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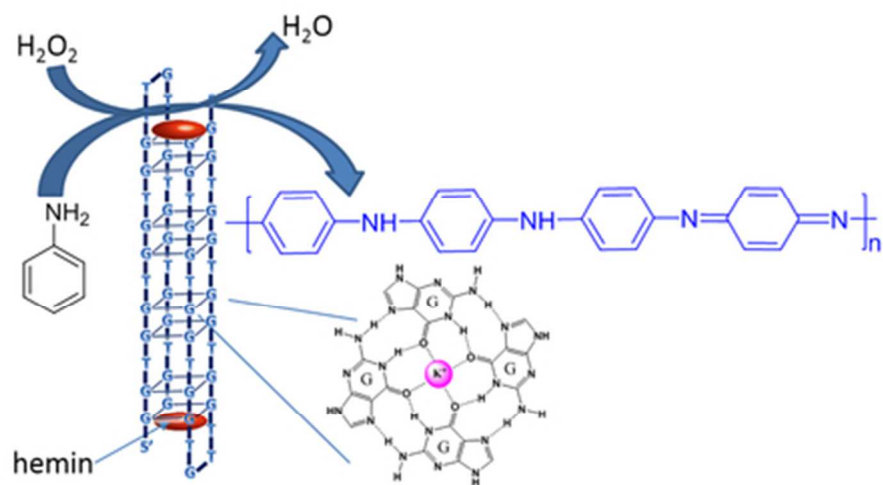


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Under simple and mild conditions, G-quadruplex DNAzyme-catalyzed oxidation and polymerization of aniline by hydrogen peroxide is achieved in aqueous medium.
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ARTICLE

Synthesis of Polyaniline via DNAzyme-Catalyzed Polymerization of Aniline

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In this report, a novel method for the synthesis of polyaniline in an aqueous medium, based on a G-quadruplex DNAzyme-catalyzed oxidation and polymerization of aniline by hydrogen peroxide in the presence of a polyanionic template, is described. The synthesis is simple and the experimental conditions are mild. The polymerization of aniline is carried out in an acidic aqueous medium with a catalytic amount of the DNAzyme. The study of pH influence on polymerization rate showed that aniline polymerization was occurring in a pH range from the pH 2.0 to 5.0 with an optimal pH of 3.0. The polymerization kinetics can be described by the classical Michaelis-Menten reaction mechanism. Comparing to the horseradish peroxidase-catalyzed polymerization of aniline, the advantages of using the DNAzyme as the catalyst in the polymerization of aniline are cost-effective and more tolerant to acidity of the reaction solution and high concentrations of hydrogen peroxide.

Introduction

As one of the important classes of conducting polymers, polyaniline (PANI) has been extensively studied due to its high conductivity in its doped (oxidized) state¹ and its intriguing electrochemical, electronic, optical, and electro-optical properties.² The conjugation mechanism of PANI is unique among the conducting polymers owing to a combination of benzenoid and quinoid rings leading to three different oxidation states, namely leucoemeraldine, emeraldine, and pernigraniline.³ It has been found that PANI exhibits insulator-to-conductor transitions and multiple color changes depending on its oxidation states and solution pH. PANI can be doped either by protonation with a protonic acid or by charge-transfer with an oxidation agent and its electronic and optical properties may be controlled reversibly by varying the doping level. Technical applications of PANI include biosensors,⁴⁻⁶ corrosion protection,⁷ energy-storage devices,⁸ and antistatic coating.⁹ PANI has also been commonly utilized to fabricate nanoelectronics including printed circuit board (PCB)¹⁰, organic light emitting diodes (LEDs)¹¹ and organic light weight batteries.¹²

PANI is commonly synthesized by oxidative polymerization of aniline in strongly acidic media either chemically¹³⁻¹⁷ or electrochemically.¹⁸⁻²⁰ Chemical polymerization of aniline is performed using strong oxidants such as ferric salts,¹⁴ bichromate,¹⁵ permanganate,¹⁶ or peroxydisulfate.¹⁷ These oxidants are able to oxidize aniline under highly acidic conditions, thus leading to the formation of chemically active cation radicals of aniline. The cation radicals formed react with aniline molecules, yielding oligomers and finally PANI. The reaction is far from being environmentally friendly because of high acid and oxidant concentrations, and the use of these oxidants also generates significant amounts of by-products

which require further steps of final product purification. Moreover, the reaction of chemical polymerization of aniline is not kinetically controllable. On the other hand, electrochemical polymerization of aniline and its derivatives typically is carried out in highly acidic aqueous solutions by the application of a constant voltage/current or by potential ramping.¹⁹ In comparison, electrochemical polymerization of aniline has several advantages over chemical polymerization since the process is clean and no toxic oxidants involved, and the synthesized PANI possess flexible electrical properties.²⁰ Electrochemical polymerization can also be used as coatings of electrodes by conducting PANI thin films because electrochemical polymerization/deposition enables coating of PANI on rather complex geometries. However, the electrochemical methods have some limitations. For instances, it is difficult to prepare a large amount of PANI in a short period of time because the polymerization is carried out only on the surface of the electrode. In addition, PANI synthesized by both chemical and electrochemical approaches is often confronted with over-oxidation state that may result in the degradation of PANI.²¹

In recent years, PANI synthesis via biocatalytic approaches using enzymes has become more and more attractive as an alternative synthetic route.²²⁻²⁸ Unlike the chemical approaches where a large amount of toxic materials are released as by-products, biocatalytic polymerization of aniline using enzymes is advantageous since it is a very simple one-step process carried under mild conditions²⁹ - does not require strong acidic media and highly toxic oxidizing reagents or additional purification steps. It is therefore an environmentally friendly approach with high potential for industrial polymer production in high yield without contaminant by products of oxidant degradation due to the efficiency of the biocatalyst.^{30,31} Moreover, the structure and solubility of PANI can be greatly

improved by optimizing the reaction conditions, which is benefit for further processing. Horseradish peroxidase (HRP) was first used for the synthesis of PANI.^{22,23} HRP is an oxidoreductase which catalyzes the radical polymerization of aniline in the presence of a mild oxidizing agent such as hydrogen peroxide. In the presence of hydrogen peroxide, HRP catalyzes the oxidation of aromatic amines and phenols to generate free radicals. The free radicals undergo coupling to produce dimers and further oxidation and coupling reactions result in the formation of PANI. Other enzymes such as laccase,²⁴ palm tree peroxidase,²⁵ bilirubin oxidase,²⁶ soybean peroxidase,²⁷ and glucose oxidase²⁸ were also used as catalysts for aniline polymerization under mild conditions in aqueous media. It should be noted that enzymes are very sensitive to hydrogen peroxide concentration which usually requires stepwise addition of diluted hydrogen peroxide to the reaction medium. Also, enzymes can be easily denatured by environmental changes because the minor alteration of their native protein conformation could result in complete loss of their catalytic activity.

More recently, it has been observed that single-stranded nucleic acids with specific sequences coupled with cofactors are catalytic through forming higher order structures – the so called G-quadruplexes – DNAzymes. DNAzymes are DNA molecules that have the ability to perform a chemical reaction, such as catalytic action. One interesting example of DNAzymes that reveals peroxidase-like activity is a supramolecular complex between hemin and a single-stranded guanine-rich nucleic acid.³² It was suggested that the intercalation of hemin into the guanine quadruplex docked layers of the nucleic acid leads to the biocatalytic functionality.³³ It has also been observed that this G-quadruplex DNAzyme can catalyze the polymerization of several aromatic compounds and produce according polymers.^{34,35} In the present work, a novel approach for the synthesis of PANI based on the G-quadruplex DNAzyme was developed which addresses limitations of both enzymatic and chemical polymerization of aniline. Comparing to natural peroxidases, the DNAzyme is much more stable and less expensive to produce by DNA synthesis. More importantly, unlike enzymes, the DNAzyme remains active in a wide range of hydrogen peroxide concentration and can be reversibly denatured and renatured many times without losing its activity. Therefore, the use of the DNAzyme as catalyst for aniline polymerization represents a viable alternative route in comparison with peroxidase-based synthesis. It is environmentally friendly and does not require a stepwise addition of diluted hydrogen peroxide to a reaction medium in contrast to the peroxidase-based approaches.

Experimental Section

Reagents and Apparatus

Aniline (> 99.5%), Polyacrylic acid (2100 sodium salt) (PAA), and hemin (> 98%, HPLC) were purchased from Sigma-Aldrich (St. Louis, USA). Hydrogen peroxide (H₂O₂) (QRec, 30–32%, AR) was obtained from ERC Sdn Bhd (Malaysia). Dimethyl sulfoxide (DMSO) was from MP Biomedicals LLC (OH, USA). H₃PO₄ (85%) was provided by Fisher Scientific Pte Ltd (Singapore). Oligonucleotide (5'-GGT GGT GGT GGT TGT GGT GGT GGT GG-3') was custom made by Integrated DNA Technologies Inc. (Iowa, USA). All the reagents were from Sigma-Aldrich and used without further purification unless specified. A 0.10 M phosphate buffer (PB) containing 0.10 M potassium chloride (KCl) was used in the aniline

polymerization study and its pH was adjusted by adding an appropriate amount of sodium hydroxide (NaOH) or phosphoric acid (H₃PO₄) solution. All aqueous solutions were freshly prepared with ultrapure water (18.3 MΩ·cm).

UV-Vis absorption measurements were carried out using an Agilent Cary 60 UV-Vis spectrophotometer (Agilent Technologies Singapore Pte. Ltd., Singapore). Fourier transform infrared (FT-IR) spectroscopic experiments were performed with a Bio-Rad Excalibur Series FTS 3000 spectrometer and the spectra were collected after 20 scans within 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. Cyclic voltammetric tests were conducted with a CHI 660D electrochemical analyzer (CH Instrument, Austin, Texas). A three-electrode system was used with a glassy carbon electrode (GCE) as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum wire as the auxiliary electrode, respectively. All potentials reported in this work were referred to the SCE. The standard four-probe technique using an Agilent 4157 parameter analyzer (Agilent Technologies, Santa Clara, CA) in conjunction with a probe station was employed to measure the electrical conductivity of compressed pellets of polyaniline samples. Molecular weight was determined by Gel Permeation Chromatography (GPC) instrumentation which includes water model 515 HPLC pumps with model 2414 refractive index detector (Alliance, USA). Scanning electron microscopy (SEM) image was collected on JEOL JSM-6701F Field Emission Scanning Electron Microscope (FESEM).

Preparation of the G-quadruplex DNAzyme

5.0 mM stock solution of hemin was prepared by dissolving 50 μmol hemin in 10 mL DMSO and stored at -20°C in dark. The working solution of hemin (100 μM) was prepared by diluting the stock solution with ultrapure water. 100 μM the oligonucleotide solution was prepared by dissolving an appropriate amount of the oligonucleotide in 0.10 M KCl and then heated to 88°C for 10 min; after which the solution was gradually cooled down to room temperature in 20 min.³⁶ The DNAzyme solution (50 μM) was prepared by adding dropwise 1.0 mL of the 100 μM hemin solution to 1.0 mL of the oligonucleotide solution. The mixture was incubated for 40 min at room temperature to fold the G-quadruplex and form the DNAzyme (G-quadruplex hemin complex).

DNAzyme-catalyzed polymerization of aniline

50 mM aniline/PAA (1:1) solutions with different pH values ranging from 2.0 to 5.0 were prepared in 0.10 M PB buffer. 2.0 μM the DNAzyme and 50 mM hydrogen peroxide (final concentration) were then added to the aniline/PAA solutions to initiate aniline polymerization. PAA in the solutions was used as a polyelectrolyte to procure a more ordered *para*-linked PANI with fewer branches and increase the solubility of the synthesized PANI in aqueous solution.³⁷ UV-Vis spectra of the reaction mixture at 750 nm were recorded with the proceeding of the polymerization. The same mixture without the DNAzyme was used as control and its UV-Vis spectra were also recorded. In the mechanistic study of the polymerization reaction, the concentration of one substrate was fixed and that of the second substrate was varied. UV-Vis spectra were collected immediately with a 15-s interval. The reciprocal of the initial reaction rate versus the reciprocal of substrate concentration was plotted. Each point was repeated for three times.

Results and Discussion

DNAzyme-catalyzed polymerization of aniline

It was reported that certain DNAzymes, such as the G-quadruplex-hemin DNAzyme, exhibit peroxidase-like activities in the presence of peroxidase substrates and hydrogen peroxide, thus offering new possibilities to engage DNAzymes in biocatalytic applications.^{32,38,39} Compared to the bulky and fragile peroxidases, their small size and high chemical stability make them attractive candidates to be used as efficient catalysts in organic synthesis and polymer synthesis. In addition, it is critical that the polymerization of aniline should be carried out in an acidic medium with a pH value below the pK_a value of aniline ($pK_a \sim 4.63$), to effectively utilize the polyanionic template by forming electrostatic adducts along PAA between cationic aniline molecules and anionic acrylic acid moieties and to minimize the parasitic branching of PANI.⁴⁰ Unfortunately, most natural enzymes are active and stable only around neutral pH values. In contrast, the chemical nature of the DNAzyme may be stable and remain active in a much wider pH range.

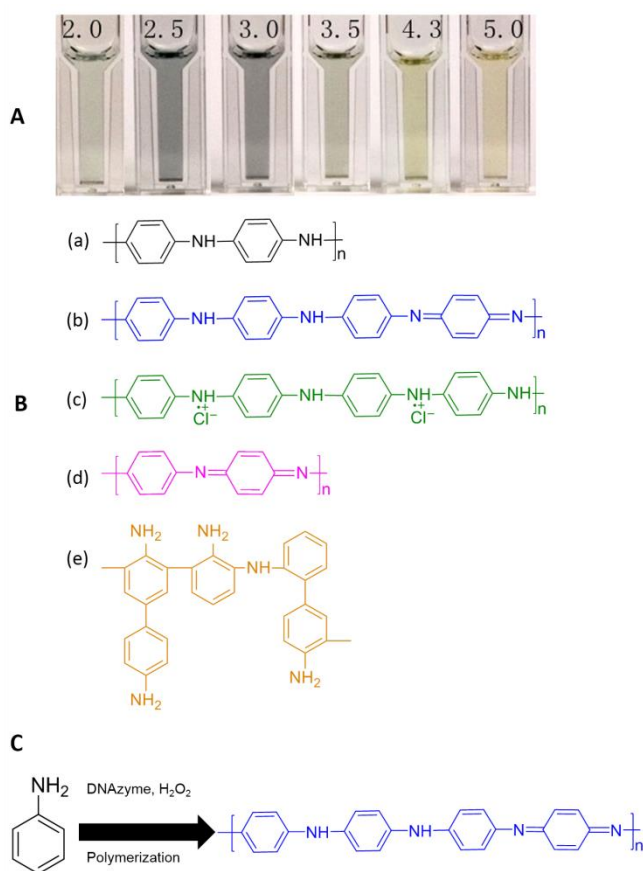


Fig. 1. (A) Photo of the results of reaction mixtures (50 mM aniline/PAA + 50 mM hydrogen peroxide + 2.0 μM the DNAzyme) at different pH values and (B) Different structures of PANI: (a) Leucoemeraldine, (b) Emeraldine base (EB), (c) Emeraldine salt (ES), (d) Pernigraniline, (e) *Ortho*- and *para*-substituted carbon-carbon, carbon-nitrogen bond structure. (C) DNAzyme-catalyzed polymerization of aniline in the presence of hydrogen peroxide.

To demonstrate this concept, we first evaluated the catalytic activity of the DNAzyme in the oxidation and polymerization of aniline. It was observed that in accordance with the HRP-catalyzed polymerization of aniline, the reaction between aniline and hydrogen peroxide in the presence of the DNAzyme produces exactly the same colored products (Fig. 1). As seen in Fig. 1A, similar to the HRP-catalyzed oxidation and polymerization of aniline,⁴¹ a blue-green color developed immediately after spiking a tiny amount of the DNAzyme ($\leq 2.0 \mu\text{M}$) into a mixture of 50 mM aniline/PAA and 50 mM hydrogen peroxide at $\text{pH} < 4.0$; while the color of the reaction mixture at $\text{pH} > 4.0$ was yellow. The blue-green product is believed to be emeraldine base, which is half-oxidized state of PANI (Fig. 1B (b)). This emeraldine base can be easily doped by proton and consequently transformed to the emeraldine salt (Fig. 1B (c)), which is the most popular state of PANI since it has an excellent electrical conductivity. The emeraldine base can also be further oxidized to the fully-oxidized pernigraniline (Fig. 1B (d)) after a prolonged period of polymerization. In addition, before forming emeraldine base, there is a state of PANI that cannot be recognized by naked eye – leucoemeraldine (Fig. 1B (a)). It is the fully-reduced state of PANI with white or clear in color. As to the yellow product, it is likely the mixture of *ortho*- and *para*-substituted carbon-carbon, carbon-nitrogen bond structure²³ and aniline oligomers⁴² (Fig. 1B (e)).

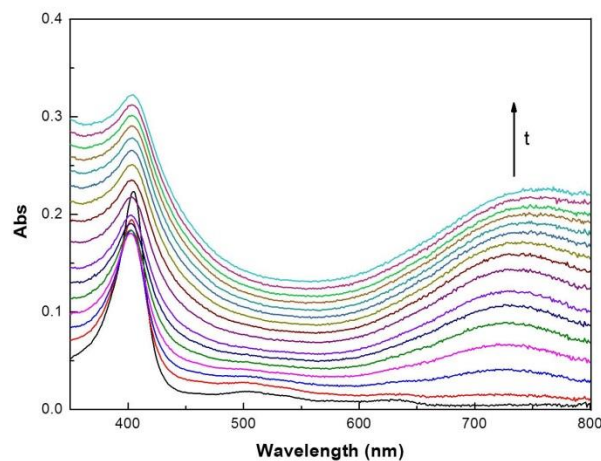


Fig. 2. UV-Vis spectra of the polymerization of aniline by hydrogen peroxide in the presence of the DNAzyme. The working solution contained 50 mM aniline/PAA (1:1), 2.0 μM the DNAzyme and 50 mM hydrogen peroxide in pH 3.0 0.10 M PB buffer. From bottom to top: 0, 15, 30, 45, 60, 75, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 s after starting the polymerization.

As shown in Fig. 2, the PANI catalytically polymerization of aniline in the presence of the DNAzyme has two UV-Vis absorption peaks, one relatively sharp peak at $\sim 410 \text{ nm}$ and another broad peak at $\sim 750 \text{ nm}$. As the polymerization proceeded, the absorbances for both peaks intensified. The UV-Vis spectra are in good agreement with those found in literature.⁴¹ Considering the DNAzyme used in this polymerization system has a sharp UV-Vis adsorption peak at $\sim 410 \text{ nm}$ due to the chromogenic hemin, which may interfere with the analysis of the polymerization process. This interference was circumvented by using the absorbance data at 750 nm. Nonetheless, all the data induced from the absorbance

at 750 nm were generally consistent with those obtained at 410 nm. Thus, the absorbance at 750 nm was therefore utilized to investigate the kinetics of the polymerization of aniline in the following sections.

Optimization

From the pH optimization experiments depicted in Fig. 3A, pH 3.0 was found to be optimal for the DNAzyme-catalyzed polymerization of aniline. When the solution pH was larger than 4.0, the polymerization rate was substantially suppressed, judging by the much slower change in the absorbance at 750 nm. Meanwhile, to rule out the possibility of the effect of pH on the extinction coefficient of PANI, the optical properties of the synthesized PANI was thoroughly investigated. PANI synthesized at pH 3.5 was separated by centrifugation at 15000 rpm. Then it was dispersed to 0.10 M PB buffers with different pH values. As can be seen in Fig. 3B, the influence of pH on the extinction coefficient of PANI was relatively negligible comparing to the drastic changes in the polymerization of aniline under different pH values. The average molecular weight of the synthesized PANI under the optimal condition was found to be 51300 through GPC.

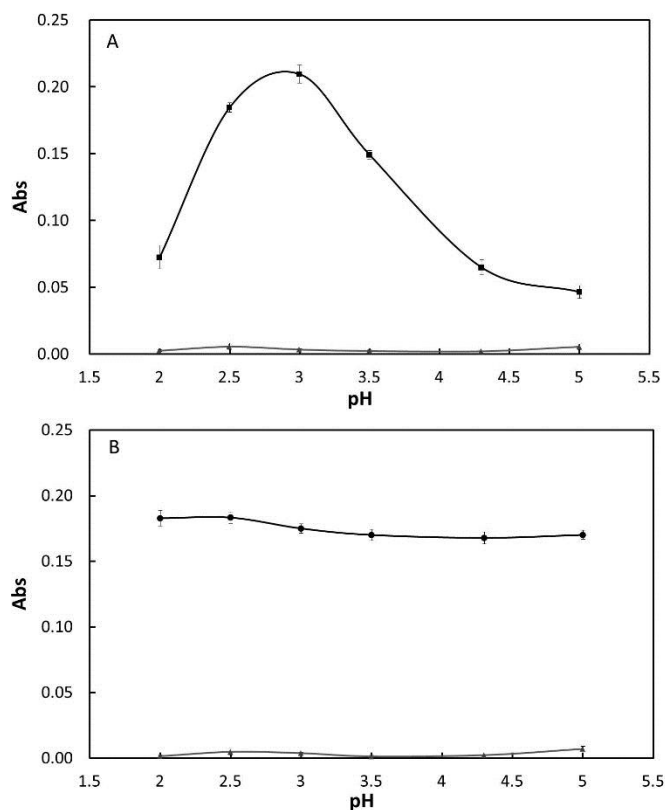


Fig. 3. (A) pH optimization of aniline polymerization. Working solution: 50 mM aniline/PAA, with (■) and without (▲) 2.0 μM the DNAzyme, and 50 mM hydrogen peroxide in phosphate buffer with different pH values ranging from 2.0 to 5.0. UV-Vis measurements were carried out 6 min later after starting the polymerizations. (B) The effect of pH on the extinction coefficient of the synthesized PANI.

As shown in Fig. 4, the reaction rate increased with the increase of the concentration of the oxidizing agent hydrogen peroxide. It was shown that the reaction rate approached to its

maximum in the presence of ≥ 50 mM of hydrogen peroxide. Also, it was shown that the reaction rate can be conveniently controlled at desired level just by simply adjusting the concentration of hydrogen peroxide. However, further increasing in hydrogen peroxide concentration was little beneficial to the polymerization of aniline. On the contrary, high concentrations of hydrogen peroxide may be detrimental since a considerable amount of the PANI may be over-oxidized or undergo the undesired *ortho*-branching which will have a negative impact on the conductivity of the PANI. On the other hand, in the commonly used HRP-catalyzed polymerization of PANI, the concentration of hydrogen peroxide can never reach such a high level as HRP will be quickly deactivated in the presence of ≥ 10 mM hydrogen peroxide.

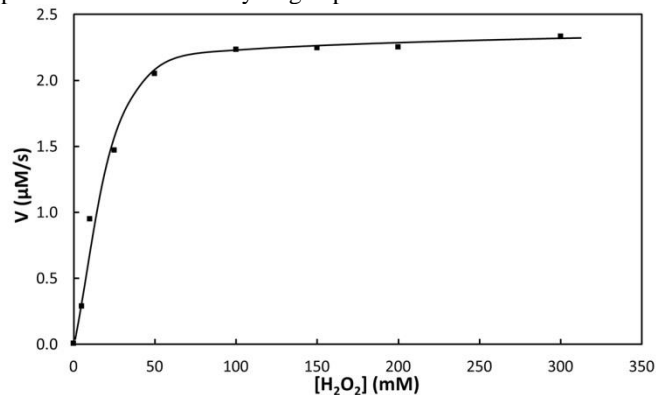


Fig. 4. Effect of the amount of hydrogen peroxide on the reaction rate of aniline polymerization. Working solution: 50 mM aniline/PAA, 2.0 μM DNAzyme and different concentrations of hydrogen peroxide in the phosphate buffer (pH 3.0).

Kinetics of the DNAzyme-catalyzed polymerization of aniline

It was found that the initial rate of polymerization varied linearly with the concentration of the DNAzyme, suggesting that the polymerization of aniline is first-order with respect to the DNAzyme. This is a good indication that the catalytic process may obey the Michaelis-Menten kinetics.⁴³ And more importantly, the linear dependence on the DNAzyme concentration strongly suggests that the DNAzyme is stable in the reaction medium. To gain insight in the mechanism of the catalytic polymerization of aniline in the presence of the DNAzyme, further investigations were conducted over wide ranges of aniline and hydrogen peroxide concentrations. Varying the concentrations of aniline and hydrogen peroxide, a series of experiments were carried out to explore the kinetics of the DNAzyme-catalyzed polymerization of aniline. Fig. 5 shows double reciprocal plots of initial polymerization rate versus one substrate concentration, obtained at predetermined concentrations of the second substrate. Good linearity ($R^2 > 0.99$) was obtained throughout the experiments. These linear plots strongly suggest that the polymerization process obeys the Michaelis-Menten kinetic mechanism as it accords with the classical Michaelis-Menten equation (Eq. 1):

$$\frac{1}{v} = \frac{K_m}{v_{max}[S]} + \frac{1}{v_{max}} \quad (\text{Eq. 1})$$

The linear correlation between the initial polymerization rate and the concentration of substrate will bring great benefit for its future applications in chemical sensors and biosensors. That is

because such a feature will simplify the relationship between the analytical signal and the target concentration, making the data process quite concise and easy to be understood.

In addition, when the concentration of one substrate was preset and the concentration of the other substrate was varied, it was found that these linear double-reciprocal curves are parallel to each other, *i.e.* the slopes of these curves are the same. This is the typical characteristic of the ping-pong mechanism,⁴⁴ demonstrating that the DNAzyme will bind and react with the first substrate and release the first product before binding and reacting with the second substrate.

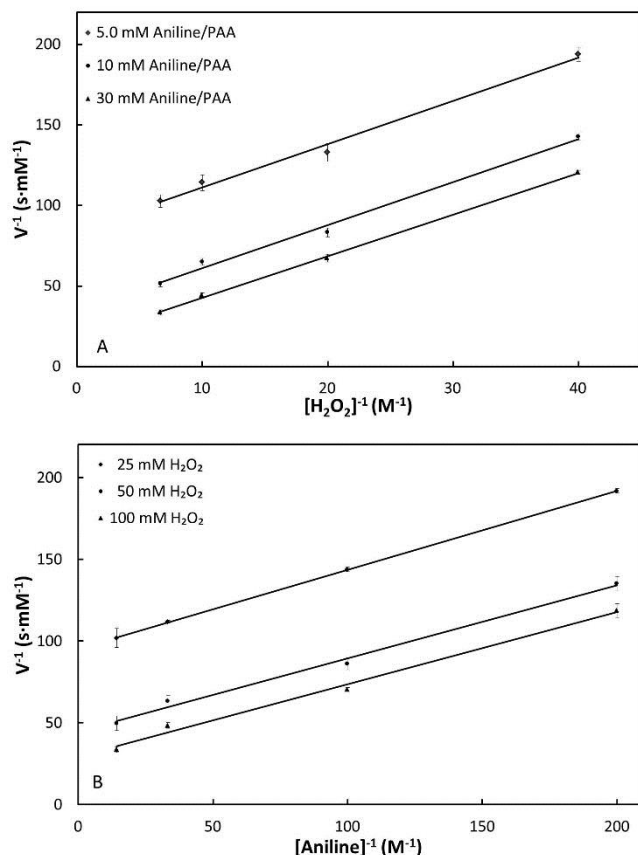


Fig. 5. Double-reciprocal plots of the catalytic activity of 2.0 μM DNAzyme at a fixed concentration of one substrate and varying concentration of the second substrate.

Characterization of the polymerization product

FT-IR spectroscopy was utilized to characterize the synthesized PANI. Fig. 6 depicts the FT-IR spectrum of the proton doped half-oxidized PANI, which was green in color. Proton doping was accomplished by treating the as-synthesized PANI in 2.0 M HCl. As seen in the spectrum, the adsorption peaks at 3450 and 3235 cm^{-1} can be assigned to the asymmetric and anti-symmetric $-\text{NH}^+$ stretching of PANI.⁴⁵ The absorption band at 2920 cm^{-1} belongs to C–H vibration.⁴⁶ The two very sharp bands at 1572 and 1500 cm^{-1} are due to quinone and benzene ring deformation.⁴⁷ The C–N stretching of the secondary aromatic amine is located at 1300 cm^{-1} . The band at 1133 cm^{-1} is originated from $\text{Q}=\text{NH}^+-\text{B}$ or $\text{B}-\text{NH}^+-\text{B}$ after doping (Q = quinoid unit, B = benzoid unit) and the band at 820 cm^{-1} is assigned to C–H out of plane bending of *para*-substitution pattern, indicating a head-to-tail coupling of aniline.⁴⁸ The FT-IR spectrum confirms that the reaction product between aniline

and hydrogen peroxide catalyzed by the DNAzyme is PANI in its emeraldine salt form.

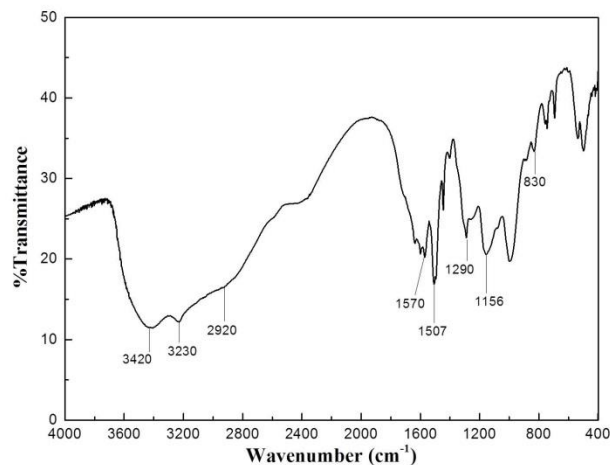


Fig. 6. FT-IR spectrum of the proton doped half-oxidized PANI (emeraldine salt).

Supportive evidence of the formation of PANI can be found in cyclic voltammogram of the reaction product coated electrode. As mentioned early, PANI exists in three different oxidation states which can be conveniently interconverted by electrochemical means and cyclic voltammetry in particular.⁴⁹ Moreover, an understanding of inter-conversion of various oxidation states of PANI produced can also be conveniently studied by cyclic voltammetry. A cyclic voltammogram of the synthesized PANI is shown in Fig. 7. Similar to PANI prepared by conventional methods,^{50,51} two pairs of current peaks centered at 0.20 and 0.49 V were observed. These peaks can be assigned to the oxidation of PANI from leucoemeraldine to emeraldine and to further oxidation from emeraldine to pernigraniline.⁴⁹⁻⁵¹ At potentials more cathodic than the first oxidation peak of 0.26 V, PANI is in its non-conducting leucoemeraldine state. As the potential is swept more anodically, the current is raised sharply and peaks at 0.26 V due to the partial oxidation of PANI to yield the emeraldine salt form. The complete oxidation peak of the polymer is then obtained at 0.51 V at which point the emeraldine salt is converted to the non-conducting pernigraniline salt. Upon potential reversal, two reduction peaks appeared at 0.47 and 0.15 V, corresponding to the reduction of pernigraniline to emeraldine and emeraldine to leucoemeraldine, respectively. The inter-conversion of different structural forms could be done repetitively without any shifts in peaks or changes in the repetitive cyclic voltammetric scans. It is the partially oxidized, protonated form of PANI, known as the emeraldine salt that is of particularly interest as it is responsible for PANI's electron conductivity.

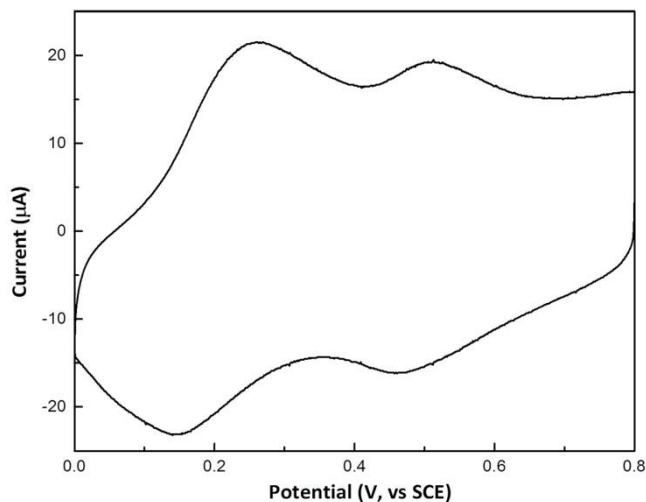


Fig. 7. A cyclic voltammogram of PANI on GCE in 2.0 M HCl aqueous solution from 0 to 0.8 V at a scan rate of 50 mV/s.

Scanning electron microscopy (SEM) image was collected in order to characterize the structure of the synthesized PANI. As can be seen in Fig. 8, the morphological characteristic of the synthesized PANI is quite similar to the one in previous study.⁵³ The linear structure with an average diameter at around 90 nm can be clearly identified, which can validate that linear PANI molecules were well formed along the PAA template.

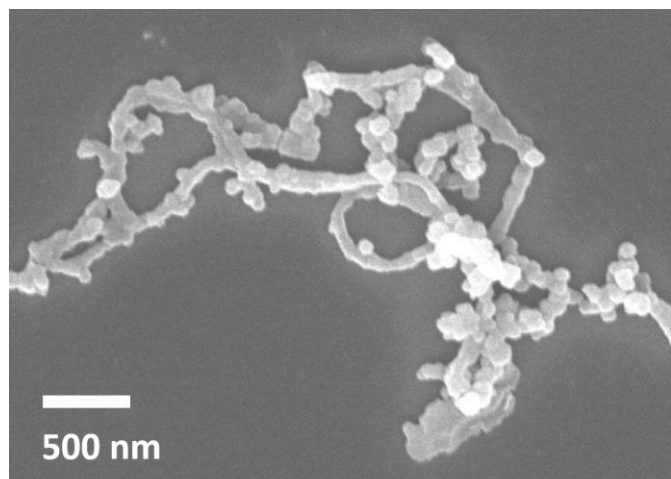


Fig. 8. Morphological characterization (SEM image) of the synthesized PANI.

Proton doping

According to previous studies, the PANI synthesized at pH 3.0 was estimated to have an electrical conductivity around 10^{-6} S/cm,⁵² which was in the semiconductor regime; while after doping, the electrical conductivity can be increased to as high as 10^{-3} S/cm,⁵³ closing to that of conducting materials. Indeed, the conductivity of the as-synthesized PANI in the pH 3.0 PB buffer was found to be $\sim 3.8 \times 10^{-6}$ S/cm, whereas the conductivity of the PANI after doping in 2.0 M HCl was significantly enhanced to 180 S/cm approaching that of metal conductors. Such a characteristic of the adjustable electrical conductivity brings a lot of convenient means to construct electrical/electrochemical bioassays considering that materials with designated electrical conductivities can now be fabricated

instead of finding various materials to fit in different devices. Furthermore, since H^+ doping is reversible,⁵⁴ PANI may also act as an “on-off” switch, *i.e.* when PANI is doped, it is conductive and thus turns on the switch that allows electric current to flow through; while after dedoping, it is insulating and turns off the switch that would block the current at that point.⁶ Based on such a simple mechanism, interesting technical applications such as environmental monitoring or biosensing are expected.

Conclusions

In summary, it was demonstrated for the first time that the G-quadruplex-hemin DNAzyme effectively catalyzes the polymerization of aniline under acidic conditions. The DNAzyme in this study consists of single-stranded DNA and hemin mimicking that of peroxidase. Such a peroxidase-mimicking catalyst is more tolerant to the environmental conditions than its natural peroxidase counterparts, which will lose the activity once the concentration of hydrogen peroxide in working solution is ≥ 10 mM or the pH is ≤ 4.5 . In contrast, the DNAzyme can still maintain a good activity under acidic conditions (e.g. pH 2.5) or a much higher hydrogen peroxide concentration up to several hundred millimolars. Due to its robustness, the DNAzyme can be employed as an attractive alternative to peroxidases under extreme conditions. Predominantly para-coupled PANI with minimal branching can be conveniently synthesized in pH 2.5–3.0 phosphate buffer with a stoichiometric amount of hydrogen peroxide. Since the reaction conditions are mild and no toxic by-products are released during the oxidative polymerization of aniline, the DNAzyme-catalyzed system is much more environmentally friendly than the conventional chemical routes. The much higher concentration of hydrogen peroxide allowed in the system implies a simpler and more efficient PANI synthesis route. Also, this approach may be extended to the synthesis of other conducting polymers such as polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene).

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Notes and references

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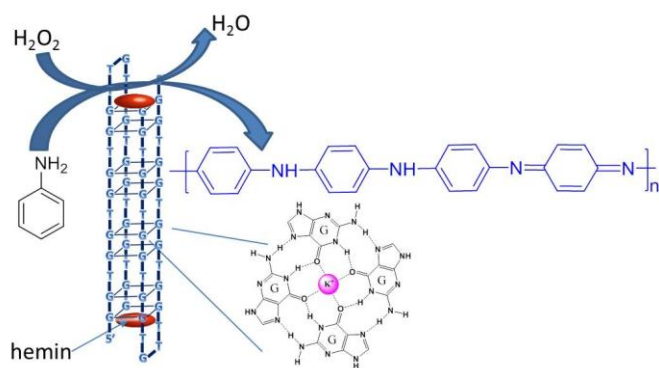
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Synthesis of Polyaniline via DNzyme-Catalyzed Polymerization of Aniline

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Under simple and mild conditions, G-quadruplex DNzyme-catalyzed oxidation and polymerization of aniline by hydrogen peroxide is achieved in aqueous medium.