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Hb-induced biocatalyzed synthesis of water-soluble polyaniline nanocomposites with controlled handedness in DBSA–CTAB mixed micelle solutions

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ABSTRACT

A new polymerization system for the synthesis of chiral conducting polyaniline (PANI) with high conductivity catalyzed by hemoglobin (Hb) in dodecylbenzenesulfonic acid (DBSA)–cetyltrimethyl ammonium bromide (CTAB) mixed micelle solutions was developed. For the first time, without any other chiral inducer, PANI with controlled handedness was found to be acquired only in the presence of Hb, indicating that Hb played the role of both the inducer and biocatalyst. The effects of reaction pH, concentrations and ratio of the mixed surfactants on the formation of chiral PANI were explored. Results revealed that the conductivity of chiral PANI was closely associated with the molar ratio of DBSA to CTAB. When the ratio of DBSA to CTAB was 3:1, the highest conductivity of 39.71 S/cm was obtained. The chiral PANI was characterized by UV–vis absorption spectroscopy, circular dichroism (CD) spectra, Fourier transform infrared spectra (FTIR), field emitted scanning electron microscopy (FESEM) and X-ray diffraction (XRD). Our results demonstrated that this novel system was specific, simple and green, in which the controlled handedness PANI was obtained with various morphologies and high conductivity.

1. Introduction

Polyaniline (PANI) is one of the most practical future functional polymer materials because of the wide range of applications in electroluminescent discoloration devices, sensors, electromagnetic shielding, antistatic protection and battery anti-corrosion coating, etc. [1–4]. Chiral conducting PANI has received wide attention in the past few decades in view of the potential applications in chiral separation, asymmetric synthesis and pharmaceutics, etc. [5–7]. Chiral PANI can be synthesized traditionally in the presence of chiral acids, like (±)-camphor-10-sulphonic acid ((±)-CSA). The chiral inducer was found to play the key role in the formation of helical packing of PANI chains. Due to the use of environmentally harmful chiral acid in the synthesis of chiral PANI, further investigation was performed to find natural and environmentally chiral inducers. In recent years, DNA, polysaccharide and cellulose has been reported to induce the chirality of PANI [8–10].

Polyaniline is the polymer with π-electron conjugated structure and conductivity is one of the most important parameters. Previous reports showed that the choice of dopants influenced the conductivity of PANI to some extent [11–13]. By now most researchers have focused on the synthesis of PANI doped with one single type of dopant. Results showed that the conductivities of these PANI complexes were mostly no more than 10 S/cm [14–16]. Recently the chemical polymerization of aniline doped with different proportions of mixed surfactants or acids was reported. It was found that the PANI obtained in the mixed reaction systems presented relatively high conductivity [13,17–19]. In comparison with the corresponding single-component dopant, the polymerization of PANI in the mixed complex system had exhibited the potential to improve the conductivity of PANI, but none of the research tried the biocatalyzed synthesis of PANI in the mixed reaction systems.

Template-guide enzymatic synthesis of chiral polyaniline, because of the mild reaction conditions and pollution-free environmental performance, has also been intensively studied in order to enhance the solubility of polyaniline. Biocatalysts including horseradish peroxidase, palmtree peroxidase, and laccase had been investigated in the synthesis of conducting polyaniline in the past few years [20–22]. Considering the expensive price and easy inactivation property of peroxidase, hemoglobin (Hb) is deserved to study further as a low-cost and efficient biological catalyst with high stability which has been

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successfully utilized in the synthesis of conducting PANI [23]. Furthermore, we had explored the polymerization of aniline in DBSA reverse microemulsions catalyzed by Hb and found that the conductivity of polyaniline can reach to 0.90 S/cm when the water content (Wo) of the reverse microemulsions was 22.5 [24]. Herein, the specific synthesis of chiral conducting PANI in DBSA–CTAB complex system catalyzed by Hb was investigated in detail. Results showed that without any other chiral inducer, the polyaniline with controlled handedness was acquired in the presence of Hb which was confirmed by CD. In addition, it was found that the chiral PANI synthesized in DBSA–CTAB complex system exhibited relatively high conductivity.

2. Experimental

2.1. Materials

Bovine Hb was purchased from Shanghai Kayon Biochemistry Company (Shanghai, China). DBSA was obtained from Tokyo Chemical Industry Co. (Tokyo, Japan). CTAB, hydrogen peroxide and aniline monomer were purchased from Shanghai Chemical Agent (Shanghai, China). Aniline was distilled twice under reduced pressure before used. All other chemicals and solvents were analytical grade.

2.2. Preparation of PANI

The polymerization of aniline in DBSA–CTAB micelle solutions was typically carried out at room temperature in 10 mL Na_2HPO_4-citric acid buffer (0.2 M, pH 1.0–4.0) which contained 17 mM DBSA and CTAB ([DBSA]/[CTAB] = 1:0, 2:1, 3:1, 4:1, 5:1, 7:1, 1:4, 1:1, 0:1 and named as sample a, b, c, d, e, f, g, h, i in turn). 12.5 mM aniline was added into the solution containing DBSA and CTAB. The solution was mixed by constant stirring for 20 min. Then 0.2 mL Hb stock solution (1 mg/mL) was added under vigorous stirring. The reaction was initiated by the stepwise addition of diluted H_2O_2 (70 mM) within 1 h. After the addition of H_2O_2, the reaction was kept stirring for 24 h to complete the polymerization. Finally methanol was added to collapse the micelles. The precipitate was centrifuged and washed to remove the remaining surfactants and organic residuals. Then the final product was dried in oven under vacuum at 50 °C for 48 h to get dark green polyaniline powders.

2.3. Product characterization

UV–vis spectra of the products were recorded on a UV–vis absorption spectra (TU-1901, China). FTIR spectra were obtained using KBr pellets on a FTIR spectrophotometer (Nicolet Avatr 370 DTGS, America). The morphology of the obtained PANI was determined by FESEM (S-4800, Hitachi Co., Japan), and the FESEM samples were gold-sputtered prior to observation. Crystallinity of the polymer was carried out by X-ray diffractometer (Rigaku D/Max 2000, Japan). The circular dichroism (CD) spectra were recorded with a Jasco 815 circular dichromator. The conductivity of the polymer was measured using a four-probe conductivity instruments (HMS-775 conductometer Lakeshore, America).

3. Results and discussion

3.1. Effect of pH

The effect of pH on the Hb-catalyzed polymerization of PANI was examined in our experiments first of all. Fig. 1 gave the absorption spectra of PANI catalyzed by Hb in DBSA-CTAB micelle solutions at various pH. As shown in Fig. 1, it was observed that the platform peak between 340 and 420 nm at pH 1.0, 2.0 and 3.0 came

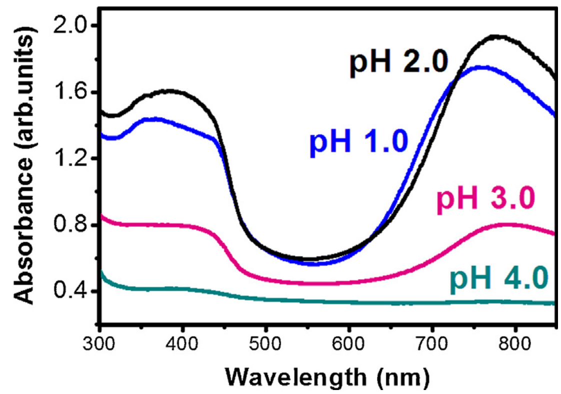

Fig. 1. UV–vis spectra of PANI (Sample d) synthesized at different pH.

from the combination of $\pi \to \pi^*$ transition energy gap (290–360 nm) and polarons band $\to \pi^*$ transition energy gap (380–440 nm) [20]. The strong absorption band at approximately 750–800 nm generated in this system indicated the formation of conductive PANI in the "compact coil" conformation [25]. While the characteristic absorption peaks were not observed at pH 4.0, suggesting that doped PANI can not be synthesized at this pH. Results indicated that the Hb-catalyzed polymerization of chiral PANI was pH-dependent in DBSA-CTAB micelle solutions, the same as other biocatalyzed synthesis systems of PANI [26].

3.2. Effect of ratios of DBSA to CTAB

Previous results had revealed that the constitution of the system influenced the formation of PANI [27]. The effects of different ratios of DBSA to CTAB on the formation of conductive PANI were determined in the following experiments. As shown in Fig. 2, it was found that when the ratio of DBSA to CTAB was 1: 0, namely, there were only DBSA as template contained in the micelles solutions, the absorption peak at 750–800 nm could be observed, suggesting the formation of conductive polyaniline (curve a). Under this most suitable surfactant concentration of 17 mM, after we raised the molar ratios of DBSA in the mixed micelles system (the total concentration of DBSA–CTAB is unchangeable, still 17 mM), the absorption peak at 750–800 nm boosted correspondingly. When the ratio of DBSA to CTAB reached to 5 or 7, the maximum of absorption peak was observed (curves e and f). However, with the increasing proportion of CTAB in the system, i.e., when the ratio of CTAB to DBSA reached to 1 or more, the absorption peak at 750–800 nm disappeared, indicating that

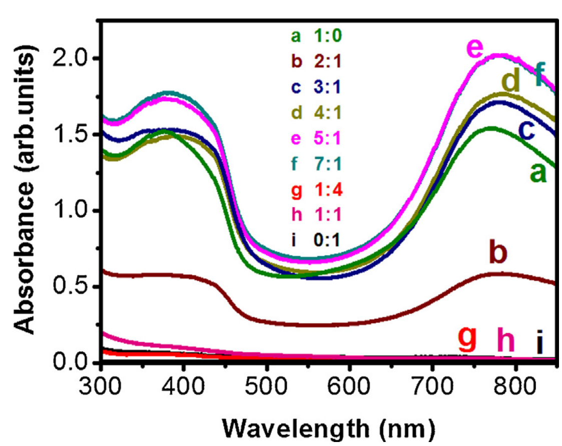

Fig. 2. The UV–vis spectra of PANI synthesized at different ratios of DBSA to CTAB.