

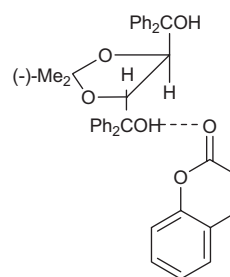
Crystalline Thin Films Formed by Supramolecular Assembly for Ultrahigh-Density Data Storage**

By Yongqiang Wen, Yanlin Song,* Guiyuan Jiang, Dongbo Zhao, Kuling Ding, Wenfang Yuan, Xiao Lin, Hongjun Gao, Lei Jiang, and Daoben Zhu

To cope with the increasing demand in data-storage capacity in this digital age, there is an urgent need to develop new technologies and materials. In the past decade, a variety of recording techniques have been proposed.^[1–5] Among them, scanning-probe microscopies (SPMs), such as scanning tunneling microscopy (STM),^[6] atomic force microscopy (AFM),^[7] and scanning near-field optical microscopy (SNOM),^[5] have proven to be competitive techniques for ultrahigh-density information storage. The ultimate level of data density has been demonstrated with the manipulation of individual atoms.^[8] During recent years, the design and synthesis of organic compounds for application as functional materials has been a field of enormous growth due to their controllable molecular structures and properties.^[1–7] From an applications point of view, a critical problem with the use of organic materials in nanoscale devices is the construction of stable, ordered, thin films on a large scale, which is only possible with crystalline materials.^[9] In contrast with small-molecule materials, supramolecular materials, which combine the benefits of polymers with those of organic crystalline systems, have been considered a promising medium in molecular electronics.^[9–13] Studies have indicated that supramolecular materials are often easier to synthesize and process than low-molecular-weight organic molecules, due to their excellent self-assembling ability. By virtue of intermolecular non-covalent interactions, chosen small molecules could be assembled into precisely ordered thin crystalline layers.^[11]

We have successfully realized ultrahigh-density data recording on several kinds of organic thin films prepared by physical vapor deposition (PVD).^[14–18] However, it was difficult to

form a large-scale, uniform film due to the lack of functional groups with strong affinities. Herein, we report a new thin-film of supramolecular (–)-TADDOL (2,2-dimethyl- α,α',α' -tetraphenyldioxolane-4,5-dimethanol) and coumarin (see below), used as a storage medium. Highly ordered crystalline TADDOL–coumarin (TC) thin films self-assembled well, due to hydrogen bonding and π -stacking among (–)-TADDOL and coumarin molecules. We successfully realized ultrahigh-density data storage in the crystalline thin film using STM, achieving a data-storage density of about 10^{13} bits cm^{-2} . The recording mechanism is attributed to the local change of the intermolecular interactions. This work has made an important step towards the practical application of organic molecules as a data-storage medium by creating self-organizing systems with a high-quality flat surface.



In order to produce a high-quality film, it is crucial to select the appropriate components and to control the growth rate. Bulk TC crystals are available in accordance with known procedures.^[19] The supramolecular crystals as a whole were 1:1 inclusion complexes of (–)-TADDOL with coumarin, which contained their respective hydrogen-bonding recognition subunits, i.e., hydroxy and carbonyl groups. To prepare films for data storage, TC crystalline complexes were re-dissolved in a 5:1 mixture of methylbenzene and dichloromethane to form a solution. The drop-casting method was used to prepare films on freshly cleaved highly ordered pyrolytic graphite (HOPG) substrates. The thickness of the film was modulated by adjusting the concentration of the solution.

Figure 1 displays a transmission electron microscopy (TEM) image of the thin film and its selected-area electron diffraction (SAED) pattern. The thin film was obtained from a 2.0×10^{-4} M solution. As can be seen in Figure 1, the TEM image shows a uniform and rather flat surface. The SAED pattern shows a fairly clear spot pattern, indicating the highly crystalline nature of the thin film. Such a uniform and smooth thin film, with a suitably large single-crystal region, is the basis for practical technological applications. The diffraction pattern, which deviates slightly from a regular hexagon, can be assigned to the reciprocal lattice of the *ac*-plane of the reported bulk crystal.^[20]

Figure 2A is a typical STM image of the thin film. Using the same tip, an atomic image of the HOPG substrate surface can be easily observed (Fig. 2A, inset). From Figure 2A, it is clear that the TC molecules are arranged periodically. The dimensions of the surface unit cell are 0.9×1.0 nm², and the angle between the *b*- and *c*-directions is about 90°, which is con-

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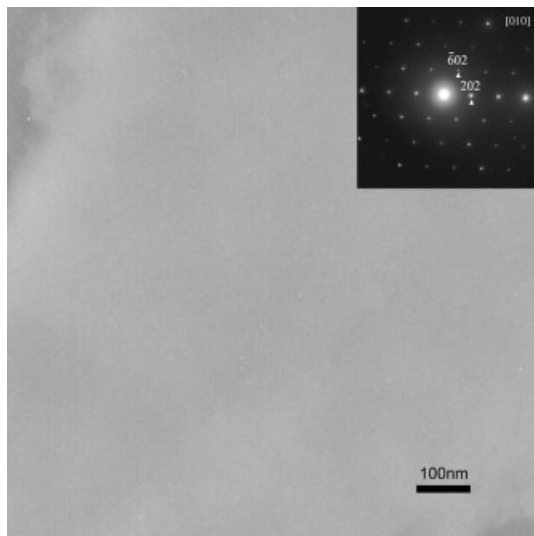


Figure 1. TEM image of the TC thin film and its electron-diffraction pattern.

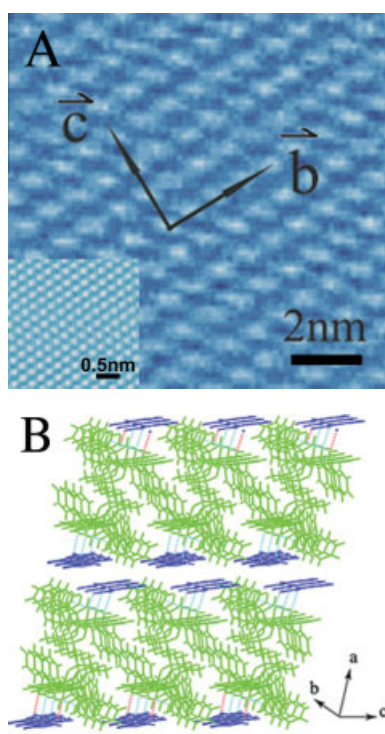


Figure 2. A) A typical STM image of the TC crystalline thin film. Scanning conditions: $V_{\text{bias}}=0.36$ V, $I_{\text{ref}}=0.32$ nA. The inset shows an STM image of HOPG. B) The stacking arrangement of (-)-TADDOL (the green structures) and coumarin molecules (the blue structures) on an HOPG substrate in the crystalline film. Dotted lines represent the stabilizing hydrogen bonds between the molecules. From the model, the hydrogen-bonding interactions between (-)-TADDOL and the coumarin molecules and the π - π interactions of the aromatic rings between the coumarin-coumarin and TADDOL-TADDOL molecules can be clearly observed.

sistent with the b and c unit-cell dimensions of the bulk crystal determined by X-ray diffraction.^[20] Generally, the structure

resulting from self-assembly at the surface strongly depends on the molecular structure and the subtle balance between intermolecular and molecule-surface interactions. Different substrate materials may result in different self-assembly processes and supramolecular structures.^[21,22] The molecular plane of coumarin is almost parallel to the HOPG substrate surface due to the strong van der Waals' forces resulting from the enforced flat adsorption geometry between them. The carbonyl groups of coumarin interact with the (-)-TADDOL molecule by hydrogen bonding, while at the same time face-to-face π - π interactions of the aromatic rings occur between the coumarin-coumarin and TADDOL-TADDOL molecules (Fig. 2B). The cooperative interaction effects lead to the highly ordered structure of the thin film on the HOPG substrate surface.

Memory recording experiments were performed with a P47 STM under ambient conditions using electrochemically etched tungsten tips. In our experiment, the STM tip was very stable, and the HOPG atomic image could be clearly observed before and after recording experiments. To induce the recording dots, pulsed voltages were applied between the STM tip and the thin film. Figure 3A shows a typical STM image of the recorded pattern on a TC thin film. The recording marks illustrate a 3×4 matrix in a scanning area of $70 \text{ nm} \times 70 \text{ nm}$.

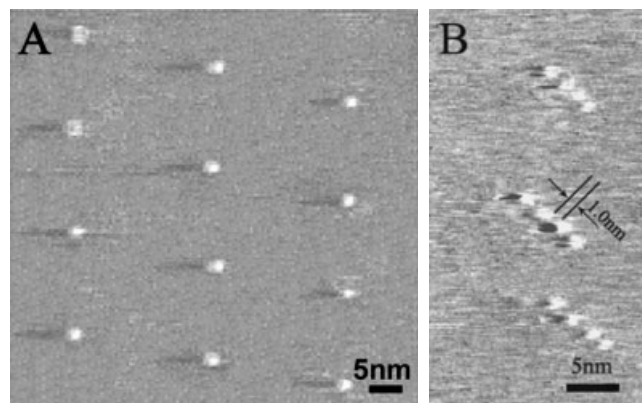


Figure 3. A) STM image of a recorded pattern obtained by applying voltage pulses of 3.4 V and 2.3 ms. The scanning area is $70 \text{ nm} \times 70 \text{ nm}$. Tunneling conditions: $V_{\text{bias}}=0.42$ V, $I_{\text{ref}}=0.62$ nA, scanning rate: $=0.2 \text{ Hz image}^{-1}$, scan mode: constant current. The average diameter of the marks is about 2.2 nm. B) Resolution test using voltage pulses of 3.2 V and 5.0 ms. The space between two information dots is about 1.0 nm.

The recording dots are about 2.2 nm in diameter. The recording dots were formed by applying a program-controlled pulsed voltage of 3.4 V and 2.3 ms. During the scanning period, the recorded marks were very stable and could last for more than 24 h.

In principle, the ultimate resolution should be the size of the molecular complex, i.e., about 1.0 nm. Figure 3B demonstrates resolution on this length scale. It is shown that the marks could be written very close to each other (the marks

are separated by approximately 1.0 nm) without merging, implying a potential recording density of about 10^{13} bits cm^{-2} . From the experiments with different pulse conditions, it was confirmed that the dot size depended strongly on the amplitude and width of the applied pulsed voltage. For voltage pulses above the threshold voltage, the probability of dot formation was almost 100%. Moreover, the dot sizes became larger as the amplitude of the applied pulsed voltage was increased from 3.2 to 6.2 V. When the value of the voltage was higher than 6.2 V, a hole could clearly be seen on the thin-film surface (Fig. S1, Supporting Information).

The marks may be formed by charge transfer,^[14] a phase transition,^[15] or some local chemical reaction.^[18,23,24] In the present case, there was no possibility for charge transfer, as studied in donor- σ -acceptor (D-A) complexes, and the possibility that the tip led to the scratches on the surface could also be excluded. In fact, to avoid running into the surface, the STM tip had been drawn 10 nm away from the tunneling position, and the feedback loop had been cut off before applying a pulse voltage.

In order to clarify the reason for dot formation, Fourier-transform IR (FTIR) spectra of a bulk TC crystal (about $0.8 \text{ mm} \times 1.2 \text{ mm} \times 1.5 \text{ mm}$) were compared with that of a crystal after the action of an electric field using a Keithley 4200 semiconductor characterization system (SCS). The junction area was about $1.2 \text{ mm} \times 1.5 \text{ mm}$. The FTIR results under different voltage conditions are shown in Figure 4. From these curves, it is clear that when the voltage reaches a

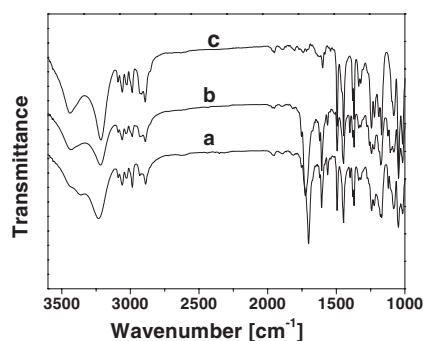


Figure 4. The FTIR spectra of a bulk TC crystal before and after applying a voltage. a) FTIR of the TC crystal; b) after applying voltage U_1 (9.6 V); c) after applying voltage U_2 (12.8 V).

certain threshold value U_1 (9.6 V), the hydrogen bonds break (Fig. 4b), leading to a shift of the characteristic IR absorption $\nu_{\text{C=O}}$ from 1700 cm^{-1} to 1724 cm^{-1} .^[25] After raising the voltage to a higher value U_2 (12.8 V), the $\nu_{\text{C=O}}$ absorption at 1700 cm^{-1} vanished, which can be attributed to the evaporation of the coumarin component from TC crystalline complexes (Fig. 4c).

On the basis of the above experimental facts, we propose the following mechanism for the formation of the information dots: when a pulsed voltage ($>3.2 \text{ V}$) is applied to a TC thin

crystalline film, hydrogen bonds between (-)-TADDOL and coumarin molecules are broken, leading to the local cracking of the crystal. This was confirmed by electron diffraction: the SAED changed from a clear spot pattern to a diffraction ring (Fig. S2, Supporting Information). When a higher pulsed voltage was applied ($>6.2 \text{ V}$), the coumarin component vaporized, leading to the formation of holes.

In conclusion, we have prepared a crystalline thin film based on the supramolecular self-assembly of (-)-TADDOL and coumarin molecules. Ultrahigh-density data storage has been successfully demonstrated with the formation of nanometer-sized dots on a thin film by applying a program-controlled pulsed voltage between a STM tip and the substrate. The size of the recording dots can be controlled at the level of the TC molecules. The demonstrated storage density is about 10^{13} bits cm^{-2} . Mechanism analyses suggest that the electric-field-induced rupture of hydrogen bonds between (-)-TADDOL and coumarin molecules is the reason the recording dots are formed. Further research into new materials possessing reversible responses to external stimuli and good self-assembling characteristics is in progress.

Experimental

TADDOL/coumarin (TC) crystals were obtained in one step from the recrystallization of (-)-TADDOL (2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenyldioxolane-4,5-dimethanol) with coumarin from an ethyl acetate/hexane solution (1:5) [19]. Subsequently, they were re-dissolved in a methylbenzene/dichloromethane mixture (5:1). A drop of this solution (typically less than 10^{-6} M) was applied to a freshly cleaved highly-ordered pyrolytic graphite substrate and studied by scanning tunneling microscopy (STM) after complete solvent evaporation at room temperature. Transmission electron microscopy (TEM) images and selected-area electron diffraction patterns were collected using an Hitachi H-8100 TEM operated at 200 kV. Amorphous carbon thin films were used to support films for TEM. The information storage experiments were performed with a P47 STM under ambient conditions, and electrochemically etched tungsten tips were used. To form the recording dots, pulsed voltages, $0 \rightarrow +8.0 \text{ V}$ in amplitude and $0.01 \text{--} 10 \text{ ms}$ in width, were applied between the conductive probe and the crystalline thin film. The Fourier-transform IR (FTIR) spectra of a bulk TC crystal, before and after applying a macroscopic electric field, were investigated with a Bruker Equinox 55 FTIR spectrometer.

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Novel Micro/Nanoscale Hybrid Reinforcement: Multiwalled Carbon Nanotubes on SiC Particles**

By Lijie Ci and Jinbo Bai*

Carbon nanotubes^[1] have been shown to have potential applications in composites due to their remarkable mechanical, thermal, and electrical properties, and because of their high

aspect ratios and low densities.^[2] However, the fabrication process of carbon-nanotube-based composites can be very complicated due to some of their nanoscale characteristics. For example, carbon nanotubes are usually provided in the form of an entangled powder, which makes it difficult to disperse them homogeneously into a matrix.^[2] The nanoscale interface between nanotubes and the matrix is another perplexing issue to deal with.^[2] Composite applications combining carbon nanotubes with well-established micrometer-scale reinforcements is potentially a good solution for improving material properties (micro/nanoscale hybrid reinforcement). By growing carbon nanotubes on the surface of carbon fibers, it has been demonstrated that the interfacial strength between carbon fibers and the matrix in a composite could be greatly improved.^[3]

Herein, we report that aligned multiwalled carbon nanotubes can be grown directly on the surface of micrometer-scale SiC particles by a floating-catalyst chemical vapor deposition (CVD) method, which has been extensively used to mass-produce aligned carbon-nanotube arrays by decomposing a ferrocene-xylene mixture at 600–900 °C in a quartz-tube reactor.^[4] Generally, aligned carbon nanotubes could be grown on large quartz substrates using this method.^[4] By combining this with a patterning technique, aligned carbon nanotubes can also be grown on microscale substrates in a controlled direction.^[5–7] SiC is a wide-bandgap semiconductor material, and has potential applications in the field of high-temperature, high-frequency, and high-power electronic devices. SiC is also an important ceramic material that is widely used for structural applications at high temperatures. Combining SiC with carbon nanotubes may create some new and exciting possibilities for their application in the fields of structural materials and electronic devices. Herein, we demonstrate that an aligned-carbon-nanotube layer grown on the surface of SiC particles can improve the interfacial properties between SiC and the matrix in an epoxy composite.

Figure 1a shows a scanning electronic microscope (SEM) image of as-received SiC particles with an average size of 17 μm. They are irregular in shape, and most of the particles have one or more flat surfaces. After the carbon nanotubes were grown on the particles, the color of the SiC powder changed to black. The layer of SiC particles became small flakes, which were very easily removed from the boat, and the surfaces of the flakes were black. This indicates that the carbon nanotubes grew evenly on the surfaces of all the SiC particles, as confirmed by SEM observations.

Figure 1b is a low-magnification SEM image of the typical product (the CVD growth duration was 25 min). Almost all the SiC particles are densely covered by carbon nanotubes. Generally, the length of the carbon nanotubes depends on the growth time at a constant growth temperature. For a growth time of 25 min at 700 °C, they were about 5–10 μm long. Figures 1c,d are enlarged images of single particles: all the surfaces of the stone-like particles are covered by carbon nanotubes. It is very interesting to note that the carbon nanotubes are aligned and perpendicular to some of the flat surfaces. On

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