Two-dimensional polyaniline nanosheets via liquid-phase exfoliation*

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Two-dimensional (2D) organic nanomaterials are fascinating because of their unique properties and pentential applications in future optoelectronic devices. Polyaniline (PANI) has attracted much attention for its high conductivity, good environmental stability and unusual doping chemistry. We report on liquid-phase exfoliation of layered PANI films grown by electrochemical polymerization. Atomic force microscopy images demonstrate that few- or even mono-layer PANI nanosheets can be fabricated. The PANI nanosheets can be transferred onto a variety of surfaces, providing a promising route to their incorporation into a variety of devices for further studies and various applications.

Keywords: two-dimensional nanosheets, polyaniline, electrochemical polymerization, liquid-phase exfoliation

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1. Introduction

Two-dimensional (2D) organic nanomaterials suitable for catalysts, energy storage, ultra-sensitive sensors and flexible optoelectronic devices have gained great attention due to their intriguing physical and chemical properties.[1–3] To date, two strategies have been adopted to fabricate 2D organic nanomaterials. One is the so-called "bottom-up" method in which monomers are confined into a surface polymerize to form 2D organic nanomaterials.[4–6] Success of this method often relies on the quality of expensive substrates, fabrication techniques and special conditions such as ultra-high vacuum which is highly energy consuming.[7,8] In addition, the transfer from the growth substrates to target surfaces often introduces residues and defects that will deteriorate their performances.[9,10] An alternative method is the "top-down" method based on the exfoliation of layered bulk material.[11,12] It is gaining more attention because it represents an extraordinarily versatile, potentially up-scalable and sustainable route to the production of a wide variety of 2D nanomaterials.[9,13,14] The approach also allows the easy transfer of the products onto a variety of surfaces.

Layered materials with inter-layer van der Waals interactions are often the start point of exfoliation. Many 2D organic nanosheets have been thus obtained from metal-organic frameworks and covalent organic frameworks.[15,16] However, the exfoliations of layered materials consisting of conventional polymer chains are rarely reported. Polyaniline (PANI) is one of the most important conducting polymers that have applications in various electronic devices due to its high conductivity, good environmental stability and unusual doping/dedoping chemistry.[17–21] PANI with nano-lamellar structure is even more useful in electronic and opto-electronic devices because of its distinctive conducting pathways and surface interactions.[22,23] In this work, we seek to grow layered PANI with the popular electrochemical polymerization method and fabricate 2D PANI via liquid-phase exfoliation.

2. Experiment

Aniline (99+%) was purchased from Alfa Aesar, and distilled prior to use. Sulfuric acid, acetone, methanol, and isopropanol were purchased from Beijing Chemical Reagents Co. and directly used without further purification. The layered PANI films were electrochemically polymerized using a CHI660A electrochemical workstation. The saturated calomel electrode (SCE) was used as the reference electrode, a silicon wafer and a polished platinum plate were used as the working electrode and counter electrode, respectively. The concentrations of aniline and sulfuric acid in the electrolytes were 0.1 M and 0.5 M respectively. The polymerization was carried out at 0.79 V versus SCE for 1000 s. The obtained PANI films were first washed using distilled water, then released by gentle solvent flow around the substrate with a micropipette. After being

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immersed in solvent for several days, sonication was adopted.

The scanning electron microscope (SEM) images were acquired using Hitachi S-4800. The x-ray reflectivity was measured by performing a θ–2θ scan on a Bruker D8-advance diffractometer, collecting diffraction peaks along the [001] direction. The rocking curve around the (001) peak was obtained by setting the 2θ angle at that of (001) peak and rocking the sample. The atomic force microscopy (AFM) images were obtained in ScanAsyst using a Bruker Multimode 8 AFM. The optical microscope images were obtained using an optical microscope (Nikon LV100ND).

3. Results and discussion

We adopt the electrochemical polymerization method, by which an extended chain conformation can be obtained,[24] to produce lamellar PANI crystals. When the potential is set to be beween 0.7 V and 0.8 V with resepct to the SCE, the polymerization goes directly towards linear PANI, favoring the formation of layered PANI crystals. The SEM image and x-ray reflection pattern (Figs. 1(a) and 1(b)) indicate that the PANI films each consist of highly ordered layers with a stacking period of 9.1 ± 0.1 Å. Furthermore, the width of the central peak of rocking curves around the Bragg peak (Fig. 1(c)), another direct criterion of the overall structural quality of lamellar films,[25] is only 0.05°, mostly limited by the instrumental resolution of 0.03°. All these results suggest that we obtain highly oriented layered PANI film with low mosaicity, which is the vital precondition to prepare 2D organic nanomaterials by liquid-phase exfoliation.

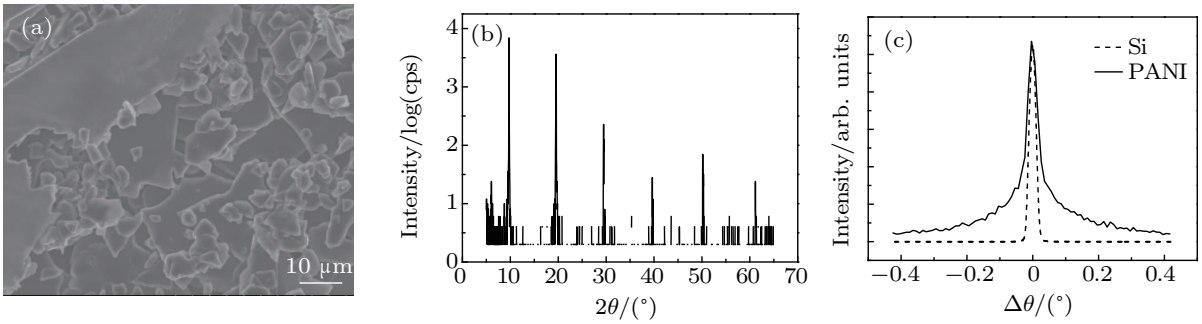


Fig. 1. Lamellar structure of PANI grown by electrochemical polymerization on silison surface. (a) Surface morphorlogy by SEM. (b) X-ray reflectivity pattern (θ–2θ scan) with a series of (00n) peaks showing the layered feature of the PANI film. (c) Rocking curve measured by rocking the sample while keeping the detector at the 2θ angle of the first Bragg peak.

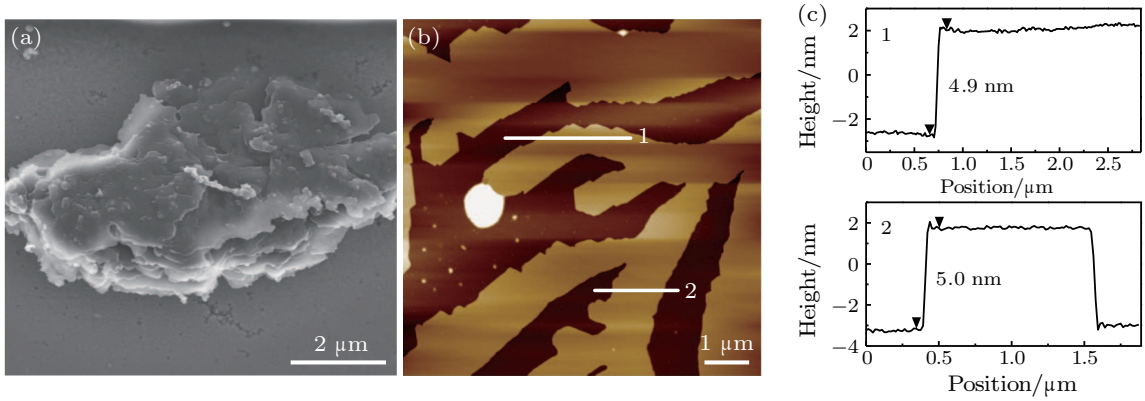


Fig. 2. (color online) Exfoliation of PANI in acetone. (a) SEM image of PANI after 3-day swelling in acetone. (b) AFM image and (c) the corresponding height profiles of the PANI nanosheets upon being transferred onto fresh mica surface after 15-min sonication at 100 W.

The key to successful exfoliation is to find appropriate solvents. The commonly used solvents are 1-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF), which have proven useful to exfoliate van der Waals crystals down to thin sheets and monolayer sheets.[26,27] However, these solvents cannot be used to exfoliate PANI crystals because they are good solvents for PANI chains. Moreover, complex processes are needed to remove these highly toxic solvents after the exfoliation. We therefore use other common solvents to exfloliate the layered PANI.

Acetone has been proved to be a suitable solvent to induce exfoliation.[28] It is one of the most common solvents with low toxicity and strong volatility, which is convenient for removing the solvent. We immerse the films in acetone for several days to swell them. After swelling, the films show loose laminar structures as shown in Fig. 2(a). We sonicate the swelled PANI at 100 W for 15 min to disrupt the interactions between layers to obtain plate-like sheets. The supernatants

are then collected after the dispersions have been centrifuged for 1 min. To determine the effect of liquid-phase exfoliation, we transfer the resulting suspension onto fresh mica for AFM characterization. Nanosheets with a lateral dimension of 1 μm∼ 3 μm can be observed from Fig. 2(b). The thickness is 4.9 ± 0.1 nm (Fig. 2(c)), or equivalently, about 6 layers according to the thickness of a monolayer deduced by the XRR measurement in Fig. 1. This indicates that liquid-phase exfoliation in acetone is an efficient approach to preparing 2D PANI and that the surface energy of acetone matches that of PANI. It is worth mentioning that the pre-swelling before sonication is important for the quality of the nanosheets (Fig. A1). Intercalation of acetone between the molecular layers of PANI during the swelling increases the interlayer spaces and reduces the van der Walls interactions dramatically, making exfoliation easier.

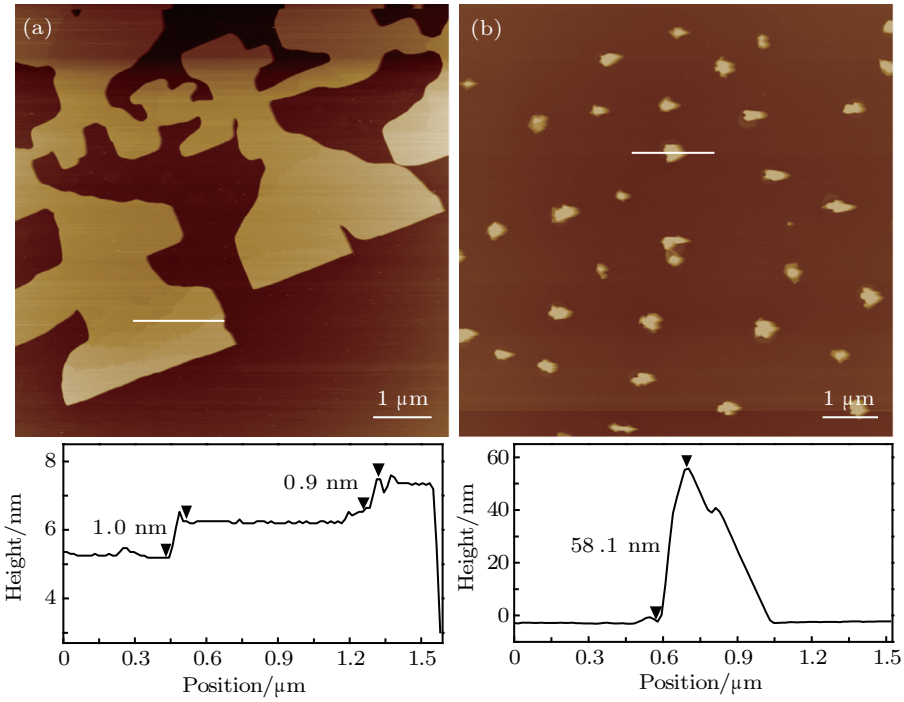


Fig. 3. (color online) AFM images and the corresponding height profiles of PANI nanosheets upon being transferred onto fresh mica surfaces after 15-min sonication at 100 W in isopropanol (a) and methanol (b).

We test two other common solvents (isopropanol and methanol) we sorted out according to the Hansen solubility parameter theory,[29] and survey their ability to exfoliate PANI films under the same condition as that in Fig. 2. After exfoliation in isopropanol, nanosheets each with a thickness of about 10 nm are obtained (Fig. 3(a)). In addition, terraces each with a height of 0.9 ± 0.1 nm are observed in these nanostructures, reflecting the layered nature of PANI. With methanol, however, only very small nanosheets with aggregated morphologies (the height is up to ∼ 60 nm) are obtained (Figs. 3(b) and A2). It is suggested that the surface energy of the solvent should be similar to that of the layered material in order to have high quality nanosheets. Otherwise, a large energy difference between the exfoliated and re-aggregated states will drive the re-aggregation.[30] All the three solvents studied here have similar surface tensions. However, the re-aggregation only occurs in methanol, indicating that the surface tension is just a crude solubility parameter although it is an excellent tool for initial solvent discovery.[28,31,32] Parameters of the solvents affecting the quality of the liquid exfoliation should be studied further.

Besides the solvents, sonication conditions also play an important role in determining the thickness and lateral dimensions of the nanosheets.[13,33] We perform additional experiments by adjusting the sonication time in different solvents in order to understand the factors that determine the quality of the nanosheets. Figure 4 shows the representative AFM images of the exfoliated nanosheets, reflecting an evolution from thick nanosheets with a thickness of 9.6 ± 0.1 nm after 10-min sonication (Fig. 4(a)) to few-layer nanosheets with a thickness of 4.0 ± 0.1 nm after 30-min sonication (Fig. 4(c)) at 100 W in acetone. We observe the same variation trend of thickness with the increase of sonication time in isopropanol. The results are in agreement with previous reports about other 2D organic nanomaterials.[13] It is obvious that the increasing of sonication time in good solvent will result in a higher degree of exfoliation. However, lateral dimensions of all of the exfoliated nanosheets under different conditions are in the same range of 1 μm∼ 10 μm and are not found to follow any trend. The results suggest that the mechanical forces under these conditions cannot break the strong in-plane bonds to reduce the lateral size.

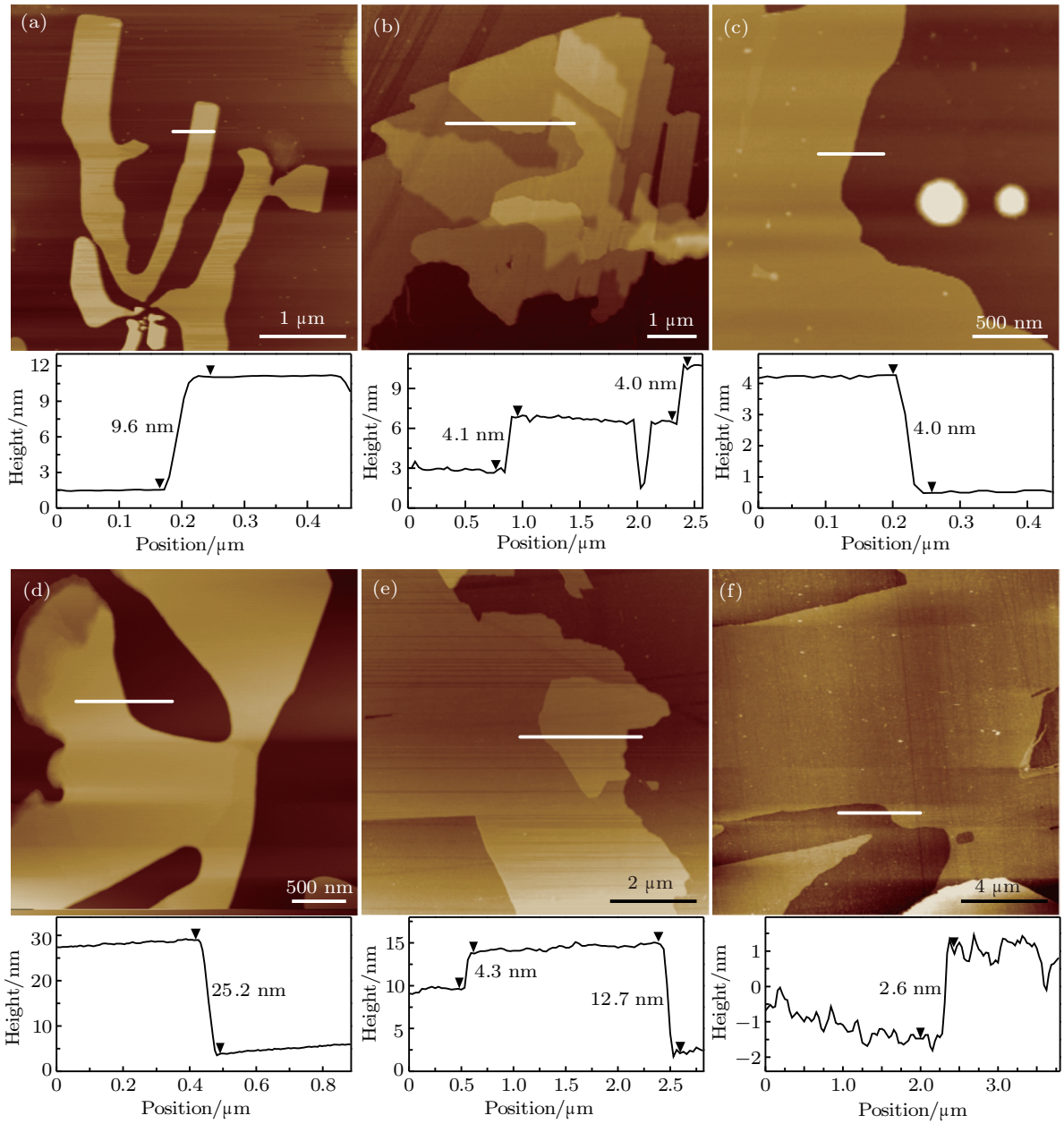


Fig. 4. (color online) AFM images and the corresponding height profiles of PANI nanosheets upon being transferred onto fresh mica surfaces after sonication in acetone ((a)–(c)) and isopropanol ((d)–(f)) for different times at 100 W. (a) and (d) 10 min, (b) and (e) 20 min, and (c) and (f) 30 min.

To see whether it is possible to push exfoliation forward to obtain single-layer PANI, we increase the sonication time and power. With the increase of time to 40 min at 100 W (Fig. 5(a)), PANI gives further exfoliation results compared with that found after 30-min sonication (Fig. 4(f)). The thickness decreases to 0.8 ± 0.1 nm, similar to the smallest height of terraces observed in Fig. 3(a) and the inter-layer period (9.1 ± 0.1 Å), indicating the PANI can be exfoliated into single layers. The same result can be achieved by increasing the sonication power to 150 W (Fig. 5(b)), when the sonication time is still 20 min. It is worth noting that the height of single-layer PANI is a little smaller than that of the expected according to the XRR results (0.97 nm). This is understandable because 1) the loading force of the AFM tip on the samples and the electrostatic attraction between the molecule and substrate often cause the measured height to be smaller than the expected value, and 2) the height measurements based on the response of piezoelectric materials may have an uncertainty of 10%–15%, mainly due to the nonlinear characteristics of the response.[34,35] This phenomenon has also been observed for other 2D organic nanomaterials.[26,27] Increasing the sonication time or sonication power, the lateral dimensions decrease to $\sim$ 300 nm after 60 min of sonication at 100 W (Fig. 5(c)) or after 20 min of sonication at 250 W (Fig. 5(d)). This suggests that the excessive sonication would induce scission of organic nanosheets as observed in graphene.[36,37]

The above results illustrate that not only the solvent, but also the sonication power and time have a significant effect on the number of layers of the two-dimensional PANI (See the following Table 1).

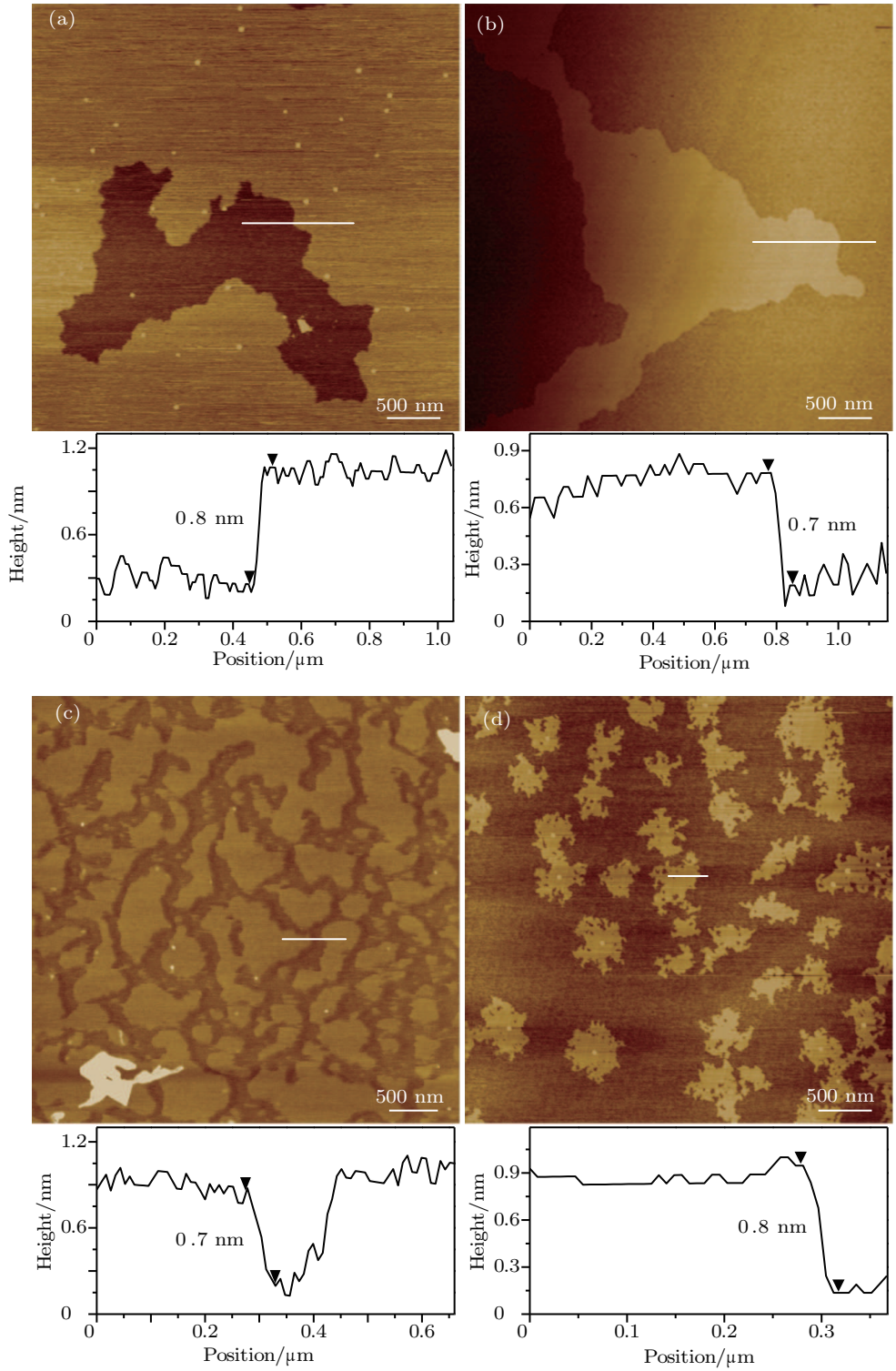


Fig. 5. (color online) AFM images and the corresponding height profiles of PANI nanosheets upon being transferred onto fresh mica surfaces after sonication in isopropanol at different powers and times: (a) 100 W and 40 min, (b) 150 W and 20 min, (c) 100 W and 60 min, and (d) 250 W and 20 min.

Table 1. Effects of sonication power (P) and time (T) on the number of layers (L) of 2D PANI.

Solvent	P/W	T/min	L/layer	Solvent	P/W	T/min	L/layer
Isopropanol	100	10	28	isopropanol	150	20	1
		15	11		250	20	fracture
		20	9	acetone	100	10	11
		30	3			15	6
		40	1			20	5
		60	fracture			30	5

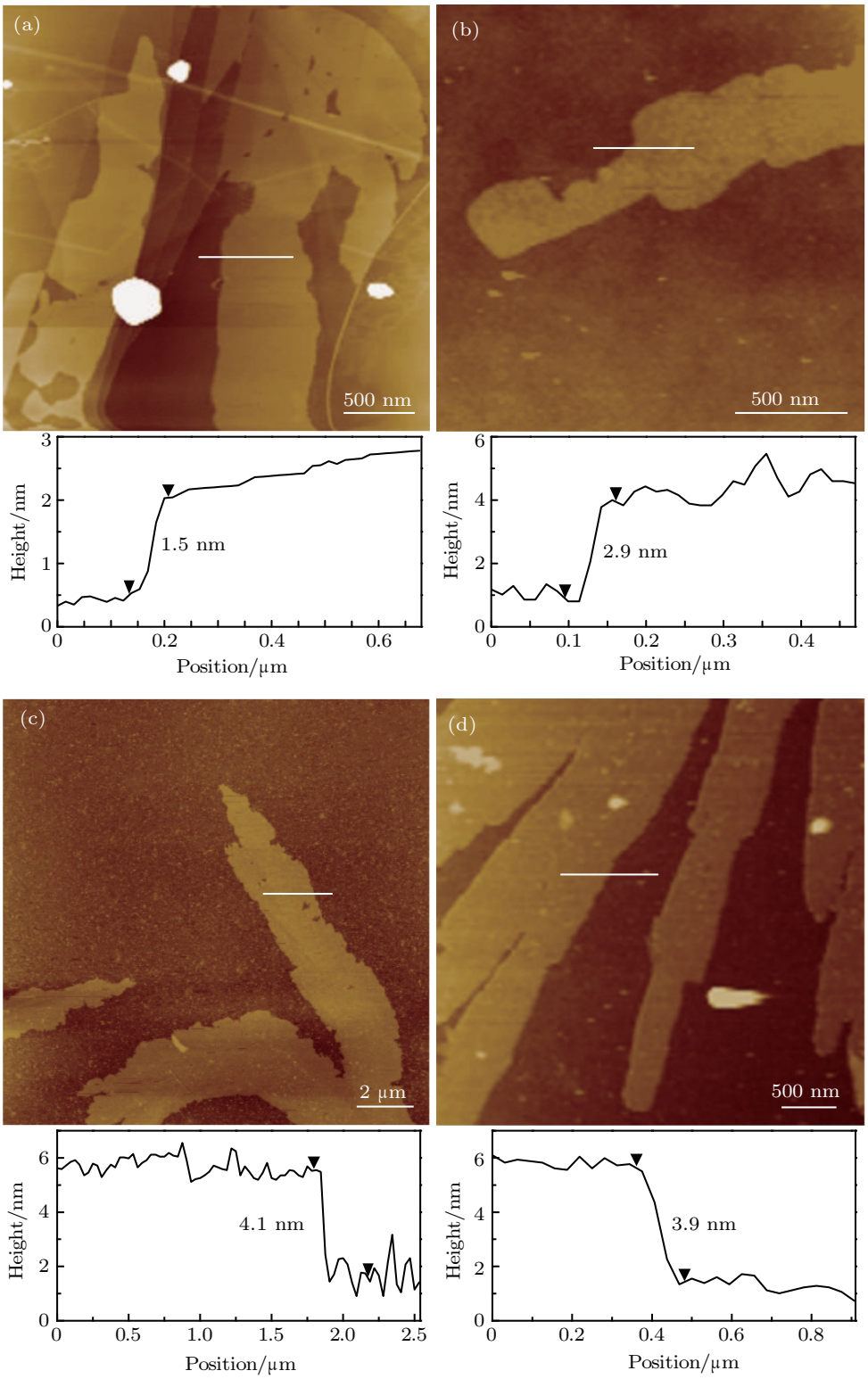


Fig. 6. (color online) AFM images and the corresponding height profiles of PANI nanosheets transferred onto HOPG (a), Si_3N_4 (b), SiC (c), and SiO_2 (300 nm)/silicon (d) surfaces.

It is noted that an advantage of the PANI nanosheets formed by liquid exfoliation is that they are transferable onto various substrates, providing a promising route to the incorporation of the PANI nanosheets into a variety of devices for further studies and various applications. We transfer the PANI nanosheets onto mica, highly oriented pyrolytic graphite (HOPG), Si_3N_4, SiC, and SiO_2 (300 nm)/silicon wafer by simply dropping the suspension (8 μl) onto the substrates (1 cm×1 cm) without other mechanical and chemical treatments (as shown in Fig. 6). The coverage ratio of the sheets on the substrates can reach up to 40%–60% (See Fig. 4, Fig. 5, and Fig. A3).

4. Conclusions and perspectives

In this work, we prepare 2D PANI nanosheets with various lateral sizes and thickness values through liquid-phase exfoliation of layered PANI films grown by electrochemical polymerization. We demonstrate that common solvents, such as acetone and isopropanol, are good solvents for preparing the 2D organic nanomaterials. Unlike previously reported solvent (NMP or DMF), these solvents are more environmentally friendly and can be easily removed through drying at room temperature. This provides a novel way of fabricating the 2D PANI nanosheets. We also show that these nanosheets can be transferred onto a variety of surfaces, which is an important step for applications.

Appendix A: Supporting information

The AFM image and the corresponding height profile of PANI and the optical microscope images of PANI nanosheets.

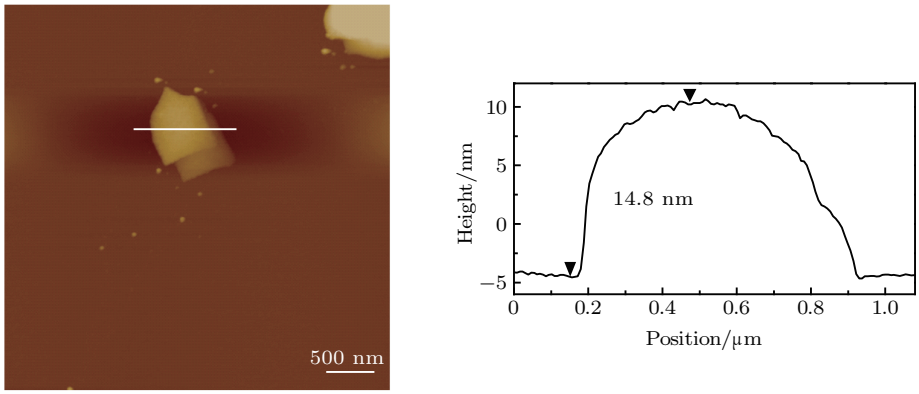


Fig. A1. (color online) AFM image and corresponding height profile of PANI sheets upon being transferred onto fresh mica surfaces after sonication of un-swelled PANI in acetone for 15 min at 100 W. This indicates that the pre-swelling before sonication plays an important role in determining the quality of nanosheets.

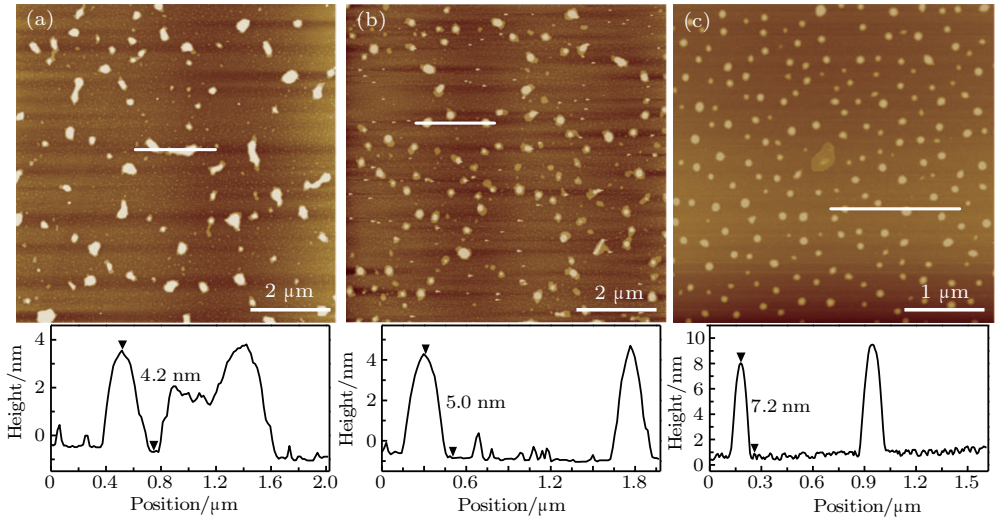


Fig. A2. (color online) The AFM images and the corresponding height profiles of PANI nanosheets upon being transferred onto fresh mica surfaces after sonication in methanol at different powers and times: (a) 100 W and 25 min, (b) 150 W and 20 min, and (c) 200 W and 15 min. We can observe that only small nanosheets with aggregated morphologies are obtained, even though we optimize the exfoliation parameters. This confirms that the methanol is bad solvent for exfoliating layered PANI.

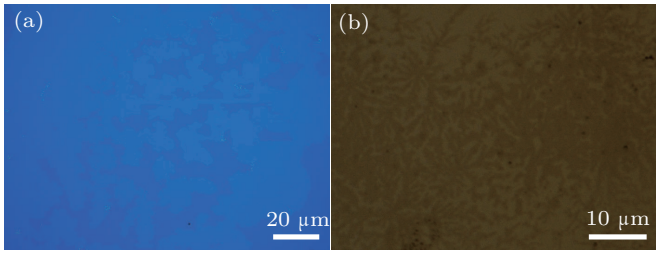


Fig. A3. (color online) Optical microscope images of PANI nanosheets upon being transferred onto SiO_2 (300 nm)/silicon (a) and Si_3N_4 (b) surfaces.

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