



Solution-grown large-area C₆₀ single-crystal arrays as organic photodetectors



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ABSTRACT

The alignment of organic single crystals with controlled placement and reasonable throughput is a practical way to realize their ultimate applications in electronics or photoelectronics, which however is still a challenging task. Here, a facile solution-processed dip-coating method is developed to construct crystalline fullerene arrays which exhibit excellent UV-light sensing performance. Our approach has realized the large-scale production of continuous C₆₀ single-crystal arrays in a controllable manner. The morphology, surface coverage and thickness of the final samples are modulated simply by adjusting the experimental conditions such as concentration, temperature and lifting speed, implying the versatility of our method. Moreover, the as-obtained C₆₀ single-crystal array demonstrates stable, highly sensitive, and fast photoresponse towards UV light illumination, promising for future high-performance integrated optoelectronic device.

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1. Introduction

Solution processed organic semiconductors are expected to pave the way towards flexible, low-cost, large-area and lightweight electronics [1–4]. Among the various organic materials reported so far, organic single crystals with few structural defects, exhibit superior performances when compared to the corresponding thin films [5–7]. However, single-crystal devices are largely limited to fundamental research because the individual devices are manually fabricated in most cases and it is rather difficult to scale up for technological applications [8]. From this perspective, it is of paramount importance to fabricate well-aligned organic single-crystal arrays over a relatively large area for future device fabrications. Over the past decade, several techniques have been developed for patterning and alignment of organic semiconductors, such as spin-coating [9], drop-casting [8], zone-casting [10], solution-shearing [11], and direct-printing techniques [12]. Nonetheless, these methods are always accompanied with some disadvantages. For instance, the products prepared with spin-coating or drop-casting often demonstrate low- or poly-crystallinity, and more

importantly, most of these techniques are inconsistent with reliable large-scale productions [13]. Therefore, the fabrication of highly-oriented organic crystals with high efficiency is particularly crucial to realize the practical applications of organic single crystals, which still remains a big challenge.

Fullerenes such as C₆₀ have attracted particular attention in the field of semiconductors, due to their extensively potential applications in electronic and optoelectronic devices [14–17]. Since the performances of these devices are sensitively affected by the size, morphology and crystalline structure of fullerene materials, great efforts have been dedicated to controllably fabricating well-defined fullerene single crystals [18–23]. To date, the zero-dimensional fullerene molecules have been successfully organized into a wide variety of self-assembled architectures ranging from one-dimension (1D) to three-dimension (3D) [18,24–27]. However, the fabrication of large-area C₆₀ crystals with desirable placement has been rarely realized. In 2012, Bao and coworkers reported a droplet-pinned crystallization method to deposit well-aligned C₆₀ single crystals on Si substrates, but the use of pinners results in discontinuous C₆₀ crystal films which hinders their practical applications [8,28]. Later, Wang and coworkers proposed a poly(-dimethylsiloxane) (PDMS)-assisted crystallization method to produce C₆₀ arrays as organic field-effect transistors. However, the preparation and detachment of PDMS slab seems to be a major hindrance for the real applications [29]. Meanwhile, fullerene

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whiskers (FWs) prepared from the liquid-liquid interfacial precipitation method were further constructed into ordered FWs through a Langmuir–Blodgett approach, but this methodology inevitably leads to a stacking of FWs which would be difficult for further semiconductor device fabrications [30]. In this regard, a new facile and efficient technique for the large-scale synthesis of continuous fullerene single crystalline arrays of high quality is urgently desirable and necessary.

In this manuscript, we proposed a simple dip-coating method to produce large-scale and well-aligned C₆₀ single-crystal arrays. Systematic studies reveal the great feasibility and versatility of our approach for the preparation of aligned C₆₀ ribbons, which can be easily modulated by changing the experimental parameters such as concentration, lifting speed and temperature. Finally, a two-terminal device using the C₆₀ array as working element was employed to determine its photoelectric performance, which demonstrates excellent photoresponsivity to UV incident light with an on/off ratio of 365 and detectivity of about 7.08×10^8 Jones at 400 nm, as well as high stability and fast response speed. These results prove that our fabrication approach is a powerful strategy to prepare fullerene single crystalline arrays for large-area photoelectronics applications.

2. Methods

2.1. Materials and sample preparation

C₆₀ crystalline arrays were grown in situ on substrates for photodetector devices fabrication. The substrates were heavily-doped Si wafers covered with a 300 nm-thick SiO₂ dielectric layer. For the assembly of the C₆₀ crystal array, the substrate was first dipped vertically into a C₆₀ solution (solvent: CS₂, concentration: 2 mg/mL or 4 mg/mL) at a constant speed of 6 mm/min, and then it was lifted out at a constant speed of 0.10 mm/min, 0.25 mm/min, 0.5 mm/min, 0.75 mm/min or 1.00 mm/min, respectively. All experiments were carried out at 20 °C or 25 °C.

2.2. Fabrication and characterization of two-terminal devices

The two-terminal devices based on C₆₀ crystalline arrays were fabricated via an electron beam lithography process (ELPHY Plus, Raith GmbH), and two electrodes together with their bonding pads were gained. Finally, Cr/Au (10 nm/50 nm) electrodes were deposited over the sample after a lift-off process via thermal evaporation (Nexdap, Angstrom Engineering). The photoelectric properties were measured on a probe station (CRX-6.5K, Lake-shore) connected with a semiconductor characterization system (Keithley 4200-SCS and 2400). For the photodetection measurements, we used a laser-driven light source (LDLS, EQ-1500, Energetiq) to provide an incident light whose intensity was calibrated by a silicon photodiode. Simultaneously, the time response property was reflected by a current meter against cyclic light stimulations.

2.3. Morphology and structure characterizations

Optical images were obtained from an Olympus optical microscope equipped with a CCD detector under bright field mode (BX51, OLMPUS). AFM images were collected using an atomic force microscope (Shimadzu, SPM9700). The crystalline structure and morphology were examined by TEM (FEI Tecnai F30, 300 kV). The thicknesses of the as-prepared arrays were measured on a Bruker, DektakXT profilometer.

3. Results and discussion

Dip-coating technique was applied to prepare C₆₀ arrays, where C₆₀ solution dissolved in CS₂ was used. In our initial attempt, the silicon substrate (2×2 cm²) covered with a SiO₂ layer was dipped vertically into the C₆₀/CS₂ solution (2 mg/mL) at a constant speed of 6 mm/min, then it was lifted out with a speed of 0.25 mm/min at a 20 °C (Fig. 1a). The as-obtained C₆₀ crystalline array is designated as CCA. The morphology and crystalline structure of CCA were characterized by optical microscopy (OM), atomic force microscopy (AFM) and transmission electron microscopy (TEM). OM images (Fig. 1b) clearly show the assembly of continuous stripes along the upward lift direction during the dip-coating process. The mean width of a single stripe is 10.20 μm, with the uniform coverage of the C₆₀ stripes extending to a millimeter range (Fig. S1-a4 shows the as-obtained C₆₀ stripes over large area). Fig. 3 shows the details to understand the growth mechanism for C₆₀ arrays. The fingering instability at the air-solution-substrate line, which has been proposed in previous works [31,32], gives rise to the regularity in initial nucleation sites of the dip-coated C₆₀ molecules (Figs. 1a and 3a), resulting in periodically segregated, continuous stripes as dip-coating proceeds. In addition, AFM image (Fig. 1c) evidently presents a relatively smooth surface of the as-obtained C₆₀ ribbons, with an average height of 264.0 nm. Moreover, Fig. 1d–f displays the TEM, HRTEM images and SAED pattern of an individual nanoribbon. The continuous lattice fringes in HRTEM image and the SAED pattern together reveal the single crystalline nature of the as-obtained C₆₀ nanoribbon. The lattice fringes in Fig. 1e are measured to be 8.62 Å and 8.24 Å, consistent with the *d*(110) and *d*(002) of a hcp structure (*a* = 10.02 Å, *c* = 16.38 Å), respectively [33], which are also in good agreement with the SAED pattern (Fig. 1f). Accordingly, millimeter-sized C₆₀ single-crystal arrays can be readily achieved through our one-step dip-coating method.

Crystallization of organic materials during dip-coating is an evaporation-induced process that occurs at the contact line, which is strongly affected by the moving of the contact line, the evaporation rate and the supplied solute [34]. Thus, we further conducted the dip-coating experiments by varying pulling speeds (*v*), temperatures (*Tem*) and concentrations (*c*), which significantly influence the morphology, surface coverage (Fig. 2 and Fig. S1, Fig. S1 represents the large-area morphologies of the as-obtained arrays) and out-of-plane thickness (Fig. S2) of the as-prepared C₆₀ microstripes. Accordingly, we can draw a schematic graph displaying the mechanism for the formation of the C₆₀ arrays, as shown in Fig. 3. It is clearly shown that uniform C₆₀ ribbons over large areas with different morphologies can be obtained under variable experimental conditions. First, the substrate pulling speed exerts great influence on the crystallization and growth of C₆₀ molecules, where a decrement in pulling speed results in drastically increments in surface coverage and out-of-plane thickness. To be specific, a slower pulling speed leads to a thicker meniscus and also a lower contact line above the solution surface (Fig. 3c), and thus more C₆₀ molecules accumulate at the contact line, resulting in stripes with higher coverage and also out-of-plane thickness. Additionally, it is obvious that the pulling speed (*v*) significantly affects the morphology of as-obtained C₆₀ array [35]. Particularly, the C₆₀ molecules stack together to form continuous microstripes along the upward lift direction at fast speeds of *v* ≥ 0.25 mm/min (*Tem* = 20 °C) or *v* ≥ 0.75 mm/min (*Tem* = 25 °C) (Fig. 3b). However, when the pulling speed is slower than the critical value of 0.25 mm/min (*Tem* = 20 °C) or 0.75 mm/min (*Tem* = 25 °C), the C₆₀ molecules tend to crystallize into discontinuous stripes (Fig. 3c). Here, the discontinuity is mainly induced by the low boiling point (≈ 46 °C) and the associated high evaporation rate of CS₂, which causes the decline speed of the mother solution exceeding the substrate lifting

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