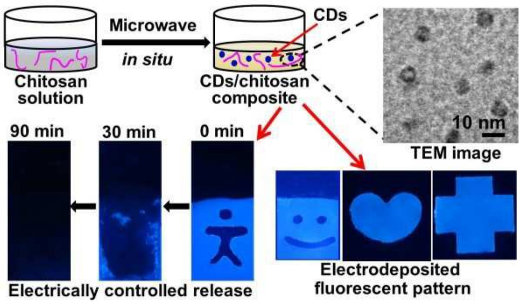
33 R. Fernandes, L. Q. Wu, T. H. Chen, H. M. Yi, G. W. Rubloff, R. Ghodssi, W. E. Bentley, and G. F. Payne, *Langmuir*, 2003, **19**, 4058-4062.

34 X. Y. Liu, P. K. Chu, and C. X. Ding, *Mat. Sci. Eng. R*, 2004, **47**, 49-121.

35 C. Joly-Duhamel, D. Hellio and M. Djabourov, *Langmuir*, 2002, **18**, 7208-7217.

36 K. Chen and S. Vyazovkin, *Macromol. Biosci.*, 2009, **9**, 383-392.

Graphical and textual abstract for the Table of contents entry



Carbon dots/chitosan composite that can be straightforward used for electrodeposition and controlled release was produced by one-step microwave method.