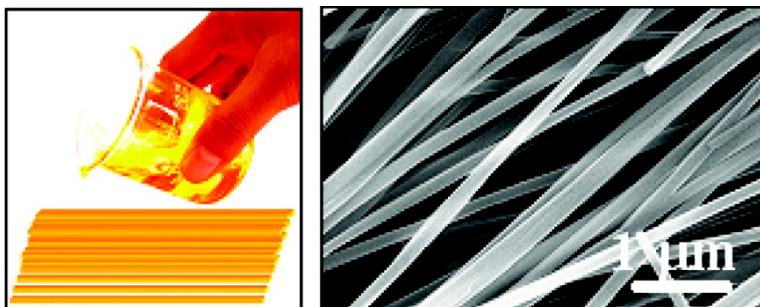Article

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Single-Crystalline, Size, and Orientation Controllable Nanowires and Ultralong Microwires of Organic Semiconductor with Strong Photoswitching Property

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Abstract: Single-crystalline, precise size-controlled nanowires and ultralong microwires with lengths reaching several millimeters of organic semiconductor **1** were prepared in large scale by cast assembly. The size and density of the nanowires and microwires could be controlled by simply adjusting the concentration of **1** in casting solutions. More importantly, the formation of these nanowires and microwires showed no substrate and solvent dependence and was orientation controllable. Highly reproducible and sensitive photo response characteristics were observed in these nanowires and microwires. Fast and reversible photo-switchers based on multiple or individual single-crystal microwires were fabricated via "multi times gold wire mask moving" technique with switch ratio over 100.

Introduction

Nanowires and nanorods can act as both active devices and interconnects and have attracted particular attention recently in nanoelectronics.[1] It is especially true for single-crystalline nanowires and nanorods of semiconductors that combine the merits of single crystal (no defect and revealing the intrinsic property of material) and the applications of semiconductors into nanostructures. To date, many studies based on carbon nanotubes[2] and nanowires and nanorods of inorganic semiconductors have been reported.[3] Compared with inorganic semiconductors, organic semiconductors offer great chemical structure variety and property tunability and are promising candidates for molecular electronics. However, there has been little in the literature about nanowires and nanorods of organic semiconduc-

tors,[4] especially for single-crystalline ones, because of the weak intermolecular interactions between organic semiconductors, complexities of the self-assembly process, and difficulties to control organic molecular packing.

In addition to the syntheses difficulty of organic semiconductor nanowires and nanorods, there are other challenges in organic semiconductor nanowires and nanorods: one is to synthesize large quantity and large-scale nanowires and nanorods easily and repeatedly at low cost. Second is to control the size and orientation of these organic semiconductor nanwires and nanorods. To synthesize nanowires and nanorods across multiple length scales (from nanometer to micrometer) and to control the orientation of these nano-objects not only have great scientific fundamentality but also are the crucial step for their applications.[5] Usually small molecules self-assemble to ordered structure from solution in nanoscale while in micrometer they exhibit disordered structure. Additionally, on the micrometer scale these nano-objects normally adopt random position and orientation. Although indirect, slow, and multistep patterning approaches have been proposed, they have lots of disadvantages,
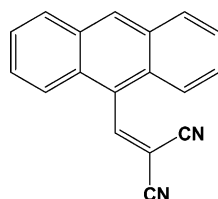
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Scheme 1. Chemical Structure of Organic Semiconductor **1**

Figure 1. Morphology of cast products of organic semiconductor **1** on glass substrate. (a−d) SEM images of cast products: (a) nanowires, (b) microwires, (c) ultralong microwires, and (d) nanowires in large area. (e) Optical image of microwires in large area.

Figure 2. (a) TEM image and (b) SAED pattern of individual nanowire.

such as involving surface-invasive steps and chemically limiting procedure and not being easily applicable on different scales.[6] The third great challenge is the application of organic semiconductor nanowires and nanorods: device fabrication. Usually, organic nanowires and nanorods are prepared through solution-based self-assembly (e.g., solution deposition), template-based methods, and vacuum sublimation.[4] By using these methods, we need to move the nanostructures to substrate for device fabrication. Currently, several methods have been developed to transfer nanostructures to substrates, namely mechanical transfer[7] and microfluidic,[1d,8] Langmuir−Blodgett,[9] and stamp techniques.[10]

Cast assembly is a method that can synthesize self-assembled nanostructures by casting a solution onto the substrate. It is low cost and can prepare nanostructures in large quantity and large area easily. More importantly, through cast assembly nanostructures can adhere to the substrate directly and further be fabricated to device in situ, which provides great advantage in device fabrication. Herein, we reported the synthesis of single-crystalline nanowires and ultralong microwires of organic semiconductor in large scale through cast assembly. The size and orientation of these wires were easily controlled by changing experimental conditions. Moreover, these nanostructures adhered to the substrate tightly and were fabricated to devices in situ. The two-end devices based on single or multiple microwires suggested these nanostructures had strong photo response and could be used as a photoswitcher.

Results and Discussion

Organic semiconductor 2-anthracen-9-ylmethylene malononitrile (**1**; Scheme 1) was synthesized by reacting 9-anthraldehyde with malononitrile in the presence of piperidine in medium yield.[11] When a solution of **1** in methylene chloride was cast on substrates, nanowires and microwires were obtained. Figure 1 shows the morphologies of nanowires (Figure 1a) and microwires (Figure 1b) cast on glass substrate. The width and height of nanowires are usually ∼50−100 nm and ∼50−80 nm (Supporting Information), respectively, while the diameter of microwires changes from hundreds of nanometers to several micrometers and the length reaches several millimeters (Figure 1c). Because the products are obtained by cast assembly, they
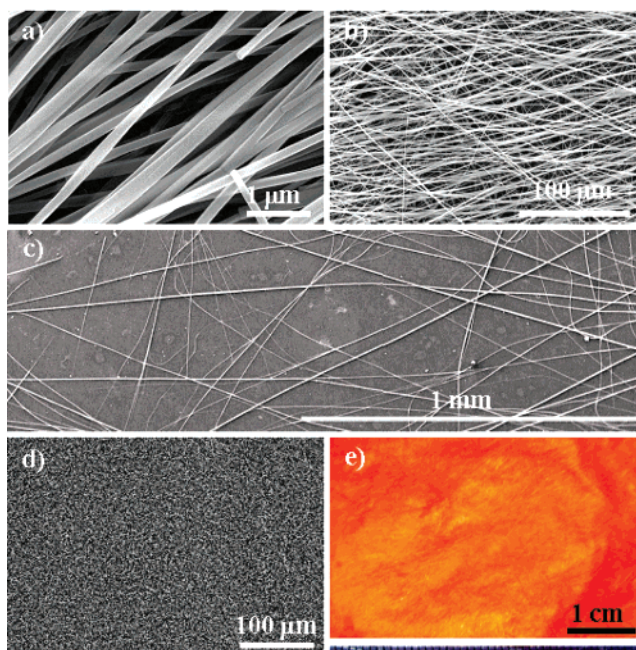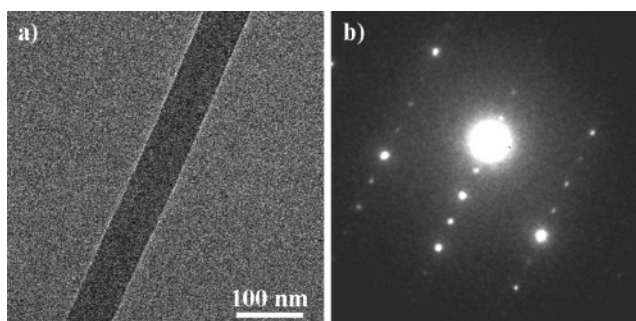
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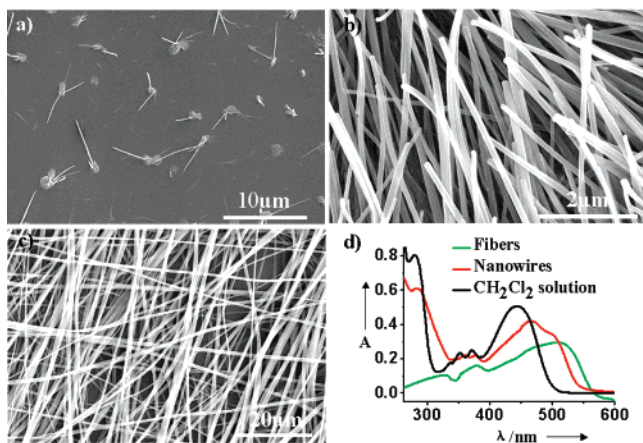
are easily synthesized in a large area as shown in Figure 1d,e. Transmission electron microscopy (TEM) image of individual nanowires and microwires and its corresponding selected area electron diffraction (SAED) patterns indicate that the whole nanowires and microwires are single crystals (Figure 2).

Experimental results showed that the size and density of nanowires and microwires of compound **1** could be controlled through simply adjusting the concentration of **1** in casting solutions (Figure 3). When **1** was at low initial concentration (0.007 M in methylene chloride), dispersed nanowires were obtained, and the diameter of these nanowires was close to 50 nm (Figure 3a). With increasing initial concentration (0.07 M), dense nanowires with well-defined shapes and diameter (∼80 nm) were formed (Figure 3b and Supporting Information). With further increasing initial concentration (close to saturation, ∼0.1 M), ultralong microwires with diameters changing from hundreds of nanometers to several micrometers and lengths reaching several millimeter were synthesized (Figure 3c). UV−vis spectra of these nanowires and microwires showed that the absorption of **1** was red shifted with increasing size (Figure 3d), which is definitely a direct proof of size effects.[12] This phenomena can be explained according to Kubo theory,[13] $\Delta E = (4E_F)/(3N) \propto$

Figure 3. (a−c) SEM images of cast products of compound **1** prepared at different concentrations from CH_2Cl_2 solution. (a) 0.007, (b) 0.035−0.07, and (c) 0.1 mol/L. (d) UV−vis spectra of **1** in CH_2Cl_2 solution (5×10^{-5} M), nanowires and microwires on quartz substrates.
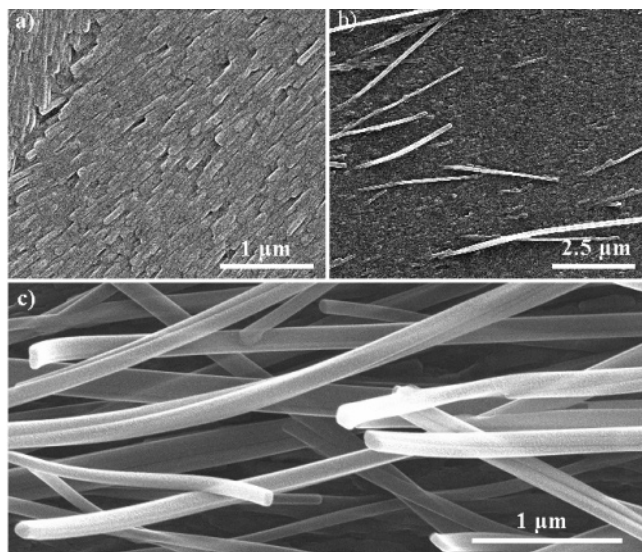

Figure 4. SEM images of the time-dependent growth process of the cast nanowires of compound **1**.

$1/d^3$, where ΔE is the energy gap of particles, E_F is the Fermi energy, N is the molecule number of the particle included, and d is the diameter of the nanostructures. With the particle size reducing, $N_\downarrow$, $\Delta E^\uparrow$, it results in a widened energy gap, which leads to the blue shift of the absorption spectrum.

The formation of nanowires and microwires of **1** might take place via a crystallization process[14−16] including nucleation and growth. First, solute molecules exist as monomer in the dilute solution. Then, with solvent evaporating, solution concentration reaches supersaturation and molecules begin to nucleate on the substrate. All nuclei clearly tend to stack in one direction as the embryonic form of nanowires (Figure 4a) and finally evolve
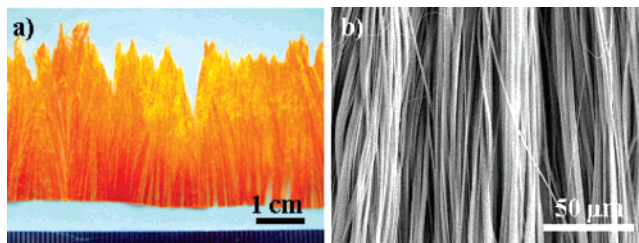
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Figure 5. (a) SEM image and (b) optical image of highly ordered microwires formed by slow solvent evaporation.

into nice nanowires and microwires with further solvent evaporation (Figure 4b,c). According to the above formation mechanism of nanowires, the concentration dependence of the morphology of **1** is well understood. Since the self-assembly of different concentration solutions is in the same environment, if we ignore the effect of concentration to the evaporating rate of solvent, we can assume the evaporating rates of the solutions (with different concentrations) are same. Thus, when different concentrations of solutions (30 μL) were drop cast to the substrates, higher initial concentration solution reaches supersaturation (at which the nuclei was begun) faster than the lower one. Hence, these nuclei have a longer time to grow, and this leads to the formation of microwires (Figure 3c and Supporting Information). To further confirm this assumption, we monitored the in situ growth process of microwires in solution by optical microscope (Supporting Information). From the growth process, we can see that, unlike the normal solution-based self-assembly in which the self-assembly is begun in solution and nano-objects are deposited on substrate, the nucleation first occurs on the side of the substrate and with the solvent evaporating microwires grow up directly from the nucleation on the substrate.

As we know, for a self-assembly system, the formation of the product is usually affected by substrates and solvents (low qualified and even no nanostructures will be formed while changing the substrates or solvents), which limit the application of the materials.[17,18] Fortunately, the formation of nanowires and microwires of compound **1** exhibited no significant difference on different substrates (glass, Si, Si/Cu (evaporated Cu film on silicon), Au). When we changed the solvents of the casting solution (hexane, toluene, methylenechloride, THF; from no polarity to high polarity), nanowires and microwires were also obtained. The excellent nanowires and microwires obtained on all kinds of substrates and solvents definitely confirmed the substrates' and solvents' independent ability of the nanowires and microwires and the greatest self-assembling property of organic semiconductor **1**.

Considering the formation mechanism of nanowires and microwires, the merits of cast assembly and the unique self-assembly property of organic semiconductor **1**, we tried to control the orientation of these nanowires and microwires. When a solution of **1** (1:2, CH_2Cl_2/petroleum ether) was added to a beaker that was covered by a perforated polyethylene sheet (the roles of polyethylene sheet are (1) to prevent the dust in air to pollute the solution and (2) to slow the evaporation rate of solvent), highly ordered microwires were obtained on the wall of the beaker with solvent evaporating (Figure 5a,b). The formation process is that nucleation first occurs at the air/

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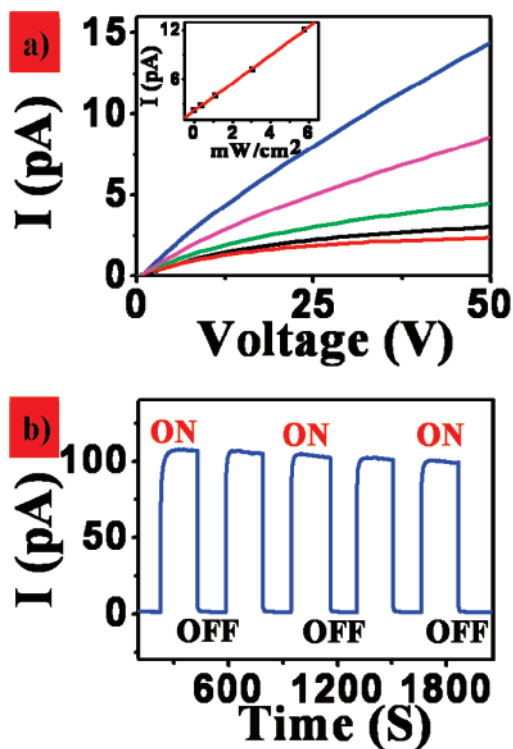(18) Tang, J.; Ge, G. L.; Brus, L. E. *J. Phys. Chem. B* **2002**, *106*, 5653−5658.

Figure 6. (a) Current−voltage characteristics of the two-end devices based on the ordered multimicrowires under illumination (the gap of the devices is 20 μm). The powers of the illumination (from bottom to top) are dark, 0.37, 1.12, 3.04, 5.76 mW/cm^2. (Inset) Linear characteristics between photo current and the power of illumination at bias 40 V. (b) Photoswitching (white light, 5.0 mW/cm^2, at bias voltage 50 V) characteristics of the two-end devices.

solution/glass wall interface since the density of solution surface is higher than that in interior solution and the glass wall provides a lower surface energy. Then microwires grow down along the glass wall with solvent evaporation. Furthermore, if we cast a solution of **1** on tilted substrates, highly ordered microwires could also be prepared. It is well known that controlling the growth orientation of nanostructures is a very important issue in nanoscience. The highly ordered microwires formed by **1** further proved the unique property of **1** in self-assembly and the great advantage of these wires in device fabrication.

As an example of potential applications for these nanowires and microwires, two-end devices were fabricated by depositing Au gap electrodes on the microwires through "multi times gold wire mask moving" technique[7] (including individual microwire; Supporting Information). It is interesting that all the single-crystalline devices exhibited high sensitivity to light. Figure 6a shows the typical current−voltage (*I*−*V*) characteristics of the single-crystalline devices in the dark and under white light illumination. It is obvious that the current of the devices increases significantly with increasing light intensity. Moreover, the current of the device increased linearly with increasing illumination power (inset of Figure 6a, at bias 40 V), indicating the extremely high sensitivity of the devices to light. We know the conductivity of the semiconductor is determined by the free carriers in conduction band ($\sigma = nq\mu$, where σ is conductivity, n is the number of free carriers, q is the charge of electrons, and μ is mobility). The energy gap of the microwires is about 2.3 eV estimated from its absorption spectra (Figure 3d). This gap is narrow enough to permit the generation of substantial numbers of charge carriers by white light. Hence, the high

sensitivity of our single-crystalline devices to light is understandable. On the basis of the high photosensitivity of the microwires, single-crystalline photoswitchers of single or multiple microwires were fabricated (Figure 6b). With the photo irradiation on/off the devices could work between low and high impedance states fast and reversibly with switching ratio over 100.

Experimental Section

Compound **1** was synthesized as follows: A solution of 0.393 g (1.9 mmol) of 9-anthraldehyde in 50 mL of CH$_3$CN was added to 0.372 g (5.6 mmol) of malononitrile and a drop of piperidine. The mixture was heated to reflux for 0.5 h. After cooling, the solvent was evaporated. The residue was purified by column chromatography on silica gel by eluting with CH$_2$Cl$_2$, affording 0.3 g of compound **1**. Yield: 62%. MS (EI) *m/z*, 254. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.94 (s, 1H), 8.66 (s, 4H), 8.09 (d, 2H), 7.94 (d, 2H), 7.70−7.54 (m, 4H).

The substrates used here were successively cleaned with pure water, hot acetone, hot ammonia/hydrogen peroxide solution (ammonia/hydrogen peroxide/water = 1:1:5), pure water, pure ethanol, and finally with argon plasma treated for 15 s. After that, 30 μL of solution at different concentrations such as 0.007, 0.07, and 0.1 M was prepared, and these solutions were cast on 1 cm × 1 cm substrates (solvent could be dichloromethane, THF, toluene, acetonitrile, *n*-hexane, etc.) for nanowires and microwires. The products were characterized by XRD (D/max2500), AFM (a Nanoscopy IIIa), SEM (Hitachi S-4300 SE), and TEM (JEOL 2010).

Two-end devices were fabricated as follows: A solution of **1** was cast assembled on a titled Si/SiO$_2$ substrate, and ordered microwires were obtained. Then Au electrodes were thermally evaporated by laying a micrometer-sized Au wire on the microwires as the mask to obtain a gap between two electrodes. Five-nanometer Ti was deposited under the Au pad electrodes to increase the adhesion between the Au electrodes and the SiO$_2$ insulator. After the first deposition of electrodes, the Au wire mask was moved slightly so that a portion of the gap area could be exposed to Au vapor again. Subsequently, Au electrodes were deposited for the second time, third time, and so forth, until the electrodes were linked by microwires. Photo response characteristics of the devices were recorded with a Keithley 4200 SCS and a Micromanipulator 6150 probe station in a clean and metallic shielded box at room temperature in air.

Conclusions

In summary, nanowires and microwires of organic semiconductor **1** were prepared by cast assembly. Because of the merits of cast assembly, these nanowires and microwires could be synthesized in large quantity and large scale at low cost. TEM images of individual nanowires and microwires and their corresponding SAED patterns indicated that the whole nanowires and microwires are single crystals. Precise size-controlled nanowires and ultralong microwires with lengths reaching several millimeters were obtained by carefully adjusting the concentrations of **1** in cast solutions. Control experiments and growth process of microwires in solution monitored in situ by optical microscope suggest the formation mechanism of nanowires and microwires is crystallization process. Moreover, the formation of nanowires and microwires showed no substrate and solvent dependence and was orientation controllable. Highly reproducible and sensitive photo response characteristics were observed in these nanowires and microwires. Fast and reversible photoswitchers based on multiple or individual microwires are fabricated via "multi times gold wire mask moving" technique with switch ratio over 100.

Supporting Information Available: Crystal structure of compound **1** and its CIF file, AFM images of nanowires, SEM images of nanowires and microwires cast from different solvents, SEM images of nanowires and microwires cast on different substrates, powder XRD of microwires, device structures for photoswitcher, current−voltage characteristics of bared Au electrodes with and without illumination, and formation process of microwires monitored by optical microscopy (this file is a flash, it can be opened by Internet Explorer). This material is available free of charge via the Internet at http://pubs.acs.org.

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