

Self-Assembly and Hierarchical Patterning of Aligned Organic Nanowire Arrays by Solvent Evaporation on Substrates with Patterned Wettability

Rong-Rong Bao,[†] Cheng-Yi Zhang,[†] Xiu-Juan Zhang,[‡] Xue-Mei Ou,[†] Chun-Sing Lee,[§] Jian-Sheng Jie,[‡] and Xiao-Hong Zhang^{*,†}

[†]Nano-organic Photoelectronic Laboratory and Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

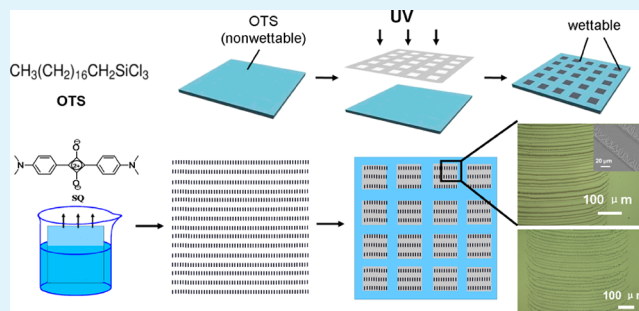
[‡]Functional Nano and Soft Materials Laboratory (FUNSOM) and Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Soochow University, Suzhou 215123, China

[§]Center of Super-Diamond and Advanced Film (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, P.R. China

Supporting Information

ABSTRACT: The controlled growth and alignment of one-dimensional organic nanostructures at well-defined locations considerably hinders the integration of nanostructures for electronic and optoelectronic applications. Here, we demonstrate a simple process to achieve the growth, alignment, and hierarchical patterning of organic nanowires on substrates with controlled patterns of surface wettability. The first-level pattern is confined by the substrate patterns of wettability. Organic nanostructures are preferentially grown on solvent wettable regions. The second-level pattern is the patterning of aligned organic nanowires deposited by controlling the shape and movement of the solution contact lines during evaporation on the wettable regions. This process is controlled by the cover-hat-controlled method or vertical evaporation method. Therefore, various new patterns of organic nanostructures can be obtained by combing these two levels of patterns. This simple method proves to be a general approach that can be applied to other organic nanostructure systems. Using the as-prepared patterned nanowire arrays, an optoelectronic device (photodetector) is easily fabricated. Hence, the proposed simple, large-scale, low-cost method of preparing patterns of highly ordered organic nanostructures has high potential applications in various electronic and optoelectronic devices.

KEYWORDS: nanodevice, organic semiconductor, nanopattern, surface wettability, optoelectronic, controlled growth



INTRODUCTION

One-dimensional nanostructures such as nanorods, nanowires (NWs), and nanotubes (NTs) are drawing tremendous attention because of their wide applications in photonics, electronics, sensing, bioscience, and energy science.^{1–10} A key requirement for these applications is the cost-effective growth of aligned NW and NT elements, as well as effective large-scale assembly with controlled orientations and at designed locations on substrates.^{11–14} For inorganic NWs to achieve these conditions, several steps are often required.^{15–19} First, inorganic NWs are first prepared by chemical vapor deposition or any other method. Then, the preprepared NWs are assembled into aligned NWs by various integrating techniques, such as electrical-field-directed assembly, the Langmuir–Blodgett technique, and directed fluidic assembly. Finally, contact-printing or other techniques are used to transfer the aligned NWs to the chosen locations on the desired substrates

or substrates with patterned wettability.^{20–23} Among these approaches, the simple evaporation of a solvent from suspensions of nanostructures on surfaces with patterned wettability shows high potential for assembling nanostructures into ordered arrays.^{24–27} The NWs are transported to the wetting regions and self-aligned by solvent wetting and dewetting processes on surfaces with patterned wettability.

For organic semiconductor materials, only a few studies have focused on the growth of patterned and aligned NWs despite the increasing need for high-performance optoelectronic devices based on organic nanostructures.^{28,29} Recently, arrays of aligned organic single crystals by solvent evaporation have been prepared and shown to have enhanced charge carrier

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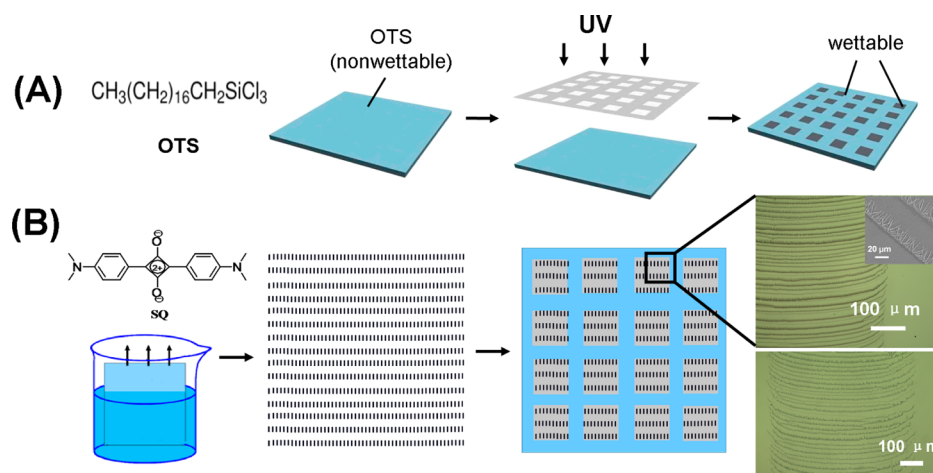


Figure 1. Schematic of the fabrication of the first-level pattern. First, the substrates with patterned wettability were modified, and a one-step solvent evaporation process was performed for the organic aligned NW arrays. The patterning of the OTS-functionalized-SiO₂ surface was performed by UV irradiation in the presence of O₂. The NWs were selectively grown on the wettable (UV exposed) region, and few NWs were found on the nonwetable region.

mobility.^{30–33} Our group has showed that periodically patterned and aligned organic NW can be synthesized by an easy one-step solvent evaporation method, such as vertical evaporation method or cover-hat-controlled method.^{34–36} We also showed that the periodic intervals between the NW arrays, NW orientation, and patterning geometry can be controlled by the solvent concentration, surface tension of the substrate, and geometry of the evaporation surface. However, the growth locations are less selective and controllable.

Here, we apply the approach of a substrate's wettability patterning to control the growth location of organic NWs and obtain the hierarchical patterning of aligned organic NW arrays. To produce a substrate with patterned wettability, we modified a clean substrate by octadecyltrichlorosilane (OTS) followed by ultraviolet (UV) irradiation through a shadow mask. Upon UV exposure, wettability of the OTS surface was considerably enhanced. The organic nanostructures were then preferentially grown on regions of high wettability. This is the first level of patterning. On top of this level of patterning by wettability, the patterning of aligned organic NWs were deposited by controlling the shape and movement of solution contact lines during evaporation on the wettable regions, which was controlled by the vertical evaporation method or cover-hat-controlled method. This pattern was of the second level. Given that these two-level patterns can be easily tunable, various new patterns of organic nanostructures can be achieved by combing these two-level patterns. The proposed approach is an easy, simple, and less-cost method for preparing hierarchically patterned organic NW arrays over a wide variety of substrates. Hence, the approach can have high potential applications in photonics, electronics, optoelectronics, microfluidic devices, nanotechnology, and biotechnology.

EXPERIMENTAL SECTION

Substrate Pre patterning. SiO₂ surfaces were modified with well-established siloxane-based condensation chemistry using octadecyltrichlorosilane (OTS). A ~0.5 vol % OTS solution in hexane was first prepared. Si/SiO₂ substrates were then treated in the solution for 3 h, followed by sequential cleaning with acetone, ethanol, and deionized water. The substrates were then dried in an oven to obtain a hydrophobic monolayer on the SiO₂ surface.

We used a deuterium lamp (L2D2 Lamp, L6309, Hamamatsu) with an emission wavelength of 185–400 nm to irradiate the OTS monolayer through a shadow mask to pattern the substrate wettability. During irradiation, the chamber was maintained at 10⁵ Pa ambient air, corresponding to ~2 × 10⁴ and 0.6 Pa oxygen partial pressure.

NW Synthesis and Patterning. The substrates used were sequentially cleaned with deionized water, ethanol, and CH₂Cl₂. 2,4-Bis[4-(N,N-dimethylamino)phenyl]squaraine (SQ) was synthesized in-house and then characterized by IR, EI-MS, and NMR spectroscopy elemental analysis. Bis(dimethylglyoximate)-nickel [Ni(DMG)₂] was also synthesized in-house and characterized by IR and EIMS. C₆₀ (>99.5% purity) and OTS (>95% purity) were purchased from Sigma-Aldrich and used without further purification. In a typical experiment, a solution of SQ in a mixed solvent of CH₂Cl₂ was prepared. The SQ concentration is 0.05 mM. In vertical evaporation method, a piece of substrate was immersed vertically into a SQ/CH₂Cl₂ solution in a cylindrical container at room temperature. After the solvent had evaporated completely, many parallel stripes or lines were deposited, extending over the entire substrate. In the cover-hat-controlled method, the covering hats and substrate were fixed with mounts. The organic solution was then loaded with a syringe into the channel formed between the substrate and covering hat to form a liquid pool. The experiments were performed at room temperature under steady conditions.

Characterization. The solvent evaporation process and cross-polarized images were observed under a microscope (Leica DM 2500M) attached to a digital camera (DH-HV3100FC). The morphologies of the nanostructures were observed using a field-emission scanning electron microscope (Hitachi S-4300), operated at an accelerating voltage of 5 kV. To minimize the sample charging, we deposited a thin layer of Au onto the samples before SEM examination.

RESULTS AND DISCUSSION

First Level Pattern. Si/SiO₂ is one of the most commonly used substrates for electronic devices. A clean silica surface has a very high surface energy and can be wet by numerous common solvents. By contrast, OTS-coated surfaces usually have low surface energies and show little wetting.³⁷ The processes for preparing substrates with patterned wettability and aligned NW arrays are illustrated in Figure 1A. First, a silicon wafer with 300 nm of thermally grown SiO₂ was treated with OTS to form a stable and nonwetable film on the substrate. UV light was then projected onto the OTS-functionalized layer through a shadow mask. The regions

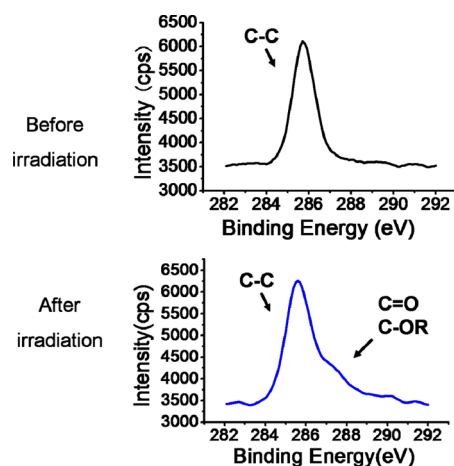


Figure 2. X-ray photoelectron spectra of the C 1s regions of OTS/SiO₂/Si substrate before (top) and after (bottom) 40 min of UV irradiation in air.

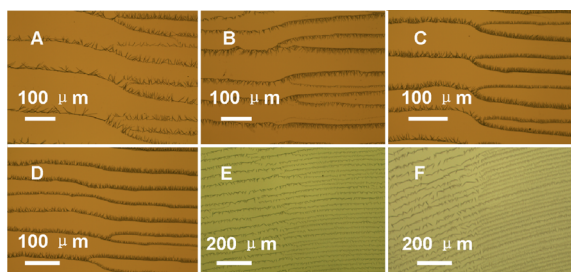


Figure 3. SQ NW arrays grown on the substrate with different contact angles. (A–D) Left parts show different exposure time as 5, 10, 15, and 20 min, and right parts of all of these photo are exposed 40 min. (E, F) 4-(Chloromethyl)phenyltrichlorosilane self-assembly layer was used for the pre patterning.

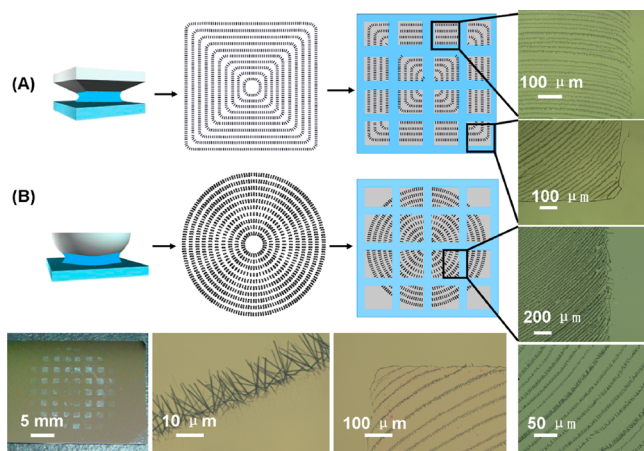


Figure 4. Schematic modulation of the shape and size of the second-level pattern by the cover-hat-controlled method. (A) Pattern growth by square rectangular pyramid. (B) Pattern grown by hemispherical.

exposed to UV light in the presence of O₂ became wettable because of the cleavage of the C–C bonds and formation of –COOH as well as –CHO functional end groups. Then, a one-step solvent evaporation process was performed for the organic aligned NW arrays, shown in Figure 1). SQ was selected because of its various optoelectronic applications.³⁸ In the typical growing experiment, the substrate with patterned

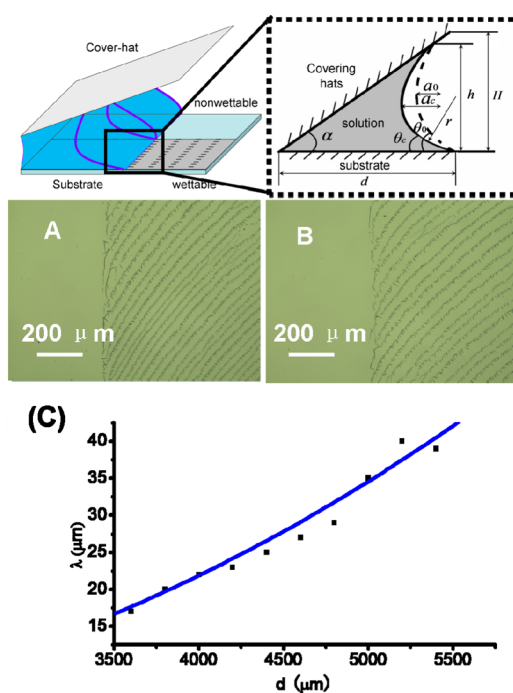


Figure 5. Patterned NW arrays. (A, B) SQ NW arrays grown with lens-shaped covering hats with surface radii R of (A) 25 and (B) 15 mm. During evaporation, the green region was nonwetable, and the large contact angle of substrate unsuitable for NW growth. The gray region was wettable and allowed the periodic growth of aligned NWs by a stick-and-slip process along the contact lines that conformed to the geometry of the covering hat. During the “slip” process, the solvent pool shrank and flowed toward the central hat-substrate contact region. This flow aligned the growth direction of the NWs. Thus, the tips of most of the NWs pointed toward the center of the covering hat, which enabled the location and orientation of the NW pattern in this one-step growth process.

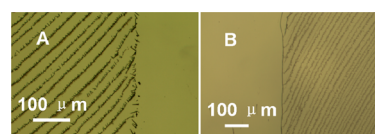


Figure 6. NW arrays of (A) C₆₀ and (B) Ni(DMG)₂ grown by the present method.

wettability was vertically immersed into an SQ/CH₂Cl₂ solution (0.05 mM). Numerous parallel stripes or lines were deposited extending over the entire substrate after the solvent had completely evaporated or by vertically pulling the substrate slowly out of solvent. The NWs were selectively grown on the wettable (UV exposed) region, and few NWs were found on the nonwetable region (Figure 1 and Figure S1 in the Supporting Information). Therefore, organic nanostructures can be grown at designated locations as defined by the pattern of wettability by designing patterns of UV irradiation.

These changes in the surface chemistry were examined by analyzing the carbon and oxygen 1s peaks using X-ray photoelectron spectroscopy (XPS). The typical XPS data of the OTS-functionalized substrate surface before and after UV exposure are shown in Figure 2. For the native OTS-functionalized substrate surface, the peaks at 284.5 eV can be assigned to the C–C/C–H bonds. After 40 min of UV irradiation in air, another peak assigned to O–C=O, C=O,

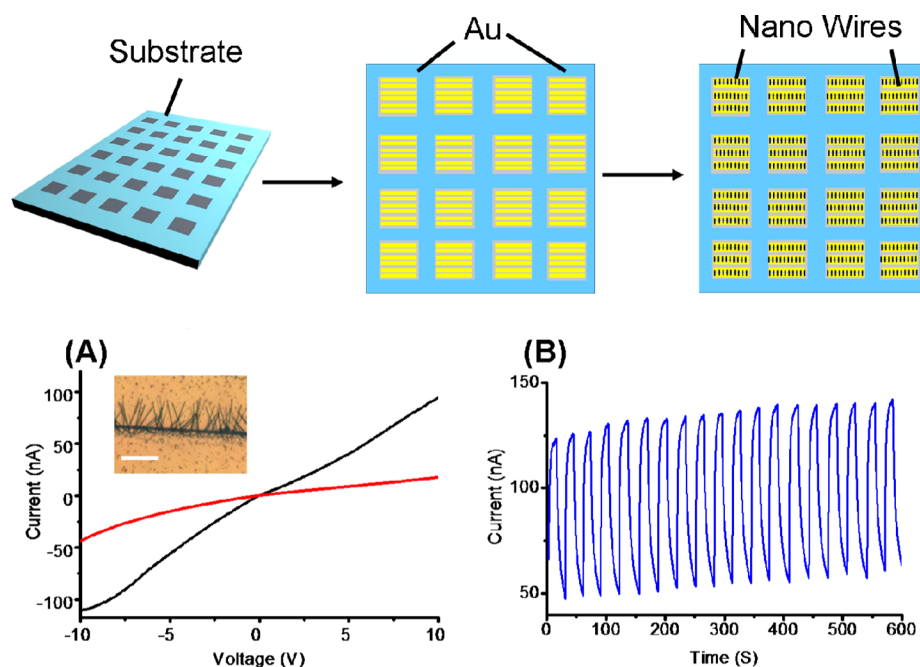


Figure 7. Top: Schematic for the fabrication of nanodevices based on the patterned NW arrays. (A) I – V characteristic of the NW device (inset of A) acquired in the dark (red line) and under white LED light illumination (black line). (B) Photocurrent response of the device with a voltage of 10 V.

and C–OR emerged (Figure 2, bottom).³⁹ These functional groups on the surface increased the surface energy and resulted in low contact angles in the wetting measurements. For example, dichloromethane (CH_2Cl_2) exhibited superior wettability on this surface than on a pristine OTS-functionalized surface. Hence, the NW arrays were grown on the UV-treated OTS regions, but not on the pristine OTS regions, considered as the first-level NW pattern.

The growth of periodically patterned NWs within each wettable region was induced by a stick-and-slip process of the solvent–substrate interface when the solvent pool shrank upon evaporation. During this growth, the nucleation of SQ crystals preferentially occurred along the edge of the solvent pool because these locations provided sites for heterogeneous nucleation. These locations also had the highest SQ supersaturation because of the highest rate of solvent evaporation at the solvent/substrate/air interface. These phenomena led to increased depinning force, which attempted to shrink the solvent–substrate contact area with decreased solvent volume because of evaporation. When the depinning force reached a value higher than the pinning force, the solvent–substrate contact line became unstable and shifted to a new position. This stick-and-slip process was repeated until all solvent had evaporated and left a periodic pattern of NW arrays. Given that the original OTS-functionalized region without UV irradiation was highly nonwettable and had a large contact angle, the stick-and-slip process did not occur and no NW nucleated along the edge of the solvent pool at these locations. Hence, highly aligned SQ NWs arrays were assembled only on the UV-exposed OTS regions. For example, complex NW patterns were grown on the glass substrate with a logo of TIPC (see Figure S2 in the Supporting Information).

By contrast, when the substrate was prepatterned into regions of different wettabilities, NWs can be grown onto both types of regions but with different distance between the adjacent lines (λ_{c-c}) values. To demonstrate this phenomenon, we make the substrate with different UV exposed time. The left

parts of substrates in Figure 3A–D had been exposed 5, 10, 15, and 20 min, respectively, and the right parts of these had all been exposed 40 min. It shown that, λ_{c-c} is larger and the NW density in every line is smaller in 5 min exposed area than in 40 min exposed area. With the increase in the UV-exposed time, both of these characters are tended to 40 min exposed area. It reveals that, after the exposure, the nonwettable region turned into wettable region where the NWs can grow. We also used a 4-(chloromethyl) phenyltrichlorosilane self-assembly layer for the prepatterning. Upon UV exposure, regions with different surface energies were formed. After the growth of NWs, NW arrays with different λ_{c-c} values grew onto regions with different surface energies (Figure 3E, F).

Second Level Pattern. The second level of patterning was achieved when aligned organic NWs were deposited through the contact lines produced during solution evaporation in the solvent wettable regions. The moving of contact lines can be controlled by the vertical evaporation method or cover-hat-controlled method. In vertical evaporation method, the distance between the adjacent lines (λ_{c-c}) can be adjusting by the evaporation rate of the solvent or pulling the substrate in a certain speed.^{34,40,41} However, it still remains an unresolved obstacle that the shapes of periodicity pattern can not be controlled. Cover-hat-controlled method is a facile one-step method for large-scale controllable patterning growth of ordered organic single-crystal nanowires through evaporation-induced self-assembly. The patterning geometry of the nanowire arrays can be tuned by the shape of the covering hats of the confined curve-on-flat geometry easily.

In the cover-hat-controlled method, a covering hat of hemispherical or other conical shapes was placed onto the patterned substrate with its pointed end facing the substrate. A solution of SQ (0.05 mM in CH_2Cl_2) was then loaded into the gaps between the substrate surface and the covering hat. The solvent was then allowed to evaporate gradually at room temperature. Upon complete solvent evaporation, the NWs were found to grow on the wettable regions of the substrate

along the contact lines that conformed to the projected shape of the covering hats. Concentric rings or parallel stripe patterns of aligned SQ NWs with different orientations and curvatures were deposited on the substrates. Thus, the pattern of the NW arrays induced by solvent evaporation can be easily tuned by the geometry of the evaporating solvent. During the evaporation controlled by covering hats, the covering hat confined the evaporation of the solvent along the side edge of the solvent pool and provided a channel for the capillary flow of the solvent. The loss of solvent mainly occurred at the contact line, which initiated NW nucleation along the same line. The shape and size of the contact line was easily fine-tuned by the geometry of the evaporation channel between the covering hats and substrate. Therefore, varied periodic patterns were obtained by controlling the shape of the covering hat. Figure 4 show that different organic NW arrays in the designated location were grown by controlling the shape of the cover hats. Hence, the various hierarchical patterns of organic nanostructures can be achieved by combing these two levels of patterns, which is advantageous for nanodevice fabrication.

During the evaporation controlled by the covering hats in wettable region, the jumping distance between consecutive contact lines mainly depended on the balance of surface tensions, which were dictated by the characteristics of interfaces and geometries of the evaporation channel. λ_{c-c} can be estimated as^{36,42}

$$\begin{aligned}\lambda_{c-c} &= \frac{1}{2} \left\{ h \left[\arctan\left(\frac{2a_c}{h}\right) - \arctan\left(\frac{2a_0}{h}\right) \right] + (a_c - a_0) \right\} \\ &= \frac{1}{2} h \left[\arctan(1 - \theta_c) - \arctan(1 - \theta_0) \right] \\ &\quad + \frac{1}{2} (\theta_0 - \theta_c) \end{aligned}$$

Once the contact angles were fixed, pattern growth was further controlled by the geometry of the covering hats. As shown in panels A and B in Figure 5, λ_{c-c} decreased with increased surface radii of the lens-shaped hats. The geometry of the formed nanowire pattern is well-defined by a surface tension model of the evaporation channel.

The simple one-step method is applicable in a wide range of organic nanostructures and substrates. For example, NW arrays of C₆₀ and an organic complex, bis(dimethylglyoximate)-nickel, were successfully grown and patterned using the same approach (Figures 6). The method was still successfully applied when the silica substrates were replaced by glass substrates (see Figure S2 in the Supporting Information).

When the silicon substrate was replaced by a substrate with prepatterned metal electrodes on the hydrophilic region (Figure 7), the aligned NW arrays were accurately deposited across the electrodes (Figure 7A inset). Here, a NW-based photodetector was fabricated by this one-step method. The as-prepared photodetector had much larger photocurrents than dark currents and photoresponse (Figure 7A, B). These results demonstrated that our method for the one-step growth of nanomaterials on prepatterned substrate was a convenient technique for device fabrication.

CONCLUSIONS

In summary, we demonstrate an easy one-step process for the growth and alignment of organic NWs with hierarchy patterning on solid substrates. On a substrate with patterned

wettability, the organic nanostructures were preferentially grown on solvent wettable regions. The growth of the periodical NW patterns was tuned by the shape and geometry of the contact line during vertical evaporation process or cover-hat-controlled evaporation method. Therefore, the proposed method can be used to obtain various hierarchical patterns based on the two-level pattern. A nanodevice can be easily fabricated based on the patterned NWs. The simplicity, controllability, and generality of the present approach suggested its good potential for the growth and patterning of a wide range of organic nanostructures for various applications.

ASSOCIATED CONTENT

Supporting Information

More photographs of pattern nanowires. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: xhzhang@mail.ipc.ac.cn. Fax: +86-10-82543510.

Notes

The authors declare no competing financial interest.

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