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Mesostructured Assemblies of Ultrathin Superlong Tellurium Nanowires and Their Photoconductivity

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Abstract: Well-defined periodic mesostructures of hydrophilic ultrathin Te nanowires with aspect ratios of at least 10^4 can be produced by the Langmuir−Blodgett technique without any extra hydrophobic pretreatment or functionalization. Packing the arrayed nanowire monolayers will allow construction of nanomesh-like mesostructures or more complex multilayered structures composed of ultrathin nanowires on a planar substrate. The well-organized monolayer of Te nanowires with periodic mesostructures can be readily used as a stamp to transfer such mesostructured nanopatterns to other substrates or can be embedded within a polymer matrix. The mesostructures of ultrathin Te nanowire films show reversibly switched photoelectric properties between the lower- and higher-conductivity states when the light is off and on, and the photocurrent is influenced by the light intensity and the number of mesostructured nanowire monolayer films. This method can be extended for fabrication of other mesostructured assemblies of ultrathin nanowires or nanotubes.

1. Introduction

One-dimensional (1-D) nanostructures,[1] such as nanotubes, nanobelts, nanowires, and especially ultrathin nanowires,[2] have attracted explosive attention in nanoscience owing to their unique structures, interesting physical properties, and potential for novel applications.[3] Some interesting phenomena will emerge after 1-D nanostructures are well assembled, which will open up many fundamental scientific opportunities, thereby further promoting related researches concerning collective magnetic, optical, and electronic properties, as well as their applications.[4]

The Langmuir−Blodgett (LB) technique[5] provides an attractive assembly strategy for its unique utilization in arranging numbers of nanostructures at the air−water interface. Up to now, soft LB technique has been used to prepare hard nanomaterials,[6] in addition to nanoparticles[7] and 2-D nanostructures;[8] recently, 1-D stiff nanostructures such as Ag nanowires,[9] $BaCrO_4$ nanorods,[10] silicon nanowires,[11] ZnSe nanowires,[12] PbS nanowires,[13] VO_2 nanowires,[14] and Ge nanowires[15] have been prepared. To our best knowledge, few studies have addressed the assembly of superlong, ultrathin, and flexible nanowires into periodic mesostructures. Despite a huge amount of experimental and theoretical work on self-assembly of nanomaterials, finding a suitable way for self-assembly of ultrathin, superlong, and flexible nanowires,[2] which easily twist around each other, is still an ongoing challenge in the research field of nanotechnology.

Herein, we report that the ultrathin nanowires with aspect ratios of at least 10^4 can be well aligned over a large area to form well-defined periodic mesostructures and their reversibly switched photoelectric properties. The hydrophilic Te nanowire−surfactant monolayers can be assembled by the Langmuir−Blodgett technique without any extra hydrophobic pretreatment or functionalization after synthesis. Packing the arrayed nanowire monolayers makes it possible to construct nanomesh-like mesostructures or more complex multilayered

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structures composed of ultrathin nanowires on a planar substrate. In addition, such uniform nanowire mesostructured patterns and their nanochannels can be easily transferred onto or embedded within an external substrate or polymer matrix.

2. Experimental Section

Synthesis of Te Nanowires. All chemicals are of analytical grade and used as received without further purification. The synthesis of uniform Te nanowires was described previously.[16] In the typical synthesis, 1.0000 g of poly(vinyl pyrrolidone) (PVP, Shanghai Reagent Company, $M_w \approx 40,000$) and 0.0922 g of Na_2TeO_3 were put into a 50 mL Teflon-lined stainless steel autoclave and dissolved in 33 mL of double distilled water under vigorous magnetic stirring for 5 min to form a homogeneous solution at room temperature. After that, 1.67 mL of hydrazine hydrate (85%, w/w %) and 3.33 mL of aqueous ammonia solution (25−28%, w/w %) were added into the mixed solution separately, under vigorous magnetic stirring for 10 min. The container was closed and maintained at 180 °C for 3 h. After that, the autoclave was cooled to room temperature naturally.

Synthesis of Ag_2Te Nanowires. In a typical synthesis, freshly prepared Te nanowires (0.1 mmol) from the previous experiment were precipitated by adding 21 mL of acetone and centrifuging at 3000 rpm for 5 min. The product obtained was washed by water and ethanol several times and dispersed in 20 mL of ethylene glycol (EG) with vigorous magnetic stirring at room temperature for 20 min. Then, 0.0669 g of $AgNO_3$ (0.4 mmol) was added into the previous solution. The mixed solution was shaken at a rotation rate of 260 rpm in the dark using an Innova 40 benchtop incubator shaker at 60 °C for 13 h.

Synthesis of Pt Nanotubes. The synthesis of uniform Pt nanotubes was described previously by our group.[17] In a typical synthesis, Te nanowires (0.05 mmol) synthesized from the above experiment were washed by water and ethanol several times and dispersed in 20 mL of ethylene glycol (EG) with vigorous magnetic stirring at room temperature for 20 min. Then, 1.29 mL of 77 mM H_2PtCl_6 solution in EG was added into the previous solution. The mixed solution was shaken at a rotation rate of 260 rpm using an Innova 40 Benchtop Incubator Shaker at 60 °C for 13 h.

Assembly of Ultrathin Te Nanowires by Langmuir−Blodgett Technique. The monolayer was prepared at 25 °C using a Langmuir−Blodgett trough (Nima Technology, 312D). The trough was filled with Millipore Milli-Q water (resistivity 18.2 MΩ cm) until it brimmed just over the top by about 2 mm. Five milliliters of the mother liquor of Te nanowires was removed and precipitated by adding about 12 mL of acetone and centrifuging at 3000 rpm for 5 min. One milliliter of *N,N*-dimethylformamide (DMF) was added to disperse the Te nanowires to form a homogeneous solution at room temperature. After that, a mixture of 5 mL of DMF and 5 mL of chloroform were added into the homogeneous solution. Too much DMF will result in the precipitation of the as-prepared Te nanowires at the bottom of the LB trough, which impedes good dispersion of the nanowires on the air−water surface, whereas it will be difficult to obtain a homogeneous solution at the very beginning if the amount of $CHCl_3$ used is too much. In this process, DMF[18] plays a crucial role in assembly of PVP-coated nanostructures, such as Ag_2Te nanowires, Pt nanotubes.

Furthermore, the present strategy can be extended to assemble other ultrathin 1-D nanostructures such as Ag_2Te nanowires, and Pt nanotubes. Te nanowires were dispensed from a 50 μL syringe drop by drop onto the water subphase. Thirty minutes later, the nanowires surface layer was then compressed slowly at 20 mm/min while the surface pressure was monitored with a Wilhelmy plate. The pressure and temperature were kept constant at least 10 h as soon as the fold formation that paralleled the barrier direction occurred (see Supporting Information, Figure S1E) The monolayer of the aligned nanowires was lifted at the pressure of 23 mN/m, and the deposition speed was maintained at 4 mm/min. The same process was repeated, and we can get more than one layer. The trough was cleaned before and after each experiment. The trough surface and barrier were then wiped with ethanol and $CHCl_3$ by tampon for several times, ensuring that there is no dust or contaminants left.

PMMA Imprinting by Te Nanowire Stamp. First, poly(methyl methacrylate) (PMMA, Sigma-Aldrich, $M_w \approx 120,000$) was dissolved in the DMF forming a 3% (w/w) solution. A 500 μL PMMA solution was dropped on the surface of the glass slide and then spin-coating proceeded at rates of 300 rpm for 30 s, and 2500 rpm for 45 s, respectively. After 8 min, the Te nanowire monolayer stamp was put onto the PMMA-coated glass slide and a moderate pressure was applied to it by a small binder clip. The stamp was pulled away from the PMMA-coated glass slide substrate rapidly, once heating was finished at 100 °C in an oven for 1 h and the slides cooled to room temperature naturally. The nanowire film glass slide was vertically separated from the PMMA-coated glass slide rapidly by hands.

Characterization. The Small-angle X-ray diffraction patterns (SAXRD) were measured on a Philips X'Pert Pro Super X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation. High-resolution transmission electron microscope (HRTEM) images were performed on a JEOL-2010 transmission electron microscope operated at an acceleration voltage of 200 kV. The energy-dispersive X-ray spectroscopy (EDS) analysis was also done with a JEOL-2010 TEM with an Oxford windowless Si (Li) detector equipped with a four-pulse processor. Field-emission scanning electron microscopy (FESEM) was carried out with a field-emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photoelectron spectrometer, using Mg Kα radiation as the exciting source. Raman scattering spectra were recorded with a Renishaw System 2000 spectrometer using the 514 nm line of Ar^+ for excitation. An Innova 40 Benchtop Incubator Shaker was used for the chemical transformation reactions. The Te nanostructures were prepared using a Langmuir−Blodgett trough (Nima Technology, 312D). FTIR spectra were measured on a Bruker Vector-22 FT-IR spectrometer from 4000 to 400 cm^{-1} at room temperature. Photoelectric properties of Te nanowire nanodevices were investigated with Micromanipulator 6150 probe station and Keithley 4200 SCS in a clean and metallic shielded box at room temperature in air. A SPA 300HV microscope (Seiko Instruments, Inc.) was used for AFM measurements.

3. Results and Discussion

In the present case, the area of the arrayed nanowires can reach up to approximately 100 squaremicrometers (see Supporting Information, Figure S2). The aligned hydrophilic Te nanowires have a diameter of 4−9 nm and aspect ratio of at least 10^4 without any extra hydrophobic pretreatment or functionalization after synthesis.[16]

First, the nanowires suspended in a mixture solvent made of *N,N*-dimethylformamide (DMF) and $CHCl_3$ were randomly distributed and enwound each other. Second, after the evaporation of mixed solvent, some ordered islands consisted of parallel nanowires are observed randomly oriented at the air/water interface. Due to the action of the interfacial tension, the

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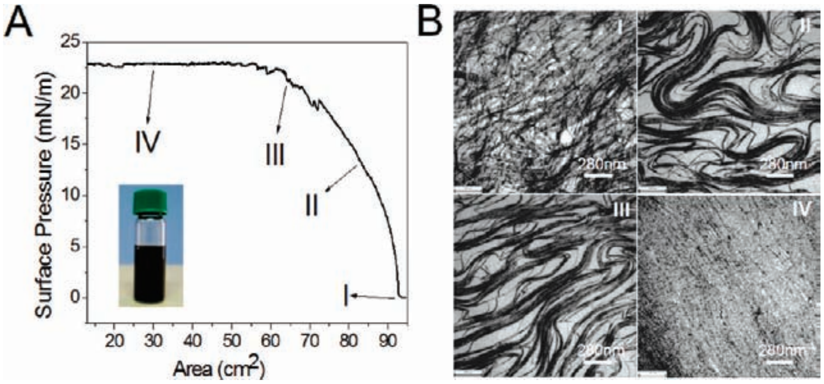

Figure 1. (A) π−A isotherms of the Te nanowire monolayer obtained at the air/water interface at 25 °C. (A, inset) Picture of Te nanowires dispersed in the mixture of $CHCl_3$ and DMF. (B) TEM images of the Te nanowire sample collected at different stages by compression of Te nanowires at 25 °C with surface pressure 0, 8.5, 19.5, and 23 mN/m (and continuously holding at this pressure for 10 h), corresponding to I, II, III, IV, respectively.

interfacial nanowires shrank to form a close-packed structure[19] and became highly arrayed after an increase in the surface pressure that should be adjusted for more than 10 h.

Figure 1A shows the surface pressure versus surface area (π−A) isotherm of the monolayer of Te nanowires. Figure 1B shows its corresponding TEM images of the Te nanowires collected during different stages. At the initial stage (I), the pressure is practically unaffected by the barrier movement. The nanowire units approach each other at small areas because of the capillary force and van der Walls attraction. At the second stage (II), an increase in the surface pressure is observed with a decrease in the trough area, indicating the formation of a condensed Te nanowire monolayer. At the last stage (III), the pressure remained constant when the areas decreased, which was a stage wherein the loosely arranged nanowires became tighter. The pressure rose steeply from 0 mN/m (II) to 23 mN/m (III) with a decreasing slope (Figure 1A). The slope of π−A isotherms directly reflects the change rate of surface pressure and indirectly reflects the behavior among the nanowires. Figure 1B shows the TEM images of a series of samples obtained after adjusting for 10 h at different surface pressures, 0, 8.5, 19.5, and 23 mN/m, respectively. Compressed uniaxially, the nanowires were arrayed with their long axis parallel to the barrier irreversibly. The best arrangement can be achieved after duration for 10 h at the surface pressure of 23 mN/m, and once this value is exceeded, the arrayed monolayer will be essentially broken into some fold that parallels the barrier direction. The corresponding TEM images after fold formation for 1, 3, 5, and 9 h, respectively, are shown in Figure S1 (Supporting Information). With the time prolonging, the ordering of the monolayer increases, which is the result of the decrease in entropy. From the data above, it is necessary to obtain a high-quality Te nanowire monolayer after waiting for at least 10 h. Figure S3 in Supporting Information shows the atomic force microscopic (AFM) topography of the Te nanowire monolayer. The compressed layer can be transferred directly to a variety of substrates (glass, quartz, silicon, polymer surfaces, etc.) by LB deposition to yield large-scale parallel nanowires. Owing to the long and flexible characteristics of Te nanowires, there are crooked and parallel Te nanowire assemblies somewhere on the substrate (see Supporting Information, Figure S4). The building blocks can be confirmed to be Te nanowires on the basis of the analysis of selected areas of the electron diffraction pattern (SAED) (insert in Figure 2B), high-resolution transmission electron microscopy (HRTEM) image (Figure 2C), X-ray photoelectron spectra (XPS), and X-ray spectroscopy (EDS) (Figure 3).

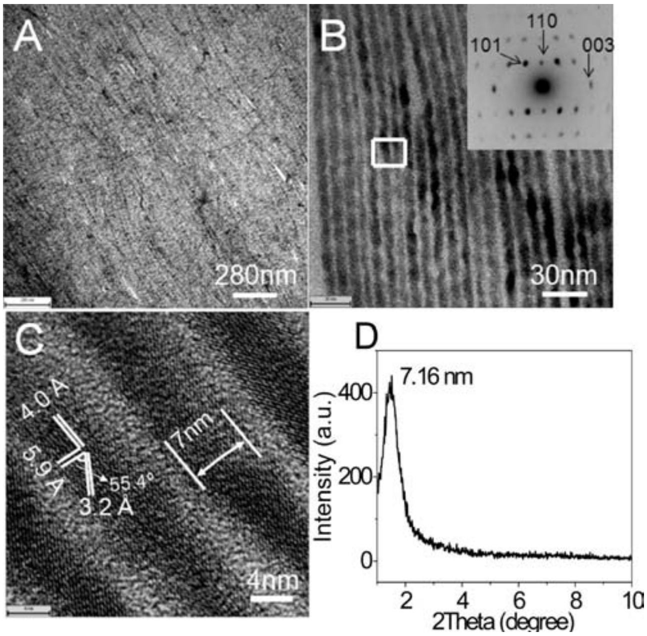

Figure 2. (A, B) Transmission electron microscopy (TEM) images of the monolayer assembly of Te nanowires at different magnification. (B, inset) Corresponding SAED pattern taken of the nanowire arrays. The electron beam was focused along [010] axis; (C) High-resolution transmission electron microscopy (HRTEM) image of the aligned Te nanowires; (D) SAXRD pattern measured on the monolayer of aligned Te nanowires. The 2θ angle of 1.44° corresponds to a d value of 7.16 nm.

TEM images in Figure 2A, B show the as-obtained assembled Te nanowire monolayer at different magnifications. The ultrathin and flexible Te nanowires which are surrounded by polyvinylpyrrolidone (PVP) are 4−9 nm in diameter and up to hundreds of micrometers in length. The inset of (Figure 2B) shows the corresponding SAED pattern of the nanowires, which was obtained by focusing the electron beam along the [010] axis. A HRTEM image in Figure 2C shows lattice spacings of 5.9, 4.0, and 3.2 Å, corresponding to the lattice spacings of the (001), (100), and (101) planes for hexagonal tellurium, respectively. Furthermore, the angle between the planes of (001) and (101) is 55.4°, which matches well with the calculated result according to its crystal structure. Both HRTEM and SAED patterns confirmed that the axis of the nanowire is along [001]

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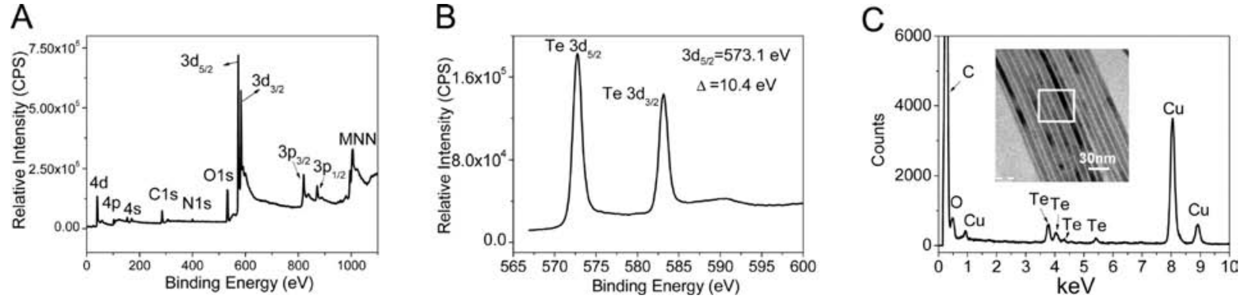

Figure 3. XPS spectra for the well-aligned Te nanowire monolayers prepared freshly. (A) Survey of the sample. Te 4d, 4p, 4s, $3d_{5/2}$, $3d_{3/2}$, $3p_{3/2}$, $3p_{1/2}$, according to the binding energy of 41, 111, 170, 573, 583, 820, 871 eV, respectively. (B) Survey of the Te 3d region. (C) EDS spectrum of the Te nanowires monolayer, confirming that the sample is composed of pure Te (the detected copper and carbon signals arise from the carbon-coated copper grid on which the tellurium samples were deposited).

direction, the nanowire was structurally uniform, and no dislocation was detected in the examined area. As shown in Figure 2C, the nanowires retain the same width after alignment, with an average diameter of 7 nm and a pitch of 10 nm. Figure 2D shows that Te nanowires are transferred from the air/water surface to a glass slide for small-angle X-ray diffraction pattern (SAXRD) measurement. Only one strong reflection peak located at $2\theta = 1.44°$ is detected, corresponding to a d value of 7.16 nm. Referring to the TEM images, the period of the Te nanowire monolayer is 7.16 nm. TEM images give intuitive periodic information, while the electron diffraction displays the indirect periodic information of the structures. Obviously, such a periodicity is varied with the diameters of the Te nanowires. In addition, multilayers of Te nanowires also show small-angle X-ray diffraction (see Supporting Information, Figure S5). From two to fifteen layers, there is no significant variability with increasing the number of layers, indicating the quality of Te nanowire films is still kept well.

Panels A and B of Figure 3 show the XPS spectra of the freshly prepared monolayer of Te nanowires, and the peak values at 284.85 and 532.05 eV can be readily assigned to the binding energies of C1s and O1s, respectively. The Te 3d peak shift displayed two strong peaks at 572.7 and 583.1 eV, corresponding to the binding energy of Te $3d_{5/2}$ and Te $3d_{3/2}$ for elemental tellurium. Energy dispersive spectrum (EDS) was measured on the Te nanowires monolayer (Figure 3C), indicating that the samples are composed of pure Te (the detected copper and carbon signals arise from the carbon-coated copper grid on which the tellurium samples were deposited).

The formation of regular mesh-like mesostructures of the order of several nanometers, the so-called nanomeshes, has recently attracted intensive attention. Commonly, nanomeshes can be obtained with a high temperature and a special substrate surface.[20] To overcome high costs and complex processes, we introduce the LB technique to fabricate two layers of periodic thin film of Te nanowires on a planar substrate which resembles a nanomesh.[12] A schematic illustration of transferring of two layers of aligned nanowires into mesh-like structures with designed crossing angles was illustrated in Figure S6 (Supporting Information). The TEM images in Figure 4 show that the Te nanowires can be tailored into nanomesh-like crossed patterns with a tunable crossed angle. The compressed monolayer in the air/water surface was then transferred directly to a planar substrate to yield a Te nanowire monolayer. After transferring the monolayer, holding 300 s, a crossed structure of two layers can be obtained by turning an angle during deposition (Figure 4). While without turning the angle, it will result in the formation of parallel nanowire layers with the same axial direction (see Supporting Information, Figure S7). Different turning angles can result in the formation of two-layer nanowire nanopatterns with different crossed angles, for example, 45°, 60°, 65°, 70°, 85°, respectively, as shown in Figure 4A−E (see Supporting Information, Figure S8). The fast Fourier transform of the mesostructures shows diffuse streaks corresponding to crossed angles made by two layers of Te nanowires, revealing that the crossed angles between two nanowires layers increase with increasing the turning angle (Figure 4A−E, and see Supporting Information Figure S8).

The present method can be extended to assemble other ultrathin nanowires or nanotubes into mesostructured assemblies as demonstrated by replacing Te nanowires with Ag_2Te nanowires and Pt nanotubes (Figure 5). Panels A and B of Figure 5 show that the Ag_2Te nanowires with a diameter of 10 nm can also be self-assembled into an ordered mesostructured monolayer. Packing a second monolayer of Ag_2Te nanowires onto the first layer perpendicularly will result in the formation of crossed Ag_2Te nanowire film mesostructures (C and D of Figure 5). The phase, composition, and morphology of Ag_2Te nanowires were confirmed by SEM, XRD, XPS, HRTEM, and TEM (see Supporting Information, Figure S9). Further extended experiments demonstrated that this method can be used for alignment of Pt nanotubes also (Figure 5E−H).

Well-ordered two-dimensional functional nanostructure arrays have a broad range of potential applications.[21] Here, we demonstrate a simple pattern-transfer method to convey nanochannels made of Te nanowires to a polymethylmethacrylate (PMMA) substrate. Figure 6A illustrates the process for creating a Te nanowire monolayer stamp in order to fabricate mesostructured nanopatterns. Glass slides were cleaned by ultrasonic wave in acetone for 10 min and rinsed with Milli-Q water. A Te monolayer on a glass slide was used as a stamp for nanocontact printing. A PMMA coated glass slide was obtained by spin-coating. After 8 min, the Te nanowire monolayer stamp was put onto the PMMA coated glass slide and suitable pressure was applied on it. The stamp was pulled away from the PMMA coated glass slides substrate rapidly when finishing heating it at 100 °C for 1 h and cooling to room temperature naturally. The XRD experiments were performed to obtain diffraction

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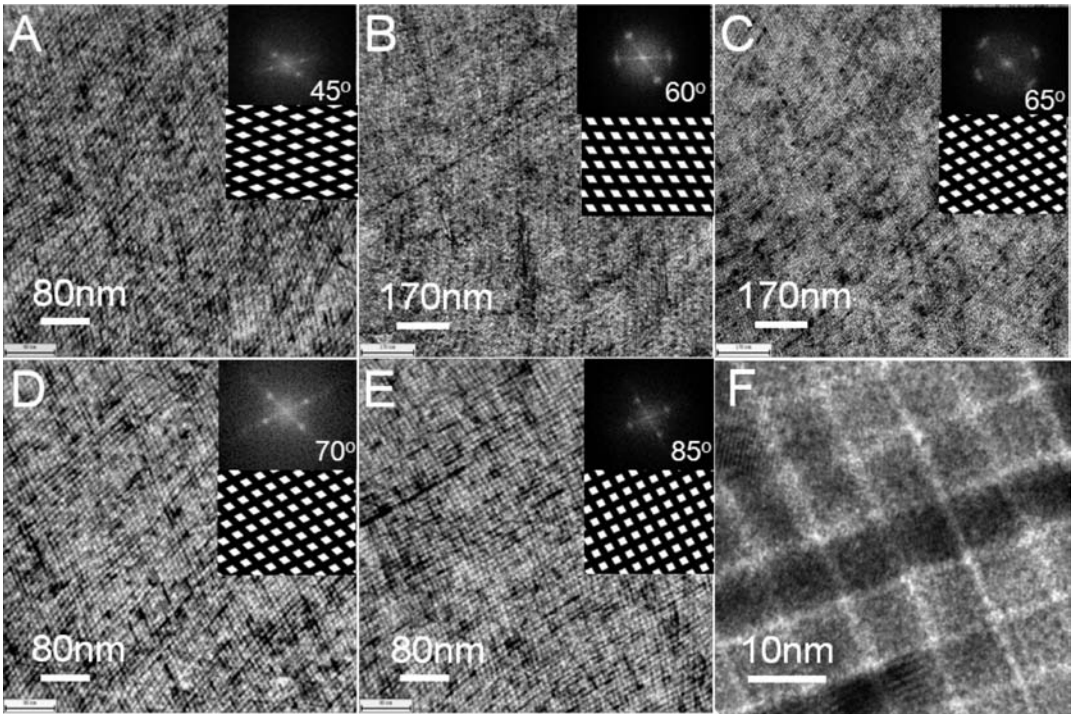

Figure 4. TEM images of the nanomesh-like assemblies formed by packing two layers of Te nanowire films with different crossed angles. (A−E) Crossed Te nanowire layers can be formed by uniformly transferring a second layer of aligned parallel Te nanowires perpendicular to the first layer and turning the angle between two monolayers of nanowires. The insets of (A−E) show the fast Fourier transform of the TEM images, and the simulation plot for the assembled mesostructures of the nanowires. (F) High resolution TEM images of crossed Te nanowires with high magnification.

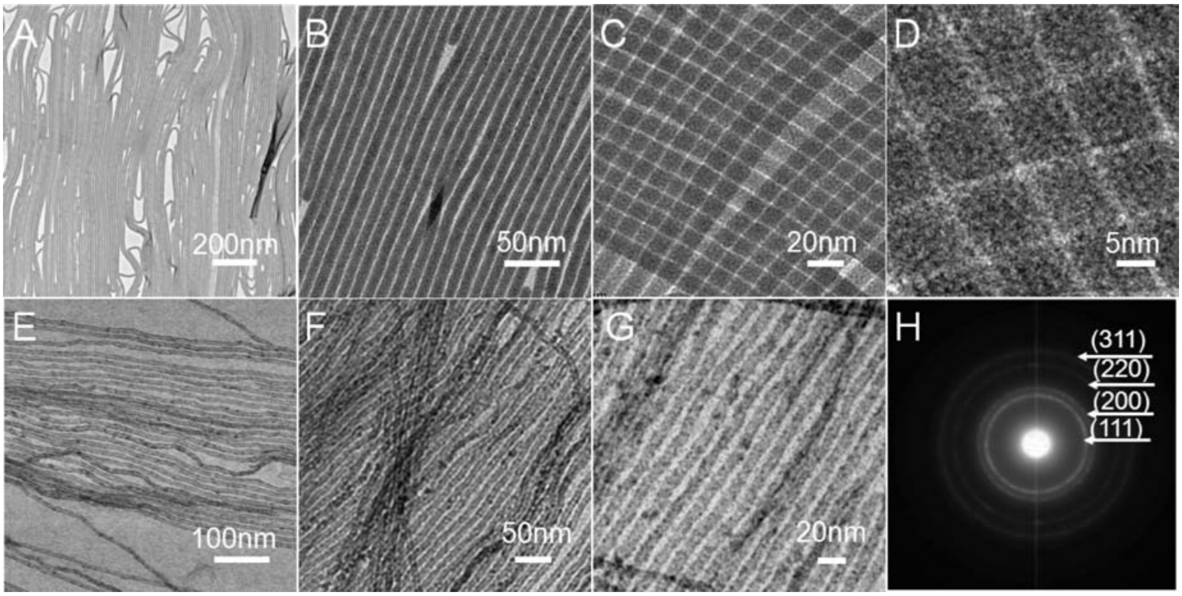

Figure 5. (A−D) TEM images of Ag_2Te assembly. (E−G), TEM images of assembled Pt nanotubes; (A, B) TEM images of monolayers of Ag_2Te nanowires with different magnification; (C, D) crossed layers of Ag_2Te nanowires are formed by uniformly transferring a second layer of aligned parallel Ag_2Te nanowires perpendicular to the first layer with different magnification; (E−G) TEM images of a monolayer of Pt nanotubes with different magnification; (H) SAED pattern taken on the Pt nanotubes shown in (G).

information on these nanopatterns. Figure 6B, C show the SAXRD patterns of Te nanowire monolayer before and after imprinting. It is found that there is no obvious change, which illuminates the mesostructures of the Te nanowire monolayer had been kept well. Figure 6D shows the SAXRD patterns of PMMA film after being detached, and the channel is 6.7 nm, which is slightly bigger than 6.3 nm of the Te nanowire monolayer in Figure 6B, C. The XPS spectrum in Figure 7A shows that no Te elements were detected on the PMMA film formed on the glass substrate after imprinting with the mesostructure stamp of Te nanowire monolayer. The FTIR spectra in Figure 7B show that the PMMA films formed on the glass substrate before (black line) and after (red line) imprinting display features similar to those of pure PMMA.[22]

The 20-layer Te nanowires with the same axial direction can be fabricated through parallel assembly of Te nanowire mono-

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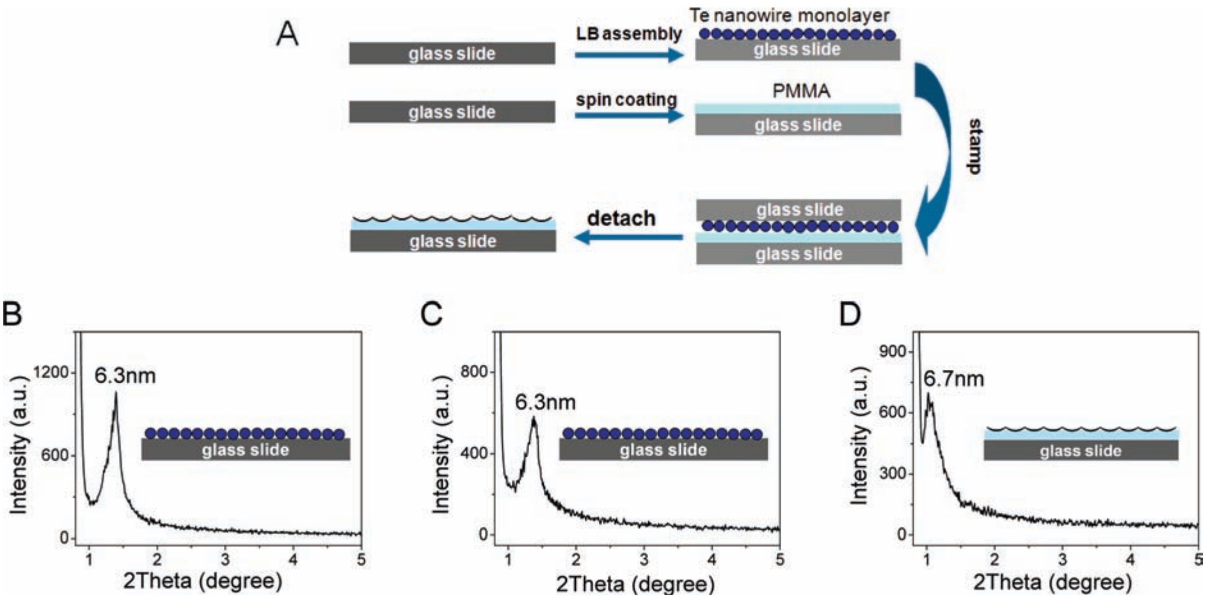

Figure 6. (A) Scheme of the process for fabricating a Te monolayer stamp for nanopatterns. (B, C) Monolayer of Te nanowires before and after the imprinting. (D) The PMMA substrate with uniform nanopatterns.

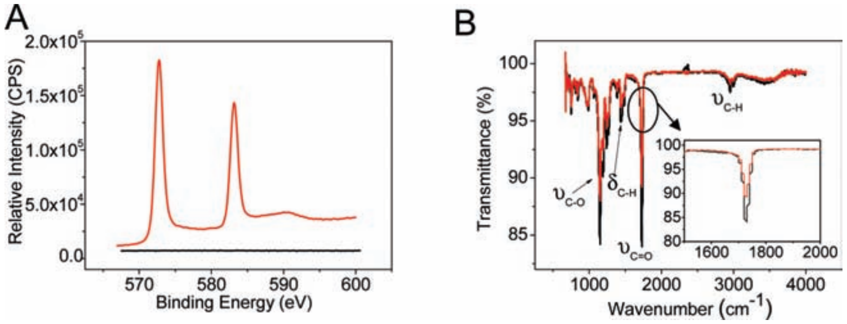

Figure 7. (A) Te 3d spectrum of the PMMA film formed on the glass substrate by spin coating and then imprinting with the Te nanowire monolayer mesostructure stamp (black line), while the red line shows the Te3d spectrum of the Te nanowire monolayer (stamp). (B) FTIR spectra of the PMMA film formed on the glass substrate before (black line) and after (red line) imprinting. Insert shows the details in the wavenumber range from 1500 to 2000 cm^{-1}.

layers on a Si/SiO$_2$ (SiO$_2$ layer with a thickness of 500 nm) substrate by LB technique, and a type of nanodevice with reversible photoelectric properties can be constructed. Then, Au electrodes were thermally evaporated via laying a micrometer-sized Au wire on the nanowires as the mask to obtain a gap between two electrodes. The Te nanowires were vertical to the electrodes (see Supporting Information, Figure S10A). Photoelectric properties of the Te nanowire nanodevice were investigated with the Micromanipulator 6150 probe station and Keithley 4200 SCS in a clean and metallic shielded box at room temperature in air. The current−voltage ($I-V$) curves measured on a Te nanowire films in the dark and white light illumination of different light intensities are shown in Figure 8,A and B. The $I-V$ curves exhibit linear behavior, confirming the ohmic contact feature. The electrical resistance of the nanowire films decreased when the light was turned on from the dark which was similar to other photoconduction materials.[23] It is obvious that the current of the devices increases significantly with the light intensity increasing. It was highly insulating in the dark with a resistivity about 9.2 kΩ (Figure 8A). When the light intensity increased from dark to 0.37, 3.04, 5.76 mW/cm^2, the electrical resistance decreased, respectively, from 9.2 to 8.4, 5.9, 4.7 kΩ (Figure 8B). Moreover, the current of the device increased linearly with increasing illumination power (inset of Figure 8B, at bias 1 V), indicating the sensitivity of the devices to light. The resistance R of the materials of uniform cross section can be calculated:[24]

$$R = \rho L/A$$

where, L is the length of the materials, A is the cross-sectional area, and ρ is the electrical resistivity (also called specific electrical resistance) of a material. Compared to the work by Wang et al,[25] the diameter of the nanowires we used is smaller and the length is much longer. According to the formula above, the resistance of the as-prepared device is thought to be larger. However, the resistance of this nanowire device is 3 orders of magnitude smaller. The reason for this could be a result of the

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[23] (a) Kind, H.; Yan, H. Q.; Messer, B.; Law, M.; Yang, P. D. *Adv. Mater.* **2002**, *14*, 158. (b) Iwasaki, A.; Hu, L. G.; Suizu, R.; Nomura, K.; Yoshikawa, H.; Awaga, K.; Noda, Y.; Kanai, K.; Ouchi, Y.; Seki, K.; Ito, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 4022.

[24] For practical reasons, any connections to real materials will almost certainly mean the current density is not totally uniform. However, this formula still provides a good approximation for long thin wires.

[25] Wang, Y.; Tang, Z. Y.; Podsiadlo, P.; Elkasabi, Y.; Lahann, J.; Kotov, N. A. *Adv. Mater.* **2006**, *18*, 518.

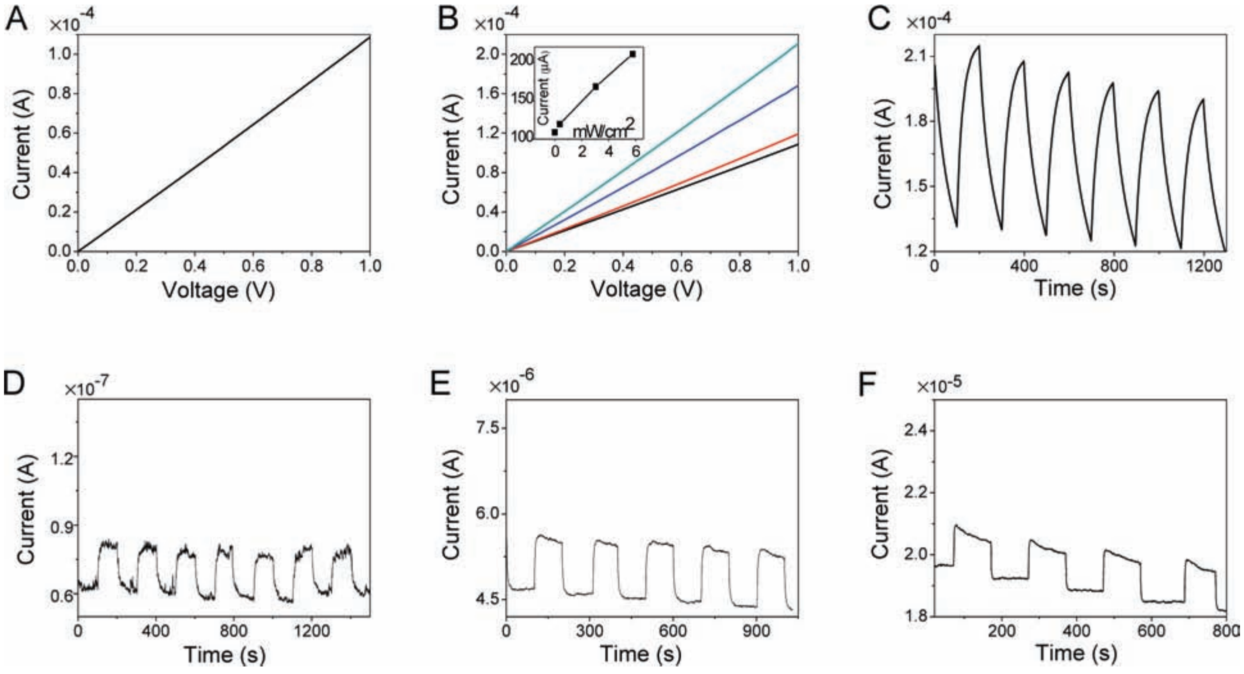

Figure 8. Photoelectric properties of the Te nanowire nanodevices. (A−C) $I-V$ curves and reversible switching photoconducting property of a 20-layer Te nanowire device. (A) $I-V$ curves measured in the dark. (B) $I-V$ curves measured under different light intensities, 0, 0.37, 3.04, 5.76 mW/cm^2, respectively. (B, inset) Linear characteristics between photocurrent and the power of illumination (0, 0.37, 3.04, 5.76 mW/cm^2) at bias 1 V. (C) Reversible switching of a 20-layer Te nanowires device between low and high conductivity states when the light was turned on and off. The bias on the nanowire films is 1 V. (D−F) Reversible switching photoconducting property of the Te nanowire films, which are composed of monolayers of three layers and five layers, respectively. All the Te nanowire films were assembled without tuning an angle, and all the nanowires have the same axial direction.

nanowires used here being arrayed in parallel with the film device containing no polyelectrolyte or polymer as used previously. Figure 8C shows a reversible switching of a Te nanodevice between low and high conductivity states when the lamp was turned on and off. The bias on the nanowires was 1 V, and the light intensity was 5.76 mW/cm^2. After test cycles, the switch ratio remained 1.6, the same as it was at the beginning, which is a little higher than that reported previously.[25] The device fabricated using ordered Te nanowires as building blocks shows a weak but detectable response to light; the further optimization of the devices is ongoing.

In order to investigate the photoswitching characteristics of the Te nanowire films in detail, a series of devices composed of different numbers of Te monolayers were fabricated, for example, monolayer, three layers, and five layers, respectively. From Figure 8D to Figure 8F, we can see that even monolayer device gives an obvious response to the white light. With increasing the number of layers from monolayer to 20 layers, the current of the device increased. From monolayer to 20 layers, the electrical resistance decreased rapidly from 1.6 MΩ to 4.7 kΩ. From Figure 8 and Figure S10B (Supporting Information), the photocurrent gradually weakened as the time was prolonged. Negative photoconductivity (PC) has been studied recently. Usually, the negative PC is attributed to two-center recombination effect[26] or caused by hole-photoemission.[27] The Te nanowire films achieved on the substrate are rather stable in the air in contrast to the poor stability of the Te nanowires dispersed in a solution,[28] which still exhibit sensitivity to light even after three months (see Supporting Information, Figure S10).

4. Conclusions

In summary, we demonstrate that large-area, well-defined, periodic mesostructures of hydrophilic ultrathin Te nanowires with aspect ratios of at least 10^4 can be produced by Langmuir−Blodgett technique without any extra hydrophobic pretreatment or functionalization. The mesostructures of ultrathin Te nanowire films show reversibly switched photoelectric properties, and the photocurrent is influenced by the light intensity and the number of mesostructured nanowire monolayers. The successful alignment of ultrathin Te nanowire mesostructures by this approach will make possible producing other hierarchical nanopatterns by combination with other techniques such as photolithography etching or depositing techniques, which can find applications such as in light detectors and switching devices for optoelectric devices. In addition, such well-organized Te nanowire monolayers with periodic mesostructures can be readily used as stamps to transfer such nanopatterns to other substrates or can be embedded within polymer matrixes. Further substitution of different nanowires and changes in structural hierarchy in different assemblies will provide us flexible and promising strategies for the fabrication of other integrated, hierarchical, and periodic nanostructures with special functionalities and multifunctionalities.

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(28) Lan, W. J.; Yu, S. H.; Qian, H. S.; Wan, Y. *Langmuir* **2007**, *23*, 3409.

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Supporting Information Available: TEM, HRTEM, SEM, AFM images, π−A isotherms of the Te nanowire monolayer, photograph of a substrate being pulled vertically through a Langmuir monolayer of Te nanowires, small-angle X-ray diffraction patterns, illustration of the steps for the assembly of Te nanowire film mesostructures, and reversible switching photoconducting property of a Te nanowire films with five layers measured after three months. This material is available free of charge via the Internet at http://pubs.acs.org.

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