

1-514

Synthesis of Polyaniline Using Electrostatically Layered Hematin Assemblies

Bon-Cheol Ku¹, Soo-Hyoung Lee¹, Wei Liu¹, Jayant Kumar², Ferdinando F. Bruno³,
Lynne A. Samuelson^{3*}

Center for Advanced Materials, Departments of Chemistry¹ and Physics², University of
Massachusetts Lowell, Lowell, MA 01854; ³Natick Soldier Center, U.S. Army Soldier &
Biological Chemical Command, Natick, MA 01760

ABSTRACT

The enzyme horseradish peroxidase has been recently used for the polymerization of water-soluble conductive polyaniline. Hematin, an ironporphyrin molecule that catalyzes the oxidative polymerization of aniline and phenol, is a robust and inexpensive biomimetic alternative to horseradish peroxidase. Composite thin film assemblies were fabricated by electrostatic layer-by-layer (ELBL) alternate deposition of a polyelectrolyte, poly(dimethyl diallylammonium chloride), and hematin. These multilayer assemblies were then used for the polymerization of aniline in the presence of a polystyrene sulfonate as a template. It was found that the polymerization rate depends on both pH and the concentration of hematin deposited and the polyaniline synthesis was possible both onto the ELBL surfaces and in solution. It was also discovered that it is possible to reuse the ELBL assembled hematin substrates for multiple aniline polymerizations.

INTRODUCTION

Conducting polymers have attracted considerable attention in many technological applications because of their wide range of electrical and optical properties as well as their good stability [1 - 3]. Polyaniline (Pani) has been investigated for such applications as a resin for coatings, lightweight-batteries, and sensors [4 - 6]. While Pani has promising properties, Pani must be cost effective to synthesize and have good processability for practical application. Many attempts have been made to improve the processability of Pani. One of them is the use of enzyme as a chemical catalyst. Enzymatic synthesis has several advantages compared to chemical preparative routes such as environmentally benign reaction conditions and the potential to produce product in high yield [7]. Recently, we reported enzymatically synthesized conducting polyaniline using horseradish peroxidase (HRP) [8 - 9]. In this system, the polyaniline formed in the presence of a template, sulfonated polystyrene (SPS), to form a water soluble Pani/SPS complex showed conductivity of 0.15 S/cm. However, the current cost and poor stability of the HRP at low pH needs to be addressed for potential large scale commercialization. Hematin, which is a hydroxyferritoporphyrine, is a promising, inexpensive, biomimetic alternative to HRP. Compared to HRP, hematin is a small molecule that is not soluble at low pH. Recently Akkara et al. reported the polymerization of phenol compounds using improved solubility and activity of hematin by increasing the pH to 11 [10]. However, this pH is prohibitive for the polymerization of conductive Pani in the presence of a polyelectrolyte template such as sulfonated polystyrene (SPS) [9]. In our reactions, a pH of 4.3 or lower is needed to form conductive Pani [11]. The poor solubility of hematin at low pH prohibits its use for aniline polymerization in its native form. To overcome these limitations, we fabricated hematin composite thin films using electrostatic layer-by-layer (ELBL) self-assembly which in general involves the stepwise adsorption of oppositely charged species onto a charged substrate. Hematin

has two carboxyl groups which can be negatively charged at high pH and thus can be easily deposited with the cationic polyelectrolyte, poly(dimethyl diallyl ammonium chloride) (PDAC). In the present work, we provide a detailed investigation of hematin multilayer film formation and the resulting catalytic activity and recyclability of these novel hematin layers for the polymerization of aniline.

EXPERIMENTAL DETAILS

Hematin was purchased from Sigma Chemical Co., St. Louis, Mo. Aniline (purity 99.5%), PDAC (20 wt% in water, Mw 100,000 – 200,000), poly (sodium 4-styrenesulfonate) (Mw 1,000,000) were obtained from Aldrich Chemical Co. Inc. (Milwaukee, WI) and used as received. Buffers of phosphoric acid (0.1M, pH 1, 2, 3) were used in the polymerization studies. The glass slides used as substrates for multilayer fabrication were purchased from VWR Scientific. Slide glasses (25x75 mm) were hydrophilized with 1% Chem-solv solution, which was obtained from Mallinckrodt, in deionized water under ultrasonication for use as a substrate.

Multilayer composite films were prepared with PDAC as the polycation and hematin as the polyanion at pH 11. All procedures were similar to that described previously except for the PDAC/Hematin concentration (5 mM/3 mM) [12]. Polymerization of aniline was typically carried out at room temperature in a 40 mL, 0.1 M phosphoric acid buffer solution, which contained a 1:1 molar ratio of SPS (Mw 1,000,000) to aniline 0.167g (0.81mmol). SPS was added first to the buffered solution, followed by an addition of 2.1 mL of aniline stock solution (0.036 mL/mL pH 1.4) with constant stirring. A 17 bilayer film of Hematin/ PDAC substrate was then immersed in the solution. To initiate aniline polymerization, 11 mL of H₂O₂ (0.25 w/w %) was added dropwise, incrementally, over 30 min. The reaction was maintained for 24 h, and carried out at different pH values (1.0, 2.0, 3.0). The rate of assembled hematin catalyzed polymerization was monitored and recorded by a Perkin-Elmer Lambda-9-UV-vis spectrophotometer at room temperature.

To monitor the recyclability of the ELBL assembled hematin catalyst for polymerization, 14 bilayers of hematin were chosen. The layered catalyst was used to polymerize aniline at pH 3.0 for 24 hours. This substrate, covered by Pani, was retested for polymerization of fresh aniline at pH 1.0. This procedure was similar to the aniline polymerization at pH 1.0 except for the H₂O₂ content, which was 5 mL (0.25 w/w %) instead of 11 mL. This test was repeated until activity of assembled hematin was undetectable.

RESULTS AND DISCUSSIONS

The multilayers were prepared by sequential deposition of PDAC and hematin from their respective solutions. The sequential absorption for the PDAC/hematin films deposited by ELBL are shown in figure 1. It was found that the deposition of hematin did not largely depend on adsorption time. Thus, a hematin adsorption of 5 min. was used throughout our deposition procedure for the PDAC/hematin film formation. The characteristic absorption peaks for hematin increased linearly and reproducibly with the number of PDAC/hematin deposition cycles.

To determine the pH effect on the catalytic activity, the polymerization of aniline was performed with pHs ranging from 1.0 to 3.0. The absorption spectra of Pani with SPS at different pHs are given both in the solution and on the substrate (Figure 2). At low pH, the polymer shows

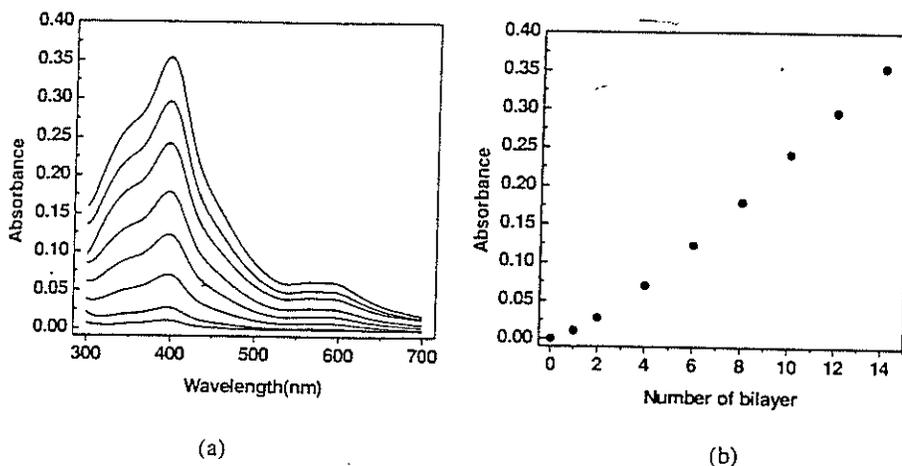


Figure 1. (a) UV-vis absorption spectra of PDAC/Hematin multilayer films as a function of the number of bilayers. (b) A linear relationship between absorbance and number of bilayer at λ_{max} (395 nm).

strong absorption bands at 700 – 800 nm and 300 – 400 nm which are due to polaron transitions [13]. At pH 3.0, the absorption of Pani/SPS complex was observed only on the substrate. Nevertheless, a pale yellow color was observed in the solution after 24 hours. However, at pH 1.0 and 2.0 the absorption characteristics of the conducting Pani/SPS complex were observed both in the solution and on the substrate. These results show that the template polymerization of aniline is strongly pH dependent.

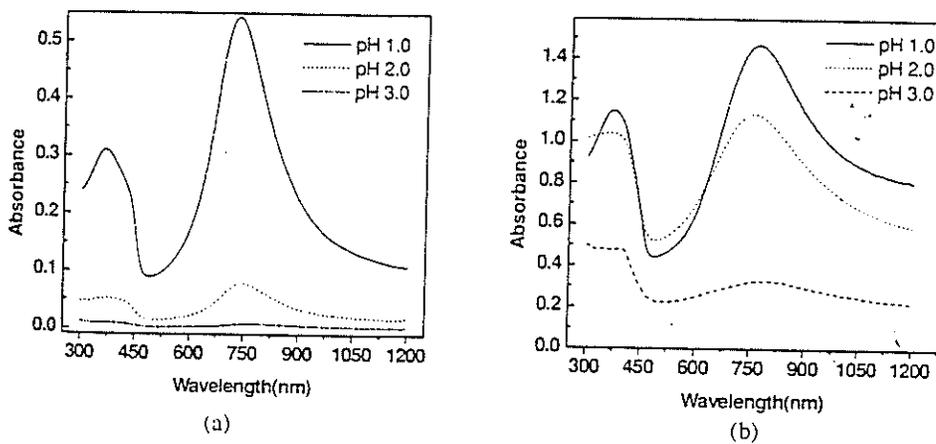


Figure 2. UV-vis spectra of SPS/Pani catalyzed using the ELBL assembled hematin substrate (a) in solution and (b) on the substrate.

To determine the redox behavior of the Pani/SPS complex in the solution, the absorption spectra of a complex prepared at pH 1.0 was studied with varying pH. Figure 3 shows the shift in absorption spectra of the complex with increasing pH from 1.0 to 11. At pH 1.0, the Pani is in the doped state as revealed by the presence of the polaron band transition at about 784 nm. As the pH of the complex is increased, the polaron bands at 784 nm gradually disappear, and a strong absorption due to exciton transition of the quinoid rings at 600 nm begins to emerge. At pH 11, the exciton band of Pani/SPS complex increased, indicating that the Pani has been fully dedoped to the emeraldine base form. To determine the redox behavior of the Pani/SPS complex on the substrate, the absorption spectra of a complex prepared at pH 3.0 was studied at different pHs. Figure 3 shows a similar shift in absorption spectra of the complex with increasing pH from 3.0 to 11. At pH 11, Pani is fully dedoped and exhibits an absorption peak at 585 nm. As the pH is decreased from 11 to 1, Pani was redoped as revealed by the absorption peak at 797 nm. However, the absorption spectra at pH 3.0 during redoping was different from the original collected at pH 3. This is possibly due to the strong interaction between Pani and the SPS molecules, which causes a pronounced delay in the redox process [14].

To test recyclability of assembled hematin substrate as a catalyst, a 14 bilayer composite hematin/PDAC film was studied. The polymerization was performed by using this substrate at pH 3.0. After 24 hours, a green film was obtained on the substrate. By using this substrate, polymerization was repeated at pH 1.0 with fresh reaction solution. It was found that the hematin substrate could be reused for several times. Figure 4 shows that intensity of the green color of the emeraldine salt form of Pani was decreased with each reaction, suggesting that the activity of hematin decreases with frequency of use. A possible explanation for this is that the hematin can leach out at low pH even though Pani covered the surface of substrate. However, it should be noted that multiple reactions could be carried out from one substrate and determination of the percent yield of the reactions is in progress.

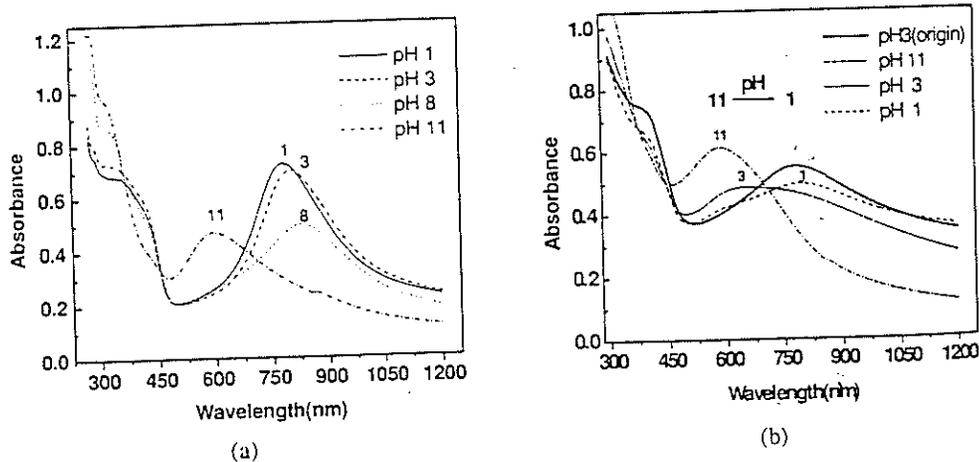


Figure 3. UV-vis spectra change of Pani/SPS complex during doping/dedoping (a) in solution and (b) on the substrate.

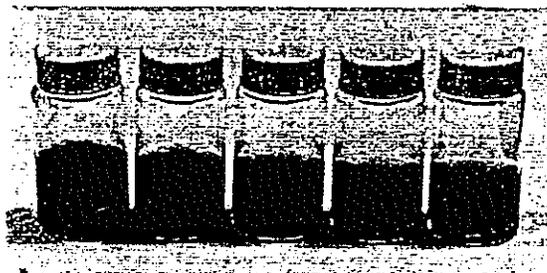


Figure 4. Photograph of a series of SPS/Pani solutions at pH 1.0. Assembled hematin was continuously used from left, 1st to right, 5th.

CONCLUSIONS

Conducting polyaniline was formed both in the solution and on the surface of an electrostatically assembled hematin substrate. It was observed that the rate as well as the concentration of polyaniline depends strongly on pH. It is believed that with further optimization, these hematin ELBL films may find wide application as catalysts for the synthesis of various polyanilines and polyphenols and also for use as potential biosensing devices.

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