Controllable fabrication of oriented micro/nanowire arrays of dibenzo-tetrathiafulvalene by a multiple drop-casting method

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A multiple drop-casting method of growing the ultralong dibenzo-tetrathiafulvalene (DB-TTF) micro/nanowire arrays has been developed which has the success ratio as high as 94%. This method enables the arrays with a length over a few hundreds of micrometers to locate between droplets with the definite orientation. The width of the micro/nanowires is controlled via tuning the concentration of DB-TTF solution in dichloromethane. The large-scale arrays can be grown onto Si, SiO₂, glass, and the flexible polyethylene terephthalate (PET) substrates. These results show the promising potential of this facile solution-based process for the growth of the high-quality organic micro/nanowires, the fabrication of high-performance and flexible devices, and the fabrication of controlled assemblies of nanoscale circuits for fundamental studies and future applications.

Introduction

Organic semiconductor micro/nanowires have attracted extensive attention recently because they combine the advantages of both organic semiconductors and micro/nanowires. On one hand, their light weight, low cost, good flexibility, and electronic tunability show a wide range of applications, for example, displays, tags, data storage, electronic papers and sensors. On the other hand, many organic micro/nanowires are capable to be easily grown by a vapor or solution method, and they generally possess the nature of the single crystal. The carriers can transport directly from one end to the other along an individual micro/nanowire, eliminating the diffusion and the traps. In this case, the high-performance organic devices can be obtained. Currently, the performance is a main challenge that limits the development of organic semiconductors in electronics and optoelectronics. Most organic semiconductor micro/nanowires have been fabricated in random locations and orientations. In comparison, the highly ordered and well-aligned micro/nanowires with the definite locations are desirable for the controlled and predictable assembly of devices and circuits. They also show a promising potential for the high-efficiency and large-scale micro/nanodevice fabrication.

Tremendous attempts have been made to grow and assemble the ordered micro/nanowire arrays of various functional semiconductor materials. One strategy is the “top-down” method, such as lithography. This method has been extensively applied in polymeric materials with excellent mechanical flexibility, but it is difficult to be applied in other fragile organic materials, especially in single crystals of small molecules. The other strategy employs the “bottom-up” process, typically the self-assembly method, to directly grow and align the organic micro/nanowires on substrates. The vapor-phase growth method with self-assembly can be carried out in a horizontal furnace tube by using organic nanocrystals as seeds. And the solution-based assembly of organic arrays is mainly performed with dip-coating, zone-casting and drop-casting methods. Among them, the drop-casting method is the most extensively used method due to the outstanding advantages such as the facile process and no requirement of specific equipment. The micro/nanowire arrays are randomly formed in the direction of the solvent evaporation. It is difficult to exactly control the location of the micro/nanowire arrays. It is requisite to further realize the controllable growth of these micro/nanowire arrays with the desired locations for their potential applications in electronic and optoelectronic devices.

Tetrathiafulvalene (TTF) and its derivatives are some of the most studied heterocyclic systems due to their outstanding advantages, such as good solubility in common solvents, easy chemical design, and good electron donors. Among them, dibenzo-tetrathiafulvalene (DB-TTF) has the high melting point of 239–243 °C, which makes it possess good air stability and hence is desirable as a candidate for organic field effect transistors (OFETs). DB-TTF is symmetric and completely conjugated, and its single crystals form the uniform stacks of the almost planar molecules due to the strong π–π interaction...
between them in a herringbone pattern along the b axis.\textsuperscript{31} Its individual microwire has shown an electron mobility \( \mu \) as high as \( 1.0 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \).\textsuperscript{31} These merits make DB-TTF a very promising candidate as building blocks for organic electronics. The single nanowire is the ideal platform for elucidating fundamental factors dictating performance. Although significant progress has been made in the fabrication of DB-TTF micro/nanowires in the past several years, no studies on the oriented DB-TTF micro/nanowire arrays have been reported until now. The assembly and scaling of the DB-TTF micro/nanowires into arrays are requisite for general purpose productions.

In this study, we develop a drop-casting method further to yield large-scale, ultralong and well-oriented arrays of DB-TTF micro/nanowires. The key improvement over the earlier studies is that our procedure yields highly ordered and well-separated DB-TTF micro/nanowire arrays in a definite location rather than randomly distributed individual DB-TTF micro/nanowires. The arrays can be obtained in large scale on various substrates, for example, Si, SiO\textsubscript{2}, even the low-cost glass and flexible polyethylene terephthalate (PET). In our work, the multiple droplets of the DB-TTF/dichloromethane solution are successively cast at predetermined regions on a substrate and allowed to evaporate slowly. The fusion of the two adjacent droplets provides a region with the lower evaporation rate, resulting in the well-aligned micro/nanowire arrays with the high success ratio and the definite location. Altogether these results demonstrate that the developed multiple drop-casting method may be used to realize the large-scale production of oriented arrays of DB-TTF micro/nanowires with high reproducibility and high crystalline quality on various low-cost substrates. It also provides a facile way to overcome the challenging problem in the controlled assembly of high-performance organic nanodevices for fundamental studies and practical applications.\textsuperscript{32}

**Experimental section**

**Growth of wire arrays**

DB-TTF was purchased from Alfa Inc. and used as received. The organic compound was dissolved in dichloromethane at a concentration of 0.00003–0.01 \text{ mol} \text{l}^{-1} (\text{M}). One to four droplets of the DB-TTF solution in dichloromethane were cast on the substrate successively and allowed to evaporate slowly. This resulted in the formation of DB-TTF micro/nanowire arrays on the substrate. In the experiment, Si, SiO\textsubscript{2}, glass, and PET were used as substrates. All substrates (except the PET substrate) were cleaned by sonication in acetone, ethanol and deionized water for 10 min. Then they were dried with nitrogen gas. After that, the substrates were dipped in the chromic acid lotion for 15 min, followed by cleaning with flowing deionized water and sonicating in deionized water. The cleaned substrates were treated with oxygen plasma right before use. For the PET substrate, it was just cleaned with deionized water, then dried with nitrogen gas, and finally treated with oxygen plasma right before use. The experiments were carried out at room temperature.

**Device fabrication**

The devices were fabricated in bottom-contact geometry. The Cr/Au electrodes were patterned on the Si/SiO\textsubscript{2} substrate using photolithography with a shadow mask and an electrode deposition process. In the process of the growth of the DB-TTF nanowire arrays, the wire arrays were connected with the microfabricated electrodes.

**Characterization**

Optical microscopy images were obtained with an Olympus BX51, SEM images were obtained with an XL30ESEM-FEG, and the electrical properties of the devices were recorded with a Keithley 4200-SCS in a clean and shielded box at room temperature in air.

**Results and discussion**

In a typical experiment, Si, SiO\textsubscript{2}, glass, and flexible PET are used as substrates. Fig. 1a shows the experimental procedure used to create the DB-TTF micro/nanowire arrays, and Fig. 1b indicates the molecular structure of DB-TTF. Two droplets of the DB-TTF solution in dichloromethane are cast on a substrate successively and fast at an optimized gap. As the evaporation proceeds, the micro/nanowire arrays are deposited in the region between the two droplets, confirming that DB-TTF has a strong tendency to self-assemble into 1D structures. Fig. 1c and d show the digital photographs of the samples. It is found that DB-TTF not only can be deposited on the rigid substrate, such as Si, SiO\textsubscript{2}, and glass, but also can be grown on the flexible PET substrate. It shows the potential of DB-TTF for applications in flexible devices.

The typical features of the DB-TTF micro/nanowire arrays are shown in optical microscopy and SEM images of Fig. 2 (Si substrate) and Fig. 3 (PET substrate). The micro/nanowire arrays are formed over the area as large as 500 \( \mu \text{m} \times 2000 \mu \text{m} \), along the evaporation direction of the solution. They exhibit good uniformity in width and consistent color along an individual micro/nanowire, indicating high crystalline quality,\textsuperscript{15,24} as shown in the SEM images. Fig. 2 shows that the length of the

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**Fig. 1** (a) Schematic illustration of the multiple drop-casting method for the growth of oriented DB-TTF micro/nanowire arrays on the substrate. (b) Molecular structure of DB-TTF. (c and d) Digital photographs of well-aligned DB-TTF micro/nanowire arrays grown on the silicon and the flexible PET substrate.
Micro/nanowires is over 400 μm. The width ranges from hundreds of nanometers to a few micrometers.

Furthermore, the width of the micro/nanowires can be controlled by tuning the solution concentration. As shown in Fig. 4, with the decreasing concentration, the width of the micro/nanowires decreases from 2–3 μm to ~100 nm. The micro/nanowire arrays can be formed when the concentration is in the range of 0.008 to 0.0003 M. When the concentration is higher, the evaporation of the solution causes the high growth speed of the crystal and produces a large number of nucleation points. As a result, as shown in Fig. 4a, the separated plate-like structures are formed when the concentration is as high as 0.01 M. As shown in Fig. 4f, when the concentration is as low as 0.00003 M, only micron-sized dots are formed as a result of the inadequate material for the continuous growth.

We have found that the formation of the micro/nanowire arrays is related to the droplet number and the distance between the droplets. Fig. 5a shows the success ratio to form the arrays as a function of the droplet number. The high success ratio is of great importance for practical applications. The conventional drop-casting method generally produces the individual micro/nanowire and/or its arrays randomly, resulting in the difficulty of device and circuit fabrication. Our experimental results show that using the multiple droplets has obviously higher success ratio than that using the single droplet. The success ratio for the formation of the micro/nanowire arrays is as high as 94%. When only the single droplet is used, the arrays are formed in random regions. However, the arrays can be controllably formed in the region between droplets when the multiple droplets are applied. The optimized gap between droplets for the high success ratio is shown in Fig. 5b, which increases with the number of droplets. These results show that our method has the promising potential for the one-step production of large-scale micro/nanowire devices.

Currently, the evaporation induced self-alignment has received special attention as a key technology for the preparation of well-ordered arrays. For example, Michael S. Strano’s group used a patterned substrate with a pinned contact area on...
the surface, to align, position, and place the individual anisotropic nanostructures, such as single-walled carbon nanotubes (SWNTs), by dip-coating and drop-casting methods. Kilwon Cho’s group modified the surface of the SiO$_2$ substrate with the different self-assembled monolayers, to obtain the trisopropylsilylethynyl pentacene (TIPS-PEN) films with significantly different morphologies and crystalline microstructures by inkjet printing. Lei Jiang’s group used the highly adhesive superhydrophobic pillar-structured silicon substrates, to obtain various polyvinyl-formal (PVF) nanowire arrays by carefully designing the micro-pillar arrangement and three-phase contact line (TCL) shrinkage direction. Conghua Lu’s group used the templates that are stable, well-controlled relaxation-wrinkles of ultrathin multilayer films in a non-stretched state, to topographically direct the colloidal crystal assembly with controlled structures by dip coating. These reports have indicated that the control over the contact line in a drying droplet plays an important role in the formation of the arrays. Following the inward shrinkage of the contact line, the oriented arrays can be fabricated by the competition between dewetting (solvent evaporation) and contact line pinning. The dewetting and contact line pinning are two generally happening processes during the solvent evaporation of a droplet. Dewetting is the shrinking of the droplet due to solvent evaporation, and the contact line pinning originates from the strong interaction between the surface and the solvent, correspondingly leading to a flow of liquid outwards to prevent the shrinkage of the solvent and to keep the contact line pinning. In fact, during evaporation of the solvent, the contact angle decreases and the meniscus interface area increases, thus causing a relative enhancement of the depinning force compared with the pinning force. As a result, the contact line becomes unstable and hops to a new position once the depinning force reaches a greater value than the pinning force, resulting in the formation of parallel arrays of micro/nanowires. As shown in Fig. 2, the ultralong single nanowire is uniform in color. It is different from our previous reports in a developed pulling method where the multiple contact lines are visible in the growth direction of the micro/nanowires. It shows that the frequent and alternate pinning and depinning processes happen uniformly in the whole process of the solvent evaporation in our multiple drop-casting method.

In order to gain insight into the process governing the spontaneous alignment of DB-TTF micro/nanowires, we have investigated the contact line dynamics of the drying droplets under the observation of the optical microscope. As shown in Fig. 6a and b, when the droplets are cast onto the substrate, they first spread on the surface from their locations, owing to the interfacial forces that are inclined to drive the droplet outwards. When the edges of the droplets contact, they mix together, resulting in a non-circular drop with the concave contact line (Fig. 6c). It has been addressed that the non-circular drops have uneven deposition rates: highly convex regions have a stronger evaporation flux and thus denser deposits. Our experiments also confirm this point. As shown in Fig. 6d and e, the contact line in the concave regions shrinks slower than that in the convex regions. The concave regions possibly provide a relatively stable environment and adequate time for the solute molecules to aggregate, crystallize, align and grow into a micro/nanowire pattern with high success ratio. The DB-TTF micro/nanowire arrays are grown along the evaporation direction of the solution near the concave regions, as shown in Fig. 6f.

In our experiments, the wire arrays grow along the evaporation direction of the solution. Therefore, the orientation of the array located at every region between droplets is predictable, even though the orientations of the arrays at different regions are different. Combined with the optimized droplet gap, the predictable orientation at the controlled location provides a facile way to device fabrication. As shown in the schematic and the typical SEM images of Fig. 7a and b, the field-effect transistors based on the DB-TTF micro/nanowire array could be fabricated on the prepared Cr/Au electrodes in one step by growing the wires perpendicular to the orientation of the electrodes. Fig. 7c and d show the typical transfer and output curves of the device. The transfer curve shows the high source–drain current at $V_G = 0$ V and the device is in its off state at $V_G > 160$ V.

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**Fig. 6** (a–f) *In situ* time-resolved optical microscopy images of the growth process of DB-TTF micro/nanowire arrays. The two droplets are successively cast on the substrate. The inset of (f) schematically shows the growth direction and location of the arrays. The scale bar is 1 mm.

**Fig. 7** Electrical characterization of a device based on the DB-TTF micro/nanowire array. (a) Schematic image of the devices. (b) SEM image of the devices. (c and d) Transfer and output characteristics of the FET.
indicating the characteristic of the depletion mode p-type field effect transistor. A FET mobility of $\sim 10^{-4}$ cm$^2$ V$^{-1}$ S$^{-1}$ was achieved, together with an ON/OFF ratio of $10^5$, and a threshold voltage of $\sim 160$ V. The low performance is ascribed to the impurity of DB-TTF used as received. It is possible to obtain the performance improvement by purifying the source materials.

Conclusions

In conclusion, we have developed a novel method for the preparation of DB-TTF micro/nanowire arrays, by allowing a few droplets to evaporate with an optimized gap on a target substrate. The location of the arrays is defined between the droplets, and the width of the DB-TTF micro/nanowires is controlled by tuning the concentration of the solution. The multiple droplets provide a unique environment for controlling the shrinkage direction and the evaporation rate of the droplets, resulting in the ordered deposition of DB-TTF micro/nanowires. Compared with the conventional drop-casting method, our process improves the success ratio for the formation of the micro/nanowire arrays. The devices can be easily realized in one step based on these micro/nanowire arrays. Such a low-cost and facile method may be used to fabricate a variety of one-dimensional organic micro/nanowire arrays in the determined area on the target substrate, and shows the potential for the large-scale fabrication in organic electronics.

Acknowledgements

The authors acknowledge the financial support from NSFC (51103018, 51273036, 61376074, 51322305, 61261130092 and 51272238), Ministry of Science and Technology of China (2012CB933703, 111 Project (B13013), 2009 National Excellent Doctoral Dissertation Award from China (201024), the Program for New Century Excellent Talents of Ministry of Education (NCET-10-317), and Fundamental Research Funds for the Central Universities (11CXPY001 and 12SSXM001).

Notes and references


