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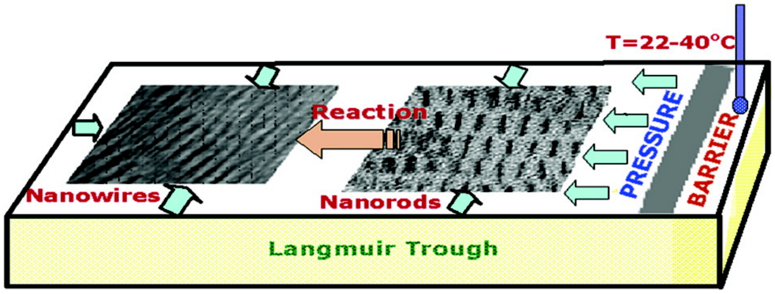

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Two-Dimensional Pressure-Driven Nanorod-to-Nanowire Reactions in Langmuir Monolayers at Room Temperature

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Abstract: Typical two-dimensional surface pressures prevalent within floating monolayer (Langmuir) films are on the order of a few dozen megapascals. One might expect, therefore, that some chemical reactions should be directly and strongly affected by this surface pressure, along with the well-known effect of pressure on the orientational order and the mere proximity of the molecules within the film. Here, we show that the two-dimensional surface pressure in Langmuir films provides a direct driving force, decreasing the activation energy of a cooperative oriented coalescence of ZnS nanorods into nanowires near room temperature. At low film surface pressure or low temperature, the nanorods do not react, while in solution, they react only above 140 °C, even though in all of these cases, the rods are organized in similar super-crystalline clusters. Electron microscopy and measurements of the reaction rates give a detailed picture of the order of the rods, their rearrangement, and their coalescence.

Introduction

Typical two-dimensional (2D) surface pressures (π) prevalent within Langmuir films run up to a few dozen megapascals (~10−50 mN/m acting on a ~1−5 nm thick film). One might expect, therefore, that some chemical reactions should be directly and strongly affected by this surface pressure, along with the well-known effect of pressure on the orientational order, parallel and perpendicular to the film, and the mere proximity of the molecules within the film. Some work involving reactions in "floating" Langmuir films has been carried out over the years.[1−20] Related studies focused on the production of particulate films under monolayers.[21−25] Most of these reactions involve compounds (reagents, initiators, catalysts, etc.) located in the subphase and are usually not confined entirely to the monolayer itself. Several involve a supply of precursors[1,3−5] or catalysts[2−4,15,16] from the ambient subphases. Others require an external initiator/driving force (for example, an oxidant,[10−14,20] a reductant,[23,25] or photons,[6−8,15,17]). At times, an external input of precursors, initiators, and a driving energy source is needed at once.[9] Most importantly, in the large majority of these cases, the surface pressure, when addressed at all, does not seem to have a direct effect on the reaction, except through its indirect effect on the orientation of some of the reacting molecules and, of course, the proximity effect. In this sense, these reactions in Langmuir films resemble analogous reactions taking place in self-assembled monolayers (SAMs)[26] where the proximity and orientational effects are dominant, while the 2D pressure is not controlled. Here, we report on an oriented coalescence reaction between capped nanorods contained within a Langmuir film, which is directly induced by the two-dimensional surface pressure. This is a 2D analogue of high-pressure reactions in bulk, especially when the free energy of the reaction and/or its transition state are pressure-dependent.[27] Furthermore, we show that in the film, this coalescence reaction occurs at nearly ambient temperatures (20−40 °C), while the same reaction in the bulk (at ambient pressure) proceeds only at much higher temperatures (typically above 140 °C).[28] We present evidence

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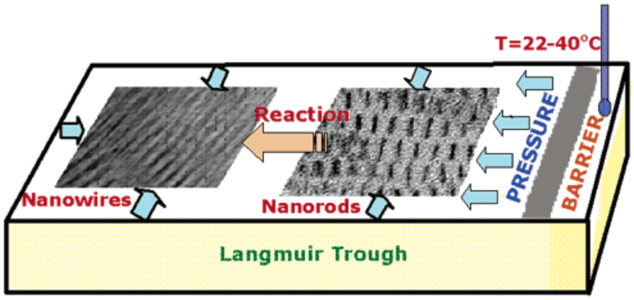

Figure 1. Cartoon of the rod-to-wire coalescence under the two-dimensional pressure in a Langmuir film of the nanorods.

that the reaction in the film is predominately a direct effect of the pressure, by comparison to the results at low surface pressures or at low temperatures (when local relative particle position and ordering are still maintained). We follow the kinetics of the reaction as a function of temperature, estimate the activation energy, and discuss the effect of the pressure on it. Transmission electron microscopy (TEM) provides detailed images of the reaction in parallel with the measurement of the reaction rates and the analysis of the kinetics.

The reaction we discuss is a transition of highly uniform (~1 × 5 nm) ZnS nanorods, capped with octadecylamine (ODA), into 100−200 nm long nanowires, retaining the extremely narrow nanowidth of the rods. This coalescence is reported here to occur in floating monoparticulate Langmuir films near room temperature, as shown in the cartoon in Figure 1.

Recently, we have shown[28] that in solution, this process takes place at temperatures above ~140 °C in super-crystalline clusters of the rods (of a structure similar to that observed in the Langmuir films). Here, we demonstrate driving these reactions by the high 2D pressure in the Langmuir films of the rods near ambient temperatures. The coalescence involves a decrease in the total area by 34−45% in the reaction temperature range of 22−40 °C, respectively, and thus can be driven by the 2D pressure even at relatively low temperatures.

One-dimensional nanostructures, such as nanorods, nanowires, and nanotubes, are expected to have unique properties due to quantum confinement in two directions and a gradual transition to the classical limit in the third (quantum wires). They also are expected to play an important role as components in fabrication of future nanoscale electronic and optronic devices. Thus, the study of these nanostructures, their reactions, and their properties is of considerable importance, scientifically and technologically. The use of the Langmuir film and the reaction in it produce a highly ordered 2D array of rods and/or wires of ~1 nm width, with a controlled (nano)distance between the particles, extending over large regions, on the order of a micron. Though this is not the focus of this report, note that such systems can provide a convenient basis for nanoscale surface patterning and derivatization.

Experimental Section

Highly uniform ZnS nanorods were synthesized from zinc ethylxanthate in ODA.[28] The rods are single crystal 1.2 ± 0.05 nm wide and 5.0 ± 0.15 nm long. The ODA coating stabilizes the rods and renders them hydrophobic, thus facilitating their spread on an aqueous subphase as Langmuir films. It also controls the distance between the rods. We subject these films to various surface pressure and temperature regimens, follow the change in film area as a function of time, and eventually view the products by TEM (JEOL 2010 HR-TEM, equipped with a Gatan CCD camera). We used a dual trough LB balance (Labcon). About 300−500 μL of ODA-capped nanorod suspension in chloroform/dichloromethane was spread dropwise at the air−water interface using a microsyringe. The LB single film transfer onto TEM grids was carried out at surface pressures of 0−50 mN/m and at 5−40 °C, at a dipping speed of 1 mm/min. A TEM grid (Ted Pella, 01883F, lacey carbon, 300 mesh) was temporarily glued onto a clean glass microscope slide, and a primer layer of ODA was deposited onto them.

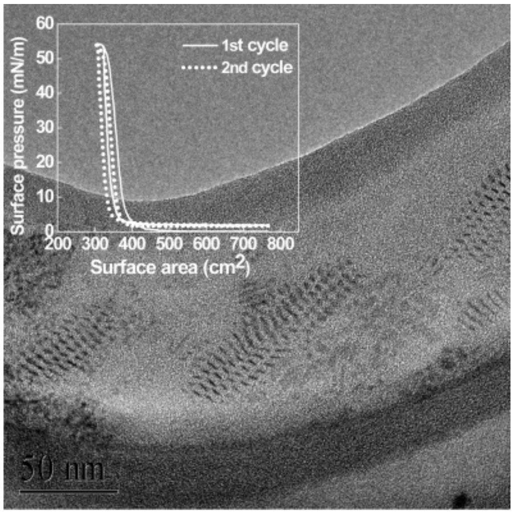

Figure 2. TEM image of ZnS nanorod islands deposited at $\pi = 0$ mN/m at 22 °C. Inset: the surface pressure/area (π−A) isotherm at 5 °C.

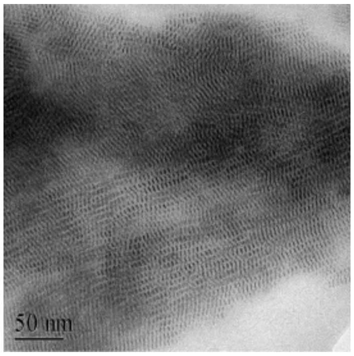

Figure 3. Representative TEM image of ordered nanorods at a surface pressure of $\pi = 25$ mN/m and at 22 °C. The deposition was performed without allowing any significant time for reaction to occur.

Results and Discussion

Figure 2, taken at low surface pressure, shows that the samples consist of well-defined rods which tend to order in super-crystalline rafts. Islands of ordered super-structures are observed with equally spaced parallel rods arranged in rows. The rods arrange in rows so that each rod is positioned between two neighboring rods in the adjacent rows. Reorientation of the rods to a head-to-tail alignment is observed in some limited regions (Figure 2, center). This is a precursor state for the subsequent coalescence.[28]

The insert of Figure 2 shows that at low temperature, when the coalescence reaction is slow, the π−A isotherms are reversible with hardly any hysteresis.

Figure 3 shows that upon compression (to 25mN/m), the individual islands of ordered rods merge to give large (over

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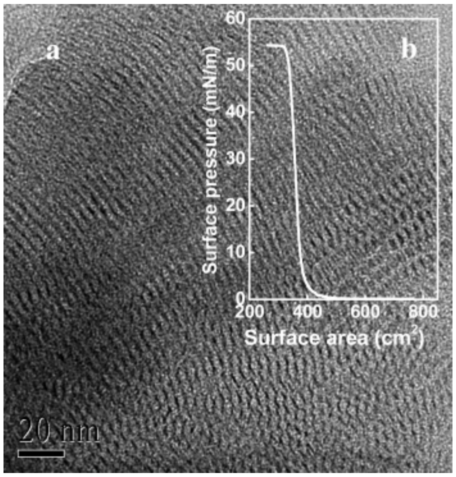

Figure 4. Nanorods deposited on a grid subjected to a surface pressure of 50 mN/m for 1 h at 22 °C. (a) A TEM image of the film showing realigned, head-to-tail regions of nanorods (lower right) and some transformation into short nanowires, consisting of 3−5 nanorods (center). At the top left, ∼50 nm nanowires are observed. (b) Surface pressure/surface area isotherm at 22 °C.

0.5 μm) ordered super-crystalline regions of rods, usually retaining the local structure of the original rafts. The original super-crystalline structure of the nanorods is maintained over large areas, with remarkable registry. However, in some areas (top right in Figure 3), some of the rods have rotated so that they assume a head-to-tail position. This appears to be a cooperative, concerted effect, occurring in tandem over a whole neighborhood. The realigned regions at this higher pressure are larger and more frequently observed compared to those of the low surface pressure.

Figure 4a shows nanorods deposited on a grid subjected to a surface pressure of 50 mN/m for 1 h at 22 °C. Compression to 50 mN/m fully aligns the nanorods in the rotated end-to-end position over almost the entire sample, and short wires consisting of 4−5 rods become apparent. Longer wires (∼50 nm) are also observed in some regions (top left of Figure 4a) where apparently the reaction is well-advanced. The widths of the nanowires are the same (1.2 nm) as those of the precursor nanorods. The tip-to-tip distance between the rods or the short wires appears to be considerably smaller than that observed in the relaxed samples. Figure 4b shows the surface pressure/surface area isotherm at 22 °C. The surface pressure ($\pi = 50$ mN/m) is nearly the collapse pressure of the film in the corresponding surface pressure/surface area ($\pi - A$) isotherm. The isotherm suggests that at large areas, the rods form individual islands that exert a vanishing pressure. When the islands start to touch at smaller areas, the pressure increases very steeply. This is in agreement with the islands observed in Figure 2 (large area) and the extended commensurate regions shown in Figure 3 (compressed film). The transfer ratios we measure at 25 and 50 mN/m are 0.97 and 1.08, respectively.

Previously, the phase behavior of hard rods[29] has been studied experimentally[30] and by simulations.[31] Side-by-side entropically driven ordering in nematic and smectic liquid crystalline phases was found. In contrast, we observe a super-crystalline state even at zero or low surface pressure, suggesting that the interparticle interactions override the entropy. However, more unusual, at high pressure, we find that the rods realign along their long axis in an end-to-end arrangement. This suggests that the alkylamines adsorbed on the caps of the ZnS rods are perhaps less dense than those along the main body of the rods (maybe because of the local curvature). This explains the relatively short end-to-end distances between the rods in adjacent rows and might hint at the reason for the subsequent coalescence, especially at the higher temperatures. The curvature and the specific crystal plane exposed at the tip might also render it more reactive, and the alkylamines might be less adsorbed to it or are probably more labile (facilitating the coalescence). This conclusion is supported by the mere fact that in our original synthesis of the ZnS particles, they grow as very narrow rods in the amine solvents.

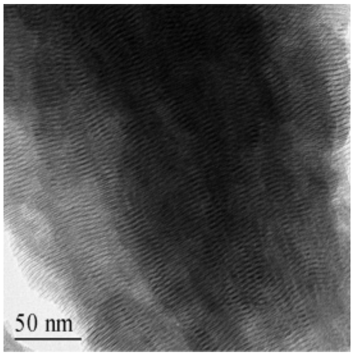

Figure 5. TEM image of close-packed nanowires formed from ZnS rods in the Langmuir film by compression to 50 mN/m at 40 °C for 60−90 min.

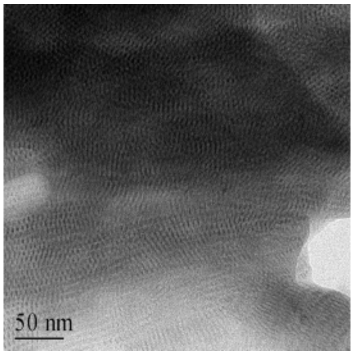

Figure 6. TEM image of a Langmuir film of nanorods kept at 5 °C and 50 mN/m for 60−90 min.

Figure 5 shows the final state, when practically all of the rods in the film coalesced into 100−200 nm long wires at a temperature of 40 °C and $\pi = 50$ mN/m. The wires assemble in large ordered regions with parallel wires. The wires are as narrow as the original rods (1.2 nm), and the interwire separation is similar to that observed with the rods (3.9 ± 0.2 nm).

In contrast, when the same experiment is performed at 5 °C, the nanorods remain intact and maintain their super-crystalline arrangement (Figure 6). Thus, a bona fide activated reaction is taking place, where temperature plays an important role alongside the surface pressure. This is expected since coalescence requires desorption of the capping molecules from the ZnS rods and perhaps some rearrangement of the metal and sulfide cores. Note that keeping the Langmuir films at low surface pressure (<25 mN/m) does not produce wires out of

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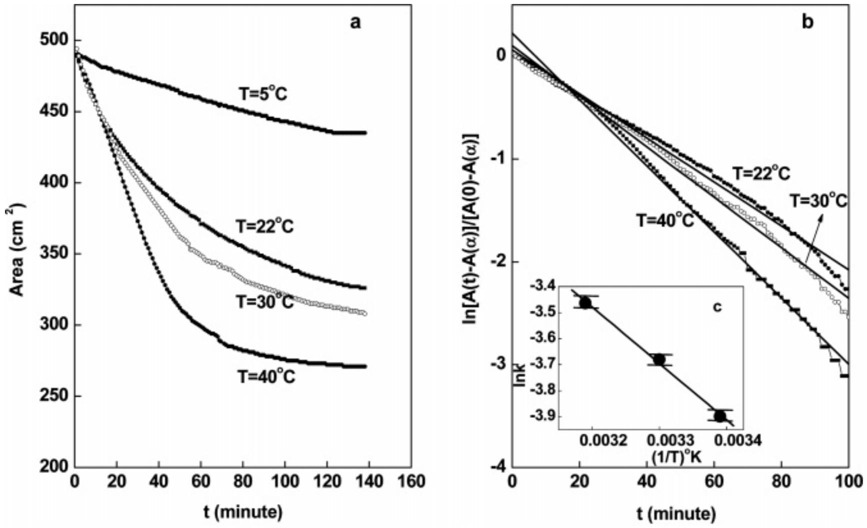

Figure 7. Kinetics of the change in surface area of a ZnS nanorod monolayer compressed to a constant surface pressure of 50 mN/m at different temperatures. (a) Area decrease with time. (b) First-order kinetics analysis of the area versus time. (c) Arrhenius plot analysis.

the rods, even at 40 °C. Pressure is certainly important for driving the reaction at a measurable rate.

Figure 7a shows that at a set surface pressure (50mN/m), the area of the films decreases with time at a rate that increases with temperature. We associate this decrease of the area to the compacting effect of the coalescence of the rods into wires. In agreement with the TEM micrographs, the degree of coalescence (i.e., the length of the wires and the reduction in the area) increases with the reaction temperature. From Figure 7a, we measure an area reduction of ~45, 39, and 34% at 40, 30, and 22 °C, respectively. Since we did not see any wires in micrographs of films compressed at 5 °C, we attribute the slow change of the area at this low temperature to rearrangement of the rods in the film (squeezing out defects, etc.) practically without coalescence. In the following kinetics analysis, we subtract this “physical” decrease of area from the area versus time curves at the higher temperatures.

We carry out a first-order kinetics analysis of the results (Figure 7b):

$$[A(t;T) - A(\propto;T)]/[A(0;T) - A(\propto;T)] = k(T) \qquad (1)$$

$A(t;T)$ is the area of a film kept at a temperature T measured at time t. $A(\propto;T)$ is the value of the area measured at long reaction times (the asymptotic area, presumably the area occupied by the wires formed at temperature T). In the actual analysis, we normalized all of the areas to $A(0;T)$ and corrected for the area changes measured at 5 °C, as noted above.

The analysis shows that, indeed, the coalescence follows first-order kinetics with rate constants, $k(T)$, of 0.021, 0.025, and 0.033 min^{-1} at 22, 30, and 40 °C, respectively. An Arrhenius analysis of the rate constants (Figure 7c), $k(T) = \nu\ \exp(-E_a/kT)$, with ν being a frequency factor and E_a the activation energy, yields an activation energy of 17.6 ± 0.6 kJ/mol. In the bulk experiment,[28] the same reaction occurs in comparable rates only at temperatures of 140−170 °C. Since in the experiment in solution the rods are clustered in super-crystalline clusters similar to those we find also in the Langmuir films, we assume that the same reaction mechanism holds in both cases, with approximately the same frequency factor. This simplifying assumption allows one to estimate approximately the activation energy for the coalescence reaction in the clusters in solution using the value found in the film.

$$\nu\ \exp[-E_a(\text{solution})/kT_{\text{solution}}] \approx \nu\ \exp[-E_a(\text{film})/kT_{\text{film}}] \quad (2)$$

$$E_a(\text{solution}) \approx E_a(\text{film})T_{\text{solution}}/T_{\text{film}} \qquad (3)$$

Taking the experimental values of $E_a(\text{film}) = 17.6 \pm 0.6$ kJ/mol, T_{film} in the range 295−313 K (20−40 °C), and T_{solution} in the range 413−443 K (140−170 °C), we obtain E_a(solution) = 23−26 kJ/mol. Thus, the difference between the activation energies in the bulk and in the compressed film is ~6−9 kJ/mol.

Presumably, this difference in the activation energy originates from the compression of the film and the free energy associated with it. The alkylamines, which are released from the rod tips to enable the coalescence, need to relocate. Since the collapse pressure of ODA is above 55 mN/m, they certainly remain in the film. We cannot tell whether they readsorb onto the sides of the rods remaining in the film or form separate 2D phases. We believe the former is more probable.

We can estimate the free energy change independently on the basis of the actual surface pressure we applied (~50 mN/m) and the typical reduction of the initial compressed area (490 cm^2) at the various temperatures. From Figure 3, there are ~100−110 ZnS rods in an area of 50 × 50 nm^2. Thus, the projected area per rod in the film or cluster, including its passivation layer of the amine, is ~25 nm^2. This value is consistent with a width of ~4 nm and a length of ~6 nm of the ODA-capped rods. The tips of the rods (with diameter of 1.2 nm) can adsorb ~10−20 amines (with a typical area of 0.2 nm/molecule). Thus, there are $\sim 3 \times 10^{16}$ alkylamine molecules, $\sim 5 \times 10^{-8}$ mol, adsorbed on the tips in the original area of 490 cm^2 on the trough. Putting all of this together, the molar free energy change associated with the pressure−area work in the film ($\pi\Delta A$) is ~20 kJ/mol. This value is of the same order of magnitude as the change in the activation energy due to the compression (6−9 kJ/mol). In fact, the agreement is surprisingly good, better than we would expect with the rough estimates we made. We, therefore, regard it only as a qualitative indication of the plausibility of our understanding of the results. Thus, we see that the surface pressure of the film indeed can significantly affect the activation energy of the coalescence and speed up that reaction, as observed experimentally. Note that one would expect the effect of the pressure–area work on the activation energy to be smaller than its contribution to the total free energy of the reaction. This feature too was captured by our rough estimates (with a reasonable Brönsted symmetry coefficient of 0.3–0.45).

The only comparison we are aware of between the activation energy for a reaction in the bulk and a similar one at the water–air surface[16] reported for an amide bond formation at 12 mN/m, a decrease from ~41–8 kJ/mol. It appears to be much too large to be accounted merely by the direct action of the surface pressure. Most likely, the detailed mechanisms in bulk and on the surface are different. A few other cases reported surface activation energies[1,2,11,12] and discussed them in terms of proximity and orientation effects. What is perhaps worthy of note in our present context is that activation energies were found to increase with surface pressure by ~25 kJ/mol with a pressure change of 12.8 mN/m for the hydrolysis of trilaurin,[1] and by 13 kJ/mol with a pressure change of 20 mN/m for the polymerization of pentadecylaniline monolayers. The former is much too large to be explained by a simple, direct effect of the surface pressure. The latter shows variation in the same order of magnitude as we observe. However, their activation energy (and enthalpy of activation) increases with pressure, even though the rate constants also increase. This suggests that in their reaction, the pressure acts in a rather complex and indirect manner, as indicated by the large negative change in the entropy of activation with pressure. In the present coalescence reaction, the pressure appears to operate in a more straightforward manner.

It is worth noting that when we use a shorter alkylamine, dodecylamine (DDA), instead of ODA, as the capping agent, the coalescence reaction in the Langmuir film is faster (results not presented here). The reaction also exhibits a weaker temperature dependence, suggesting a smaller activation energy compared to that of the case of ODA, as might be expected since the rod–rod distance is smaller with DDA. Incidentally, with DDA, the reduction of the area due to the coalescence is also smaller than with ODA, ~26% compared to 34% at 22 °C, respectively, as is expected from the shorter alkyl chain length.

In summary, we have shown here a unique reaction in a monoparticulate film, driven directly by the 2D surface pressure which decreases the free energy of the reaction by ~20 kJ/mol and its activation energy by ~6–9 kJ/mol compared to the same process in clusters in the bulk (with an estimated activation energy of ~23–26 kJ/mol). The reaction in the film thus proceeds at room temperature, while in the bulk, it takes place at a comparable rate only above 140 °C. The reaction obeys first-order kinetics. The effect of the surface pressure is not a simple alignment or proximity effect since the rods are already aligned in the bulk and in rafts at low pressure in the Langmuir film. It appears that the pressure induces an orientational, cooperative "phase transition" to a less stable state, affecting the arrangement of the capping molecules at the tips of the rods or their partial desorption. In this intermediate state, the rods are mutually aligned in an orientation convenient for coalescence, and they readily join, provided that the temperature is sufficiently high (though considerably lower than required in an analogous bulk reaction). The rods form extended 2D super-crystalline arrays and transform into highly ordered, parallel wires, retaining the ~1 nm width.

Summary

In this report, we show a unique reaction where two-dimensional surface pressure in Langmuir films provides a direct driving force in the coalescence of ZnS nanorods into nanowires. The activation energy of a cooperative oriented coalescence decreases during this process. At low film surface pressure or low temperature, the nanorods do not react, while in solution, they react only above 140 °C, even though in all of these cases, the rods are organized in similar super-crystalline clusters. Electron microscopy and measurements of the reaction rates give a detailed picture of the order of the rods, their rearrangement, and their coalescence. The ability to arrange the nanorods in one direction could be an important aspect in the design of nanoelectronic devices. It is a very simple and highly convenient way to produce nanowires of such low dimension with high aspect ratio in the nanoregime in a highly controllable fashion near room temperature.

Acknowledgment. We thank Narayan Pradhan and Asit Baran Panda for the synthesis of the ZnS rods.

Supporting Information Available: Additional figure showing wires produced from coalescing nanorods. This material is available free of charge via the Internet at http://pubs.acs.org.

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