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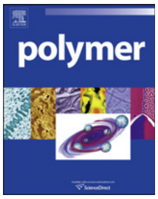

3D-boxlike polyaniline microstructures with super-hydrophobic and high-crystalline properties

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ABSTRACT

Three-dimensional boxlike microstructures assembled from 1D-nanofibers of polyaniline (PANI) were synthesized by a template-free method in the presence of perfluorosebacic acid (PFSEA) as the dopant for the first time. The 3D-boxlike microstructures show both super-hydrophobic and high-crystalline properties. The trick of forming such complex micro/nanostructures is that the PFSEA not only serves as both dopant and soft-template, but also provides hydrogen bond and hydrophobic interactions as driving forces for self-assembly from 1D-nanofibers to 3D-boxlike microstructures due to low-surface energy perfluorinated carbon chain and two hydrophilic –COOH end groups.

1. Introduction

Synthesis of nanomaterials with well-controlled morphology and size is a key issue in current nano-science research because they are key parameters to determine the optical, electronic, magnetic, and chemical properties [1–7]. In particular, to synthesize complex three-dimensional (3D) architectures in nanometer or micrometer is desirable for advanced functional nanomaterials via a self-assembly process [4,5]. Self-assembled flowerlike boehmite, nanorods-based [6,7], and curved structure of gold-polypyrrole [5] have been recently prepared via a self-assembly process.

Polyaniline (PANI), as one of the most promising conducting polymers, has received considerable attention because of its reversible doping/de-doping function through a simple acid/base reaction [8]. The electronic and optical properties of nanostructured PANI have triggered several promising applications in gas and chemical sensors, actuator, drug delivery systems and tissue engineering [9]. Hard-template [10], interfacial polymerization [11], seeding [12] and electrospinning techniques [13] have been widely employed to synthesize PANI nanostructures. More recently, hierarchical structures of PANI directly oxidized by ammonium persulfate (APS) in dilute aniline aqueous solution have been also reported [14]. However, 3D-micro/nanostructures assembled from 1D-nanostructure of PANI are seldom reported. Therefore, design and synthesis of multifunctional 3D-microstructures assembled from 1D-nanostructures of PANI are still challenge.

It has been widely demonstrated that template-free method created by Wan is a simple and universal route to synthesize micro/nanostructures of PANI even its multifunctional composite [15–18]. In particular, the super-hydrophobic rambutan-like hollow spheres [19] and dandelion-like 3D-microstructures [20] assembled from 1D-nanofibers of PANI were synthesized by template-free methods. Regarding the formation of such complex micro/nanostructures, one trick is a cooperation effect of the micelle acting as the soft-template and non-covalent interactions, such as Van der Waals forces, hydrogen bonding, π–π stacking and hydrophobic interactions as the driving forces of a self-assembly process. According to the micelle model proposed by Wan et al. [18], the micelle formed by dopant, dopant/aniline monomer even aniline monomer itself can be served as the soft-template in the formation of self-assembled micro/nanostructures of PANI by a template-free method. However, morphology and competition of these micelles are strongly affected by the nature of dopant and reaction conditions including the concentration of dopant, oxidant and monomer as well as the molar ratio of dopant and oxidant to aniline monomer even reaction temperature and stirring fashion. Here we show the template-free method to synthesize 3D-boxlike microstructures of PANI assembled from 1D-nanofibers in the presence of perfluorosebacic acid (PFSEA) as the dopant. The resulting 3D-boxlike microstructures show super-hydrophobic and high-crystalline properties. The structural characteristic, room temperature conductivity, wettability, and self-assembly mechanism of the 3D-boxlike microstructures of PANI-PFSEA are reported.

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2. Experimental details

2.1. Reagents

Aniline (Beijing Chemical Co.) was distilled under reduced pressure. Ammonium persulfate (APS, Beijing Yili Chemical Co.), Perfluorosebacic acid (PFSEA, Acros Organics), and other reagents were all of AR grades and used as-received without further treatment.

2.2. Synthesis of PANI

3D-boxlike microstructures of PANI assembled from 1D-nanofibers were synthesized by a template-free method in the presence of PFSEA as both dopant and soft-template. A typical synthesis is as follows: 0.02 mmol PFSEA dissolved in 18 mL de-ionized water were mixed with 0.4 mmol aniline monomer under supersonic stirring for 3 min. Then 2 mL aqueous solution of APS (0.4 mmol) was added into above mixture and the reaction continued to the stationary state at room temperature for 24 h. In this case, the molar concentration of aniline was 0.02 M, and the molar ratio of PFSEA and oxidant to aniline was 0.05:1 and 1:1, respectively. The resulting product was washed with water, methanol, and ether several times, consecutively. In order to remove the reaction by-products completely, the product was again immersed in methanol, and ether for 15 min before filtrating every time. Finally, the products were dried under vacuum at room temperature for 24 h.

2.3. Characterization

Scanning electron microscopy (SEM) images were measured using a JEOL JSM-6700F field-emission scanning microscope. Transmission electron microscopy (TEM) images were obtained using a Hitachi-9000 transmission electron microscope. Infrared (IR) spectra in the range 400–4000 cm^{-1} on sample pellets with KBr were conducted by means of an infrared spectrophotometer (Bruker Tensor 27). UV–visible (UV–vis) spectrum was measured in *N*-methyl-2-pyrrolidinone (NMP) solution on a HITACHI 4100 UV–visible spectrophotometer. X-ray diffraction (XRD) patterns were measured on Micscience M-18XHF (with a Cu Kα radiation) instrument. X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB 220i-XL instrument with a monochromatic Al Kα X-ray source. The conductivity of the compressed pellets at room temperature was measured by a standard four-probe method, using a Keithley 196 system DMM Digital Multi-meter and an Advantest R1642 programmable DC voltage/current generator as the current source. Contact angles (CAs) were measured on a data physics OCA20 contact angle system at ambient temperature. The average CAs value was obtained by measuring at five different positions of the same sample.

3. Results and discussion

Fig. 1a is typical SEM image of 3D-boxlike microstructures of PANI assembled from 1D-nanofibers. The average side lengths of these 3D-boxlike microstructures is estimated to be ca. 3–4 μm. The high-magnification SEM image shown in Fig. 1b presents the shape of single 3D-boxlike microstructure with 3.7 μm in average side length and 1 μm in average height. The high-magnification SEM image also shows that 3D-boxlike microstructure are assembled from the cross-junction nanofibers (40 nm in an average diameter). Moreover, morphology of the 3D-boxlike microstructures is still reserved after supersonic for 4 h, indicating that the 3D-boxlike microstructures assembled from 1D-nanofibers are stable. The

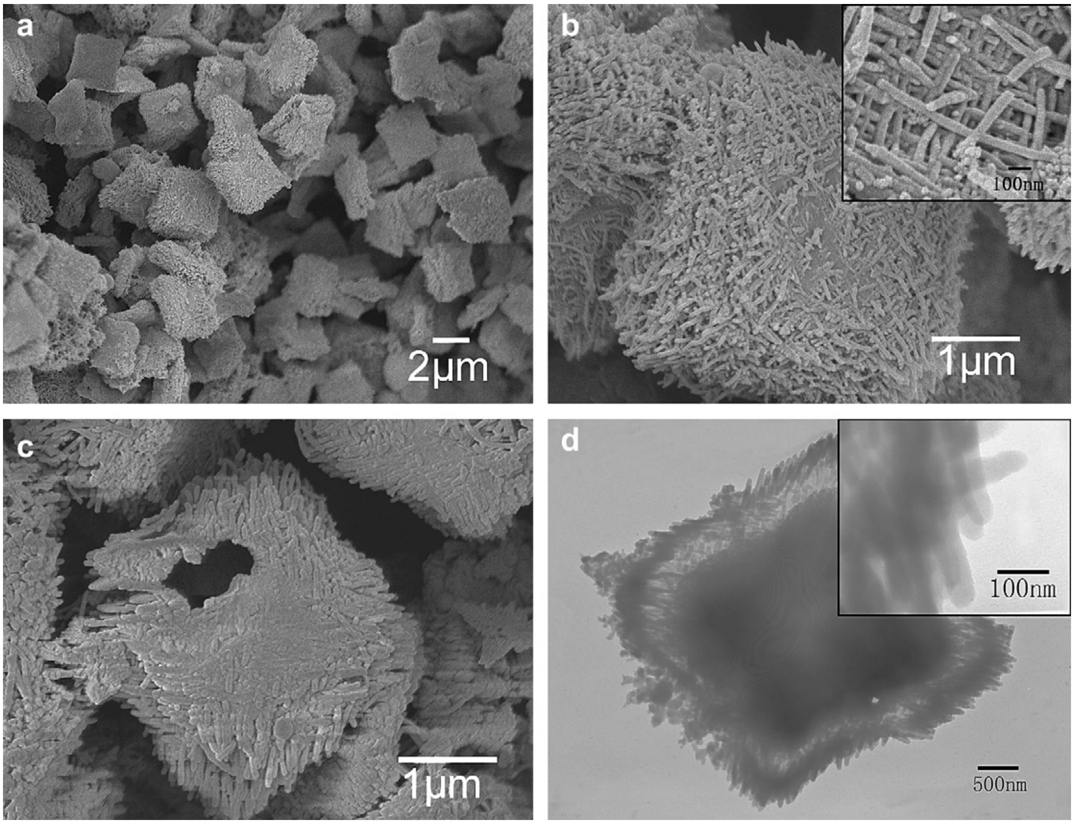

Fig. 1. (a) SEM image of the 3D-boxlike PANI microstructures assembled from 1D-nanofibers; (b) high-magnification SEM image of one 3D-boxlike microstructure, inset shows typical cross-linked nanofibers; (c) SEM image of broken 3D-boxlike microstructure; (d) TEM image of the 3D-boxlike microstructures, inset shows typical cross-linked nanofibers.

hollow structure of these 3D-boxlike microstructures is further conformed by TEM, as shown in Fig. 1d. The average shell thickness and interior diameter of 3D-boxlike microstructures are estimated by means of TEM to be ca. 290 nm and 2.7 μm, respectively. As shown in the inset of Fig. 1d, moreover, the uniform nanofibers with a diameter of ~40 nm are crossed each other to form nanofiber junctions. These across-junction nanofibers might be regarded as cell unit for self-assembly from 1D-nanofibers to 3D-boxlike microstructures.

Typical FTIR spectrum of 3D-boxlike microstructures assembled from 1D-nanofibers is shown in Fig. 2. All characteristic peaks of PANI at 1583 and 1500 cm^{-1} (quinoid and benzenoid ring, respectively), 1303 cm^{-1} (C–N stretching), 1146 cm^{-1} (C=N stretching), and 830 cm^{-1} (1,4-substituted phenyl ring stretching) appear in the spectrum of the boxlike microstructures, which are identical to the emeraldine base form of PANI [21]. However, the relative intensity of the quinoid ring to the benzenoid ring (as presented by I_{1500}/I_{1583}) is ca. 1.30 due to a higher extent of chain cross-linking [22]. Two absorption peaks at around 756 and 696 cm^{-1} assigned to the 1,2-substituted and 1,2,4-substituted aromatic ring are observed [23], further proving the above conclusion. These might be a reason of forming cross-junction nanofiber, which is regarded as self-assembled unit to form 3D-boxlike microstructures self-assembled from 1D-nanofibers via a self-assembly process. In addition, a strong and broad band at 3234 cm^{-1} assigned as the hydrogen bonded N–H vibration is observed [24] that is a evidence of hydrogen bond existing in 3D-boxlike microstructures and can be regarded as a driving force for 1D-nanofibers forming 3D-boxlike microstructures via a self-assembly process. In addition, there is a carbonyl absorption of the carboxylic acid end groups in PFSEA at 1679 cm^{-1} that is assigned to a hydrogen bonded C=O stretch [25], indicating that PFSEA acts as the dopant. Moreover, the vibration bands at 1155 and 1248 cm^{-1}, which are ascribed to the symmetric and asymmetric CF_2 stretches, are also observed [26], further indicating that the 3D-boxlike microstructures are doped with PFSEA as the dopant. The results obtained from XPS revealed that the component of 3D-boxlike microstructures consists of C, N, H, F and O elements, where F element is contributed to hydrophobic function. Fig. 2c shows that the band energy of amine (–NH–) and imine (–N=) nitrogen is at 399.6 and 398.5 eV, respectively, whereas the positive charged nitrogen (N^+) is at 401 eV, which is consistent with previous results [27]. According to the above results of structural characterizations, the PFSEA not only serves as the dopant, but also provides hydrophobic interaction and hydrogen bonds as the driving forces for the self-assembly of the 3D-boxlike microstructures through cell units of the across-junctions. As shown in Fig. 2d, a strong absorption peak and a weak absorption peak at 370 and 617 nm are observed that is neither typical emeraldine base nor salt form of PANI [28], suggesting that the 3D-boxlike microstructures are a low molecular weight and high oxidation state of PANI, leading to poor conductivity of less than 10^{-8} S cm^{-1} as measured by four-probe method.

To investigate self-assembly mechanism of the 3D-boxlike microstructures assembled from 1D-nanostructures, SEM images of as-synthesized PANI at different reaction times are measured, as shown in Fig. 3. For a short polymerization time (e.g. 35 min), a large number of the quadrangle in shape are observed (Fig. 3a), which are composed of nanofibers crossed each other (Inset in Fig. 3a). With the polymerization time prolonging 10 h, square microstructures assembled from nanofibers are observed (Fig. 3b). The completed 3D-boxlike microstructures assembled from nanofibers are finally formed after polymerization for 15 h. As well known, PFSEA is a bola-amphiphilic molecule that consists of both hydrophobic perfluorinated carbon chain and two hydrophilic

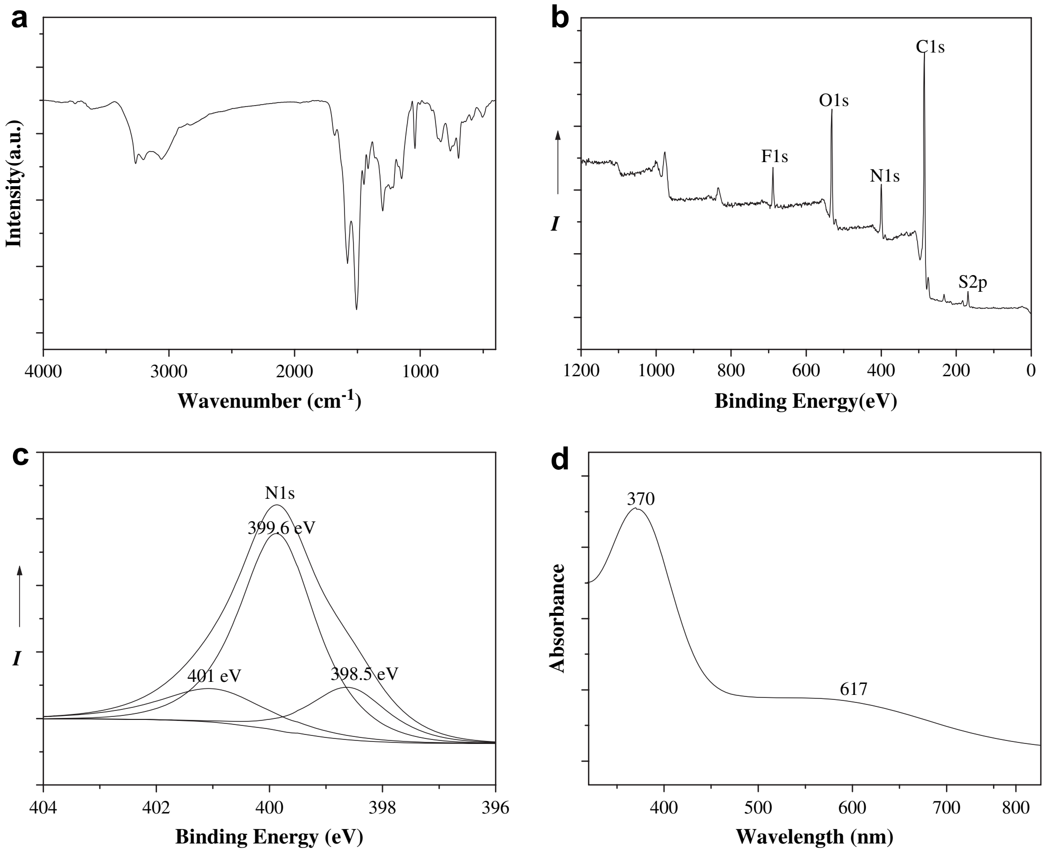

Fig. 2. (a) FTIR spectrum; (b) XPS; (c) N1s XPS; (d) UV–vis spectrum of the 3D-boxlike microstructures dissolved in NMP.

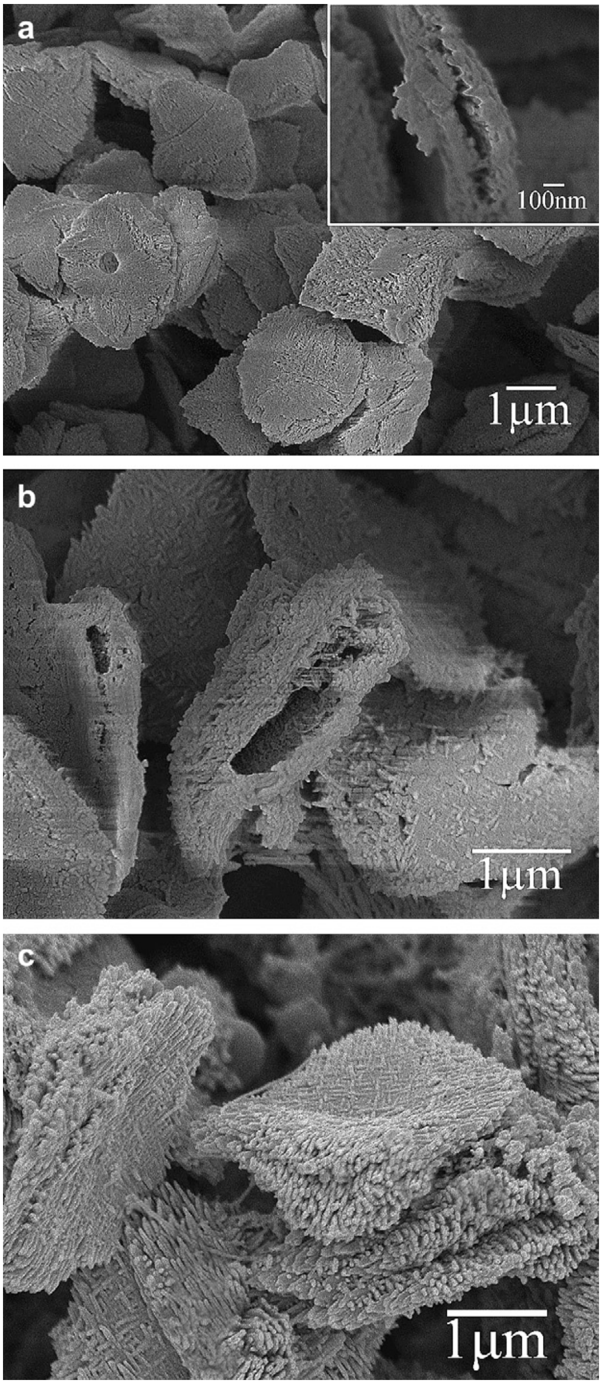

Fig. 3. SEM images of the 3D-boxlike microstructures as-synthesized at different polymerization times: (a) 35 min; (b) 10 h; (c) 15 h.

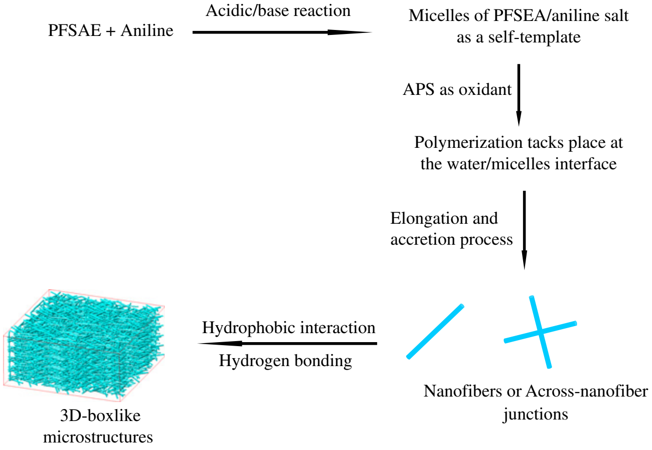

Fig. 4. Schematic illustration of the possible self-assembly mechanism for the 3D-boxlike microstructures assembled from 1D-nanofibers.

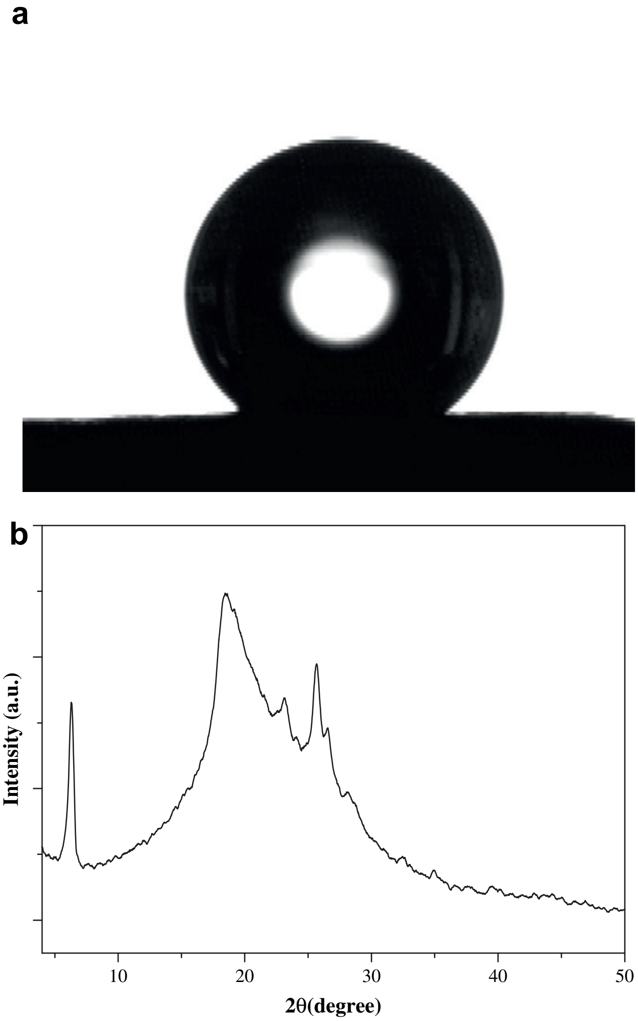

Fig. 5. (a) Images of a 4 μl water droplet residing on the surface of the 3D-boxlike microstructures; (b) XRD pattern of the 3D-boxlike PANI microstructures.

–COOH end groups. Thereby two hydrophilic –COOH groups of the PFSEA are served as the dopant and providing hydrogen bond at the same time. According to micelle model previously proposed [15], micelles formed by PFSEA itself and PFSEA/aniline salt are existed in the reaction solution at the same time due to the surfactant character of PFSEA and acidic/base reaction between acidic PFSEA and basic aniline, which can be served as the soft-templates in the formation of micro/nanostructures of PANI. However, the competition between them is dependent upon the reaction conditions. Based on our previous studies [20], the PFSEA/aniline micelles in this study are served as the soft-templates in the formation of nanofibers of PANI. Since APS is hydrophilic, the polymerization only takes place at the interface of water and PFSEA/aniline micelle to form nanofibers through accretion and elongation processes [15]. As increasing polymerization time, moreover, cooperation of hydrogen bond and hydrophobic interaction might result in the aggregation of these nanofibers to form across-nanofiber junctions [20]. These across-nanofiber junctions as the self-assembled units can be further aggregated to form 2D-platelike structured with across-nanofiber junctions through hydrophobic interactions due to hydrophobic perfluorinated carbon chain of PFSEA. Thereby, the formation of 3D-boxlike microstructures assembled from 1D-nanofibers results from a cooperation of various effects mentioned above. The schematic of formation mechanism of 3D-boxlike microstructures assembled from 1D-nanofibers is shown in Fig. 4.

The surface wettability of the 3D-boxlike microstructures was evaluated by means of water contact angle (CA) measurements. A water CA for the surfaces of the 3D-boxlike microstructures was estimated to be ca. 151.7°, showing a super-hydrophobic property, as shown in Fig. 5. The reasons for super-hydrophobic properties are as follows [19]: one is the micro- and nano-scale hierarchical structure proved by SEM images. Another is the low-surface energy of hydrophobic perfluorinated carbon in the PFSEA as the dopant, as demonstrated by XPS. Interestingly, the 3D-boxlike microstructures can float on the surface of the water for several weeks due to the hollow and super-hydrophobic characteristics. The crystalline property of 3D-boxlike microstructures was characterized by XRD is shown in Fig. 5b. Two peaks centered at $2\theta = 18.6°$, and 25.4° were observed that are ascribed to periodicity parallel and perpendicular to the polymer chain, respectively [29]. However, a strong peak at $2\theta = 6.4°$ assigned as the periodicity along the polymer chain is also observed [30], indicating that the 3D-boxlike microstructures assembled from 1D-nanofibers are highly crystalline that might be related to its low molecular weight and special box structure.

4. Conclusions

Supper-hydrophobic and high-crystalline 3D-boxlike microstructures of PANI assembled from 1D-nanofibers were synthesized by using PFSEA as the dopant. It is proposed that a cooperation effect of the PFSEA/aniline micelles as the soft-templates of the nanofibers, and hydrogen bond and hydrophobic interactions as the driving forces on the formation of 3D-boxlike microstructures assembled from 1D-nanofibers. Such novel 3D-boxlike microstructures of PANI combined with super-hydrophobic and high-crystalline properties may have some promising potential applications in the fields of nanoelectronic devices, chemical sensors, confined reaction vessels, controlled release, delivery, separation systems.

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