Chemical Nano-Gardens: Growth of Salt Nanowires from Supramolecular Self-Assembly Gels

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ABSTRACT In this article, we examine the phenomenon of single-crystal halide salt wire growth at the surface of porous materials. We report the use of a single-step casting technique with a supramolecular self-assembly gel matrix that upon drying leads to the growth of single-crystal halide (*e.g.*, NaCl, KCl, and KI) nanowires with diameters ~130—200 nm. We demonstrate their formation using electron microscopy and electron-dispersive X-ray spectroscopy, showing that the supramolecular gel stabilizes the growth of these wires by facilitating a diffusion-driven base growth mechanism. Critically, we show that standard non-supramolecular gels are unable to facilitate nanowire growth. We further show that these nanowires can be grown by seeding, forming nanocrystal gardens. This study helps understand the possible prefunctionalization of membranes to stimulate ion-specific filters or salt efflorescence suppressors, while also providing a novel route to nanomaterial growth.
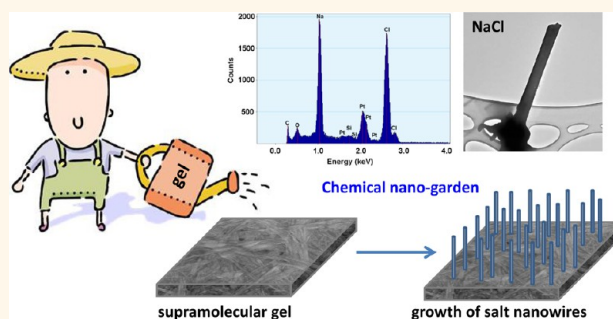
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The chemical garden, a terminology known by most children and applied to the crystal growth of inorganic salts that have plant-like hollow fiber forms, was first observed by Johann Rudolf Glauber in 1646.[1] In its original form, the chemical garden describes a process that takes place between crystals of ferrous chloride ($FeCl_2$; though many other salts can be used) in an aqueous solution containing silicate or aluminate anions. This growth solution leads to the formation of crystals that grow upward by breaking through an insoluble semipermeable membrane consisting of colloidal metal silicate material. Today, membranes are typically formed using polymeric materials through the polymerization of one or more "*single*" monomers, to yield closely packed and dense networks (or materials) with various physical properties. Equivalently, gels are colloidal material formed from single molecules, or gelators, that gelate in the presence of liquid, such as water in the case of hydrogels. These give rise to the formation of novel macroscopic materials

which are mostly liquid in composition.[2,3] Over the past decade, supramolecular self-assembly processes driven by the use of noncovalent reversible bond formation between molecules have been employed in the formation of supramolecular polymers.[4,5] Such polymers are formed from one or more complementary building blocks, also referred to as low molecular weight gelators (LMWGs), generated through intermolecular interactions using weak forces such as hydrogen bonding, $\pi-\pi$ stacking, *etc.* as well as coordination bonds. These can subsequently give rise to the formation of further highly ordered self-assembled materials through intramolecular interactions leading to the generation of one-, two-, or three-dimensional structures and networks.[6–8] It is well-established that gels made from *classical gelators* such as agarose, polyacrylamide gelatin, silica, *etc.* can also be used in the growing of crystals, a method commonly used for instance in the crystallization of proteins for use in X-ray crystallography.[9] However, the use of supramolecular

self-assembly gels for such an application is quite recent and of particular interest because supramolecular gels are formed through reversible bond formation. This allows an external *trigger* by changes in pH, temperature, sonication, *etc.* that may lead to dissociation of the gel, facilitating the isolation of the crystals. Steed and co-workers have recently demonstrated that supramolecular gels, formed from aryl-urea-based LMWGs, can be used to grow crystals of a variety organic compounds, such as known pharmaceuticals, and demonstrated that these can also be recovered/isolated by using *anion-triggered gel dissolution*.[2] Also, Cronin and co-workers showed that an inverse chemical garden methodology may be used for assembly of high aspect ratio micrometer-scale hollow microtubes from polyoxometalate-based inorganic solids in conjunction with a polyaromatic phenanthridinium-based cation.[10]

In this article, we report the first example of a single-step technique whereby high aspect ratio nanowires are grown from a dropcast supramolecular gel, containing dissolved salt ions of common halide salts (*e.g.*, NaCl, KCl, and KI), with the smallest wire diameters being 130–200 nm in diameter. We also describe the selection of individual nanowires from the nanocrystal garden, to allow closer examination by transmission electron microscopy (TEM). This shows clearly their single-crystal structure, composition, and growth direction. We demonstrate the applicability of this method to other halide salts, along with the potential for forming wires from different combinations of ions during the crystallization process.

Understanding the mechanism for the growth of nanomaterials and ways of controlling morphology of wires is of great current interest in the field of molecular nanotechnology.[11,12] Halide wires in particular have been studied as they represent model systems to test theories of growth and the electrical and mechanical properties of near perfect materials.[13–15] A wide range of approaches have been developed to date for controlling anisotropic growth of crystals such as melt, solution, flux, and hydrothermal growth[16] as well as vapor–solid–liquid[14,17] and surface-tension-driven methods.[18] However, the prospect of generating new forms of material through the use of supramolecular gels and/or understanding the role of the supramolecular structure itself could potentially open up new avenues within the field of molecular nanotechnology.[19]

The supramolecular gels employed in our current study consist of LMWG based on structure **L** (Scheme 1) that has a C3-symmetrical benzene-1,3,5-tricarboxamide (BTA) central core connected to three 2,2′:6′,2″-terpyridyl (*terpy*) moieties through a carboxamide spacer, which form two-dimensional supramolecular polymers (Figure 1a) through hydrogen bonding and $\pi-\pi$ interactions of the central BTA cores. Using Eu(III)
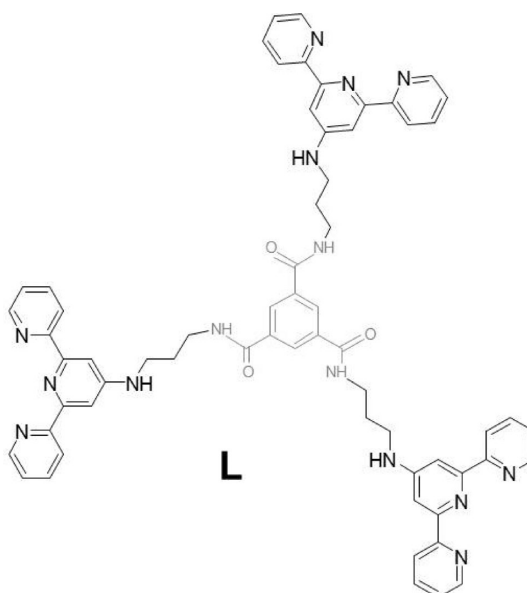
Scheme 1. Chemical structure of the ligand L.

ions (EuCl₃), the concomitant formation of higher order self-assembly gel was also achieved (EuCl₃-**L**), which is three-dimensional in its nature (Figure 1b).[20] Here, individual supramolecular polymeric strands are connected together through coordination to the Eu(III), which can be described as functioning as a *supramolecular glue* (Figure 1b), and it is from this material that nanowires are observed to grow (Figure 1c).

RESULTS AND DISCUSSION

Porous Matrix and Wires. A scanning electron microscopy (SEM) image of the supramolecular Eu(III) gel is presented in Figure 2a, showing the rope-like bundles formed by the self-assembled helical structure of the gel strands where the distance between the central BTA cores corresponds to 0.36 nm as it was identified in our earlier work.[20]

The typical binding energy between BTA moieties self-assembled into an infinite polymeric structure through hydrogen bonding depends on the number of monomers involved and was not estimated within the current work. However, an extensive study performed on very similar molecules reveals that it may vary from ~20 to ~116 kJ/mol.[21] It was observed, initially by SEM and confirmed by TEM and energy-dispersive X-ray spectroscopy (EDX) that micrometer-scale euhedral-like sodium chloride crystals formed at the surface of such ambient-dried films and smaller crystals on the order of 200 nm have been identified within the matrix (Figure 2b). Their origin is believed to be a 1.3%_{w/w} impurity level of NaCl in the powder ligand, based on the thermogravimetry results shown in the Supporting Information.

The gel viscosity is controlled by the cosolvent mix and weight percentage of ligand. In the case shown in Figure 2a, the gel was of sufficient viscosity to hold irregular shapes, and so when dosed onto a silicon
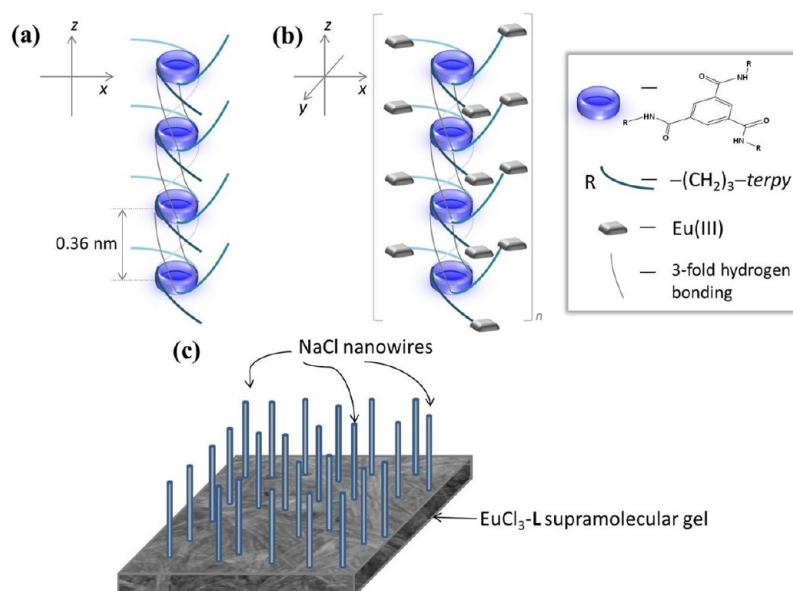
Figure 1. Schematic representation of (a) two-dimensional supramolecular polymers formed through hydrogen bonding between L molecules and (b) three-dimentional supramolecular network of $EuCl_3$-L along with (c) formation of NaCl nanowires.

wafer, the dried film thickness was uneven across the sample, giving rise to a heterogeneous distribution of crystallites. A drying step under vacuum ensured removal of almost all water. Following 3−4 days storage at ambient conditions after the vacuum dry, re-examination by SEM showed signs of thin wires growing from the surface of the dried gel (Figure 2c−e), giving rise to large areas of growth resembling tree trunks in a garden, hence, the generation of nanocrystal gardens. Crystals are found at various stages of anisotropic growth, with the most developed on the order of 130−200 nm in diameter and often 10 μm in length. It is important to note that (i) initial imaging of the dropcast film directly after deposition and drying does not reveal nanowire growth; and (ii) some dropcast films begin to crack and delaminate post-dehydration during the storage time, and such samples exhibit identical nanowire growth at both gel−air interfaces, as shown in Figure 2e. It can be concluded that the wires are not formed as part of the initial bulk drying step. Figure 2c,d shows examples of nanowires that are straight and uniform along their length, growing from the supramolecular gel, and there is no evidence of branched growth using the growth technique detailed in this report. Moreover, nanowires frequently show evidence of gel at their base (see Figure 2d), which is consistent with a base growth mechanism.

The growth of halide salt *needles* was first reported by percrystallization in 1932,[22] leading to a sustained interest in growth from porous materials and membranes.[23−26] Initial studies related directly to desalination techniques by reverse osmosis, where a saturated salt solution was observed to reject crystalline needles to the opposite side of the porous membrane (usually a ceramic or cellulose acetate). Significant work since

then has looked at this behavior using saturated solutions in porous membranes.[27,28] It is generally agreed that the solution penetrates the porous matrix and begins to evaporate from the free surface. While the matrix is replenished by diffusive flow, there is a buildup of salt until it reaches supersaturation levels, following which nucleation and growth of crystals begins to occur within the surface pores.

It is noted by Lonsdale and Podall[29] and summarized by Yellin et al.[30] that ion diffusion will only occur in a hydrated sample, and so it is important to consider the bound water that cannot be removed by vacuum pumping and the very low volumes of moisture reabsorbed by the dried film under ambient conditions. While solid-state NMR would be required to examine the low level of water incorporated in the gel, it is clear that the presence of water is essential in facilitating ion transport and anisotropic growth. It has been shown by Zehnder et al.[28] that dry upper surfaces are necessary for salt growth, where diffusing species can only approach from one facet. This, coupled with our evidence of base growth where growing crystals appear to pull some of the gel strands up from the substrate (Figure 2d), strongly suggests that nanowire growth results from the diffusion and crystallization of ions at the lower face of a small seed crystal formed within the gel surface. This is similar to the base growth mechanism suggested for the porous membrane wire growth.[26,28,31] The nanowire growth itself is driven by the exothermicity of crystallization and is facilitated by the presence of water that provides a constant feed of the required salt ions.

Wire Growth. For the nanowire shown in Figure 2c, the mass is calculated as 0.33 pg assuming growth starts at the gel−air interface and the wire density is that of bulk sodium chloride. This equates to 5×10^{-15}
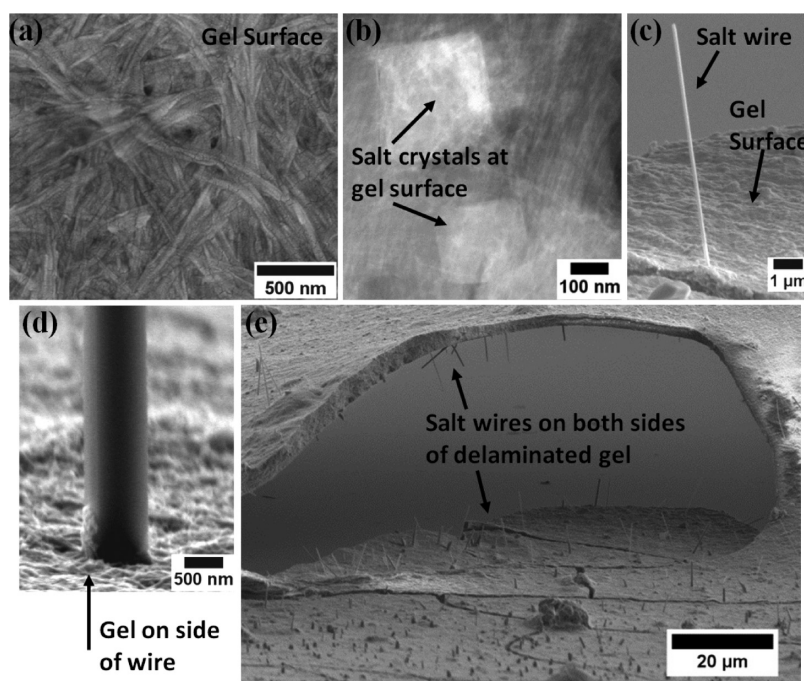
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Figure 2. (a) Eu(III) gel showing bundles formed by the self-assembled helical structure of the gel strands. (b) Small NaCl crystals observed in gel matrix observed by TEM. (c) NaCl nanowires grown from a Eu(III) gel. (d) Gel observed on the side of nanowires. (e) Growth of nanowires seen on both sides of delaminated gel film.

moles or 3.4×10^9 molecules of NaCl. Using the measured salt content in the pure ligand and assuming an even distribution of ions throughout the film, this will require all of the salt ions from approximately 25.4 fL of the surrounding gel. This volume is illustrated (to scale) as a hemispherical region centered on the base of a wire in Figure 3a, with a scaled diagram of the system shown in Figure 3b. Thus, the supply of ions from the gel clearly controls the density of wire growth using this method. Whereas the density of wires can be increased by increasing the salt concentration, too high a concentration actually leads to a disruption of the gel matrix (see below).

As noted earlier, due to the semisolid and heterogeneous nature of the gel, the repeatability of the sample drying was quite poor and crystals were present in different geometries, orientation, and concentrations across the film. This accounts for the poorly controlled spatial distribution of wires and varying angles of the wires emerged from the gel. The uniformity and repeatability were improved by using a less viscous formulation of the same supramolecular gel and adopting a standardized drying protocol in which initial drying was carried out in an argon-rich vacuum desiccator. After 24 h, the sample was evacuated to a high vacuum (10^{-6} mbar for approximately 15 min) prior to standing in ambient conditions for 3−4 days and then examined by SEM.

This drying approach, illustrated in Figure 4a, led to a repeatable circular gel film with a thick central ring of euhedral-like crystals, as shown in the high-tilt-angle SEM image in Figure 4b with the outer border shown at higher magnification in Figure 4c. Importantly, the nanowire morphology was only observed at the outer border of

this ring where there is a transition from a higher to lower seed crystal concentration. As the gel dries, it is not pinned, and so the outer perimeter retracts as the volume decreases. Once water evaporation leads to a supersaturated salt concentration, the nucleation of crystals commences, leading to the ring shape shown in Figure 4a,b. This ensures that, at the outer rim, the smallest crystals and those most likely to be single crystal are formed (i.e., while the gel is at a low salt supersaturation). This indicates that there is an optimum concentration whereby the nucleating crystals are sufficiently small, of single-crystal composition, and there is sufficient salt content remaining nearby to allow further ion diffusion and wire growth.

Wire Analysis. Analysis of the EDX spectra of wires on the gel surface confirms the presence of sodium chloride. However, the background signal from the substrate is large, and it was important to analyze isolated nanowires to confirm their composition and structure. Individual wires were plucked and transferred to a carbon mesh grid for TEM and EDX analysis (see Figure 5a−c and Supporting Information for additional details). As shown in Figure 5e, EDX spectroscopy confirms the expected 1:1 stoichiometry of sodium chloride in the absence of a background signal from the substrate, while the TEM diffraction pattern indicates cubic, single-crystal morphology. The electron diffraction pattern in Figure 5d reveals the crystal orientation as a $\langle 110 \rangle$ type zone axis for a cubic face-centered crystal structure.

The measured distance of the $\{200\}$ and $\{111\}$ type reflections indicates a lattice parameter of 5.64 Å. This is consistent with reported values for sodium chloride. The growth direction of the wire can be identified as a
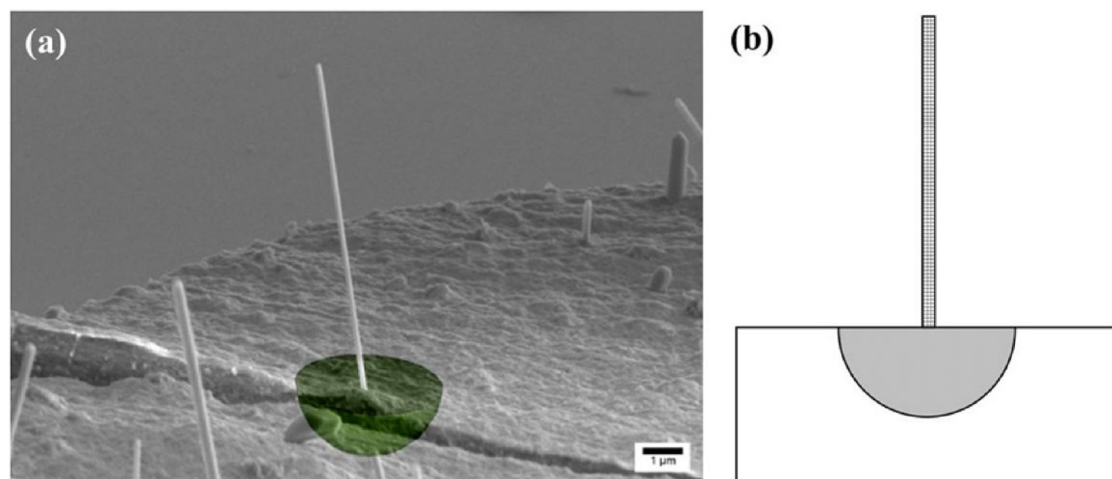
Figure 3. (a) Eu(III) gel with nanowire and illustrated region from which salt ions are required. (b) Scaled diagram shows the volume required to feed a single-crystal nanowire.
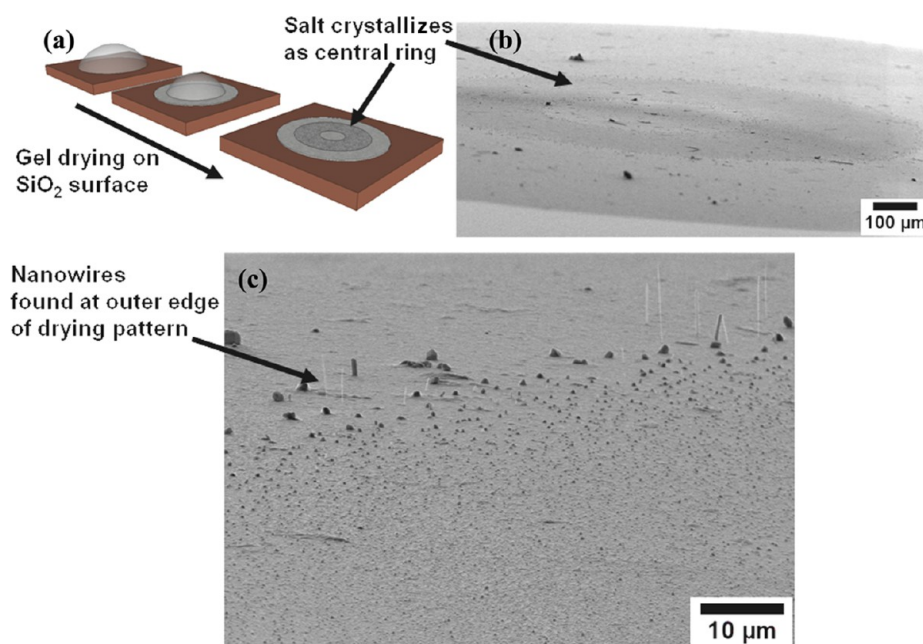

Figure 4. (a) Diagram of gel drying on SiO_2/Si surface. (b) Highly tilted image showing the dried gel sample with a large ring of euhedral crystals. (c) Transition region at the outer edge of the ring from euhedral crystals to nanowires.

⟨110⟩ direction by comparing the diffraction pattern and the bright-field image of the wire. Note that the image rotation between diffraction pattern and bright-field image has been compensated for in this study.

Recombination of Ions. To test the generality of this approach, a range of salts were intentionally added to the pure ligand gel. Initially, sodium chloride was added at a range of concentrations between $0.05-0.5\%_{w/w}$, which translates to an approximate increase in salt concentration of $55-550\%_{w/w}$. As seen in Figure 6a, the addition of $0.05\%_{w/w}$ NaCl leads to a more densely packed growth of nanowires across the surface. This is consistent with a significant reduction in the volume of gel required to nucleate and feed the growth of each wire, as indicated in Figure 3. For the samples with no

additional inclusion of salts, it is estimated that only approximately 5% of the dosed sample area can grow nanowires. With added NaCl salt at $0.05\%_{w/w}$, nanowires are found over almost the entire surface. There is also a slight increase in wire density, from approximately 1.5 to 2 wires per micrometer with addition of salt. A further increase in concentration, however, results in the destabilizing of the gel structure and the development of unusual surface morphologies, with wire growth only occurring interspersed between these regions. Images of these destabilized morphologies are included in the Supporting Information.

Potassium chloride and potassium iodide were also added to the pure ligand gel at $0.05\%_{w/w}$, and samples prepared for SEM in the manner described earlier.
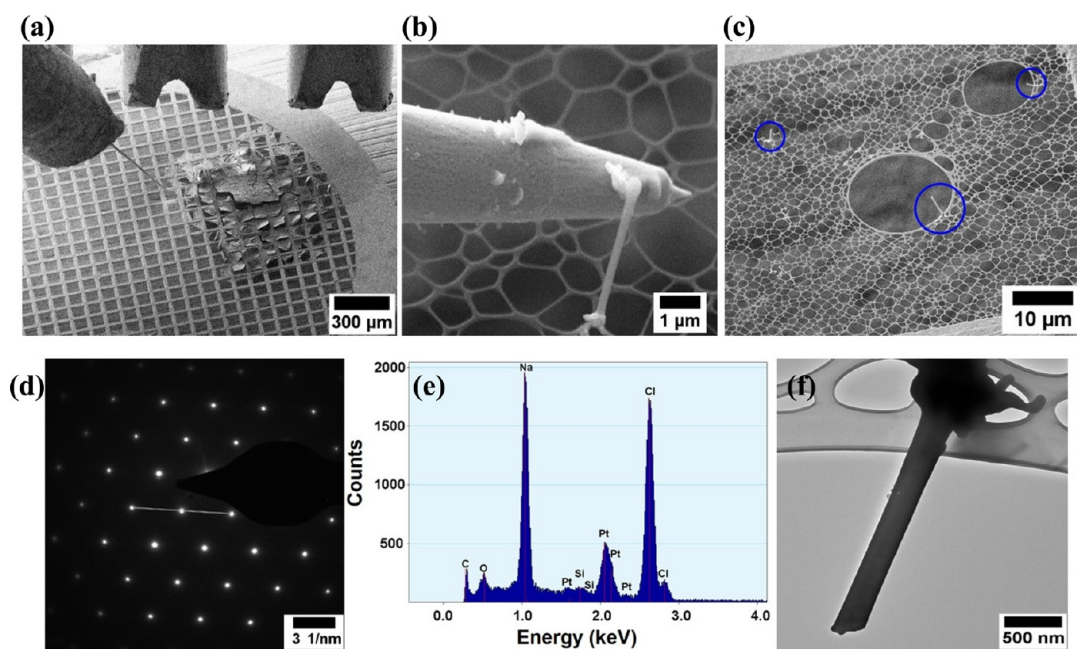
Figure 5. (a–c) Steps used to transfer a single nanowire from a gel surface to a clean TEM mesh for analysis. (d) Diffraction pattern obtained for the wire shown in (f). (e) EDX spectra for the wire shown in (f). (f) Salt wire plucked from the Eu(III) supramolecular gel in (a).
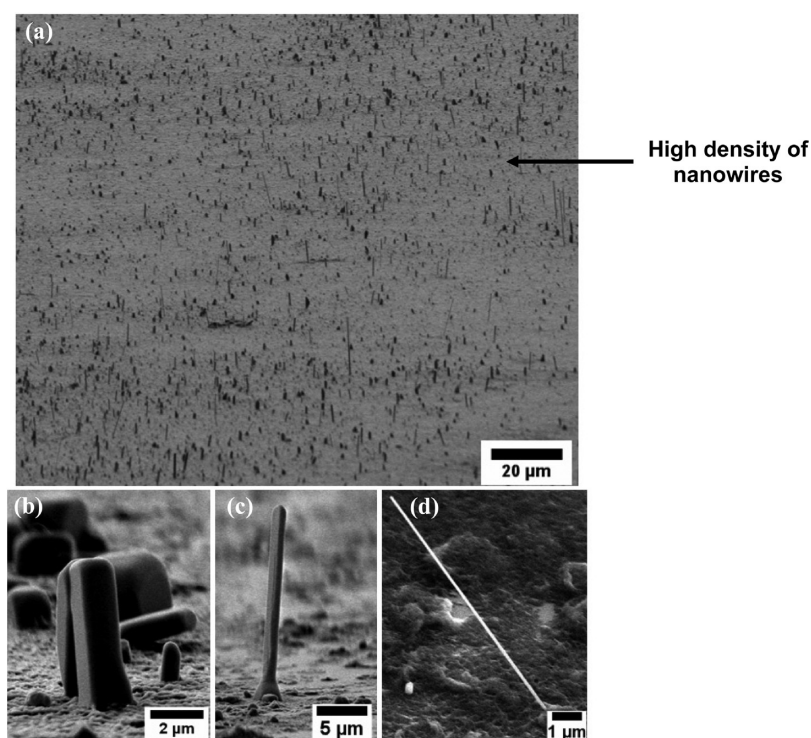

Figure 6. (a) Dense wire growth over larger area upon addition of 0.05%$_{w/w}$ NaCl. (b) As well as KCl nanowires, larger wires are also observed; (c) large KI wires are observed. (d) Upon addition of KI, recombination with Cl$^-$ ions leads to KCl nanowires.

It was found that nanowires and larger wires of potassium chloride could also be grown but in lower density than sodium chloride samples. The chemical nature of the wires was confirmed by EDX mapping, as shown in Supporting Information. Addition of potassium iodide to the pure ligand gel showed some large wire growth,

more similar to those formed in less dry surfaces[31] and more euhedral crystals on the surface. Importantly, it was also found that, with the addition of 0.05%$_{w/w}$ potassium iodide, nanowires were also identified as KCl by EDX mapping. In this case, the added potassium ions compete to recombine with the chloride ions

(from NaCl in the gel) in addition to the iodide ions from the added KI salt.

Clearly, recombination involves interplay between kinetic and thermodynamic factors, where the relative ion concentrations and the ionic lattice energies are important, with the latter favoring recombination of ions with the smallest radii. The observation of KCl wire growth clearly shows that the gel can facilitate the formation of the thermodynamically more stable nanowire product.

Although the specific role of the supramolecular gel facilitates the diffusion of ions and single-crystal nanowire growth, it needs to be explored further as standard gels do not facilitate nanowire growth. The addition of similar quantities of NaCl to Laponite and Carbopol gels show crystal formation in a range of morphologies, as detailed in the Supporting Information, but in neither case was it possible to grow nanowires of the type described here, thus supporting the observation that the self-assembled supramolecular gel has a specific role in the controlled nucleation and growth process.

CONCLUSIONS

In this article, we have demonstrated the growth of single-crystal halide salt wires, facilitated by a self-assembled supramolecular gel (**L** and EuCl$_3$-**L**).[20] The inclusion of a halide salt in the developed supramolecular gel leads, upon dehydration, to the formation of small seed crystals and evidence of diffusion-driven base growth of nanowires. Since ion diffusion requires hydration, outgassing must remove all of the bound water and the remaining but limited supply of water facilitates slow diffusion and anisotropic crystal growth. Although the detailed growth mechanism is not understood and will be the focus of future work, it is already clear that the supramolecular gels play an important role is directing anisotropic wire growth, in contrast to the growth modalities observed when conventional gels are employed. The approach developed here provides a straightforward and scalable method to synthesize pristine single-crystal nanowires of unprecedented dimensions and an opportunity to test the properties of these important nanoscale material systems.

MATERIALS AND METHODS

The synthesis and physical characterization of the supramolecular gel have recently been reported,[20] but the ligand was synthesized in two steps from commercially available starting materials. SEM and EDX was carried out using the Zeiss ULTRA Plus focused ion beam, and platinum deposition for TEM preparation was carried out in the Zeiss Auriga while combined TEM and EDX analysis was carried out in a FEI Titan field emission TEM. The supramolecular gels were prepared for analysis on a thermally annealed silicon dioxide surface. Fresh wafers were always used and cleaned initially with HPLC-grade acetone, propan-2-ol, and deionized water prior to high-pressure nitrogen and oven drying steps. Detailed sample preparation steps are included in the Supporting Information. Sodium chloride, potassium chloride, and potassium iodide were purchased from Fisher Scientific laboratory reagent grade. Laponite RD (hydrous sodium lithium magnesium silicate) was from Rockwood Additives Ltd., and Carbopol 940 polymer from Lubizol Corporation was neutralized using triethanolamine from Sigma Aldrich.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Additional information on materials and methods, thermogravimetry experiment data of **L** along with experimental details on the addition of salts to gel samples and microscopy data. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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