Nanostructures

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Synthesis of Nanoscopic Optical Fibers Using Lipid Membranes as Templates**

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Nanostructures of various materials with different sizes and shapes have been synthesized and studied in the past few years as a result of their high impact in optoelectronic applications. In particular, one-dimensional (1D) nanostructures (nanowires, nanorods, nanotubes, etc.) show optical and electronic properties[1] that are of importance to downsize optoelectronic components to the nanometer scale.[2] The development and integration of such 1D nanostructures relies on suitable synthetic procedures. Several methods have been designed such as template-directed synthesis,[3–6] solvothermal synthesis,[7] microfabrication,[8] metal-nanocluster-catalyzed growth,[1a] and surfactant-mediated self-assembly.[9] In particular, template-directed synthesis offers significant advantages: ease of performance, the possibility to work under mild reaction conditions, and above all the control over unique, well-defined morphologies of the resulting nanostructures. Various kinds of templates, such as porous alumina,[3] molecular sieves,[4] proteins,[5a] DNA,[5b] viruses,[5c] and self-assembled monolayers,[6] have been reported to guide the synthesis of 1D nanostructures. The critical issues in many template-directed syntheses are to obtain high yields and to achieve monocrystallinity.

Until now, lipid bilayers have not been used as templates for asymmetric synthesis although they are well-known self-organized nanostructures. The closed compartments of single phospholipid vesicles have already been used as nanoreactors to perform simple chemical reactions.[10,11] Upon drying from aqueous dispersions, many phospholipids spontaneously form well-organized periodic multilayers of lipid membranes separated by distinct nanometer-thick water films.[12] The rich variability of the lipid hydrocarbon chains and lipid polar head groups results in numerous lyotropic and thermotropic phases.[12] Of particular interest in the present context are lipid polar head groups that bind certain cations selectively and reversibly. This opens the possibility to modulate the concentration of precursor ions, for example, when a second reactant is added, and thus control the synthesis of nanomaterials in the confined, nanometer-sized water films of multilamellar lipid phases. Here, we have applied this strategy to synthesize high-aspect-ratio (≈ 1000) cadmium chloride nanowires, which exhibit interesting optical properties when doped in situ with fluorescent CdS quantum dots.

The nanowires were synthesized in hydrated, multilamellar stacks of lipid bilayers comprising lipid-bound Cd^{2+} ions. A proper design of the lipid template was crucial for the formation of nanowires. The lipid bilayers comprised 70 mol% of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC), which acts as a stable matrix, and 30 mol% of a thiolipid, 1,2-dilauroyl-*sn*-glycero-3-phosphothioethanol (DLPSH), which was added for its strong ability to bind Cd^{2+} ions through the -SH groups (see Supporting Information). With a molar ratio of lipid/Cd^{2+} of about 2, large quantities of Cd^{2+} ions were complexed by the lipid head groups. Upon exposure to HCl vapor, Cd^{2+} ions were released as a result of competitive binding of protons to the polar lipid head groups,[13] leading to supersaturation of Cd^{2+} ions in the nanometer-sized water film and finally to the initiation of growth of nanowires. When either the concentration of Cd^{2+} was reduced by a factor of two or DLPSH was omitted, no nanowires were formed which shows that a critical concentration of Cd^{2+} is necessary (see Supporting Information).

The nanowires show high aspect ratios with a narrow distribution of diameters ranging from 80 to 200 nm and lengths extending up to 170 μm (Figure 1a). The lengths of the nanowires could be tuned by varying the duration of exposure to HCl while the diameters showed little variation. Transmission electron microscopy showed that the nanowires are monocrystalline along their entire lengths (Figure 1b). Selected-area electron diffraction patterns revealed that the nanowires are composed of orthorhombic $CdCl_2 \cdot 4H_2O$ crystals grown along the [100] direction (Figure 1c).

The synthesis of anisotropic structures requires that the template, here the lipid lamellar phase, restricts or promotes the growth in specific directions. Orthorhombic $CdCl_2 \cdot 4H_2O$ consists of [001] molecular chains formed by edge-sharing $[CdCl_4(H_2O)_2]^{2-}$ octahedrons (Figure 2a) that define a preferential growth direction along the octahedral chain axis to result in slightly elongated crystals of $CdCl_2 \cdot 4H_2O$ when

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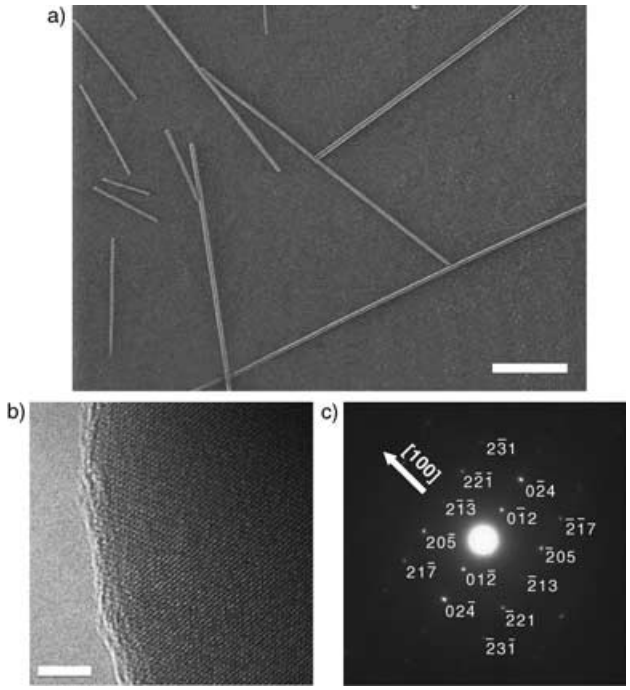

Figure 1. a) Scanning electron micrograph of typical $CdCl_2{\cdot}4\,H_2O$ nanowires illustrating the high aspect ratios. In this particular image, diameters of the nanowires are around 100 nm and lengths range from 1.5 μm up to more than 20 μm (scale bar = 2 μm). b) High-resolution transmission electron micrograph of the edge of a nanowire showing the regular atomic arrangement in the crystal lattice (scale bar = 5 nm). c) Selected-area electron diffraction pattern on a nanowire, with indexation corresponding to orthorhombic $CdCl_2{\cdot}4\,H_2O$. The arrow indicates the [100] direction, which is the long axis as well as the growth direction of the nanowires.

grown in aqueous solution.[14] It is remarkable that the growth direction of our nanowires is perpendicular to the preferential growth direction of bulk $CdCl_2$ crystals. Online monitoring of the synthesis of nanowires indicates that the initiation of growth critically depends on a rate-limiting step. Two sequential phases were observed with the rapid appearance of small nucleation points followed, after a certain delay, by the sudden and continuous, nonsynchronous 1D growth of the crystals (see Figure 2b and Supporting Information). By using fluorescent lipids, a close colocalization of lipids and nanowires was observed which demonstrates that the lipid membranes are intimately involved in the growth of the nanowires (Figure 2c). Taking these observations together, we propose a mechanistic model for the unusual, asymmetric growth of the nanowires. $CdCl_2{\cdot}4\,H_2O$ crystal nuclei grow unperturbed up to a critical size, at which point a collective binding of numerous protonated, positively charged head groups of the planar lipid membranes to the crystal planes that are rich in Cl^- (i.e. high negative-charge density) becomes favorable. This occurs for all crystal planes except the (100) plane, in which Cl^- ions are shielded by a layer of coordinated water molecules, thus inhibiting growth in these directions.

While $CdCl_2{\cdot}4\,H_2O$ crystals are nonfluorescent, CdS compounds and particularly their nanocrystals, show size-dependent fluorescence. To provide the nanowires with fluorescence properties, HCl vapor was supplemented with H_2S during the growth process. As a result, the nanowires became intensely fluorescent with high photostability as shown in the confocal image of Figure 3a, while a weak diffuse background fluorescence was observed within the lipid bilayer stacks. The diffuse fluorescence in the lipid stacks featured a broad emission band upon excitation at 458 nm, with a maximum at 522 nm typical for CdS nanoparticles (see Figure 3b and Supporting Information). TEM images revealed a heterogeneous mixture of crystallites of CdS nanoparticles (Figure 3c). Single nanoparticles were also detected by optical microscopy at high excitation intensities as diffraction-limited spots[15] in the middle of a fluorescent background (see Figure 3d and Supporting Information). The nanowires exhibited spectra that are identical to that of the diffuse background in the lipid stacks which shows that their fluorescence results from associated CdS nanoparticles. No nanoparticles could be observed by TEM on the surface of the nanowires which suggests that they intercalate in the $CdCl_2{\cdot}4\,H_2O$ lattice during crystal growth (see Supporting Information).

The extended length of the nanowires as well as their diameter, which is on the order of 100 nm, make them

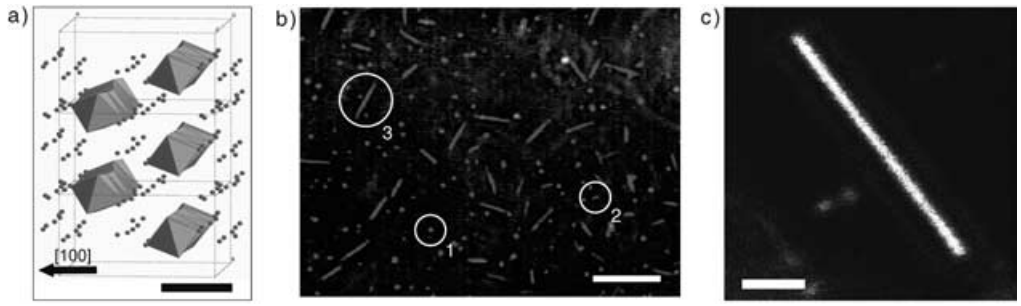

Figure 2. a) Crystal structure of orthorhombic $CdCl_2{\cdot}4\,H_2O$ showing the 1D molecular chains formed by edge-sharing $[CdCl_4(H_2O)_2]^{2-}$ octahedrons. The arrow indicates the [100] growth direction (scale bar = 6 Å; see Supporting Information for a more-detailed crystal structure). b) White-light transmission image of growing nanowires. As the initiation of growth is asynchronous, the various phases of the growth of the nanowires are present in a single image. Growth of nanowires occurs in two distinct steps: first, numerous nucleation points appear (1); after a while, some nucleation points grow into small nanowires (2); these latter continuously elongate upon addition of HCl vapor (3) without noticeable change in the diameter (scale bar = 60 μm). c) Fluorescence confocal image showing colocalization of a nanowire and rhodamine-labeled lipids (scale bar = 2 μm, λ_{ex} = 543 nm, λ_{em} = 560–610 nm).

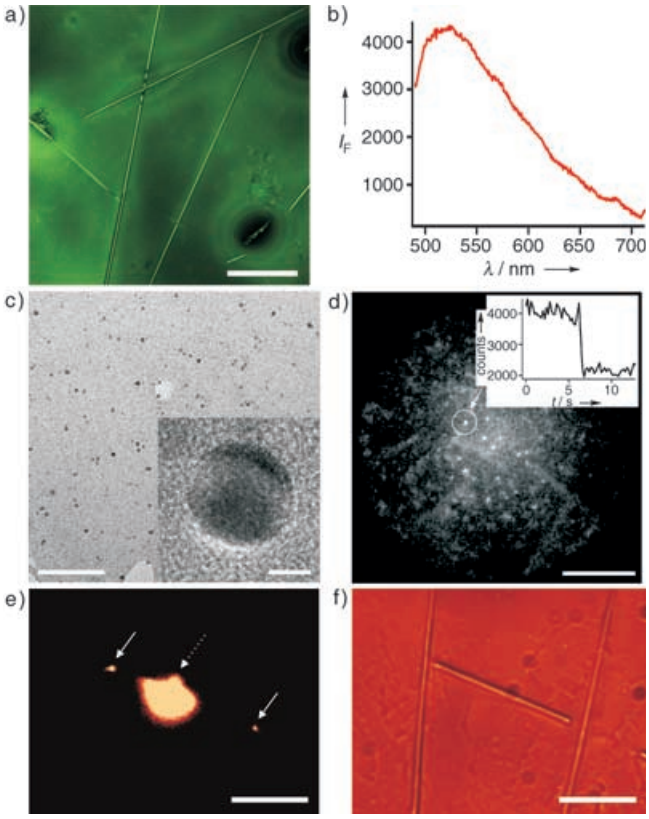

Figure 3. a) Fluorescence confocal image of nanowires (false color) grown in presence of H_2S showing that the as-prepared 100 μm-long nanowires are intensely fluorescent (scale bar = 20 μm, λ_{ex} = 488 nm, λ_{em} = 505–550 nm). b) Fluorescence emission spectrum of a single washed nanowire upon excitation at 457.9 nm. The emission maximum is at 522 nm with a full width at half-maximum larger than 100 nm. The spectrum of the fluorescent background is identical. c) Transmission electron micrograph of the background lipid multilayers showing the presence of a heterogeneous mixture of nanometer-sized CdS crystallites (scale bar = 200 nm). The inset shows the high-resolution transmission electron micrograph of a CdS nanoparticle (scale bar = 5 nm). d) Wide-field image showing single quantum dots, recognized as diffraction-limited spots, which appear in a structureless fluorescent background. Only a small fraction of the quantum dots is observed at the single-quantum-dot level owing to the stringent requirements for such observations, while the major fraction contributes to the structureless fluorescent background. The inset shows a time trace of the emission from the encircled quantum dot which features the characteristic single-step photobleaching (scale bar = 10 μm, λ_{ex} = 457.9 nm, integration time = 100 μs, measurement frequency = 5 Hz). e) False-color photoluminescence image of a nanowire upon local excitation at the middle (dotted arrow) with excitation at 488 nm. Luminescence is observed at the excitation location (dotted arrow) and from both ends (solid arrows) as result of optical waveguiding along the nanowire (scale bar = 10 μm). f) The corresponding false-color white-light transmission image of the nanowire (scale bar = 10 μm).

attractive candidates for optical waveguiding.[1a,16] When fluorescent nanowires were locally excited, fluorescence emission was detected not only at the excitation spot but also from the ends of the nanowires (Figure 3e and f). Nanowires waveguide light over tens of micrometers, thus acting as effective nanoscopic optical fibers. The ability to waveguide light is associated with the high refractive index of the nanowires, n_{nw}, which is expected to lie between the refractive indices of pure $CdCl_2 \cdot 2.5\,H_2O$ ($n = 1.65$) and CdS ($n = 2.5$). The corresponding minimal diameters, D, needed for the nanowire to act as a single-mode optical waveguide at the emission maximum at $\lambda = 520$ nm are thus between 80 and 190 nm by using the relationship, $D = (\lambda/\pi)(n_{nw}^2 - n_{medium}^2)$, where n_{medium}, the refractive index of the medium, is 1.4. The range of diameters found for the nanowires fall well within the theoretical sizes of the optical waveguides.

In conclusion, a novel synthetic route for state-of-the-art nanowires has been presented based on lipid membranes as an anisotropic template. This allows a straightforward, high-yield production of high-aspect-ratio monocrystalline nanowires under mild reaction conditions. The synthesized $CdCl_2 \cdot 4\,H_2O$ nanowires can be furthermore endowed with fluorescent properties by addition of H_2S. The appearance of highly fluorescent CdS quantum dots demonstrates that such nanoparticles can be synthesized in the confined interlamellar water film which might open novel synthetic routes for quantum dots. Our fluorescent nanowires could find a broad range of applications in optoelectronics, for instance in the development of nanolasers, as a complement to CdS nanowires.[1a] We furthermore speculate that this novel procedure using lipid membranes as templates may be extended to the synthesis of other materials by exchanging the thiolipid with other lipids that have suitable head groups which reversibly bind various ions. The possibility to manipulate the nanowires laterally, for instance by using laser tweezers (see Supporting Information) encourages the use of these nanowires for the nanofabrication of devices. In this respect, particularly attractive are the recent developments to form networks of lipid vesicles and lipid nanotubes,[11] which may be used as a template to build an array of connecting nanowires, opening a way to preassemble nanocomponents for future optoelectronics.

Experimental Section

Synthesis of nanowires: Solutions of DMPC (4 mM (Fluka); 100 μL) and DLPSH (16 mM (Avanti Polar Lipids); 10 μL) in chloroform were mixed and dried in vacuum, and the resulting lipid film was hydrated in deionized water (110 μL) at room temperature for 10 min. An aqueous solution of $CdCl_2$ (10 mM (Fluka); 30 μL) was added, then the mixture was dispersed for 5 min in a bath sonicator. A 15-μL aliquot of the obtained clear solution of vesicles was transferred onto a microscope glass coverslip and dried in vacuum. The resulting transparent lipid film was rehydrated in a 100 % humid atmosphere in a closed desiccator at 60 °C for 3 h. Then, a recipient containing 32 % hydrochloric acid (Merck) was inserted in the desiccator, and the lipid film was incubated for another 2 h with maintained humidity while the temperature was slowly decreased from 60 °C to room temperature. To produce fluorescent nanowires, the procedure was identical except that HCl was mixed with a small flake of FeS (Fluka, Germany) to produce H_2S while the dessicator was evacuated (400 mbar) to enhance the production of H_2S. A typical synthesis yielded around 1×10^6 nanowires of which 10–20 % showed lengths that exceeded 20 μm (see Supporting Information). Changing the ratio of DLPSH to DMPC reduced the yield and afforded shorter nanowires. Lipids could be removed from the produced nanowires by washing with toluene (Fluka). To observe colocalization of lipids and

nanowires, 1% rhodamine-labeled lipids (TRITC-DHPE, Molecular Probes) was added. See Supporting Information for further experimental details.

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