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Complicated nanopattern composed of crosswise aligned nanoribbons and its application for integrating anisotropically aligned polypyrrole nanoparticles

Penglei Chen*, Peng Gao, Minghua Liu*

Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun North First Street 2, Beijing 100080, China

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Abstract

Complicated nanopattern composed of crosswise aligned nanoribbons of the supramolecular assemblies of a triangular molecule, tri-L-(glutamic diethyl ester)-1,3,5-benzenetricarboxamide (T-L-Glu-BB), can be easily constructed by the extremely simple Langmuir–Blodgett (LB) process. The application of such nanopattern by templated chemical polymerization strategy to integrate anisotropically aligned polypyrrole (PPy) nanoparticles is described. We have showed that not only parallel arranged but also crosswise aligned PPy nanobelts composed of anisotropically arranged nanoparticles of the polymer can be integrated easily over large area silicon surface. More importantly, the width of the parallel aligned PPy nanobelts and the interspace between them can be dexterously regulated to some extent by using distinct silicon substrates that have different hydrophobicities or by altering the synthesis process. A plausible mechanism has been proposed for the described strategy.

Keywords: Polypyrrole; Nanoarray; Templated strategy

1. Introduction

Nanopatterns featured with regularly aligned nanoarrays have currently received increasing attention due to their potential applications in various scientific and technical fields [1–5]. Generally, top-down and bottom-up strategies are widely employed to fabricate the well-ordered nanopatterns [2]. The former one is a physical technique and the expenses are of great high, while the latter one, based on the supramolecular assemblies, shows diverse merits and thus is of increasing interest. It has been reported that Langmuir–Blodgett (LB) technique can be used to produce ordered nanopatterns through supramolecular assembling at the air/water interface. For example, Chi and coworkers have reported that regular nanostripes of supramolecular assemblies of L-α-dipalmitoylphosphatidylcholine can be produced by withdrawing a solid substrate with extremely high speed (60 mm/min) during the LB film deposition process [2a,3,6]. They also have reported a periodic nanostructure composed of parallel arranged nanofibers of the supramolecular assemblies of methyl and ethyl esters of *ent-threo*-2,3-dihydroxy fatty acids with different chain length [7]. Some other authors have also fabricated regularly aligned nanoarrays patterned surface through the LB process [8]. Besides amphiphilic molecules, some prefabricated inorganic nanofibers can also be aligned to some extent by the LB strategy. For example, Yang's and Lieber's groups have reported a “logs-on-a river” process to align one-dimensional inorganic nanomaterials on water surface [2b,5]. In their cases, nanowires of inorganic materials are parallel aligned by using the sophisticated LB technique through controlling the lateral forces.

It, however, seems that the ever addressed regular nanopatterns produced by LB process mainly focus on various parallel

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* Corresponding authors. Tel.: +86 10 82612655; fax: +86 10 62569564.
E-mail addresses: chenpl@iccas.ac.cn (P. Chen), liumh@iccas.ac.cn (M. Liu).

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aligned one-dimensional nanostructures, and that more complicated nanoarrays composed of crosswise aligned one-dimensional nanostructures are seldom addressed [5a]. It is suggested that this kind of complicated nanopattern is critical to the realization of integrated electronic and photonic nanotechnologies [2d,5a]. The subject concerning the hierarchical organization of such nanopattern is one of the most significant issues in the nanoscience and nanotechnology, and thus has recently attracted considerable interest from nowadays scientists [2d,5a]. Accordingly, developing simple processes to fabricate intricate nanoarray patterned surface composed of crosswise aligned nanostructures is a significant subject required to be explored intensively.

From the point of view of functionalities, fabricating patterned surface covered by regularly aligned nanoarrays of polypyrrole (PPy), one of the significant π-polyconjugated conducting polymers, is one of the most vital issues [9]. Various nanostructures of PPy such as nanotubes, nanowires and nanoparticles, and nanocomposites of PPy with some other components have been synthesized [10–14] and the properties of these nanostructures have been intensively investigated. The subject focusing on the fabrication of ordered nanopattern of PPy, however, has been hampered by the intractability of PPy, as it is known that PPy has poor solubility in common solvents due to its rigid and highly conjugated backbone [9d–f]. Recently, Goren and Lennox have demonstrated that nanoarrays of PPy dots in a parallel fashion can be achieved by using micelles of block copolymer as the polymerization template, which is produced by the LB technique. They have also found that another micelles template synthesized by the self-assembly of the block copolymer gives out a complex PPy nanostructure, which, however, shows no distinct regularity [15]. Grady et al. have claimed that nanopatterns of polyaniline (PAni) and PPy with controllable morphologies can be organized on planar surface using adsorbed surfactant molecules as polymerization template [16]. Parallel aligned nanowires of PAni have been successfully integrated, whereas there was no remarkable regularity in the case of PPy. Besides these excellent works, some other groups have also reported their endeavors based on the template-assistant strategies, and great achievements have been obtained [9c–f,17–24]. Nevertheless, these methods are either too tedious or too costly, since the fabrication of the templates is a complicated process itself and sometimes expensive apparatus are required [9c,17–21]. More importantly, there is no obvious lateral regularity in the alignments of the PPy nanostructures from the viewpoints of the two-dimensional planar surface, even though the PPy nanostructures are found to align vertically on the substrate surface [21,22,9f]. Additionally, the dimensions of the aligned PPy wires and/or the controllable PPy structures sometimes are in the range of micrometer but not nanometer scope [9d,23]. Considering the large-scale fabrication and practical applications, it is understandable that much more convenient, simple, low cost, and high efficient strategies are still imperatively desired for constructing complicated as well as regularly aligned nanoarrays of PPy.

Previously, we have showed that long, straight as well as parallel aligned nanoribbons of supramolecular assemblies of a triangular amphiphilic molecule, tri-L-(glutamic diethyl ester)-1,3,5-benzenetricarboxamide (T-L-Glu-BB), can be easily constructed by LB process [24]. Herein, we describe an extremely simple process for constructing a more complicated nanopattern, consisting of crosswise aligned nanoribbons of the supramolecular assemblies of the compound. We depict that not only parallel arranged but also crosswise aligned nanobelts of PPy composed of anisotropically arranged nanoparticles of the polymer can be easily integrated over large area silicon surface by using LB films of T-L-Glu-BB as the chemical polymerization template. More importantly, the width of the parallel aligned PPy nanobelts and the interspace between them can be dexterously regulated to some extent by using distinct silicon substrates that have different hydrophobicities or by altering the synthesis process.

2. Experimental part

2.1. Materials and LB substrates

T-L-Glu-BB was synthesized as described elsewhere [24]. Ammonium persulfate was purchased from Beijing Yili Fine Chemical Co., Ltd. and used without further purification. Pyrrole monomer was purchased from Chinese Academy of Military Medical Sciences and purified by distillation under reduced pressure before use. Silicon wafer (111, single face polished) with a diameter of 200 mm and thickness of 400 μm was purchased from National Grinm Semiconductor Materials Co., Ltd. and knifed to quadrate shaped slices with a width of 1 cm and length of 3 cm. Before being used as the substrate for T-L-Glu-BB LB film deposition, the silicon slices were treated roughly by the similar processes reported by others in order to obtain hydrophobic and/or hydrophilic surfaces [25]. For the hydrophobic one, the silicon slices were washed with diluted soapy water under sonication for 30 min, after which great deal of Milli-Q water was used to wash the slices vigorously. Then it was washed with acetone under sonication for another 30 min, also followed by washing with Milli-Q water. Subsequently, it was put into the piranha solution ($H_2SO_4/H_2O_2 = 7/3$), which was kept at 80 °C, for an hour. After being washed with Milli-Q water, the slice was dipped into the basic hydroxide solution ($H_2O/H_2O_2/NH_3 = 5/1/1$) for another hour at 80 °C, followed by washing with Milli-Q water. Subsequently, it was dipped into 5% HF solution at the room temperature for 10 min. After being washed with Milli-Q water and dried with nitrogen gas, the treated silicon wafer can be used as hydrophobic substrate for LB film deposition. In the case of hydrophilic substrate, almost exactly the same process was performed, except that the 5% HF rinsed silicon slice was required to be further dipped into the acidic solution ($H_2O/H_2O_2/HCl = 5/1/1$) for 10 min before use.

2.2. LB template fabrication

LB films featured with parallel aligned T-L-Glu-BB nanoribbons were deposited as described elsewhere [24]. In the case of

LB films featured with crosswise arranged T-L-Glu-BB nanoribbons, two continuous depositions on the hydrophobic silicon surface by horizontal lifting LB technique were performed. The employed substrate was kept parallel and perpendicular to the barrier for the first and the second depositions, respectively.

2.3. Chemical polymerization of pyrrole at the template surface

Twenty micro liter of newly distilled pyrrole monomer was added to 60 ml of 0.1 M ammonium persulfate aqueous solution in Milli-Q water, the mixture was sonicated at 5 °C for 5 min to make the monomer disperse uniformly. Generally, the alignment of PPy nanopattern was accomplished by dipping the T-L-Glu-BB LB template in this freshly prepared polymerization solution at 5 °C. After an appointed polymerization time, the template was removed and washed with plenty of Milli-Q water. Before the atomic force microscopy (AFM) investigation, the template was dried by nitrogen gas.

2.4. AFM, Fourier-transform infrared (FTIR) spectroscopy investigations, and scanning electron microscopy (SEM) measurements

FTIR and tapping mode AFM height images of the produced nanostructure were investigated as described elsewhere [24]. SEM measurements were carried out on Hitachi S-4300 at 15 kV and 10 mA. In order to make clear contrast, the samples employed for the SEM investigations were covered with 30–40 nm platinum by vacuum deposition, since flat and even PPy nanopatterns were produced by using the LB film as the polymerization template [26].

3. Results and discussion

We have found previously that the aligned direction of T-L-Glu-BB nanoribbons is parallel to the compressing barrier of the LB film deposition apparatus [24]. Based on this interesting ground, we hereby tried to fabricate the T-L-Glu-BB LB film by two continuous depositions onto the hydrophobic silicon surface by horizontal lifting technique, during which the substrate was kept parallel and perpendicular to the barrier for the first and the second depositions, respectively. Experimentally, PPy nanoarray patterned surface was achieved by putting such T-L-Glu-BB LB films into newly confected mixed aqueous solution of pyrrole monomer and ammonium persulfate that worked as oxidant for the chemical polymerizations of PPy [15]. Tapping mode atomic force microscopic (AFM) height images of the produced nanostructure were detected after the polymerization reaction went along for an appointed time and the sample was adequately washed with Milli-Q water [26]. The morphology evolution process as a function of polymerization reaction time is shown in Fig. 1. As we have expected, the AFM image of thus freshly deposited LB film displays a nanostructure consisting of crosswise aligned T-L-Glu-BB nanoribbons (Fig. 1(a)). The AFM image after short polymerization reaction time (Fig. 1(b), 30 min) gives out a similar nanopattern with more sharp vacancies, where small PPy nanoparticles can be seen by careful observation. A longer polymerization reaction time (Fig. 1(c), 120 min) results in a nanostructure, where crosswise aligned PPy nanobelts consisting of anisotropically arranged nanoparticles of the polymer is observed.

In order to disclose the possible mechanism, we have tried to use the T-L-Glu-BB LB films, which were fabricated by a single deposition (the substrates were kept either parallel or perpendicular to the compressing barrier), as the chemical polymerization templates. As we have described in our former results, the AFM image of the freshly deposited LB film of T-L-Glu-BB displays a nanostructure composed of straight and parallel aligned nanoribbons (Fig. 2(a)), under and between which a sublayer exists [24]. The width of these T-L-Glu-BB nanoribbons and interspace between them are about 100–150 nm and 100–300 nm, respectively. After the LB template has been placed in the polymerization solution for 30 min, the AFM image of the resulted film shows a nanopattern similarly composed of parallel aligned nanoribbons, the relative altitude of which, however, becomes larger compared with that detected from the original LB film before PPy deposition, as revealed by the sectional analysis shown at the bottom of Fig. 2(a) and (b). Accordingly, the gaps between the T-L-Glu-BB nanoribbons become sharper. Simultaneously, small PPy nanoparticles are examined in the gaps' areas between the nanoribbons by careful observation, while there are almost no such nanoparticles on the T-L-Glu-BB nanoribbons. When the polymerization time increases to 90 min (Fig. 2(c)), these gaps are found to be filled with nanoparticles that have a height of about 7–10 nm and a diameter of about 27–35 nm. At the same time, a few nanoparticles are absorbed on the T-L-Glu-BB nanoribbons sporadically at this stage. However, the number of T-L-Glu-BB nanoribbon-attached nanoparticles is apparently much fewer than that in the gaps. An even longer polymerization reaction time (120 min) results in a nanopattern that is composed of parallel aligned straight and long nanobelts consisting of nanoparticles that have a height of about 25–40 nm and a width of about 45–50 nm (Fig. 2(d)). The width of these nanobelts is about 100–400 nm and the distance between the nanobelts is about 100–150 nm, which are very close to the interspace between T-L-Glu-BB nanoribbons and the width of T-L-Glu-BB nanoribbons themselves, respectively. The T-L-Glu-BB nanoribbons, however, cannot be observed at this stage, since they are suggested to be buried by the nanopatterns of PPy. It should be noted that the borderlines between the nanobelts are not so sharp, since a few nanoparticles are observed to be enchased sporadically in the gaps between them. This can also be confirmed by the SEM images of the resulted nanopattern, as shown in Fig. 3, straight and parallel aligned nanobelts of PPy consisting of the nanoparticles of the polymer were indeed produced. There are also a few PPy nanoparticles located in the gaps' region.

As demonstrated by Whitesides et al. and Goren and Lennox, pyrrole monomers were inclined to nucleate and polymerize preferentially on hydrophobic relative to the

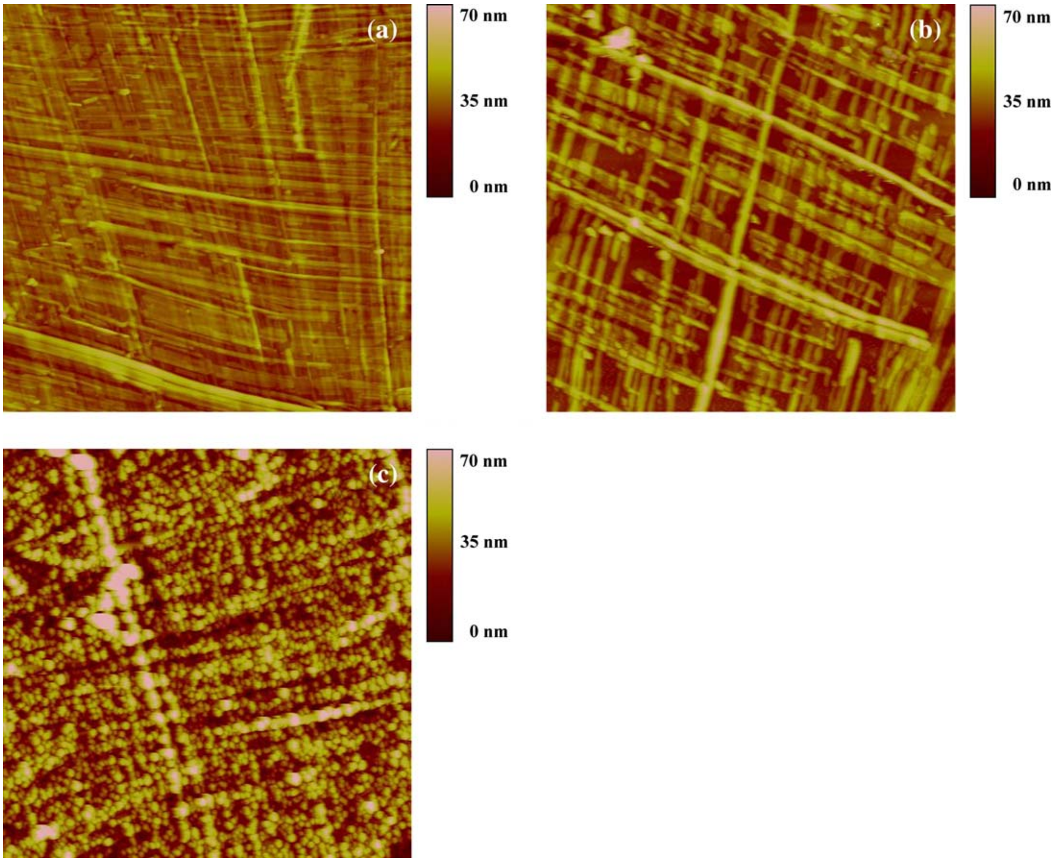

Fig. 1. AFM images of the evolution of PPy polymerized on T-L-Glu-BB LB films as a function of polymerization reaction time: (a) 0 min (freshly deposited T-L-Glu-BB LB film before polymerization), (b) 30 min and (c) 120 min. The templates employed for the polymerization reaction were fabricated by altering the substrate's direction orthogonally during a twice-transferred T-L-Glu-BB LB film deposition process. Hydrophobic silicon substrates were used as the solid supports. Image size: 5 μm × 5 μm.

hydrophilic sites [9e,15]. Accompanied by this deduction, the data and phenomena in our case suggested that the sublayer between the T-L-Glu-BB nanoribbons was peeled off the solid support, leaving behind the bare hydrophobic silicon surface which is exposed to the polymerization solution, when the LB film was dipped into the reaction system, whereas the most of the T-L-Glu-BB nanoribbons still kept their alignments on the substrate. At the same time, adsorption, nucleation and polymerization of PPy preferentially occurred on the bare hydrophobic silicon surface. Nevertheless, the polymerization of PPy was almost interdicted on the nanoribbons at the initial stage of the polymerization reaction, since the T-L-Glu-BB molecule in the nanoribbons was proved to stand vertically on the substrate with one of its hydrophilic arms pointing outwards [24]. With the further proceeding of the polymerization reaction, it is understandable that a few PPy nanoparticles can sporadically grow on the T-L-Glu-BB nanoribbons, since the polymerization of pyrrole monomers on the bare hydrophobic silicon surface would make the polymerization sites to be covered by the PPy nanoparticles, which could reduce the hydrophobicity of the polymerization regions. Consequently, the driven force for the PPy localized nucleation and polymerization is not strong enough for polymerization reaction to strictly happen at the beginning sites. And the result is that the position occupied by the parallel aligned PPy nanobelts (which were obtained by a polymerization time of 120 min and were consist of anisotropically arranged PPy nanoparticles) is roughly the original location of the gaps between the T-L-Glu-BB nanoribbons observed at the initial stage. Similarly, the area inhabited by the gaps between the PPy nanobelts is generally the location that is occupied by the T-L-Glu-BB nanoribbons detected at the early stage.

In order to disclose if the sublayer in the LB template was supplanted by the PPy nanoparticles, we dipped a freshly deposited LB template into the pure Milli-Q water for 30 min and checked its AFM images after drying the surface by nitrogen gas. We found that the sublayer was peeled off the solid support, which left behind parallel aligned T-L-Glu-BB nanoribbons with distinct gaps again (the morphology of the resulted film is extremely similar to that exhibited in Fig. 2(b), figure is not shown). This indicates that the sublayer was peeled off the hydrophobic silicon surface neither by the PPy nanoparticles nor by ammonium persulfate but by water molecules. As we found that the T-L-Glu-BB molecules in the sublayer lay flatly on the substrate surface and connected by the intermolecular hydrogen bonds, whereas they were packed closely in the nanoribbons and linked together not only by the intermolecular hydrogen bonds but also by the $\pi-\pi$ stacking [24]. This probably made it relatively easier for the water molecules to chisel into the sublayer between

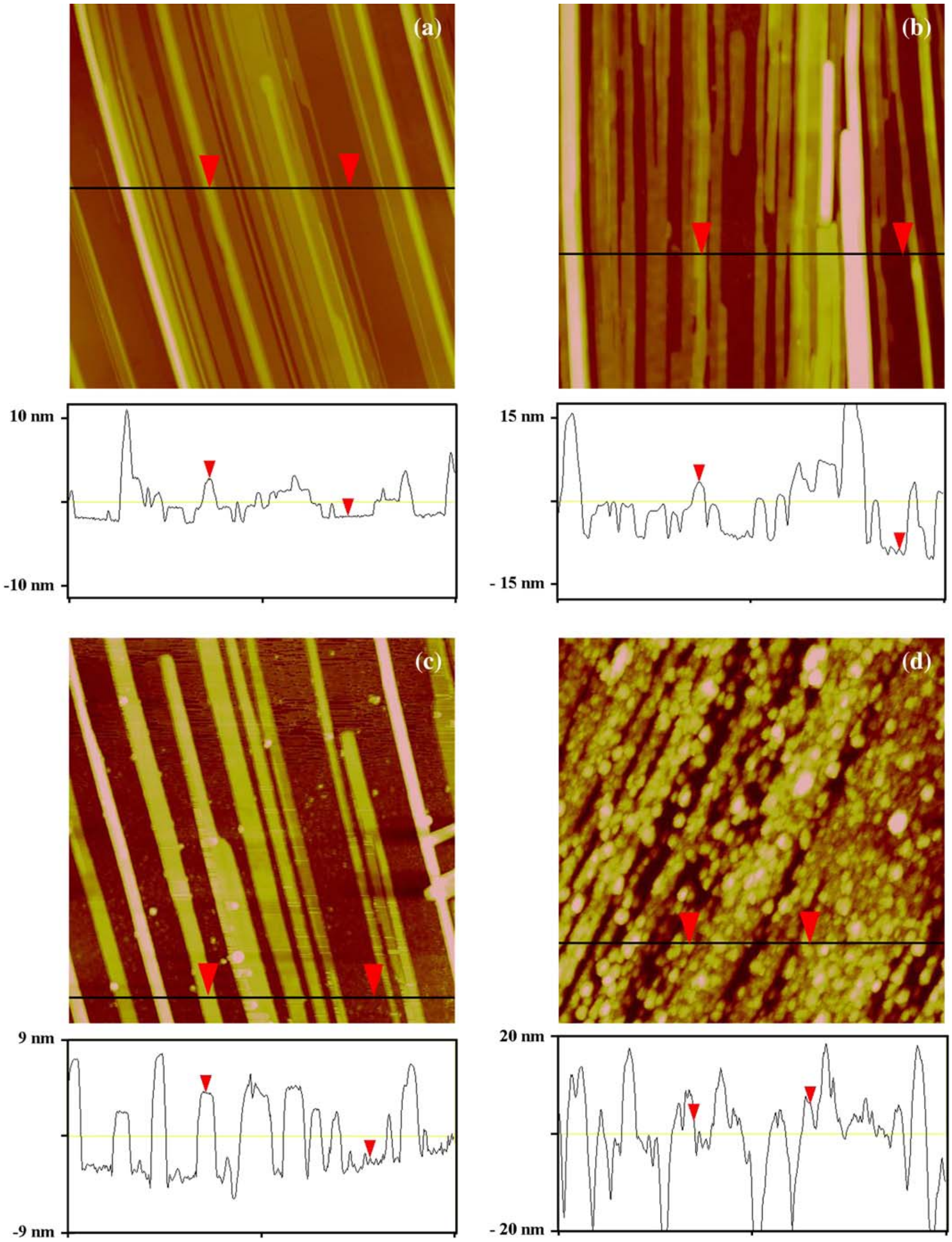

Fig. 2. AFM images of the evolution of PPy polymerized on T-L-Glu-BB LB films as a function of polymerization reaction time: (a) 0 min (freshly deposited T-L-Glu-BB LB film before polymerization) [24], (b) 30 min, (c) 90 min and (d) 120 min. The templates used for the polymerization were fabricated by a single deposition. Hydrophobic silicon substrates were used as the solid supports. Image size: 2 μm × 2 μm.

the T-L-Glu-BB nanoribbons and disintegrated the supramolecular aggregations by destroying the intermolecular hydrogen bonds between the T-L-Glu-BB molecules. When this nanopattern without the sublayer was used as the template for PPy polymerization, the produced nanopattern similarly exhibits as parallel aligned nanobelts that are composed of PPy nanoparticles. The width of thus fabricated nanobelt, however, shows a broader width (about 450–750 nm, Fig. 4, polymerization time is 120 min) compared with that fabricated by using the freshly deposited T-L-Glu-BB LB film as the template directly. This suggests that discontinuously dipping the LB film into aqueous system will not only scrape off the sublayer but also some of the T-L-Glu-BB nanoribbons.

We have also tried to fabricate the PPy patterned surface by using the T-L-Glu-BB LB film transferred by a single deposition on hydrophilic silicon substrate as the polymerization template. Fig. 5(a) gives the AFM image investigated after the polymerization reaction develops for 90 min, from which loosely and parallel aligned nanobelts consisting of PPy nanoparticles with a height of about 2–5 nm and a diameter of about 30–35 nm are observed. The width of the nanobelts and interspace between them are about 35–70 nm and

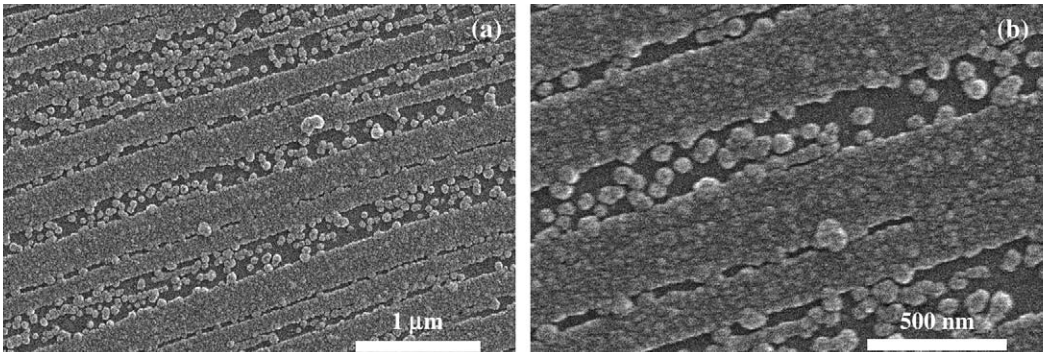

Fig. 3. SEM images with different image size of PPy polymerized on T-L-Glu-BB LB films. The T-L-Glu-BB LB films, which were fabricated by a single deposition, were used as the polymerization templates. The polymerization reaction time was 120 min both for (a) and (b). Hydrophobic silicon substrates were used as the solid supports.

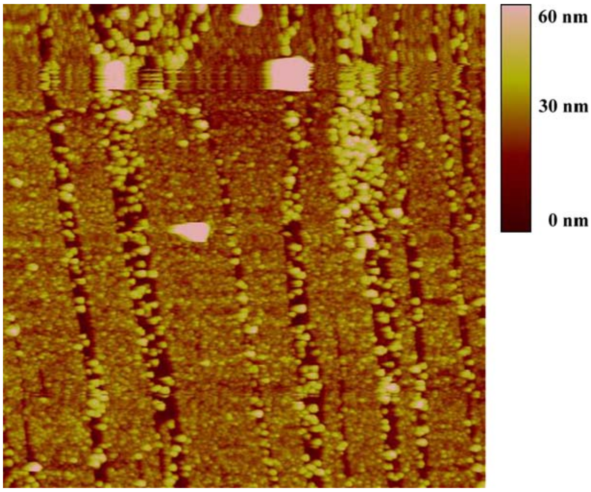

Fig. 4. AFM image of PPy polymerized on T-L-Glu-BB LB film. The T-L-Glu-BB LB film, which was fabricated by a single deposition and was pre-dipped in Milli-Q water for 30 min, was used as the polymerization template. The polymerization time was 120 min. Hydrophobic silicon substrate was used as the solid support. Image size: 5 μm × 5 μm.

150 nm−1.2 μm, respectively. Dotted nanolines consisting of aligned PPy nanoparticles also appeared in the figure. And a few nanoparticles are found to localize sporadically in the areas between these nanobelts. Short reaction time (30 min, figure is not shown) gives the similar results and a longer reaction time (120 min) presents almost the same morphological feature except that nanobelts with a broader width are detected (Fig. 5(b)). The T-L-Glu-BB nanoribbons in all these cases, however, are not observed. These results confirm that PPy is indeed inclined to polymerize preferentially at hydrophobic sites relative to the hydrophilic ones, since it is reasonable to speculate that the hydrophobicity of the T-L-Glu-BB nanoribbon template is stronger than that of the hydrophilic silicon surface. We also can deduce that both the sublayer and the T-L-Glu-BB nanoribbons are easier to be peeled off the solid supports when they are deposited on the hydrophilic silicon surface.

The same processes have also been tried by using T-L-Glu-BB LB films featured with crosswise aligned T-L-Glu-BB nanoribbons deposited on the hydrophilic silicon substrate as the polymerization template. We, however, found that T-L-Glu-BB LB film deposited during the first transferring was peeled off the substrate surface during the second deposition, and as a result we could not get the crosswise aligned T-L-Glu-BB nanoribbons template on the hydrophilic silicon surface. This demonstrated that the T-L-Glu-BB supramolecular aggregations were easier to be peeled off the hydrophilic silicon surface when they were exposed to the aqueous circumstance.

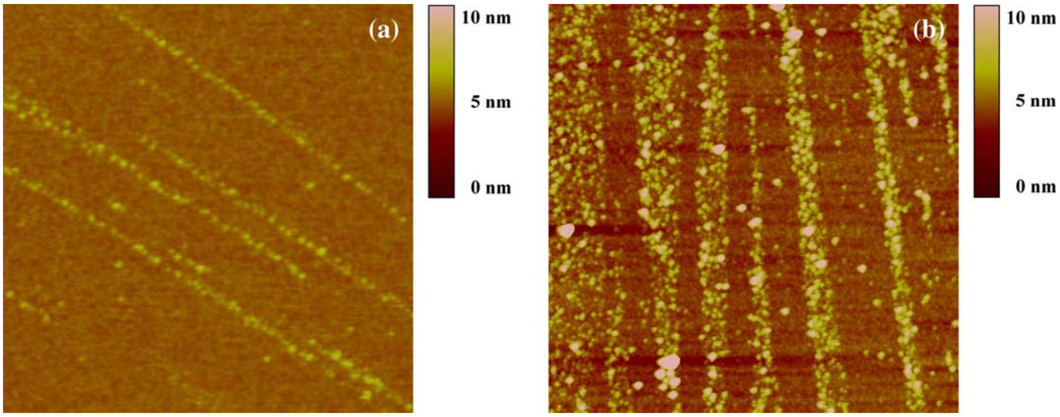

Fig. 5. AFM images of PPy nanoparticles patterned surface. The polymerization reaction time was (a) 90 min and (b) 120 min. The T-L-Glu-BB LB films that were deposited on hydrophilic silicon wafers by a single deposition were used as the polymerization templates. Image size: 2 μm × 2 μm.

Additionally, we tried to rinse out the T-L-Glu-BB nanoribbons in the LB template by a great deal of chloroform after the polymerization reaction went along for a designated time, in order to see if the PPy nanopattern could hold its morphology after the T-L-Glu-BB nanoribbons were washed off. For the sample fabricated on hydrophobic silicon surface with a short polymerization time (30–90 min), the morphology of the chloroform rinsed nanostructure is observed to be composed of PPy nanobelts, between which nanoribbon-shaped vacancies exist (Fig. 6(a), corresponding to Fig. 2(b) and (c)), while the T-L-Glu-BB nanoribbons disappeared. This makes it clear that the T-L-Glu-BB nanoribbons, working as the template for the PPy nanopattern construction, can be washed off by chloroform, whereas the PPy nanopattern can keep its basic feature when the template is removed. For the samples constructed with a longer polymerization time (120 min), the morphology of the PPy nanopattern keeps almost unchanged before and after rinsing with chloroform (Fig. 6(b) and (c), corresponding to Fig. 2(d) and Fig. 1(c), respectively), since the T-L-Glu-BB nanoribbons are suggested to be buried by the nanopatterns of PPy at this stage.

In order to disclose if the buried T-L-Glu-BB nanoribbons can indeed be removed by rinsing, a comparison of the FTIR of the newly deposited T-L-Glu-BB LB film on hydrophobic silicon surface, the PPy nanoarrays covered surface formulated by 120 min polymerization reaction on the above template before and after rinsing was performed, as shown in Fig. 7. The FTIR spectrum of the freshly fabricated T-L-Glu-BB LB film on hydrophobic silicon surface by a single deposition before the PPy polymerization shows several vibration bands at 1742, 1729, 1644, 1563 and 1260 cm^{-1}, which can be ascribed to the characteristic vibrations of T-L-Glu-BB, affirming the existence of T-L-Glu-BB molecules on the solid support surface [24]. The FTIR of the PPy nanoarrays covered surface constructed by 120 min polymerization reaction on the above template before rinsing shows several characteristic vibrations at 1567, 1391, 1187, 1044, 781 cm^{-1}, which can be assigned to the C═C backbone stretching of PPy ring, N–C stretching vibration, ═C–H in-plane deformation, C–H deformation, and C–H out of plane bending, respectively, indicating that the observed nanoparticles described above are indeed the PPy polymer [27,28]. The vibration bands at 1706 cm^{-1}, which can be assigned to carbonyl stretching vibration, indicate the overoxidation of pyrrole rings [21,29]. The indistinct shoulder peaks at around 1210 cm^{-1} and the middle vibration at 926 cm^{-1} can be assigned to bipolaron bands, which are normally named as "doping-induced bands", indicating that the synthesized PPy polymer is in a doped state [21,28]. Most of the peaks ascribed to T-L-Glu-BB molecules, however, disappear, except a weak

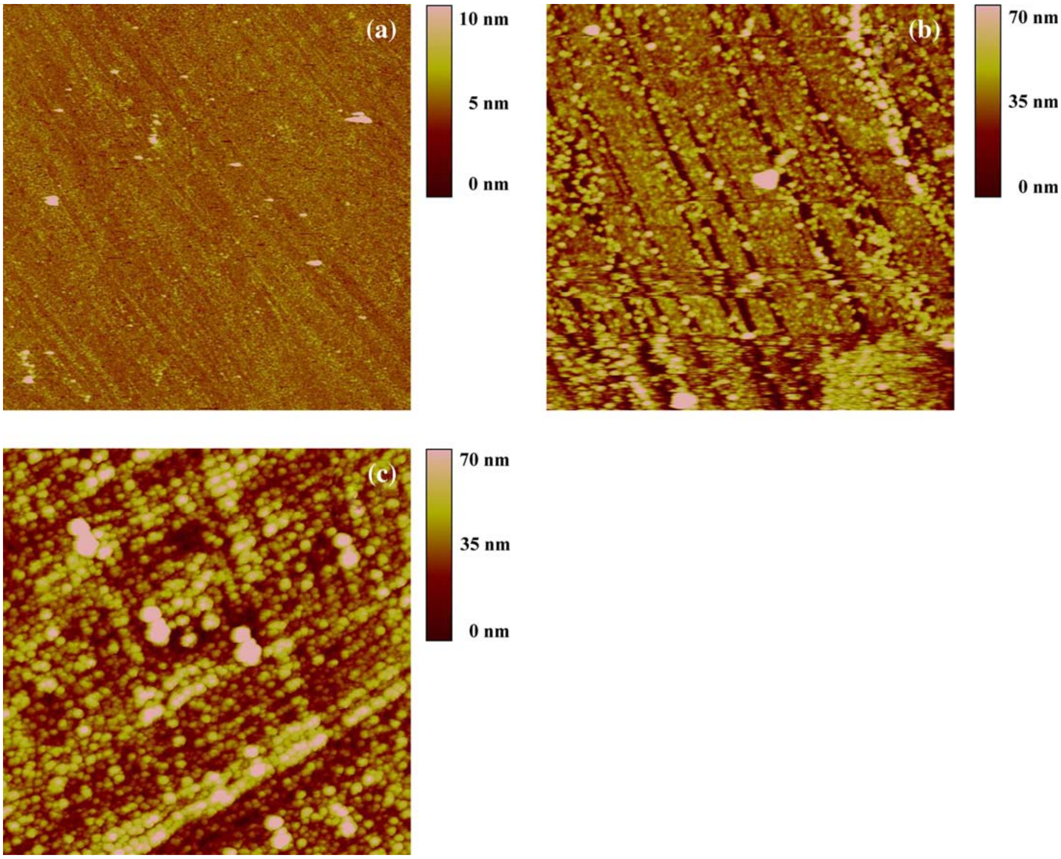

Fig. 6. AFM images of PPy polymerized on the parallel aligned T-L-Glu-BB nanoribbon templates. The polymerization reaction time was (a) 30 min and (b) 120 min. The samples were rinsed with great deal of chloroform to remove the T-L-Glu-BB nanoribbon template; (c) was the same as that of (b) except that a crosswise aligned T-L-Glu-BB nanoribbon template was employed. Hydrophobic silicon substrates were used as the solid supports. Image size: 5 µm × 5 µm.

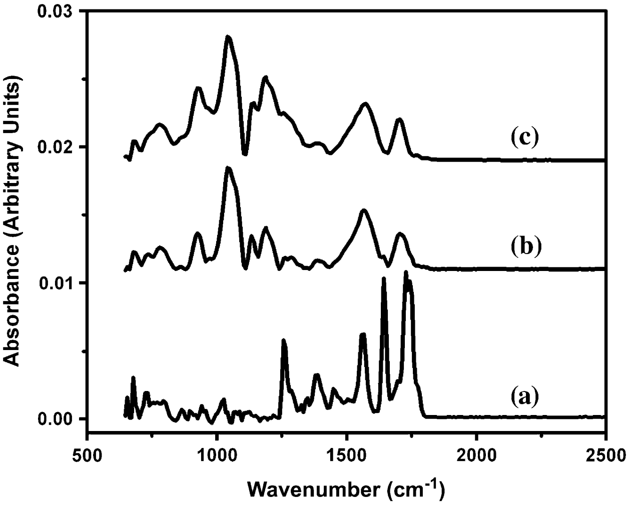

Fig. 7. FTIR spectrum of freshly deposited T-L-Glu-BB LB film (a) before the polymerization reaction [24] and FTIR spectrum of PPy polymerized on T-L-Glu-BB LB film (b) before and (c) after rinsing with chloroform. The polymerization reaction time was 120 min. Hydrophobic silicon substrate was used as the solid support.

shoulder vibration at around 1644 cm^{-1}, confirming the peeling off of the sublayer when the LB template was dipped in the aqueous circumstance. After rinsing the film with chloroform, this shoulder vibration disappeared totally, whereas the vibration assigned to PPy is almost kept unchanged. These results suggest that T-L-Glu-BB nanoribbons, buried between the gaps of PPy nanobelts, can indeed be washed off by rinsing with chloroform, while the PPy nanopattern can keep its basic feature when the template is removed.

Finally, we tried to synthesize PPy nanopattern on the bare silicon solid support that did not deposited with T-L-Glu-BB LB films. The same chemical polymerization process was performed. As shown in Fig. 8, the morphology of the resulted PPy nanostructure covered surface exhibits as a homogenous film that is composed of isotropically distributed PPy nanoparticles. And there is no obvious anisotropic alignment of these PPy nanoparticles on the solid support surface. The result confirms that the regular nanopattern that is composed of anisotropically aligned PPy nanoparticles described in the context is indeed printed by T-L-Glu-BB nanoribbon template.

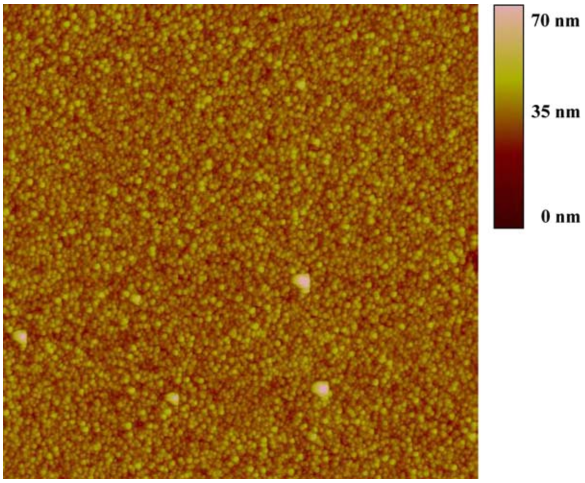

Fig. 8. AFM image of PPy polymerized for 120 min on the bare silicon solid support that did not deposited with T-L-Glu-BB LB films. Hydrophobic silicon substrate was used as the solid support. Image size: 5 μm × 5 μm.

4. Conclusions

Complicated nanopattern over large surface area composed of crosswise aligned nanoribbons of supramolecular assemblies of T-L-Glu-BB can be dexterously constructed by employing an ingenious twice-deposited strategy, which was constructed by altering the substrate's direction orthogonally when the second T-L-Glu-BB LB film deposition was carried out. A complicated PPy nanopattern, consisting of crosswise aligned nanobelts of the polymer that are composed of anisotropically arranged PPy nanoparticles along two orthogonal directions, can be readily accomplished simply by a templated chemical polymerization process. We have showed that parallel aligned PPy nanobelts over large area, consisting of anisotropically arranged nanoparticles of the polymer, can also be handily achieved using T-L-Glu-BB LB film, which was fabricated by a single deposition, as the polymerization template. The width of the PPy nanobelt and the space between them can be readily regulated to some extent by employing different technical strategies or by using solid supports with different hydrophobicities. Thus synthesized PPy nanoarrays can retain their basic patterns even after the T-L-Glu-BB nanoribbon template is washed off the solid support by rinsing with chloroform. The strategy described here likely opens a handy way for fabricating the complicated, morphology controllable nanopatterns of PPy. We, however, should also point out that the exact reason why the T-L-Glu-BB sublayer is easier to be flaked off the solid support than that of T-L-Glu-BB nanoribbons, is still kept unknown, although a plausible discussion has been performed in the present paper.

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References

[1] (a) Purrucker O, Foetig O, Lüdtke K, Jordan R, Tanaka M. J Am Chem Soc 2005;127(4):1258−64;
(b) Keting CD, Natan MJ. Adv Mater 2003;15(5):451−4;
(c) Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, et al. Adv Mater 2003;15(5):353−89;
(d) Kang M, Yu S, Li N, Martin CR. Small 2005;1(1):69−72.
[2] (a) Lu N, Chen X, Molenda D, Naber A, Fuchs H, Talapin DV, et al. Nano Lett 2004;4(5):885−8;
(b) Whang D, Jin S, Lieber CM. Nano Lett 2003;3(7):951−4;

(c) Service RF. Science 2001;293(5531):782–5;
(d) Huang Y, Duan X, Lieber CM. Small 2005;1(1):142–7.

[3] Lenhert S, Zhang L, Mueller J, Wiesmann HP, Erker G, Fuchs H, et al. Adv Mater 2004;16(7):619–23.

[4] Messer B, Song JH, Yang P. J Am Chem Soc 2000;122(41):10232–3.

[5] (a) Whang D, Jin S, Wu Y, Lieber CM. Nano Lett 2003;3(9):1255–9;
(b) Kim F, Kwan S, Akana J, Yang P. J Am Chem Soc 2001;123(18):4360–1;
(c) Yang P. Nature 2003;425(6955):243–4.

[6] (a) Gleiche M, Chi L, Gedig E, Fuchs H. ChemPhysChem 2001;2(3):187–91;
(b) Gleiche M, Chi LF, Fuchs H. Nature 2000;403(6766):173–5.

[7] Chi L, Jacobi S, Anczykowshi B, Overs M, Schaefer HJ, Fuchs H. Adv Mater 2000;12(1):25–30.

[8] (a) Pignataro D, Sardone L, Marletta G. Langmuir 2003;19(14):5912–7;
(b) Devereaux CA, Baker SM. Macromolecules 2002;35(5):1921–7;
(c) Moraille P, Badia A. Langmuir 2002;18(11):4414–9.

[9] (a) Holdcroft S. Adv Mater 2001;13(23):1753–65;
(b) Ramanathan K, Bangar MA, Yun M, Chen W, Mulchandani A, Myung NV. Nano Lett 2004;4(7):1237–9;
(c) Ikegame M, Tajima K, Aida T. Angew Chem Int Ed 2003;42(19):2154–7;
(d) Gorman CB, Biebuyck HA, Whitesides GM. Chem Mater 1995;7(3):526–9;
(e) Huang Z, Wang PC, MacDiarmid AG, Xia Y, Whitesides G. Langmuir 1997;13(24):6480–4;
(f) Seo I, Pyo M, Cho G. Langmuir 2002;18(20):7253–7.

[10] (a) Lu G, Li C, Shi G. Polymer 2006;47(6):1778–84;
(b) Lan Y, Wang E, Song Y, Song Y, Kang Z, Xu L, et al. Polymer 2006;47(4):1480–5;
(c) Yang X, Dai T, Lu Y. Polymer 2006;47(1):441–7.

[11] (a) Lee H-T, Liu Y-C. Polymer 2005;46(24):10727–32;
(b) Fujii S, Armes SP, Jeans R, Devonshire R. Chem Mater 2006;18(11):2758–65;
(c) Zhang X, Manohar SK. J Am Chem Soc 2004;126(40):12714–5.

[12] (a) Hama HT, Choib YS, Jeongc N, Chung IJ. Polymer 2005;46(17):6308–15;
(b) Baea WJ, Kima KH, Joa WH, Park YH. Polymer 2005;46(23):10085–91;
(c) Zhong W, Liu S, Chen X, Wang Y, Yang W. Macromolecules 2006;39(9):3224–30.

[13] (a) Chronakis IS, Grapenson S, Jakob A. Polymer 2006;47(5):1597–603;
(b) Boukerma K, Piquemal J-Y, Chehimi MM, Mravčáková M, Omastová M, Beaunier P. Polymer 2006;47(2):569–76.

[14] (a) Zhang X, Manohar SK. J Am Chem Soc 2005;127(41):14156–7;
(b) Wu A, Kolla H, Manohar SK. Macromolecules 2005;38(19):7873–5;
(c) Jang J, Yoon H. Langmuir 2005;21(24):11484–9;
(d) Hermsdorf N, Stamm M, Forster S, Cunis S, Funari SS, Gehrke R, et al. Langmuir 2005;21(25):11987–93.

[15] Goren M, Lennox RB. Nano Lett 2001;1(12):735–8.

[16] Carswell ADWE, O'Rear A, Grady BP. J Am Chem Soc 2003;125(48):14793–800.

[17] (a) Demoustier-Champagne S, Ferain E, Jérome C, Jérome R, Legras R. Eur Polym J 1998;34(12):1767–74;
(b) Demoustier-Champagne S, Stavaux PY. Chem Mater 1999;11(3):829–34.

[18] Martin CR. Chem Mater 1996;8(8):1739–46.

[19] (a) Liang L, Liu J, Windisch CF, Exarhos GJ, Lin Y. Angew Chem Int Ed 2002;41(19):3665–8;
(b) Duchet J, Legras R, Demoustier-Champagne S. Synth Met 1998;98(2):113–22;
(c) De Vito S, Martin CR. Chem Mater 1998;10(7):1738–41.

[20] Cai XW, Gao JS, Xie ZX, Xie Y, Tian ZO, Mao BW. Langmuir 1998;14(9):2508–14.

[21] Zhang W, Wen X, Yang S. Langmuir 2003;19(10):4420–6.

[22] Yoo SI, Sohn BH, Zin WC, Jung JC. Langmuir 2004;20(24):10734–6.

[23] Rozsnyai LF, Wrighton MS. Langmuir 1995;11(10):3913–20.

[24] Chen P, Gao P, Zhan C, Liu M. Chem Phys Chem 2005;6(6):1108–13.

[25] (a) Bae SS, Lim DK, Park JI, Lee WR, Cheon J, Kim S. J Phys Chem B 2004;108(8):2575–9;
(b) Li ZF, Ruckenstein E. Macromolecules 2002;35(25):9506–12;
(c) Sfez R, Liu DZ, Turyan I, Mandler D, Yitzchaik S. Langmuir 2001;17(9):2556–9.

[26] Flat and even films are always produced by the LB process, which would make it difficult for the SEM observation. Experimentally, in order to catch the SEM morphologies easily, about 30–40 nm of platinum has to be deposited by vacuum deposition onto the patterned surface to make clear contrast. This would make the gaps between the PPy nanobelts become more faint, especially in the case of crosswise aligned PPy nanobelts. As a result, we herein mainly present AFM results. In order to shorten the paper, we only provided two SEM results of the fabricated PPy nanopatterns in the context.

[27] Allen NS, Murray KS, Fleming RJ, Saunders BR. Synth Met 1997;87(3):237–47.

[28] (a) Oyaizu K, Haryono A, Shinoda H, Tsuchida E. Macromol Chem Phys 2001;202(7):1273–9;
(b) Tian B, Zerbi G. J Chem Phys 1990;92(6):3886–91;
(c) Tian B, Zerbi G. J Chem Phys 1990;92(6):3892–8.

[29] (a) Liu Y, Shi G, Li C, Liang Y. J Appl Poly Sci 1998;70(11):2169–72;
(b) Mathys GI, Truong VT. Synth Met 1997;89(2):103–9.