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Orientated Langmuir—Blodgett Assembly of VO₂ Nanowires

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ABSTRACT

We report Langmuir–Blodgett (LB) based assembly of vanadium dioxide (VO₂) nanowires. VO₂ nanowires were functionalized with stearic acid (SA) and cetyltrimethylammonium bromide (CTAB) and then spread on the surface in an aqueous phase in a LB trough. Surface pressure–area (π –A) isotherms were recorded on the LB trough and show hysteretic behavior. Scanning electron microscopy investigations of morphology and alignment of the VO₂ nanowire films transferred at different points on the π –A curve demonstrate that with increasing surface pressure there is a transition from well-separated domains of nanowires to compact and locally ordered nanowire monolayers, while aggregates of raftlike nanowire structures remain after expansion. Interestingly, X-ray diffraction studies show that VO₂ nanowire LB films exhibit (00*I*) crystal plane orientation, which is attributed to preferential coordination of SA and CTAB–SA complex to (001) surface of VO₂ nanowires thereby driving this orientation.

One-dimensional (1-D) nanostructures, such as nanotubes, nanobelts, and nanowires, have attracted increasing attention in nanoscience due to their unique structures, interesting physical properties, and potential for novel applications.^{1–6} A formidable challenge, however, is the hierarchical organization of these nanoscale building blocks into organized assemblies and, ultimately, useful systems.^{7–10} For example, rational assembly of these 1-D building blocks into well-defined two- or three-dimensional architectures will open up many areas of nanoscience from nanoscale electronics,¹¹ optoelectronics,¹² solar cells,¹³ spintronics,¹⁴ and piezoelectronics¹⁵ to biosensing.¹⁶

To this end, the Langmuir–Blodgett (LB) technique is an attractive methodology because it can readily help to assemble 1-D nanostructures into large-area ordered monolayer arrays at the air–water interface. The feasibility of transferring multiple or alternating layers of metal or semiconductor 1-D nanostructures onto flexible substrates also points to new directions for flexible electronics and optoelectronics. Kim et al.¹⁷ applied the LB technique on 1-D nanostructures and succeeded in assembling short aspect ratio nanowires on a water surface to create textures that resembled liquid crystals. Up to now, LB films of various 1-D nanostrctures such as silicon nanowire,^{10,25} carbon nanotubes,^{18–20} BaWO₄ nanowires,¹⁷ ZnSe nanowires and nanowires,^{21,22} Ag nanowires,²³ and Ge nanowires²⁴ have been prepared. Notably, Whang et al.^{10,25} used the LB method to control organization and hierarchy of silicon nanowires in parallel and crossbar arrays over many length scales.

Recently, vanadium oxide nanomaterials, especially nanowires, have been the focus of intensive investigation due to their interesting electric and magnetic properties, where properties can be tuned by oxygen stoichiometry in structures with the general formula VO_{2+x} .^{26–28} In the present work, we report the stable surface functionalization and LB assembly of VO₂ nanowires with diameters of 30–60 nm and aspect ratios of 20–50.

The VO₂ nanowires with 30–60 nm in diameter and 1–5 μ m in length were prepared via a hydrothermal method previously described.^{31–33} Briefly, V₂O₅ and CTAB were mixed with distilled water and, after aging, were transferred to an autoclave and heated at ~180 °C for ca. 7 days. The resulting VO₂ nanowires were washed with distilled water and dried. To facilitate assembly, VO₂ nanowires were functionalized with steric acid in toluene,³⁴ followed by CTAB, centrifuged, and then resuspended in chloroform. The chloroform VO₂ nanowire suspension was spread dropwise (typically 2 mL of 1 mg/mL) on the aqueous phase of a Langmuir–Blodgett trough (KSV5000). The nanowire surface layer was compressed slowly while the surface pressure was monitored with a Wilhelmy plate 30 min (or later) after

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Figure 1. Schematic view of the surface functionalization of VO_2 nanowire. (a) A great number of hydroxyls exists on the VO_2 nanowire surface. (b) Stearic acid molecules surround nanowire by coordination and/or hydrogen bonds. (c) Nanowire is surrounded by a CTAB–SA complex layer.

spreading to ensure evaporation of the solvent (chloroform) and equilibration of the film. The π -A isotherms at 298 K were recorded at a barrier speed of 10 mm/min. The films were prepared at the surface pressures of 15 and 40 mN/m during compression process and at the surface pressure of 2 mN/m during expansion on the tank. After each compression step, the surface was allowed to relax for 30 min. Nanowire transfer was performed using hydrophilic glass at a speed of 2 mm/min by a vertical dipping method. Sufficient time (10 min) was allowed for drying of the film between successive cycles.

To achieve Langmuir–Blodgett assembly, it is necessary that nanowires were rendered hydrophobic and monodispersed in organic solution.³⁵ Figure 1 illustrates schematically the process of surface functionalization of the nanowires. In general, hydroxyl groups on the VO₂ nanowire surface (Figure 1a) cause unfunctionalized nanowires to aggregate.³⁵ During surface modification (Figure 1b), stearic acid (C₁₇H₃₅COOH, SA) molecules can coordinate and/or hydrogen bond to the VO₂ surface. During the modification process of microemulsion (Figure 1c), water-soluble cetyltrimethylammonium bromide (C₁₉H₄₂NBr, CTAB) has the following interaction with SA on the surface of nanowires, resulting in the formation of a CTAB–SA complex.³⁶

$$C_{17}H_{35}COO^- + C_{19}H_{42}N^+ \rightarrow CTAB-SA$$
 Complex

Therefore, the functionalized VO₂ nanowires consist of an inorganic core surrounded by a CTAB–SA complex layer (Figure 1c). Notably, the nanowires can be monodispersed in organic solution by SA and CTAB functionalization while the monodispersed degree is worse only by SA or only by CTAB functionalization. To understand the reason, we prepared VO₂ nanowires using a microemulsion method and found that the attained VO₂ nanowires were easily monodispersed in orgnic solution. It is reasonable to attribute this phenomenon to the fact that there are some organic molecules on the surface of VO₂ nanowires by the microemulsion method while the organic molecules are absent on the surface of those nanowires by the hydrothermal method.



Figure 2. (A) π –A isotherm of VO₂ nanowires floating on the water during compression and expansion cycle. (B) Schematic illustration of the behavior of nanowires during compression and expansion cycle. (a) Nanowire units floating on water after dispersion are fairly monodispersed with no superstructures, and the directions of the nanowires are isotropically distributed. (b) Wires with uniform size and small aspect ratio form raftlike aggregates of generally three to five wires by aligning side-by-side after compression. (c) With further compression the nanowires isotropically distributed align with their long axis at local areas. (d) Raftlike aggregates remained after relaxation.

Figure 2A shows the surface pressure versus surface area $(\pi - A)$ isotherm of VO₂ nanowires functionalized by SA and CTAB on water. During compression, at the initial stage (from I to II) the nanowire units approach each other at smaller areas, and the nanowires with uniform size and small aspect ratio form raftlike aggregates of generally three to five nanowires by aligning side-by-side due to the directional capillary force and the van der Waals attraction.³⁷ As the pressure rises gradually from 0 (II) to 13 mN/m (III) with a slope of 0.26,³⁸ the raftlike aggregates further coalesce and

the nanowires align along long axes in local areas. The pressure rises steeply from 13 mN/m (III) to 40 mN/m (IV) with a slope of 0.73 without a kink due to any phase transition, indicating a formation of a compact monolayer. In the last isotherm (from IV to V) with a slope of 0.6, a small shoulder that seems to be characteristic of collapse appears at about 40 mN/m. The smoothly rising surface pressure suggests, however, that the nanowires do not collapse during compression.³⁹ During expansion, the surface pressure initially declines rapidly from V to VI, and then the monolayer area decreases significantly after relaxation (from VI to VII). Comparing compression and expansion of VO₂ nanowires monolayer, a substantial hysteresis is observed in the π -A isotherm.

Figure 2B provides schematic explanation for the observed hysteretic π -A data recorded during compression and expansion. At zero surface pressure, the nanowires are monodispersed on the trough's water surface with an isotropical distribution (Figure 2B,a). When the nanowires are compressed with increasing surface pressure, the nanowire with uniform size and small aspect ratio approach each other at smaller area and form raftlike aggregates; the raftlike aggregates approach each other and the nanowires are aligned locally (Figure 2B,b). When the surface pressure increases still further, a compact monolayer is formed (Figure 2B,c). However, during expansion, the nanowire monolayer yields raftlike aggregates that do not return to the fully dispersed starting point (Figure 2B,d).

To probe experimentally these ideas, we have carried out scanning electron microscopy (SEM) imaging of nanowires films transferred at different surface pressures to glass substrates. Figure 3 shows typical SEM images of VO₂ nanowire LB films deposited at surface pressures during compression of (a) 15 mN/m and (b) 40 mN/m and (c) at surface pressure during expansion of 2 mN/m. When surface pressure increase from 0 to 15 mN/m during compassion, isotropically distributed VO₂ nanowires approach each other at smaller areas and nanowires with uniform size form raftlike aggregates of generally three to five nanowires by aligning side-by-side (Figure 3a). With the gradual increase of pressure from 15 to 40 mN/m, the nanowires become tightly packed and the compact monolayer is formed (Figure 3b), in which obviously ordered VO₂ nanowire in local area can be seen (the inset of Figure 3b). In the process of expansion, there is a fast decrease in the surface pressure. When the pressure becomes very small (~ 2 mN/m), the nanowires in raftlike aggregates are retained after relaxation (Figure 3c), in which the irreversibility is related to the size of the nanowires. Hence, the SEM data confirm our analysis based on the π -A isotherm.

For comparison, Figure 4A shows the π -A isotherm of VO₂ nanowires only functionalized with SA on water. At the initial stage during compression, the pressure rises gradually from 0 (I) to 11 mN/m (II) with a slope of 0.22. With further compression (from II to III), the increase of the pressure becomes slow with a slope of 0.1. In the last isotherm, the surface pressure increase rapidly from 16 mN/m (III) to 39.5 mN/m (IV) with a slope of 1.6. Figure 4B



Figure 3. Typical SEM images of VO₂ nanowire LB films deposited at surface pressures of 15 mN/m (a) and 40 mN/m (b) during compression and at surface pressure of 2 mN/m (c) during expansion in the pure water subphase. Scale bars represent 2 μ m (a) and 5 μ m (b) and the inset is the high magnification image showing the alignment at local area (scale bar is 1 μ m). In (c), the scale bar represents 5 μ m.

exhibits the typical SEM image of VO₂ nanowire LB films deposited at surface pressures of 39.5 mN/m. It is shown that the surface of the nanowire film is not smooth and some nanowires are aggregated, and the nanowire monolayer is not attained, which is because of the worse monodispersed degree of nanowires functionalized by only SA in comparison with that functionalized by SA and CTAB.

In addition, we have carried out X-ray diffraction (XRD) analyses of the transferred films of VO₂ nanowires functionalized by SA and CTAB to probe for additional structural order. Notably, the typical XRD pattern of VO₂ nanowire Langmuir—Blodgett films at surface pressures of 40 mN/m (Figure 5A,a) only exhibits (00*l*) peaks, while diffraction peaks characteristic of other crystalline planes are absent. These observations contrast XRD analyses of VO₂ nanowires transferred to the same substrates without LB assembly process (Figure 5A,b). Hence, we can conclude that the VO₂ nanowires in LB film have a well-defined (00*l*) crystal plane orientation. To investigate the cause of orientation, we



Figure 4. (A) The π -A isotherm of VO₂ nanowires only functionalized with SA on water. (B) Typical SEM image of VO₂ nanowire LB films deposited at surface pressures of 39.5 mN/m during compression. (Scale bar represents 2 μ m.)

deposited Langmuir–Blodgett film under low surface pressure and the same phenomenon occurred, suggesting that the observed orientation is not caused by pressure. Meanwhile, we also observed the well-defined (00*l*) plane orientation of the transferred films of VO₂ nanowires functionalized only by SA. We speculate that the VO₂ nanowires on water subphase reorient such that their (00*l*) crystal planes are parallel to the water/air interface, which results in the formation of oriented VO₂ nanowire Langmuir–Blodgett film. During the transfer process, this ordered structure remains.

Although the mechanisms for (00l) plane orientation of VO₂ nanowire LB films are still being investigated, we believe that monodispersed functionalization and resulting uniform distribution provide the possibility for orientation of VO₂ nanowire LB film. Because the VO₂ nanowire surface has a large number of O-H bond and V-O bond groups, and the most closely packed (001) crystal planes have the higher energy and more atoms (Figure 5B), SA molecular and CTAB-SA complexes preferentially coordinate to the (001) surface thereby driving the orientation. In order to explain this further, representative TEM and high-resolution TEM images of individual nanowire together with corresponding fast Fourier transformation (FFT) are shown in Figure 5C, exhibiting clear lattice fringes without defects or dislocations and further confirming the nature of high crystallinity. The clearly marked interplanar spacing is 0.35





Figure 5. (A) The X-ray diffraction (XRD) patterns of VO_2 nanowire LB films (a) and as-synthesized VO_2 nanowires without LB assembly (b). (B) The schematic diagram of crystalline structure of B phase VO_2 . (C) TEM image of VO_2 nanowires. (Scale bar represents 20 nm.) The inset of Figure 5c is the nanowire's high-resolution TEM image and the corresponding FFT pattern.

nm, corresponding to the *d* spacing of the (110) plane of monoclinic VO₂ (B), which indicates a [110] growth direction combined with the result of FFT analysis. Obviously, although (110) crystal planes also have the high energy and large amount of O–H bond and V–O bond groups, it seems impossible for them to be parallel to the water surface because (110) crystal planes are the axial end planes of nanowires confirmed by TEM and corresponding FFT

diffraction (see the inset of Figure 5C); otherwise, the nanowires would stand on the water surface in this case, which is not in accord with the lowest barycenter principle.

In conclusion, we have described LB-based assembly of VO₂ nanowires. Compression–expansion π –A isotherms of VO_2 nanowires, which were functionalized with SA and CTAB, on the LB trough indicate hysteretic behavior. SEM investigations of the VO₂ nanowire films transferred at different points on the π -A curve demonstrate with increasing surface pressure there is a transition from well-separated domains of nanowires to compact and locally ordered nanowire monolayers, while raftlike nanowire structures remain after expansion. Interestingly, XRD studies show that VO₂ nanowire LB films exhibit (00l) crystal plane orientation, which is attributed to preferential coordination of SA and CTAB-SA complex to (001) surface of VO₂ nanowires thereby driving to expose (00l) crystal planes parallel to water/air interface. The novel orientation of VO₂ nanowires by LB assembly and the general applicability of this approach to other nanowire and nanotube building blocks could enable the assembly, interconnection, and intergration of a broad range of functional nanosystems.

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