

Electron Transfer in Ferrocene-Containing Functionalized Chitosan and Its Electrocatalytic Decomposition of Peroxide

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Functional polymeric materials that have the ability to participate in electron-transfer processes have become increasingly important in recent years, in particular in the fields of catalyst, biotechnology, environmental protection, and illumination.^{1–3} As for polymeric catalysts, the most recent efforts in the development of cleaner sustainable systems are being driven by a shift from petrochemical-based feedstocks toward biological materials.^{4,5} Given these developments, it seems clear that there will be a key role to be played in the development of natural polymers (or biopolymers) for use as polymeric catalysts. A unique feature of natural polymers compared with synthetic ones is their ability to undergo degradation by specific microorganisms.^{6,7} Chitosan, an abundant biopolymer obtained from a fully or partially deacetylation of its parent polysaccharide chitin, has attracted significant interest in the broad range of scientific research, including biomedical, agriculture, and environmental protection fields, due to its biodegradability, biocompatibility, and bioactivities.^{8–11} A large number of chitosan's hydroxyl and amino groups not only provide sites for numerous chemical modifications but also are excellent functional groups for the anchoring of a large variety of organometallic complexes, making chitosan a good candidate as a precursor for molecular catalysts.^{9,12–14} Moreover, the amino groups are potential base catalysts.⁴ These features allow for great flexibility in manipulating chitosan and leading to a unique potential as a catalyst.^{14–16}

On the other hand, macromolecules containing organometallic units combine potentially useful chemical, electrochemical, optical, and other interesting characteristics with the properties and processability of polymers.^{17–19} In particular, ferrocene-based polymers, which are redox-active materials, have received a great deal of attention in light of their uses as electrocatalysts, chemical sensors, modified electrodes, photoactive molecular devices, and medicine.^{19,20–25} The covalent attachment of ferrocene and chitosan could offer a way for building novel polymeric systems, which combines redox activity and biocompatibility as well as opens applications in catalysis, biosensors, photochromic devices, nonlinear optics, antibodies diagnostic tests, and antiproliferative chemotherapeutic agent in cancer research. Herein, we synthesized the ferrocene-containing chitosan and investigated the photoinduced electron-transfer processes in this functionalized chitosan as well as the electrocatalytic decomposition of peroxide, which could lead to its applications in catalysis, antiexplosion agent, photosensitizer, peroxide sensor, etc.

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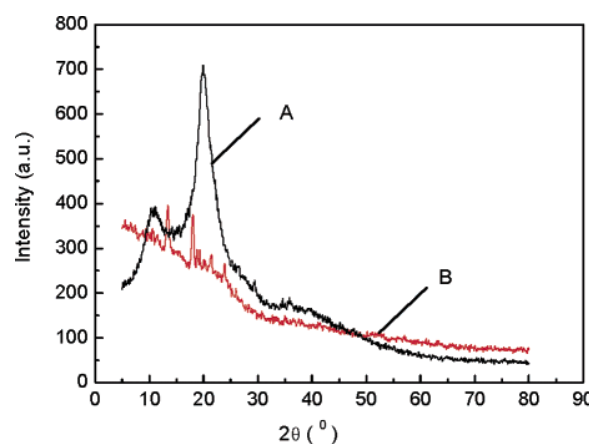


Figure 1. WAXD profiles of chitosan and the ferrocene-containing chitosan: (A) chitosan; (B) ferrocene-containing chitosan.

In methanesulfonic acid solution in our experiment, the amino groups of chitosan are protonated, and this is disadvantageous for the nucleophilic displacement reaction. Therefore, the substitution is supposed to happen preferentially onto the hydroxyl groups (see Scheme 1). This has been confirmed by FTIR, ¹H NMR, and ¹³C NMR spectra. Compared with the IR spectrum of the starting material chitosan, the IR spectrum of ferrocene-containing chitosan shows a strong absorption band at about 1720 cm⁻¹, which can be assigned to the ester carbonyl group, and the bands around 3085, 830, 770, and 740 cm⁻¹ corresponded to the cyclopentadienyl ring. The ¹H NMR spectrum exhibited the signals in the range of 4.2–5.0 ppm, assigned to the protons of cyclopentadienyl moieties. In the ¹³C NMR spectrum, the signal at 166 ppm is attributable to the ferrocenecarbonyl group (C=O). On the basis of the NMR measurements, it can be calculated that the degree of substitution is about 1.

For further insight into the microscopic structure of the polymer, wide-angle X-ray diffraction (WAXD) measurement was conducted. The WAXD profiles were presented in Figure 1. The diffraction peaks centered at 2θ 10° and 20° are indicative of the crystalline morphology of chitosan. While as for the ferrocene-containing chitosan, no diffraction peaks could be observed at 2θ 10° and 20°, but some weak diffraction peaks centered at 2θ 13° and 18° appeared; this could be attributed to the generally amorphous state of the polymer upon the incorporation of ferrocene moieties onto the molecular chains.

To investigate the ability of the ferrocene-containing chitosan to participate in the photoinduced electron-transfer process, methyl viologen dichloride (MV²⁺) was used as the electron acceptor. The photographs of the ferrocene-containing chitosan solution (DMSO + 30 wt % H₂O) in the presence of MV²⁺ upon UV irradiation (λ = 350 nm) are shown in Figure 2A–C. It can be seen that, in the presence of MV²⁺, upon UV irradiation the ferrocene-containing chitosan (CpFeC) solution turned from yellow to dark blue; this is due to the reduction of MV²⁺ into the MV^{•+} radical by electron transfer. The electron transfer is from the singlet excited state of CpFeC to MV²⁺. This electron-transfer process could be described as follows: CpFeC^{1*} + MV²⁺ → CpFeC⁺ + MV^{•+}. The MV^{•+} radical, formed after electron transfer, is blue in color and shows characteristic maximum absorption at 395 and 600 nm.^{26,27} Figure 2D shows the UV–vis absorption spectra of the

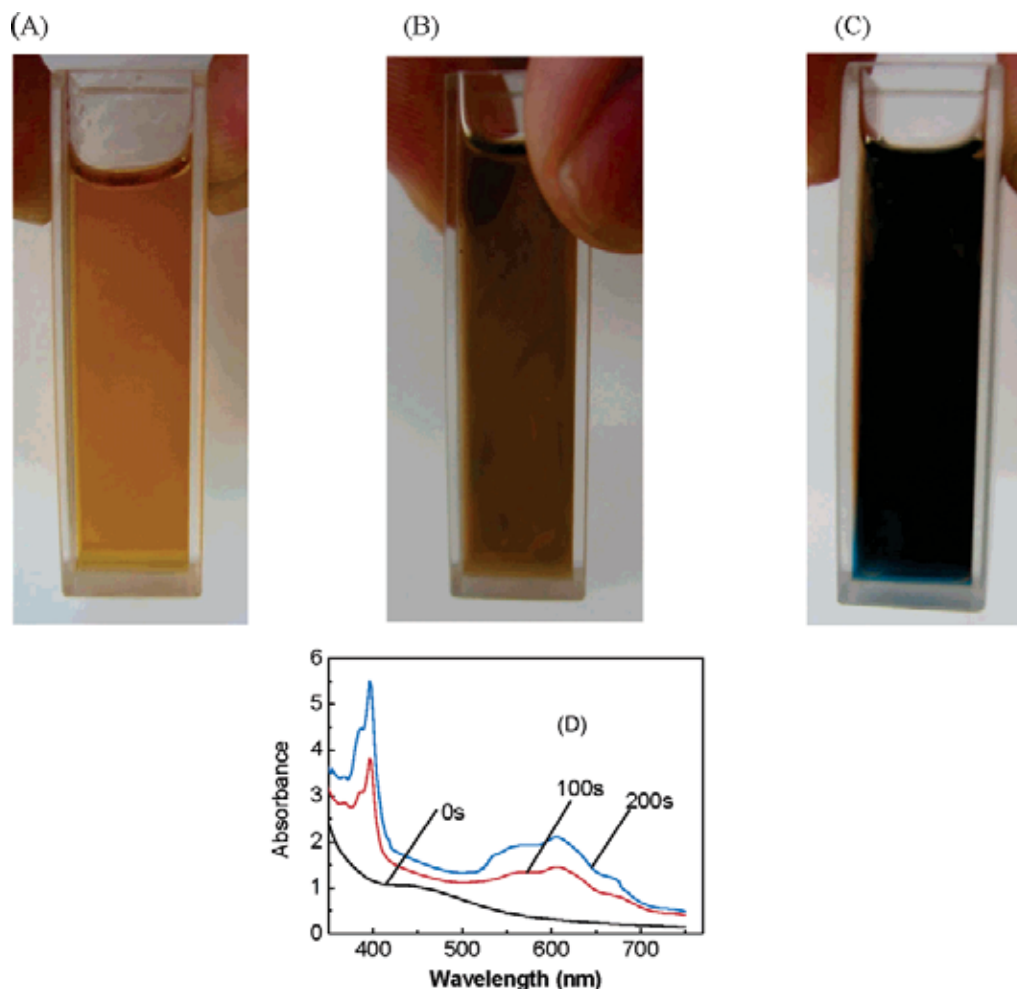
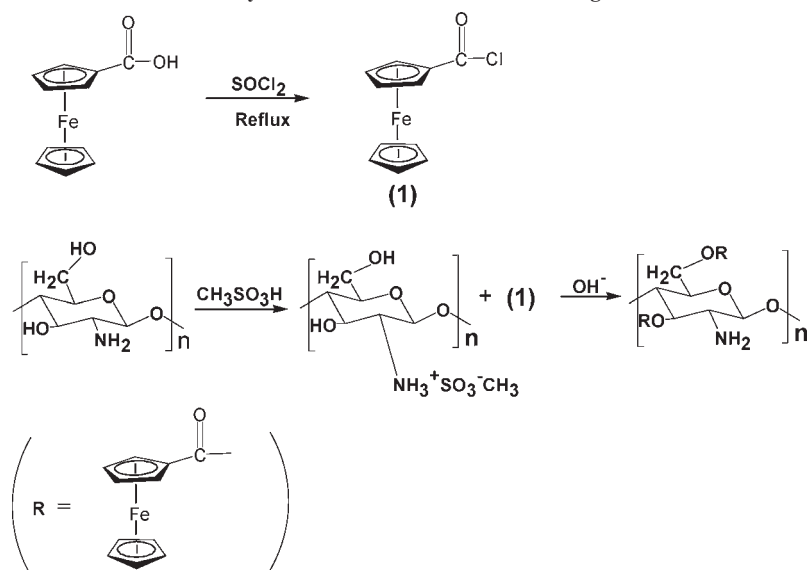


Figure 2. Photographs of the ferrocene-containing chitosan solution in the presence of MV^{2+} upon UV irradiation and the UV-vis absorption spectra of the ferrocene-containing chitosan in the presence of MV^{2+} as a function of irradiation time: (A) 0 s; (B) 100 s; (C) 200 s; (D) UV-vis absorption spectra. The concentration of ferrocene-containing chitosan and MV^{2+} is 0.1 wt %.

Scheme 1. Synthesis of the Ferrocene-Containing Chitosan



ferrocene-containing chitosan in the presence of MV^{2+} as a function of irradiation time. Without UV irradiation, MV^{2+} shows no absorption in the wavelength range of 350–800 nm; the absorption at about 450 nm was attributable to the pendant

ferrocenyl groups along the chitosan polymer chains. Upon UV irradiation and as the time of irradiation ($\lambda = 350$ nm) increases, the polymer system's absorption at about 400 and 600 nm increases; this indicates that the electron-transfer process

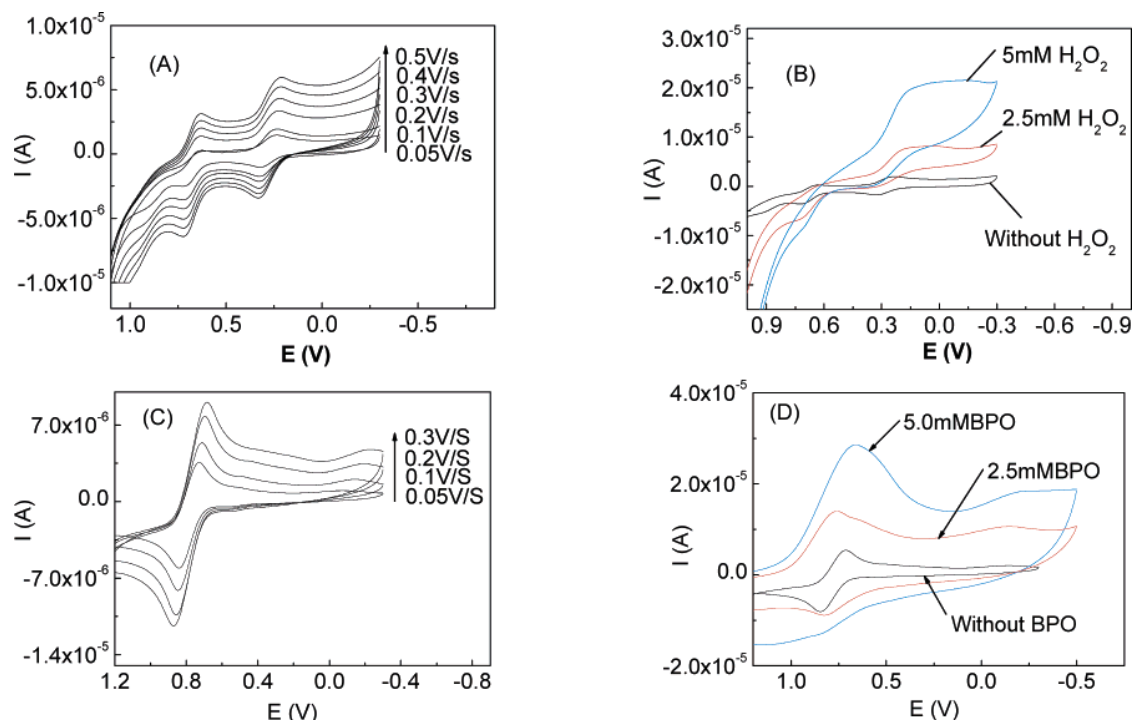


Figure 3. Cyclic voltammograms. (A) Ferrocene-containing chitosan in DMSO without H_2O_2 (the concentration of ferrocene-containing chitosan is 0.1 wt %). (B) Ferrocene-containing chitosan in DMSO in the presence of H_2O_2 (scan rate 0.1 V/s). (C) Ferrocene-containing chitosan in dichloroethane without BPO (the concentration of ferrocene-containing chitosan is 0.3 wt %). (D) Ferrocene-containing chitosan in dichloroethane in the presence of BPO (scan rate 0.1 V/s).

proceeds continuously. The experimental results indicate that the ferrocene-containing chitosan could act as promising photosensitizer for the reaction of organic compounds through photoinduced electron transfer and have the potentials in the applications of the environment-friendly photocatalytic system for efficient degradation of a wide range of pollutants.

The facile measurement and determination of the amount of hydrogen peroxide and organic peroxides is of great significance for pharmaceutical industry and analytical purposes, while electrocatalysts for efficient peroxide decomposition are fundamentally important for the catalyst development in energy devices as well as antiexplosion application. Herein, the electrocatalytic activity for peroxide decomposition and the electrochemical properties of the ferrocene-containing chitosan were studied by using cyclic voltammetry (CV). Measurements were performed in both high-polar solvent DMSO and less-polar solvent dichloroethane containing the supporting electrolyte tetra-*n*-butylammonium hexafluorophosphate (0.1 M) under a N_2 atmosphere, and the results are shown in Figure 3. In DMSO, the cyclic voltammograms recorded for the electroactive polymer CpFeC show two reversible redox peaks associated with the stepwise, one-electron oxidation of the iron centers in the ferrocene units. Peak splittings (ΔE_p) were found to be about 90 mV. In the high-polar solvent DMSO, the hydrophobic ferrocene moieties along the hydrophilic polymer chain tend to aggregate due to hydrophobic interaction. This could lead to the repulsive interactions between the electroactive centers in the polymer. A ferrocenium group increases the oxidation potential of neighboring unoxidized ferrocene centers and was even found to weakly affect the oxidation potential of the next nearest ferrocene centers. Thus, the first oxidation wave is attributed to oxidation of ferrocene centers at alternating positions along the chain. In the second wave, at higher potentials, oxidation of the remaining ferrocene centers, in positions close to oxidized units, is completed; this result is

similar to what was observed by other researchers.²⁸ In the presence of hydrogen peroxide (in DMSO and the potential range of +1.1 to -0.3 V, H_2O_2 solution shows no obvious redox reaction), only one irreversible redox couple could be observed; both the anodic and cathodic currents were found to increase, while the cathodic peak current value was substantially higher, indicating the electrochemical catalytic current was formed, and the cathodic peak shifted to more negative potential compared with that of CpFeC. As the concentration of hydrogen peroxide was increased, the peak current value increased as well.

Benzoyl peroxide (BPO) was selected as the representative of organic peroxides. Since BPO is insoluble in the high-polar solvent DMSO, its electrocatalytic property was investigated in the less-polar solvent dichloroethane. In the solvent dichloroethane and the potential range of +1.2 to -0.3 V, benzoyl peroxide (BPO) solution exhibits no obvious redox reaction. As for the ferrocene-containing chitosan, in the less-polar solvent dichloroethane, only one reversible redox couple could be seen in the cyclic voltammograms, in contrast to what was observed in the high-polar solvent DMSO. It indicates that the ferrocene moieties appended along the chitosan polymer chain may have little interaction with one another in the less-polar solvent. Upon the addition of BPO, the current peak values increased obviously, with a larger increment in the cathodic current, displaying a response typical of catalytic behavior. As the BPO concentration was increased, the current peak value increased proportionally. The proportional current response to peroxide concentration indicates that the redox-active chitosan could be used as peroxide sensor.

In summary, ferrocene groups were successfully incorporated into chitosan polymer chains; thus chitosan, the initially only acid soluble polysaccharide, was turned into the solvent-soluble material. This ferrocene-containing chitosan shows efficient photoinduced electron transfer and electrocatalytic activity for peroxide decomposition. This environment-friendly polymer

could be used in catalysis, antiexplosion agent, photosensitizer, peroxide sensor, etc. The study could offer a strategy for developing environment-friendly photoactive and electroactive polymers.

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Supporting Information Available: Details of experimental procedures, FTIR spectra, ^1H NMR spectrum, and ^{13}C NMR spectrum. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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