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Scalable Alignment and Transfer of Nanowires in a Spinning Langmuir Film

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Abstract

Many nanomaterial-based integrated nanosystems require the assembly of nanowires and nanotubes into ordered arrays. A generic alignment method should be simple and fast for the proof-of-concept study by a researcher, and low-cost and scalable for mass production in industries. Here we have developed a novel Spinning-Langmuir-Film technique to fulfill both requirements. We used surfactant-enhanced shear flow to align inorganic and organic nanowires, which could be easily transferred to other substrates and ready for device fabrication in less than 20 minutes. The aligned nanowire areal density can be controlled in a wide range from 16/mm² to 258/mm², through the compression of the film. The surface surfactant layer significantly influences the quality of alignment and has been investigated in detail.

Introduction

Assembly of one-dimensional nanostructures is a critical aspect in the development of bottom-up nanodevices. Sophisticated approaches can accurately position nanowires through predefined patterns or localized forces,^{1, 2} while many applications require aligned nanowire arrays without registering each individual nanowire. Non-registering alignment of nanowires is desired for

various reasons. For electronic devices, aligned nanowires greatly simplify the design and fabrication of electrode pattern. In nanowire-based composites, the direction of nanowires determines their mechanical, thermal, and electric behaviors.³⁻⁵ A good alignment enables the anisotropic property of individual nanowire, such as piezoelectricity and lasing,^{6, 7} to have macroscopic effect. For instance, nanowire alignment is a major hurdle for energy harvesters based on piezoelectric nanowires.⁸

Many alignment techniques have been explored for the alignment of specific nanowires.. Alignment with electric field or magnetic field,⁹⁻¹² as one of the earliest techniques, requires specific electromagnetic properties from the nanowire. Contact printing has minimum misalignment,^{13, 14} but it mainly works for nanowires grown on a substrate. Spincoating aligns and sorts nanowires simultaneously,^{15, 16} and the surface chemistry between the substrate and nanowires needs to be optimized.

Control over the density of aligned array is also important. Langmuir-Blodgett alignment produces dense nanowire arrays.^{17, 18} When random number of nanowires can work together for one functional unit like a transistor, a high density facilitates the device integration. However, if the number of functional nanowires in a device is important or the whole array functions as one component, the density of nanowires determines device properties like conductivity, transparency, stiffness, piezoelectricity, *etc.*, which makes the density control necessary.

Compared with the other methods, alignment based on shear flow has minimum requirement on the property of nanowires, and usually allows the array density to be tuned.¹⁹⁻²² The shear stress in fluids depends on the shear rate and the viscosity. In order to align nanowires, most approaches use either a high shear rate in a confined space^{19, 20, 22} or a viscous fluid²¹ to produce sufficient shear stress. The confined space limits the scalability of the alignment, while the viscous fluid

completely encapsulates the nanowires. On the other hand, a thin layer of molecules floating on the surface of fluids, called a Langmuir film, can increase the surface viscosity without changing the bulk property of fluids.²³ By adopting the Langmuir film as a shear medium,²⁴ we have developed a simple and versatile alignment technique with the capability of density control.

Results and discussion

The alignment consists of five steps - nanowire spread, compression (optional), shear, nanowire transfer, and surfactant removal, as illustrated in Fig. 1. First, a solvent containing nanowires and surfactant is spread on the deionized water surface to form a mixed Langmuir film, Fig. 1(a) and (f). Surfactant molecules can raise the surface viscosity of water to facilitate the nanowire alignment. The density of aligned nanowires can be increased when the top surface is shrunk, Fig. 1(b) and (g). The spread-compression process is different from the conventional Langmuir techniques in that the commonly used rectangular trough with a movable barrier is eliminated. The compression is realized by draining the water through a PTFE funnel outlet, which avoids the complex moving mechanism and provides a centrosymmetric compression.²⁵⁻²⁷ Following the compression, a PTFE rod is spinning along the center of the funnel, generating an azimuthal flow, Fig. 1(c). Because of the small size of nanowires and the high surface viscosity, the nanowires are able to trace the flow, and the shear between the steady funnel and the rotating rod gradually aligns the nanowires along the streamlines, Fig. 1(h). After the rod stops, a receiving substrate is brought into contact with the water surface so that the aligned nanowires can be transferred (Langmuir-Schaefer deposition), Fig. 1(d) and (i). If the substrate is much smaller than the funnel, the nanowires will be approximately unidirectional on the substrate. The surfactant molecules are also transferred onto the substrate, but most of them can be easily removed on a hotplate (95 °C when 1-octadecylamine is used as surfactant), Fig. 1(e) and (j), and Fig. S1.

Surfactant serves as a temporary shear medium. The setup in Fig. 1 is low-cost and easy to operate, and the clean and aligned nanowire array can be achieved in about 20 minutes (see the Experimental section).

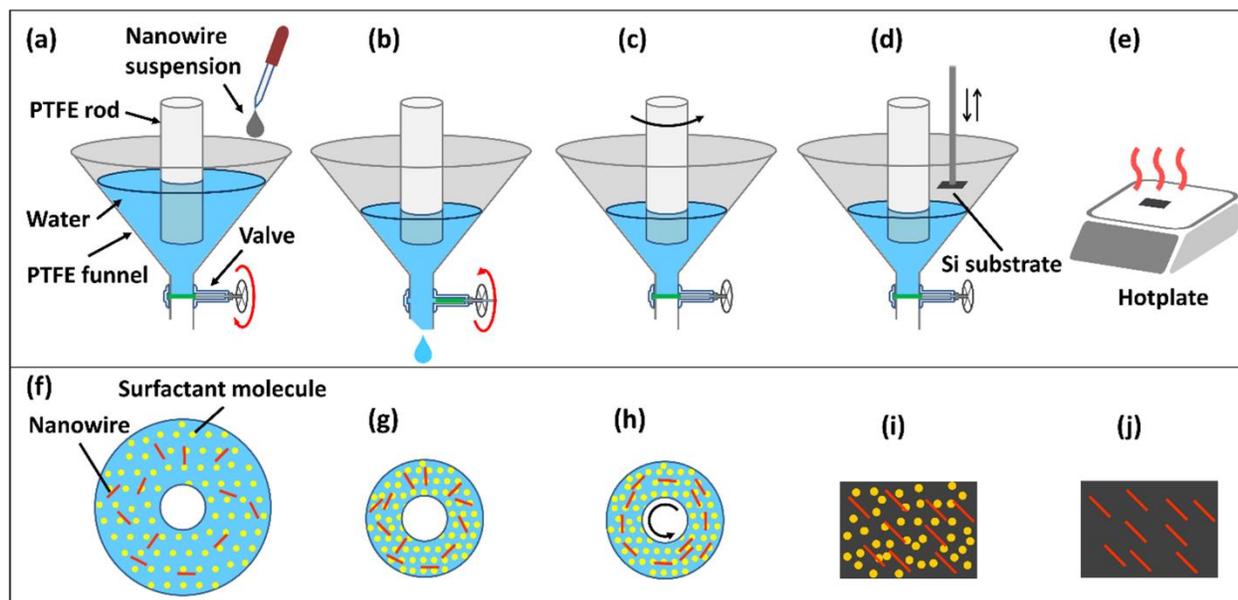


Fig. 1. Schematic illustration of the alignment process. (a) Spread of nanowires and surfactant molecules on the water surface to form a composite Langmuir film. (b) Compression of the Langmuir film by draining the water. (c) Shear of the Langmuir film with a rotating rod. (d) Transfer of nanowires onto a receiving substrate. (e) Surfactant removal on a hotplate. (f)-(j) Top views of the water surface or substrate surface, corresponding to (a)-(e) respectively. Figures are not drawn to scale.

This approach can be applied to various one-dimensional nanomaterials. In this work we demonstrated its generality with zinc oxide nanorods and diphenylalanine peptide nanotubes (FF PNT). The nanostructure does not need to be hydrophobic. With a proper spreading solvent, the surface tension at the water-air interface is sufficient to support even the hydrophilic nanostructures.²⁸ Fig. 2(a) and (b) are the typical optical microscopy images of aligned zinc oxide

nanorods and FF PNT on silicon substrates. The inserted scanning electron microscopy images in Fig. 2 show that the zinc oxide nanorods are short and conical, and that FF PNT have various lengths. Therefore, the Spinning-Langmuir-Film method can align one-dimensional nanostructures with different sizes and aspect ratios. It is worth noting that the nanowires on the most part of the water surface are aligned under the shear flow, although there are much fewer nanowires adjacent to the spinning rod or the funnel edge, as is shown in the supplementary material, Fig. S2. Different spinning rates between 60-180 RPM produce similar aligned nanowire arrays. Even at a low spin rate of 60 RPM, the nanowires close to the spinning rod start to align with respect to the shear field in less than 1 sec and the aligned area grows continuously toward the steady funnel wall with a speed of a few millimeters per second, as shown in Fig. S4.

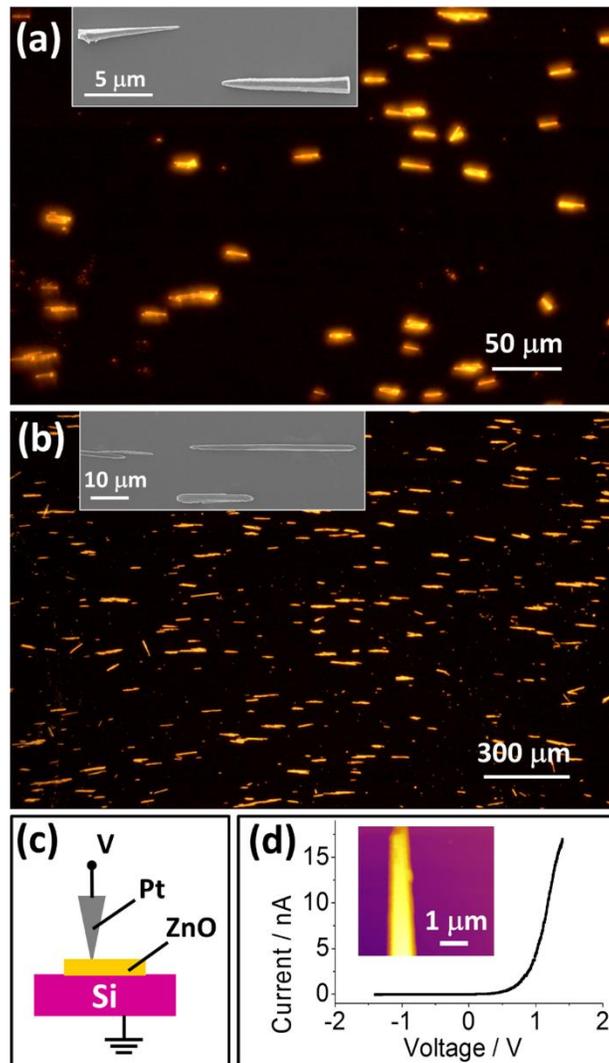


Fig. 2. Alignment and electric characterization of one-dimensional nanostructures. (a) Dark-field optical microscopy image of aligned zinc oxide nanorods on a silicon substrate. Inset: Scanning electron microscopy image of individual nanorods. (b) Dark-field optical microscopy image of aligned diphenylalanine peptide nanotubes on a silicon substrate. Inset: Scanning electron microscopy image of individual nanotubes. (c) Schematic diagram showing the electric characterization of aligned zinc oxide nanorods based on Atomic Force Microscopy. (d) A typical current-voltage curve of a nanorod. Inset: Topographical scan of the nanorod on the silicon substrate.

After the alignment from the chemical solution, a good interface between the nanowire and other materials is critical for the device fabrication. The electric contact of the aligned n-type zinc oxide nanorods was tested with conductive Atomic Force Microscopy (AFM). As illustrated in Fig. 2(c), an AFM platinum probe forms one electric contact with the nanorod, while the silicon substrate serves as the bottom electrode. The current-voltage curve of the nanorod in Fig. 2(d) shows rectifying characteristics, which is due to the Schottky barrier between zinc oxide and platinum. The electric characterization confirmed that the aligned nanorod formed good electric contacts with both the metallic probe and the silicon substrate.

This technique controls nanowires areal density via the height of water in the funnel. Alternatively, the density can also be controlled by adding different amounts of nanowires onto the water surface. However, nanowires may overlap if too many nanowires are added during the spread (Fig. S3). Starting with a sparse array ensures the formation of monolayer nanowires on the water surface. Fig. 3(a)-(c) show the aligned FF PNT at relatively low (*ca.* 16/mm²), medium (*ca.* 41/mm²), and high (*ca.* 258/mm²) densities, collected at different water levels. The inserted histograms show the angular distribution of nanotubes; more than 85% of the nanotubes are within $\pm 10^\circ$ of the shear direction in all the three images. At the low density end, this technique is a complement to the conventional Langmuir-Blodgett assembly approach,^{17, 18} where sparse nanowires could not be aligned due to the absence of nanowires interaction. At the other end, large area reduction from the dropping water level can produce denser array, as shown in Fig. 3(c). Aligned arrays with much higher density can also be achieved, as provided in the supplementary information, Fig. S3.

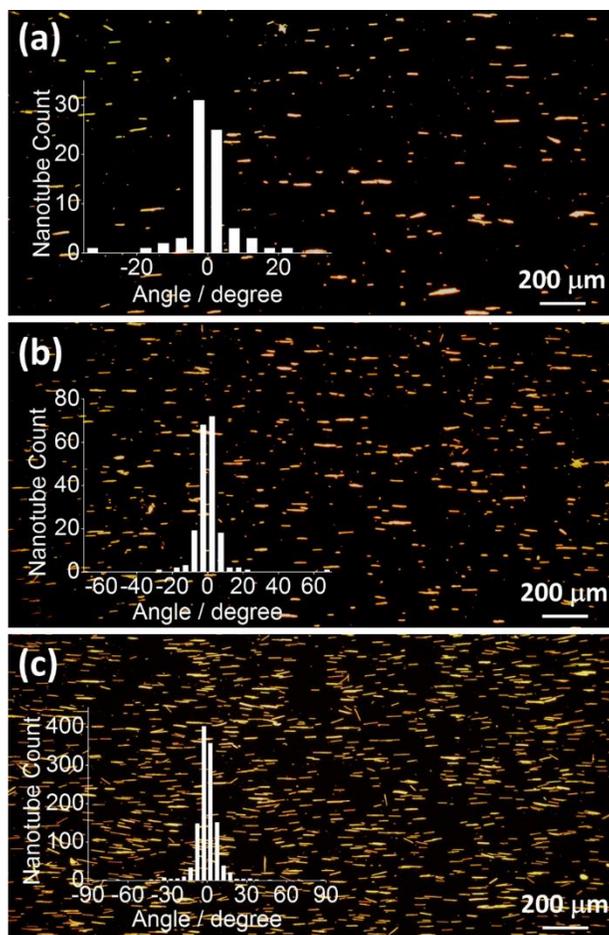


Fig. 3. Aligned nanotubes with different areal densities through compression. (a) Low density nanotube array from a high water level in the funnel. Inset: Angular distribution of the nanotubes. (b) Medium density nanotube array from a medium water level in the funnel. Inset: Angular distribution of the nanotubes. (c) High density nanotube array from a low water level in the funnel. Inset: Angular distribution of the nanotubes.

Compared with the conventional Langmuir trough with a movable barrier, a distinguishing trait of the conical trough is the movement of the three-phase contact line during the compression. We observed a “stick-slip” behavior when the contact line was moving along the funnel, indicating the pinning of the contact line.²⁹ The pinning force is due to the surface roughness and/or the chemical heterogeneity of PTFE,^{30, 31} and it caused the nanowire monolayer to deposit on the

funnel wall before high-density nanowires formed on the water surface. The stick-slip problem can be mitigated by keeping a layer of nonpolar solvent, such as isooctane (the one in the spreading solvent), on top of the water during the compression. The nonpolar solvent is believed to wet the PTFE and serve as a “lubricant” at the contact line,^{32, 33} such that the nanowire array can be compressed smoothly until they are closely packed.

The shear force on the water surface is critical to achieve the unidirectional alignment. When we simply compressed the Langmuir film to a high density, the nanowires were roughly along the circular three-phase contact line, similar to the existing Langmuir-Blodgett alignment approach; however, the angular deviation was large. Fig. 4(a) shows the compressed nanotube array without rotation of the PTFE rod. There is no obvious long-range orientation in the array, whereas some short-range alignment is present due to the interaction between adjacent nanotubes. It is worth noting that vast majority of the nanotubes in Fig. 4(a) are still in a monolayer, although collapse occurs at some places due to the high compressive pressure.

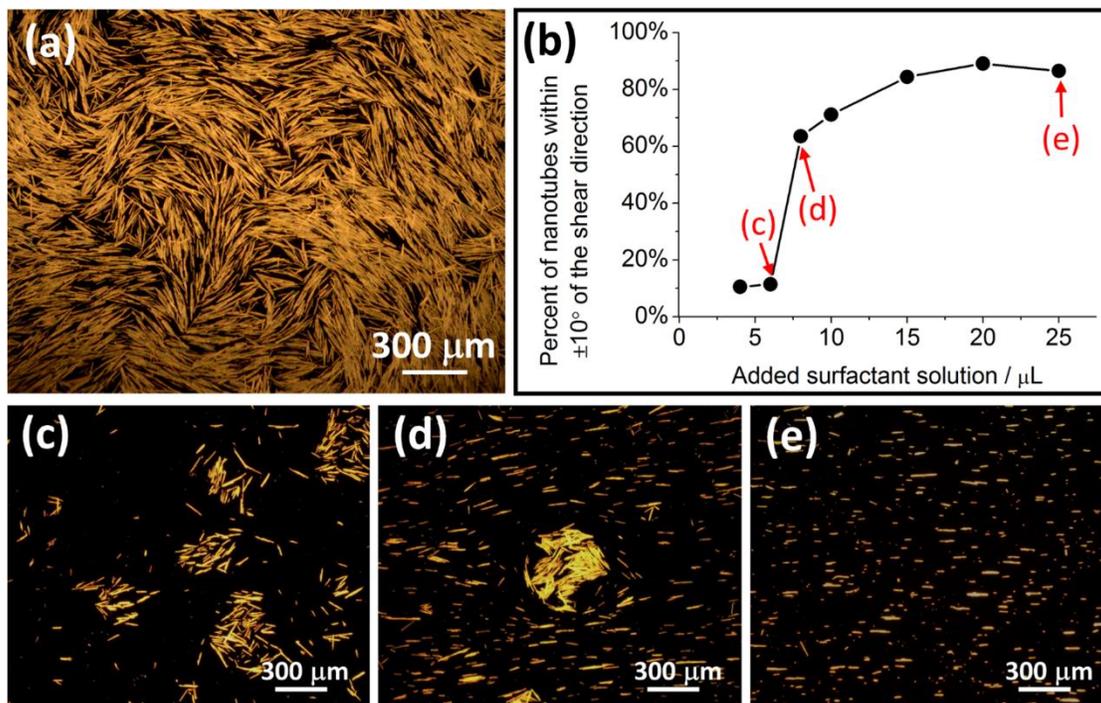


Fig. 4. Shear effect on the nanotubes alignment. (a) Compressed monolayer of nanotubes without shear. (b) Relationship between the quality of alignment and the amount of added surfactant. A higher percentage of nanotubes within $\pm 10^\circ$ of the shear direction indicates a better alignment. (c) Nanotubes after shear alignment with 6 μL surfactant. (d) Nanotubes after shear alignment with 8 μL surfactant. (e) Nanotubes after shear alignment with 25 μL surfactant.

The role of the surfactant during shear needs to be emphasized. Before the added surfactant reaches a threshold amount, the surface viscosity is insufficient so that the nanowires would move freely and aggregate on the water surface without alignment. We have characterized the quality of alignment with different amounts of surfactant being added. The result is given in Fig. 4(b). When the surfactant is less than 8 μL (*ca.* 20 molecules/ nm^2 on the water), nanotubes have random orientation and agglomeration is observed after the shear, as shown in Fig. 4(c). When the surfactant amount is increased into the transition region, the agglomeration is significantly reduced and the dispersed nanotubes start to be oriented in the shear flow direction, Fig. 4(d). When the surfactant amount exceeds the transition region, the agglomeration completely disappears and the dispersed nanotubes are well aligned, as shown in Fig. 4(e). Therefore, the high viscosity from the surfactant not only aligns the nanotubes but also prevents them from aggregating.

Finally, we compared the Spinning-Langmuir-Film approach to an early technique. Decades ago, researchers used the circular shear flow to align fibers in viscous suspensions to study the orientation dependence of composite materials.³⁴ Those fibers embedded in a matrix cannot be easily transferred onto a planar substrate with the alignment maintained for device fabrication. Taking advantage of the Langmuir film on the water surface, we produce the aligned nanowire array with desired density on a selected substrate which is ready for the device fabrication with current microfabrication technologies.

Conclusion

The Spinning-Langmuir-Film technique combines several advantages: 1) the setup is simple, low-cost, and feasible for scale-up; 2) the areal density of aligned nanostructures can be controlled in a wide range; 3) the aligned nanostructures can be transferred onto receiving substrates and form good electric interface with other materials. We demonstrated its feasibility by aligning zinc oxide nanorods and diphenylalanine peptide nanotubes on silicon substrate, and this method can be applied to other nanostructures and substrates as well. Despite the simplicity of the aligning setup, the alignment mechanism is based on the complex interaction between molecules and mesoscopic objects in a two-dimensional phase, and in-depth investigation is required to fully understand and optimize the alignment process.

Experimental section

Preparation of Zinc Oxide Nanorods Suspension: The zinc oxide nanorods were synthesized on glass slides. Briefly, ammonia solution (3.6 mL, approx. 30 wt%) was added into an aqueous solution (100 mL) of hexamethylenetetramine (10 mM) and zinc chloride (10 mM). Clean glass slides were placed floating on the top surface of the growth solution in a glass jar which was kept in an oven at 80 °C for 16-20 hours. After zinc oxide nanorods grew on the glass slides, they were detached from the substrates by mild ultrasonication, and dispersed in a mixed solvent of isooctane and isopropanol (3:1 by volume).³⁵

Preparation of Diphenylalanine Peptide Nanotubes Suspension: A vial containing diphenylalanine (10 mg, Bachem, Switzerland) and water (5 mL) was put in an oven at 80 °C until the white suspension became visually transparent. A second vial containing diphenylalanine (10 mg) and water (10 mL) was ultrasonicated vigorously until the white suspension became uniform

without lumps. Then suspensions from both vials (2 mL and 2 mL) were mixed in a third vial and kept still overnight. The synthesized nanotubes were filtered out of the suspension and dispersed in a mixed solvent of isooctane and isopropanol (3:1 by volume).³⁶

Preparation of Subphase for the Formation of Langmuir Film: For water insoluble nanostructures such as zinc oxide nanorods, deionized water can be directly used as subphase. However, since diphenylalanine peptide nanotubes dissolve in water, the subphase needs to be saturated with diphenylalanine prior to the nanotube spread. Diphenylalanine (20 mg) was added into water (20 mL), followed by vigorous ultrasonication for 1 hour. The suspension was filtered, and the clear filtrate was used as subphase.

Alignment of Nanorods and Nanotubes: The basic procedure has been explained in the main text. Specifically, the PTFE funnel (SonomaTesting) was 70 mm in diameter and 50 mm in height, and the PTFE rod (McMaster-Carr) had a diameter of 25 mm. The surfactant was 5 mM 1-octadecylamine in hexane. In a typical alignment, solvent (0.2 mL) containing nanowires and surfactant (20 μ L) was ultrasonicated for 20 seconds for mixing, and then added onto the water surface. Depending on water surface area and ambient ventilation, the spreading solvent evaporated in 2-5 min, during which an optional compression could be performed. The shear flow was induced when the PTFE rod was rotating at 60-180 rpm, for a period of 1-3 min. Various substrates, including silicon, silicon with native oxide, glass slide, Kapton polyimide film, polyethylene terephthalate (PET) film, and PET film coated with copper, were used as receiving substrates. After the aligned nanowires were transferred, the substrate was put on a hotplate at 95 $^{\circ}$ C for 5-15 min to evaporate the surfactant residue. A short oxygen plasma cleaning may be necessary if surfactant molecules form strong bonds with nanowires.

Image Processing: The optical microscopy images were processed in MATLAB[®] to obtain the angular distribution of nanotubes. All optical images had 3039-by-2014 pixels, and objects that had fewer than 80 pixels were considered particles and excluded from statistics. In addition, objects that had an aspect ratio ≤ 3 were not considered wire structures, and thus were excluded from statistics.

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