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Single-crystalline 2D erucamide with low friction and enhanced thermal conductivity

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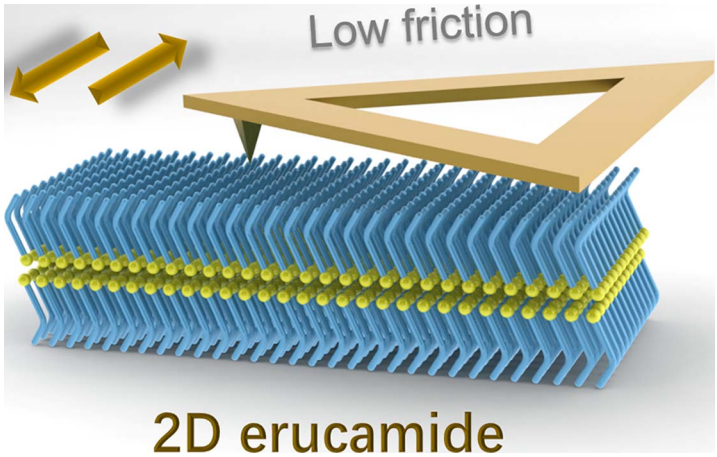
GRAPHICAL ABSTRACT



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ABSTRACT

Two-dimensional (2D) organic materials attract much research interest because of their unique properties and potential applications in catalysis, lubrication, and biological medicine. Erucamide is an unsaturated aliphatic primary amide that is widely used to reduce friction in the production of various polymers. In this work, we synthesize single-crystalline 2D erucamide with a facile and scalable method. The thinnest 2D erucamide is ~4 nm thick, containing two layers of erucamide molecules; and its lateral size is a few micrometers. We observe a crystalline-to-amorphous transformation for 2D erucamide under electron beam irradiation. More importantly, we systematically investigate the influences of crystallinity on the tribology and thermal properties of 2D erucamide. The crystalline 2D erucamide demonstrates an ultralow friction and enhanced thermal conductivity, which makes it a promising material used in nanoscale lubrication and thermal management.

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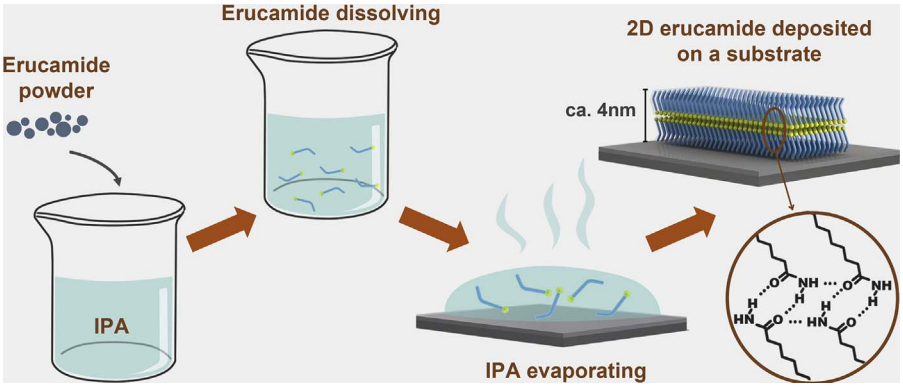

Fig. 1. Synthetic route of 2D erucamide.

1. Introduction

Recently, Two-dimensional (2D) materials have drawn a lot of research interest [1–10], because they exhibit unique properties such as good flexibility and large specific surface area in comparison with their bulk counterparts due to the reduction of dimension [6,7]. 2D organics refer to single- or few-layer organics whose thickness is a few nanometers and is several orders of magnitude smaller than the lateral sizes [11]. Much effort has been paid in the design, synthesis, and characterization of highly ordered, sheet-like 2D organic materials. 2D supramolecular organic frameworks (SOFs) [12–15], covalent organic frameworks (COFs) [16,17], and polymers [18–21] are synthesized successfully. These 2D organic layers show great potential in various applications such as sensing [17], energy storage [20], and catalysis [22].

Erucamide is an unsaturated aliphatic primary amide that is widely used to reduce friction in the production of various polymers [23]. It also has extensive applications in drug delivery [24] and corrosion inhibition [25]. In this work, we synthesize single-crystalline 2D erucamide material with a lateral size of 2–10 μm for the first time. The thinnest 2D erucamide is ~4 nm thick, containing two hydrogen-bonded single layers. We observe a crystalline-to-amorphous transformation for 2D erucamide under electron beam irradiation of scanning electron microscopy (SEM) or transmission electron microscopy (TEM). More importantly, we systematically investigate the friction and thermal transport behavior of crystalline and amorphous 2D erucamide and explore the influences of crystallinity on the tribology and thermal properties of 2D erucamide. The crystalline 2D erucamide demonstrates an ultralow friction and enhanced thermal conductivity, which makes it a promising material used in nanoscale lubrication and thermal management.

2. Experimental

A facile method was used to synthesize 2D erucamide. 1 mg as-received commercial erucamide powder (98% purity, Usoft, China) was dissolved in 10 g isopropanol (IPA, 99.8% purity, Acros, Belgium) to form a solution. The solution was then dropped on SiO_2 (200 nm, thermally grown oxide)/Si substrate and dried naturally to form 2D erucamide. The crystal structure of the bulk erucamide was determined by X-ray diffractometry (XRD, D/max-2500/PC, Rigaku, Japan) using the commercial powder. The morphology of 2D erucamide was observed by SEM (Merlin, Zeiss, Germany), TEM (JEOL 2100, JEM, Japan), and atomic force microscopy (AFM, AR Cypher, Oxford, UK). The chemical structure of 2D erucamide was studied by Fourier transform infrared spectroscopy (FT-IR, Bruker, Horiba, Germany). The composition was analyzed by time of flight secondary ion mass spectrometry (TOF-SIMS, TOF.SIMS 5, ION-TOF GmbH, Germany).

The thickness of 2D erucamide was measured by AFM on contact mode with a TR400 PSA tip at a scan rate of 2 Hz. Lateral force images were taken with PNP-TR probes at a scan rate of 40 Hz. The tip was calibrated with an improved wedge method [26]. The normal spring constant k_n and lateral spring constant k_l were calculated to be 0.267 and 15.7 Nm^{-1}, respectively. The friction force was determined by dividing the difference between trace and retrace signals by two.

Thermal conductivity of 2D erucamide was measured using a well-established suspended thermal bridge method [27]. The micro-device consists of two suspended membranes, serving as the heat source and heat sink, respectively. A Platinum coil was patterned on each membrane, acting as a heater to increase the temperature of the suspended membrane (heat source), as well as a resistance thermometer to measure the temperature of each membrane (heat source or heat sink). The 2D erucamide sample was aligned bridging two membranes with a home-made micromanipulator. A Wheatstone bridge was employed on the sensing side to eliminate the contribution of the background conductance [28]. The thermal conductance G of the 2D erucamide was extracted by solving the heat transfer model of the micro-device. Then, the thermal conductivity was calculated according to $\kappa = G \times l/(d \times w)$, where l, w, and d were the suspended length, sample width, and sample thickness, respectively. The l and w were measured by SEM and d was obtained by AFM.

3. Results and discussion

For erucamide, hydrogen bonds play important roles in its structure. Each amide head group can form two hydrogen bonds. Two amide molecular chains are bonded head to head with hydrogen bonds to form a dimer and further hydrogen-bonded with neighboring molecular chains to form a lamella [29]. The crystal structure of bulk erucamide was determined by XRD. The interlayer spacing and the side to side packing distance are calculated to be 4.36 and 0.48 nm, respectively. The details of the structural analysis are shown in Fig. S1 and Table S1 (Supplementary information).

Fig. 1 shows the synthetic route of 2D erucamide. Erucamide molecules are homogenously distributed in IPA after the powder is dissolved. Then, the solution is dropped onto a SiO_2/Si substrate. While IPA evaporates, 2D erucamide is formed through layer-by-layer assembly of molecules, which is usual for organic layers [30,31]. First, a dimer is formed by linking two erucamide molecular chains with two hydrogen bonds. Then, neighboring dimers are assembled to form a bilayer that is the structural unit of 2D erucamide. The bilayers are periodically stacked to form a nanosheet. A bilayer (structural unit) is shown in Fig. 1. The thickness of bilayers and nanosheets is measured by AFM, which is shown later.

Fig. 2a is the SEM image of 2D erucamide layers. The layers typically show a parallelogram-like shape with a lateral size of 2 − 10 μm. The thickness of 60 erucamide layers was measured by AFM. The thickness histogram is shown in Fig. S2 (Supplementary information) and the average thickness of the erucamide layers is 16 nm. The thinnest layer measured by AFM is about 4.5 nm (Fig. 2b), which is well