Cetyl trimethyl ammonium bromide (CTAB) micellar templates directed synthesis of water-dispersible polyaniline rhombic plates with excellent processability and flow-induced color variation

Yong Ma, Chongyin Zhang, Chunping Hou, Hao Zhang, Hepeng Zhang, Qiuyu Zhang, Zhanhu Guo

Key Laboratory of Applied Physics and Chemistry in Space of Ministry of Education, School of Science, Northwestern Polytechnical University, Xi’an 710072, PR China
Integrated Composites Laboratory (ICL), Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA
Shanghai Aerospace Equipments Manufacture, China Aerospace Science and Technology Corporation, NO.100, Huaning RD, Shanghai 200245, PR China

A R T I C L E   I N F O
Article history:
Received 2 March 2017
Received in revised form 30 March 2017
Accepted 4 April 2017
Available online 6 April 2017

Keywords:
Template
PANI rhombic plates
Water dispersibility

A B S T R A C T

Well-defined PANI rhombic plates are produced via a cetyl trimethyl ammonium bromide (CTAB) micellar soft template route in low acid environment. Lamellar micelles consisting of CTAB and ammonium persulfate (APS) molecules not only serve as both soft templates and oxidant for oxidative polymerization of aniline, but also provide intermolecular interactions to assemble two-dimensional PANI sheets to three-dimensional rhombic plates. Detailed mechanistic studies meanwhile reveal that fabricating such regular rhombic plates cannot be separated from the synergistic effect of the optimal pH value and suitable anions. The prepared PANI rhombic plates exhibit water dispersibility, processability, and flow-induced color variation, which is supposed to be attributed to the intermolecular interactions between residual CTAB molecules and PANI molecules. Using these rhombic plates as a model system, the results and strategies presented here provide insight into the general scheme of morphology and dimension control in the low acid environment for conducting polymers.

© 2017 Published by Elsevier Ltd.

1. Introduction

Because morphology and dimension are the decisive factors in controlling the practical properties and performance of materials, the synthesis of inorganic and organic materials with uniform morphologies and special dimensions has become the focus of attention [1–5]. As one of the intensively investigated conducting polymers, polyaniline (PANI) is unique for its environmental stability, nonredox acid/base doping, and controllable electrical and optical properties [6]. Compared to its bulk aggregates, regular PANI micro/nanostructures have advantages in wide applications [7–9]. Many studies have lately focused on one-dimensional (1D) PANI nanostructures since their low dimensions and high surface area are of interest for development of enhanced conductivity and improved sensitivity and responsibility of chemical sensors [10–13]. In comparison with 1D nanostructures, multi-dimensional (MD) morphologies of PANI provide a great deal of opportunities to explore new significant performance and uses. For example, PANI nanorices assembling into hexagonal microplates aligned shoulder to shoulder exhibited anisotropic characteristics of electrical transport [14]. Chiral PANI nanospheres induced by proteins had enantiospecificity [15]. Self-healing reagents encapsulated into the PANI capsules could be controllably released by adjusting the redox state of capsules [16]. Additionally, PANI capsular structures were able to measure diffusion coefficient of ions [17] and worked as the materials for a dye-sensitized solar cell [18].

PANI is commonly polymerized by oxidizing aniline molecules either electrochemically or chemically in an acid environment. There are some pioneering works reported to fabricate PANI MD morphologies. With the aid of electrodeposition, PANI nanobelts were prepared directly onto Ti sheets [19]. Leaf-like PANI were synthesized in the presence of amphiphilic triblock copolymer F127 [20]. By etching hard templates such as metallic oxide, PANI...
nanorings [21], hollow spheres [22], and chain-like hollow spheres [9] were produced. PANI from plate-like structures to flower-like superstructures had been tailored by altering the molar ratio of oxidant to monomer in the range of 0.1:1–0.8:1 [23]. Wan’s group reported PANI boxes [24], brain-like structures [25], rambutan-like spheres [26], as well as junctions and dendrites [27] by employing different organic acids. In a separate study, different dimensional PANI morphologies could be obtained by controlling the nucleation of the crystals and the non-covalent interactions between the doped oligomers [28]. Although so many PANI MD morphologies have been reported, the synthesis of regular PANI rhombic plates still remains scientifically challenging. The difficulty in obtaining this structure is the lack of adequate guidance of PANI nucleation and growth. In recent years, cationic surfactant cetyl trimethyl ammonium bromide (CTAB) has been researched as an additive for forming MD structures of conducting polymers including nanobelts, ribbon, nanoplates, etc. [29–33]. Furthermore, the low concentration of acid solution resulting in slow polymerization of aniline allows enough time for the ordered arrangement of freshly formed PANI building blocks [34]. Therefore, it is promising to obtain PANI rhombic plates by means of using surfactant CTAB in a low acid environment.

Herein, we report the successful synthesis of regular PANI rhombic plates by utilizing surfactant CTAB micellar soft template in a static 0.010 M HCl solution at room temperature. The formation mechanism and the growth process of the rhombic plates are clarified, for which the significance of the dosage of CTAB, pH value, and the kinds of anion are also illuminated. The rhombic plates display water dispersibility, processability, and flow-induced color variation, which promises this structure for multifunctional applications in optical devices.

2. Experimental section

2.1. Materials

Aniline (Hongyan Chemical Reagent Co., Ltd.) was purified by distilling it under reduced pressure and storing it in a refrigerator. Hydrochloric acid (HCl; Beijing Chemical Works), cetyltrimethyl ammonium bromide (CTAB; Kemiou Chemical Reagent Co., Ltd.), cetyltrimethyl ammonium chloride (CTAC; Shanpu Chemical Reagent Co., Ltd.), ammonium persulfate (APS; Hongyan Chemical Reagent Co., Ltd.), and absolute ethanol (Fuyu Chemical Reagent Co., Ltd.), ammonium bromide (CTAB; Kemiou Chemical Reagent Co., Ltd.) were of analytical grade and used as received. Deionized water was applied throughout all the synthetic processes. The conductivity value of the sample, which was pressed into pellets beforehand, was received by a RTS-9 four probe measurement. The transmission spectra were measured by a LabTech UV Power spectrophotometer.

2.2. Synthesis of PANI rhombic plates

In a typical run, purified aniline (0.30 mL) and CTAB (0.50 g) were sequentially dispersed in an HCl solution (90 mL, 0.010 M) to form a homogeneous solution via ultrasonic stirring for half an hour. Another HCl solution (10 mL, 0.010 M) containing APS (164.2 mg) was quickly injected into the foregoing solution all at once to initiate the polymerization. The white flocculent precipitate appeared immediately, which gradually turned brown in color with increasing the reaction time. The polymerization was left to stand at room temperature for 10 h. The sediment was suction filtered with ethanol and deionized water several times and dried in vacuum oven at 70 °C for 12 h. The purified PANI rhombic plates were obtained.

2.3. Growth process of PANI rhombic plates

A series of experiments were carried out, and their reaction conditions were the same as those of aforementioned quintessential synthesis of PANI rhombic plates with the exception of changing the dosage of CTAB: 0.050, 0.10, 0.20, 0.30 g.

2.4. Effect of pH value and kinds of surfactant

Many experiments proceeded and their polymerization conditions were the same as those of above typical synthesis of PANI rhombic plates except that 0.0, 0.030, 0.10, 0.50, and 1.0 M HCl solution were separately used.

An experiment was carried out and its experimental conditions were as same as those of synthesis of PANI rhombic plates but in the presence of CTAC (0.50 g) instead of CTAB.

2.5. Characterization

Field emission scanning electron microscopy (FE-SEM) images were generated with a ZEISS MERLIN microscope; samples dispersed in ethanol were deposited onto silicon wafers and sputtered with platinum by a JFC-1600 auto coater at a 20 mA current for 300 s prior to observation. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-3010 microscope with Oxford 794-CCD camera at an accelerating voltage of 300 kV; samples suspended in ethanol were dropped onto copper grids coated with a carbon support film before observation. Fourier transform infrared spectrum (FTIR) was taken from 4000 to 400 cm\(^{-1}\) on a Bruker TENSOR 27 spectrometer. X-ray diffraction pattern (XRD) was determined on a Shimadzu XRD-7000S diffractometer with Cu\(_{\text{Kα}}\) radiation (λ = 1.548 Å) from 5 to 50°. The conductivity value of the sample, which was pressed into pellets beforehand, was received by a RTS-9 four probe measurement. The transmission spectra were measured by a LabTech UV Power spectrophotometer.

3. Results and discussion

Our experimental results indicate that regular PANI rhombic plates are produced by adding CTAB to the polymerization of

Scheme 1. Molecular formula and 3D mode of CTAB molecule.
aniline in a still 0.010 M HCl solution at room temperature. As evident from SEM image of Fig. 1 (a), the as-synthesized PANI rhombic plates have smooth surface and sharp angles, with 3.0–7.7 μm in thickness, horizontal and vertical diameters of 19.1–46.0 and 27.1–90.2 μm. A compared PANI sample obtained in the same reaction conditions of rhombic plates but without adding CTAB is displayed in Fig. S1 (Supplementary Material). From the SEM images at different magnifications, it is easily found that the as-synthesized PANI is in the shape of sheets and like-spheres. A closer look at the like-spheres indicates that they have a rough surface. The appearance of these irregular agglomerates having coarse surface is supposed to be a result of poor solubility and quick precipitation of the freshly formed PANI. In the low concentration of HCl solution, because the doping level is insufficient, the long-chain oligomers with lower solubility coagulate into irregular agglomerates [35,36]. Furthermore, for reducing the interfacial energy between the newly formed PANI and water molecules, these PANI agglomerates favor the formation of rough surfaces [37].

FTIR spectrum of PANI rhombic plates is given in Fig. 1 (b) (blue). The N-H stretching vibrations appear at 3000–3500 cm⁻¹; there are two sharp peaks due to the different types of hydrogen bonded N-H stretching vibrations of secondary amines at 2979 and 2856 cm⁻¹; the peaks at 1590 and 1485 cm⁻¹ correspond to the C=C stretching deformation of quinonoid and benzoid rings; the peak at 1269 cm⁻¹ is attributed to the C-N stretching vibrations; the 1108 and 717 cm⁻¹ are ascribed to C-H in plane and out of plane deformation, respectively [38,39]. The FTIR spectrum convincingly confirms the formation of PANI, Fig. 1 (b) (black) represents the XRD pattern of the rhombic plates. A sharp peak at 8.3° is a result of the periodic distance between N atom and dopant acid on adjacent main chains [10]. The peaks at 18.8 and 25.2° are relative to the periodicity in the direction parallel and perpendicular to the polymer chains [40]. In addition to these dominant characteristic peaks, several peaks including those at 6.4, 15.8, 16.7, 20.9, 22.7, 24.9, 29.5, 41.3 and 42.8 appear, which are caused to the introduction of CTAB (JCPDS 25-1588, shown at the bottom of Fig. 1 (b)). Besides, the conductivity value of PANI rhombic plates is in the range of 10⁻⁴–10⁻⁵. The low conductivity is thought to be ascribed to the low acid environment, the addition of CTAB surfactants, and unfriendly conducting morphology.

To clearly reveal the mechanistic rationale of formation of PANI rhombic plates, PANI morphological evolution is investigated with increasing the dosage of CTAB. A series of electron microscope images of the resulting samples are shown in Fig. 2. In SEM image of Fig. 2 (a), when the dosage of CTAB is 0.050 g, a variety of truncated irregular sheets with 6.5–15.9 μm in long axis are obtained. At a closer observation, inset TEM image manifests the emergence of the smooth margin and sharp angle of the sheet. As CTAB increases to 0.10 g, quadrilateral and zigzag sheets are formed (SEM image of Fig. 2 (b)), whose sizes are bigger than that of truncated irregular sheets. The rough edges of quadrilateral sheet and the wide middle with two pointed ends of zigzag sheet are clearly observed in inset TEM images. From SEM image of Fig. 2 (c), one can find that cloud-like plates dominate the PANI morphology with adding 0.20 g CTAB, and their diameter further increases in contrast with the quadrilateral and zigzag sheets. Inset SEM image demonstrates that the cloud-like plates are composed of stacked sheets, implying that there is a self-assembly process happened from the sheets to cloud-like plates. When CTAB is up to 0.30 g, less regular PANI rhombic plates are discerned in SEM image of Fig. 2 (d). Of particular attention is that there are PANI debris decorating the surface of rhombic plates, which suggests that the inadequate CTAB dosage presents a limited control to PANI orchestration. Based on the experimental results, it is likely that the morphologies of PANI experience a bottom-up self-assembly process from small, thin, irregular sheets to big, thick, regular plates with increasing the dosage of CTAB.

Towards the aniline polymerization, PANI often imparts a tolerance to completely different morphologies in other concentrations of HCl solution [41,42]. With regard to CTAB polymerization system, the pH value also has an important influence on the resulting PANI structures. When the polymerization is carried out in 0.0, 0.030, 0.050, 0.10, 0.50, and 1.0 M HCl solution, respectively, distinct morphologies instead of desired rhombic plates are attained. From SEM image of Fig. 3, it is readily observed that both of two PANI samples produced in 0.50 and 1.0 M HCl solution are made up of disordered agglomerates. The scattered structures obtained in other concentrations of HCl solution can be seen in SEM image of Fig. S2 (Supplementary Material). The formation of these agglomerates is a consequence of the water solubility increase of aniline molecules. With increasing the concentration of HCl solution, more aniline molecules are dispersed in the solution rather than in the inside of CTAB micelles, since water-soluble aniline cations form by electrostatic attraction between aniline molecules and H⁺ [43]. In this case, the polymerization of aniline takes place in the solution. Due to the lack of the guidance of CTAB micelles, disordered agglomerates are formed. On the basis of morphologies obtained in other pH values, we clarify that the amount of aniline cations in the polymerization system is a key element to the fabrication of PANI rhombic plates.

In order to elucidate the impact of electrostatic interactions resulting from surfactant molecules, a comparative experiment is carried out in the presence of cetyl trimethyl ammonium chloride (CTAC). The size of irregular PANI plates is about 1/3 times as big as

Fig. 1. (a) SEM image and (b) FTIR spectrum and XRD pattern of PANI rhombic plates.
Fig. 2. SEM images of PANI samples synthesized with different dosages of CTAB: (a) 0.050, (b) 0.10, (c) 0.20, and (d) 0.30 g, magnified samples shown in their corresponding inset TEM (a, b) and SEM (c) images.

Fig. 3. SEM images of PANI samples separately obtained in (a) 0.50 and (b) 1.0 M HCl solution, other reaction conditions the same as those of the PANI rhombic plates.

Fig. 4. (a) Low magnification and (b) high magnification of irregular PANI plates obtained in the presence of CTAC, other reaction conditions the same as those of the PANI rhombic plates.
that of rhombic plates, as shown in SEM image of Fig. 4 (a). Magnified SEM image of Fig. 4 (b) confirms that the irregular plates are adhered with each other. The sticking phenomenon is ascribed to the differences of electrostatic interactions and size of anions. During the reaction process, for maintaining the charge balance, surfactant micelles are encased with a myriad of anions. Cl\(^-\) has stronger electrostatic attraction and smaller size compared to Br\(^-\), which on the one hand favors the attraction of the micelles, on the other hand weaken steric hindrance of micelle movement. Accordingly, the polymerization yields effortless aggregation and fusion of freshly formed PANI building blocks. This situation seriously damages the self-assembly process of the building blocks, and thereby impairs their possibility to grow into regular structures. Through the CTAC experiment, suitable intermolecular interactions between micelles are another indispensable factor for the development of PANI rhombic plates.

Correlating the morphology evolution of rhombic plates associated with the effects of pH value and intermolecular interactions on the PANI morphologies, a lamellar micelles mechanism is believed responsible for orchestrating PANI rhombic plates, as shown in Fig. 5. In the polymerization solution, chemical structures ([CTA]\(_2\)S\(_2\)O\(_8\)) consisting of two cetrimonium cations and one S\(_2\)O\(_8\)\(^{2-}\) anion are generated immediately after pouring into APS solution [32]. Afterwards, the lamellar micelles composed of sheet-like complex of ([CTA]\(_2\)S\(_2\)O\(_8\)) whose formation is favored by the inherent amphiphilicity of ([CTA]\(_2\)S\(_2\)O\(_8\)), are spontaneously fabricated. Such structure with cetrimonium cations in the middle and S\(_2\)O\(_8\)\(^{2-}\) anions in the two terminals is beneficial to reduce the contact of hydrophobic cetrimonium cations to water and increase the contact of hydrophilic S\(_2\)O\(_8\)\(^{2-}\) anions to water, respectively. Aniline molecules migrate to the interior of lamellar micelles from the solution owing to their poor water solubility. The migration process in 0.010 M HCl solution extremely differs from that in 1.0 M HCl solution where the aniline cations prefer to migrate to the interface between the micelles and aqueous HCl medium [32]. Thereafter, aniline molecules are oxidatively polymerized by the S\(_2\)O\(_8\)\(^{2-}\) anions of the ([CTA]\(_2\)S\(_2\)O\(_8\)) concurrently reducing S\(_2\)O\(_8\)\(^{2-}\) anions to SO\(_4\)\(^{2-}\) anions. After aniline polymerization and reduction of APS, lamellar micelles gradually degrade leaving behind the PANI sheets. Because the polymerization usually proceeds preferentially and continuously in the close proximity of existing PANI [22], these PANI sheets can further enlarge and thicken themselves. During this process, zigzag sheets and cloud-like plates are successively generated, since the active centers are concentrated on the top of plates. In the meantime, under the optimal intermolecular interactions, these building blocks assemble into rhombic plate along their large facets. As time goes by, regular PANI rhombic plates are ultimately fabricated.

The glass vial containing the resulting PANI rhombic plates in water is displayed in optical image of Fig. 6 (a). Amazingly, the plates with micron level size in the dedoping state exhibit good dispersibility even though standing undisturbed for 6 h. The reason is that there are residual CTAB molecules attaching on the surface of rhombic plates. The existence of these surfactant molecules plays roles in dispersing and stabilizing the rhombic plates in water [44]. For visual clarity, PANI samples acquired in other dosages of CTAB (0.0, 0.050, 0.10, 0.20, 0.25, 0.30 g) are shown in optical image of Fig. 5 (Supplementary Material). It is worth noting that although regular rhombic plates have much larger size than the others, they possess far better water dispersibility. Because of maximum dosage of CTAB used, relatively more CTAB molecules remain on the periphery of the rhombic plates, giving rise to the best water dispersibility.

The good water dispersibility makes it very convenient to process the rhombic plates for practical applications [45]. Continuous films or coatings can be easily obtained through solution processing methods such as drop-casting or spray-coating [46,47]. In optical image of Fig. 6 (b), casting film of rhombic plates not only exhibits a smooth surface with uniform brown color, but also possesses outstanding transmission. The good transmission of film can be affirmed by the plastic ruler shown under the glass slide, which is better than that of films prepared by electrochemical process [48]. Moreover, the transmission spectra of glass slide and as-formed PANI film are shown in Fig. 7. The transmission of them in the visible region is about 90% and 65–70%, respectively. The spectra further demonstrate that the PANI film has good transmission. The ease of process, with the combination of film-forming and good transmission, promises these PANI rhombic plates for potential application in optical devices.

Interestingly, when shaking the vial, the rhombic plates display...
nacreous color as shown in optical image of Fig. 6 (c). All other samples also have the same but weak color change with the exception of one obtained without CTAB. Moreover, CTAB solution (0.50 g dissolved in 100 mL water or 0.010 M HCl solution) and pure PANI samples dispersed in 100 mL water with CTAB added don’t have the ability of color change as well. Hence, it is deemed that when only hydrogen bonding formed between CTAB molecules and PANI molecules during the polymerization process, as proved in aforementioned FTIR spectrum, the phenomenon of color change happens. Although the reasons are yet to be fully ascertained, this color change has been postulated to the collision of the rhombic PANI molecules during the polymerization process, as proved in 

4. Conclusions

Regular PANI rhombic plates are prepared by adding CTAB to the reaction system in the static 0.010 M HCl solution at room temperature. On the basis of the discussions of evolution process, pH value, and kinds of surfactants, the lamellar micelles mechanism is proposed and rationalizes the formation process of rhombic plates. These rhombic plates have good water dispersibility, excellent processability, and flow-induced color variation, and the possible reasons for these properties are also explained. The remarkable performances make the PANI rhombic plates work as functional building blocks for fabricating optical devices. The method presented herein also affords the possibility to realize the regular MD structures of other conducting polymers.

Acknowledgment

We gratefully appreciate the support of the National High Technology Research and Development Program of China (863 Program) (Grant 2012AA02A404), the National Natural Science Foundation of China (Grant 51603168), and the National Natural Science Foundation of Shannxi (Grant 2015JM2050). This research is supported by NPU Foundation for Graduate Innovation.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2017.04.010.

References

[16] L.-P. Lv, Y. Zhao, N. Vilbrandt, M. Galle, A. Vimalanandan, M. Rohwerder,