ACS Macro Letters

Letter

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Protein-Induced Synthesis of Chiral Conducting Polyaniline Nanospheres

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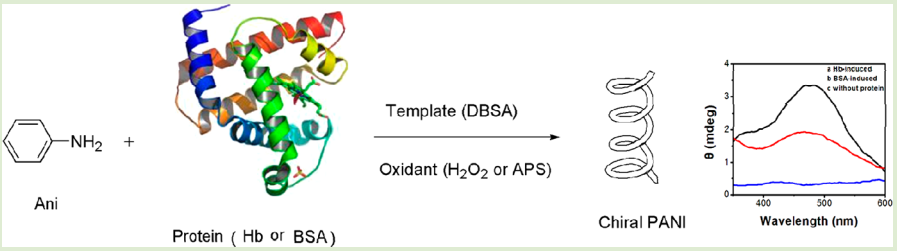
Supporting Information



ABSTRACT: A green and novel method for the synthesis of chiral conducting polyaniline was developed. Chiral polyaniline induced by protein was obtained by using the template-assisted polymerization route. The experimental results demonstrated that proteins such as bovine hemoglobin and bovine serum albumin had the capacity to direct enantio specificity of PANI which may be ascribed to the α-helix structure within the proteins. The achieved chiral conducting polyaniline exhibited nanometered, spherical shape according to scanning electron microscopy and transmission electron microscopy images. Moreover, the high degree of crystallinity and conductivity of chiral polyaniline induced by protein was acquired.

In recent years, chiral conducting polymers have attracted great attention for the potential applications in materials science, chemical and biological sensors, catalysis, pharmaceutics, enantioselective separation, and so on.[1] Especially, there has been increased interest in synthesizing chiral conducting polyaniline (PANI) due to the high environmental stability, simple synthesis, and low cost.[2] In general, chiral PANI was synthesized by chemical, electrochemical, or enzymatic in situ polymerization methods in the presence of chiral inducers.[3−5] Besides, chiral conducting polyaniline can also be synthesized via doping emeraldine base with a chiral inducer in organic solvent.[6] The chiral inducer was found to play the key role in the formation of helical packing of the polymer chains. Chiral acid, typically (+) or (−)-10-camphorsulphonic acid (CSA) has been intensively studied as the chiral inducer. In addition, aniline oligomers, DNA, polysaccharide, and cellulose have never been used to induce the chirality of PANI.[7−10]

However, the protein, which is the other kind of the natural chiral macromolecules, has never been noticed to fabricate the chiral PANI yet. In this paper, we presented a protein-induced synthesis of chiral conducting PANI, which had not been reported before. The synthesis of chiral conducting PANI was carried out at room temperature in dodecylbenzenesulfonic acid (DBSA) micelle solutions. Protein was used as chiral inducer. Oxidant (H_2O_2 or ammonium persulfate) was added to initiate the polymerization of aniline. The CD spectra of PANI synthesized in DBSA micelle solutions with the addition of aniline, hemoglobin (Hb) and H_2O_2 were shown in Figure 1A. It was found that PANI has an absorbance peak maximum at around 450 nm, which is a signature of the optical active PANI. With the increased concentration of Hb, the absorbance peak appeared at longer wavelength (475 nm) owed to the different oxidation states of PANI.[11,12] Hb had been reported to be utilized to catalyze the synthesis of PANI.[13] This result indicated that Hb can not only catalyze the polymerization of aniline, but also induces the chirality of polymer without any assistance of chiral inducer.

As is known to us all, Hb is a common mimic enzyme that is made of hematin and globin. However, it had been proved that the hematin has no capacity to direct enantiospecificity for the PANI chains,[14] which suggested that the protein (globin) possibly induced the chirality of PANI. In order to verify the hypothesis, the polymerization reaction was carried out in DBSA micelle solutions with the addition of aniline, 2 mg Hb, H_2O_2, and different amounts of bovine serum albumin (BSA) instead of the equal quantities of Hb. The results in Figure 1B, as expected, showed that PANI was optical active which can be seen from the characteristic peak at around 450 nm. And the amount of the BSA was found to affect the strength of the CD signal. To further confirm the role of protein, the chemical polymerization of PANI by the addition of aniline, Hb or BSA, and ammonium persulfate into DBSA micelle solutions was performed. As shown in Figure 1C,D, from which we got to know that chiral PANI was obtained in the presence of Hb or BSA, indicating that protein

Received: January 4, 2014
Accepted: March 10, 2014
Published: March 11, 2014

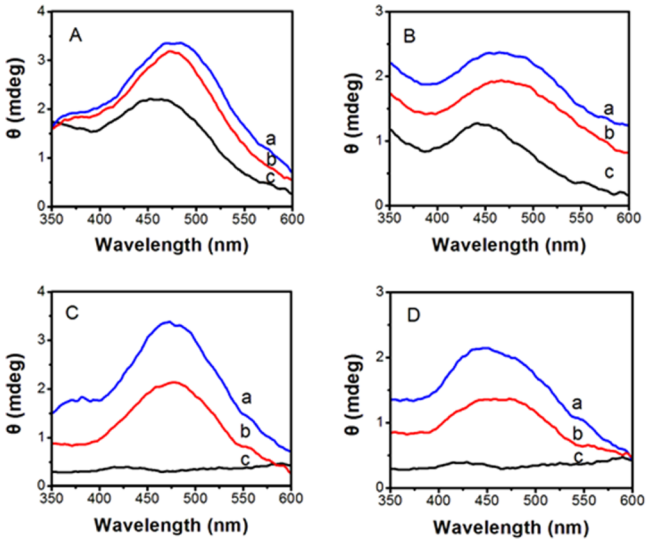


Figure 1. (A) CD spectra of chiral PANI in the presence of (a) 10, (b) 8, and (c) 6 mg Hb and H_2O_2; (B) CD spectra of chiral PANI in the presence of 2 mg Hb, H_2O_2, and (a) 8, (b) 6, and (c) 4 mg BSA; (C) CD spectra of chiral PANI in the presence of ammonium persulfate and (a) 10, (b) 6, and (c) 0 mg Hb; (D) CD spectra of chiral PANI in the presence of ammonium persulfate and (a) 8, (b) 4, and (c) 0 mg BSA.

prominently induce the chirality of PANI. Besides, the dissymmetry *g*-values ($\Delta\varepsilon/\varepsilon$) of chiral PANI induced by Hb and BSA as shown in Table 1 indicated that with the increasing of

Table 1. Dissymmetry *g*-Values of Chiral PANI Induced by Hb and BSA

sample	protein content (mg)	g ($\times 10^4$)
Hb-PANI	6	1.11
Hb-PANI	10	1.52
BSA-PANI	4	0.98
BSA-PANI	8	1.16

protein content, the *g*-value was also improved.[15] This is the first time to report the phenomenon that protein can act as the chiral inducer, which was significantly distinctive compared with previous reports.[1−11]

Subsequently, the pH-dependent experiment was used to investigate the chirality of PANI conducted by doping and dedoping process. Figure 2 showed the UV−vis and CD spectra of chiral PANI under various pH conditions. As is commonly known, the color as well as the UV−vis spectrum of PANI can be reversibly switched by changing the pH. After dedoping process

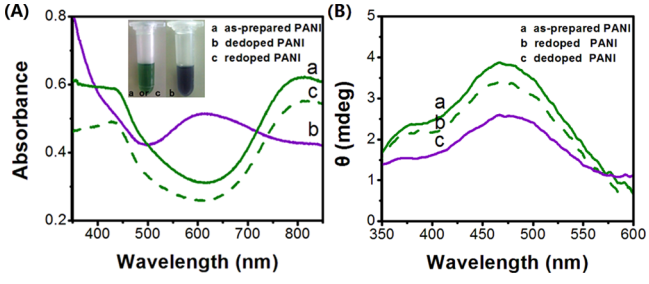


Figure 2. Typical UV−vis (A) and CD (B) spectra of as-prepared chiral PANI induced by Hb, dedoped by NaoH to pH 10, and redoped by H_3PO_4 to pH 2, respectively.

the color turned to violet (inset photo b) and UV−vis spectra of dedoped PANI salt exhibited an absorbance band at around 600 nm corresponding to emeraldine base. But when the pH was adjusted to 2, the olive green color was back again (inset photo a or c). The peaks at 800 nm reappeared in UV−vis spectra indicated that doped PANI was obtained once again. Meanwhile it was also observed that the CD spectra of the dedoped PANI still exhibited a lower peak at around 450 nm, suggesting that dedoped PANI had not lost the chirality completely at pH 10, which also can be proved from the *g*-values in Supporting Information (Table S1). Furthermore, we removed the chiral protein after polymerization and repeated the dedoping-redoping experiment. The CD signal of the polyaniline at 475 nm revealed that the memory effect was present possibly(data was not shown). It manifested that protein has the similar inducing function as the traditional inductive agents such as CSA or DNA and so on.[8,16,17]

The elemental compositions of the chiral PANI induced by Hb and BSA were tested. From Table 2, we can see that the more

Table 2. Elemental Compositions of Chiral PANI Induced by Hb and BSA

sample	N (%)	H (%)	C (%)	S (%)
control PANI	8.54	6.64	64.46	4.90
Hb(6 mg)-PANI	9.72	6.89	61.12	4.40
Hb(10 mg)-PANI	10.27	7.05	59.58	4.13
BSA(6 mg)-PANI	9.78	6.85	60.69	4.53
BSA(10 mg)-PANI	10.07	7.03	59.36	4.46

protein, the more N% and H% and the less C% and S% in PANI. The slight increase of N% and H% with the increasing of protein may be assigned as the formation of hydrogen bond between L-amino acids residues inside the proteins and chains of PANI,[18] and the characteristic FTIR bands of PANI located at 2800 cm^{-1} to 3200 cm^{-1} confirmed the presence of hydrogen bond (Figures S1 and S2). On the other hand, part of proteins may combine with DBSA via electrostatic interactions and reduce the quantities of DBSA doped into PANI and thus, led to the decrease of C% and S% in PANI chains. These are all strong evidence to prove that the protein has the interaction with the PANI chains so as to facilitate the formation of chiral PANI.

Additionally, in the present investigation, we observed that all of the CD spectra of chiral PANI synthesized in the presence of proteins exhibited positive signals, indicating that the proteins play the role of preferentially directing PANI to a specific chiral conformation. Our results agreed with the report on horseradish peroxidase (HRP) that catalyzed the synthesis of specific one-handed helical conformational conducting PANI, which showed positive signal from the CD spectra.[19] Similarly, chiral PANI with positive CD signal was synthesized by using DNA served as the chiral inducer with a right-handed double helix structure.[17,20] In that most enzymes and globular proteins have a significant α-helical content (e.g., HRP, bovine hemoglobin, bovine serum albumin),[21−23] it is supposed that the right handedness of the α-helix structure in these natural proteins resulted in the right-handed chiral PANI, and that is why the positive peak was presented in the CD spectra.

The spherical morphology of chiral PANI samples was recorded by SEM (Figure 3A) and TEM (Figure S4). The nanometered, spherical conformation of chiral PANI induced by Hb or BSA was observed. Unexpectedly, it was found that the nanometered, spherical conformation of chiral PANI induced by

dx.doi.org/10.1021/mz500008f | ACS Macro Lett. 2014, 3, 295−297

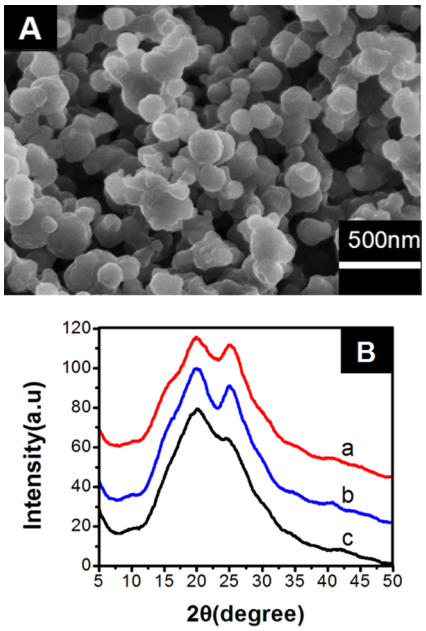


Figure 3. (A) SEM of PANI nanostructures induced by Hb; (B) XRD of PANI induced by Hb and BSA (a, b) and control PANI (c).

Hb was only observed at pH 2.0, whereas the irregular and amorphous granules were found at pH 1.0 or 3.0 (Figure S5).The possible reason for this phenomenon was that DBSA formed the spherical micelles at pH 2.0. Otherwise, the shape of micelles will be changed to amorphous at other pH. The XRD spectra of chiral PANI induced by Hb and BSA were examined as shown in Figure 3B. The peak centered at $2\theta \sim 19.9°$ may be ascribed to the periodicity parallel to the polymer chain, which was a characteristic peak of amorphous emeraldine base form of PANI.[24] While the peaks at $2\theta \sim 25.1°$ may be caused by the periodicity perpendicular to the polymer chain which was the mark of the highly ordered crystalline structure.[25] Our results indicated that the chiral PANI induced by protein had the conspicuous degree of crystallinity that can be found from the higher peak of $2\theta \sim 25.1°$ than that of the control PANI. The conductivity of conducting PANI induced by Hb was measured and the conductivity of 7.3×10^{-1} S·cm^{-1} was much higher than that of chiral PANI induced by CSA reported by Thiyagarajan et al.[14]

In summary, we successfully synthesized the optical active polyaniline nanospheres induced by proteins for the first time. We demonstrated that protein can act as a chiral inducer to preferentially direct polyaniline to a specific chiral conformation. Most importantly, we also open possibilities to develop artificial helical polymers, supramolecules, and oligomers with a controlled handedness. Up to now, much more studies on the protein-induced chiral polyaniline are still in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, synthesis of chiral conducting polyaniline induced by protein, FTIR, SEM, and TEM of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation (No. 21303105), Shanghai Normal University foundation (No. SK201229), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (No. ZX2012-05), and Innovation Program of Shanghai Municipal Education Commission (No. 11YZ227).

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