



One-step electrodeposition of chitosan/phosphonate iron(III) hybrids film and its pH-controlled switchable electrocatalytic behavior



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ABSTRACT

The switchable/tunable electrocatalysis is of great importance in both fundamental and application research. In this work, we synthesize the CS–Fe(notpH₃) hybrids film by the simple one-step electrodeposition technique (CS: chitosan; Fe(notpH₃): 1,4,7-triazacyclononane-1,4,7-triyl-tris methylene-phosphonic acid iron(III) complex). The stable immobilization of Fe(notpH₃) in CS polymer originates from the strong electrostatic and/or hydrogen bonding interactions between Fe(notpH₃) and CS, which also enhances the insolubility of CS in acidic solution. The immobilized Fe(notpH₃) complex undergoes an effective direct electron transfer reaction and shows a particular pH-sensitive electrochemical property. Based on the particular formal potential hopping mechanism of Fe(notpH₃) complex, the CS–Fe(notpH₃) hybrids film can be further used to realize pH-controlled switchable electrocatalysis toward H₂O₂ reduction.

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1. Introduction

In recent years, the stimuli-responsive functional materials which are sensitive to various external physical/chemical signals have drawn much attention due to their potential applications in various fields such as controlled drug delivery, wastewater treatment, bio-separation, sensor, and molecular device [1–8]. In particular, the integration of the stimuli-responsive materials with electrode surface allows their operation as electrochemical gates switching “on–off” or tuning rates of interfacial redox reactions by external signals change. The controllable or “signal-triggered” electrocatalysis has demonstrated great potential applications in information storage, data processing, signal transduction and amplification, electrochemical sensor and other electronic device [9–19].

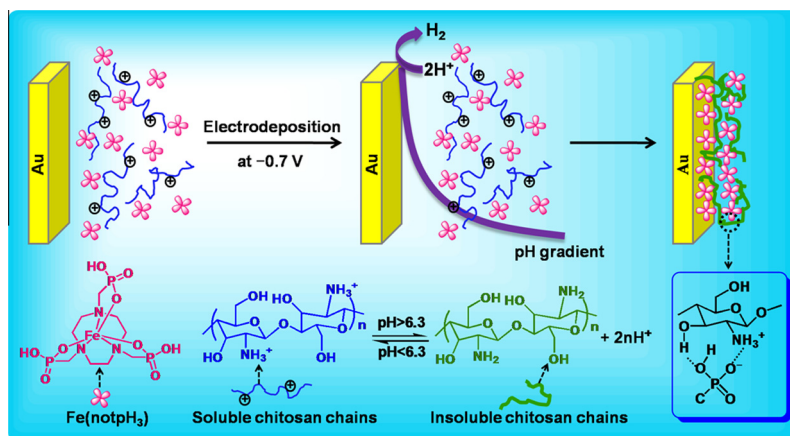
The switchable/tunable electrocatalysis based on polymer films, which do not directly participate in the electron-transfer process but rather affect the access of redox active species from bulk solution to electrode surface, have been successfully developed to control electrode interfacial properties by changing temperature, electric field, pH, ionic strength and potential [9–19]. Among various external stimuli-switchable/tunable electrocatalysis, pH-switchable/tunable electrocatalysis is the most studied one.

In general, the switchable/tunable electrocatalysis is achieved by incorporating redox probe (such as Fe(CN)₆^{3–}, Fc(COOH)₂ and Ru(NH₃)₆³⁺) into pH-sensitive polymer films, which are switchable between charged swollen and uncharged shrunken states upon changing protonation/deprotonation of acid/base groups in polymer. For example, Prof. Hu has fabricated various polymer-based layer-by-layer films that exhibited pH-sensitive permeability toward electroactive probes, which can be applied to control electrocatalysis [20–26]. However, these modified electrodes generally suffer from a leakage of redox probe during their storage and running, resulting in unsatisfactory stability and switchable times [9]. Therefore, it is highly essential to explore novel stimuli-responsive functional materials with high stability and reusability.

1,4,7-Triazacyclononane-1,4,7-triyl-tris methylene-phosphonic acid iron(III) complex [Fe(notpH₃), Scheme 1], a macrocyclic metal complex with three uncoordinated –P–OH groups, is a pH-sensitive redox molecule. It shows an interesting formal potential hopping behavior in the pH range of 3.4–4.0 (–585 mV pH^{–1}, ten times bigger than theoretical shift value of –58 mV pH^{–1} for a single proton-coupled single electron transfer reaction, owing to the protonation/deprotonation of the uncoordinated –P–OH groups [8]. The effective and stable immobilization of redox molecule on electrode surface is a key point for the fabrication of electrochemical sensors. Chitosan (CS), a linear hydrophilic polymer obtained by deacetylation of nature chitin, has been extensively used as an excellent immobilization matrix due to its good film-forming ability, nontoxicity, high mechanical strength, cheapness and good water permeability [27–42]. In this work, *in situ* incorporation of

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Scheme 1. Schematic illustration of the fabrication process and mechanism of CS-Fe(notpH₃)/Au electrode.

pH-sensitive Fe(notpH₃) complex into CS hydrogel was achieved through simple and convenient one-step electrodeposition technique. The pH stimuli-responsive films could be further used to realize switchable electrochemical reduction of H₂O₂.

2. Experimental

2.1. Reagents and chemicals

Chitosan (CS, 95% deacetylation, *M* = 1,50,000) was obtained from Nantong Xincheng Biological industry Co., Ltd. Fe(notpH₃) (Scheme 1) was prepared according to the previous work reported by us [8]. Elemental analysis calcd. (found) for C₉H₂₁N₃P₃O₉Fe: C 23.29 (23.20), H 4.53 (4.60), N 9.06 (9.01)%. IR (KBr, cm⁻¹): 3437(b), 1638(m), 1477(m), 1291(m), 1257(w), 1012(s), 1017(s), 778(m), 587(s), 523(s). All other chemicals were of analytical grade. The solution pH was adjusted by the addition of dilute KOH or HCl solution.

2.2. Preparation of the CS-Fe(notpH₃) modified electrode

The electrodeposition was carried out by dipping a pre-cleaned Au disk electrode (2 mm in diameter) in a pH 3.0 deposition solution containing 0.5 mg mL⁻¹ CS and 0.05 M Fe(notpH₃) at -0.7 V applied potential for 30 min. After rinsing with water, the fabricated electrode was denoted as the CS-Fe(notpH₃)/Au electrode. For comparison, the CS/Au electrode was also fabricated by the similar procedure.

2.3. Instruments

Scanning electron microscopy (SEM) was performed on a JEOL JSM-7600F scanning electron microscopy. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo VG Scientific ESCALAB 250 spectrometer. The binding energy was calibrated by the Au 4f_{7/2} peak energy of 84.0 eV. Ultraviolet–visible (UV–vis) spectra were recorded on a Hitachi UV3600 spectrophotometer. All electrochemical experiments were carried out on a CHI 660 C electrochemical workstation (CH Instruments, Shanghai, Chenghua Co.) at 25 ± 1 °C. A Pt wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used. All potentials refer to SCE.

3. Results and discussion

3.1. Characterization of the CS-Fe(notpH₃) hybrids film

The electrodeposition of CS-Fe(notpH₃) hybrids film on Au substrate was carried out in a pH 3.0 mixed solution containing

0.5 mg mL⁻¹ CS and 0.05 M Fe(notpH₃) at -0.7 V (vs. SCE) applied potential for 30 min. Formation mechanism of CS-Fe(notpH₃) hybrids film is schematically illustrated in Scheme 1.

As a pH-shift biopolymer, CS is ideally suited for electrodeposition because its net charge and solubility are pH dependent [31]. At -0.7 V applied potential, the reduction of H⁺ gradually increases the local pH near Au electrode surface, which results in the deposition of CS on Au electrode when the pH exceeds the pK_a of chitosan (about 6.3) [43]. As an electroactive redox molecule with three uncoordinated -P-OH arms, the strong electrostatic and/or hydrogen bonding interactions between -P-OH groups at Fe(notpH₃) and -NH₂ groups at CS also assist the coacervation of CS due to the ionotropic crosslinking interactions, similar to the case of polyphosphonate crosslinked CS [32]. As confirmed, the yellow flocculent precipitation generates slowly after addition of the Fe(notpH₃) solution (pH 5.0) to the transparent CS solution (pH 5.0) (Fig. 1). Thus, Fe(notpH₃) coexisted with CS can be *in situ* entrapped in the formed CS film during the electrodeposition.

The evidence for the formation of CS-Fe(notpH₃) hybrids film was firstly determined by XPS. The appearance of Fe 2p and P 2p peaks confirms the *in situ* incorporation of Fe(notpH₃) in CS film during electrodeposition (Fig. 2). The native CS is soluble in acid conditions. However, it is worth noting that the -P-OH group assistant ionotropic crosslinking interactions are irreversible. No dissolution of CS-Fe(notpH₃) precipitation is observed in 40 days under pH 2.0 conditions, which improves the applicability of CS-based electrochemical devices in acidic solution. (Noting: CS cannot interact with Fe(notpH₃) at pH 2.0 solution to generate CS-Fe(notpH₃) precipitation, which in turn confirms the -P-OH

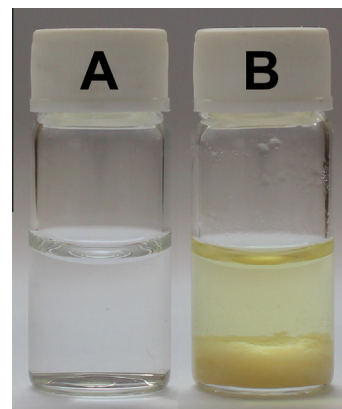


Fig. 1. Digital photographs of the native CS solution (pH 5.0) (A) before and (B) after addition of the Fe(notpH₃) solution (pH 5.0).

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