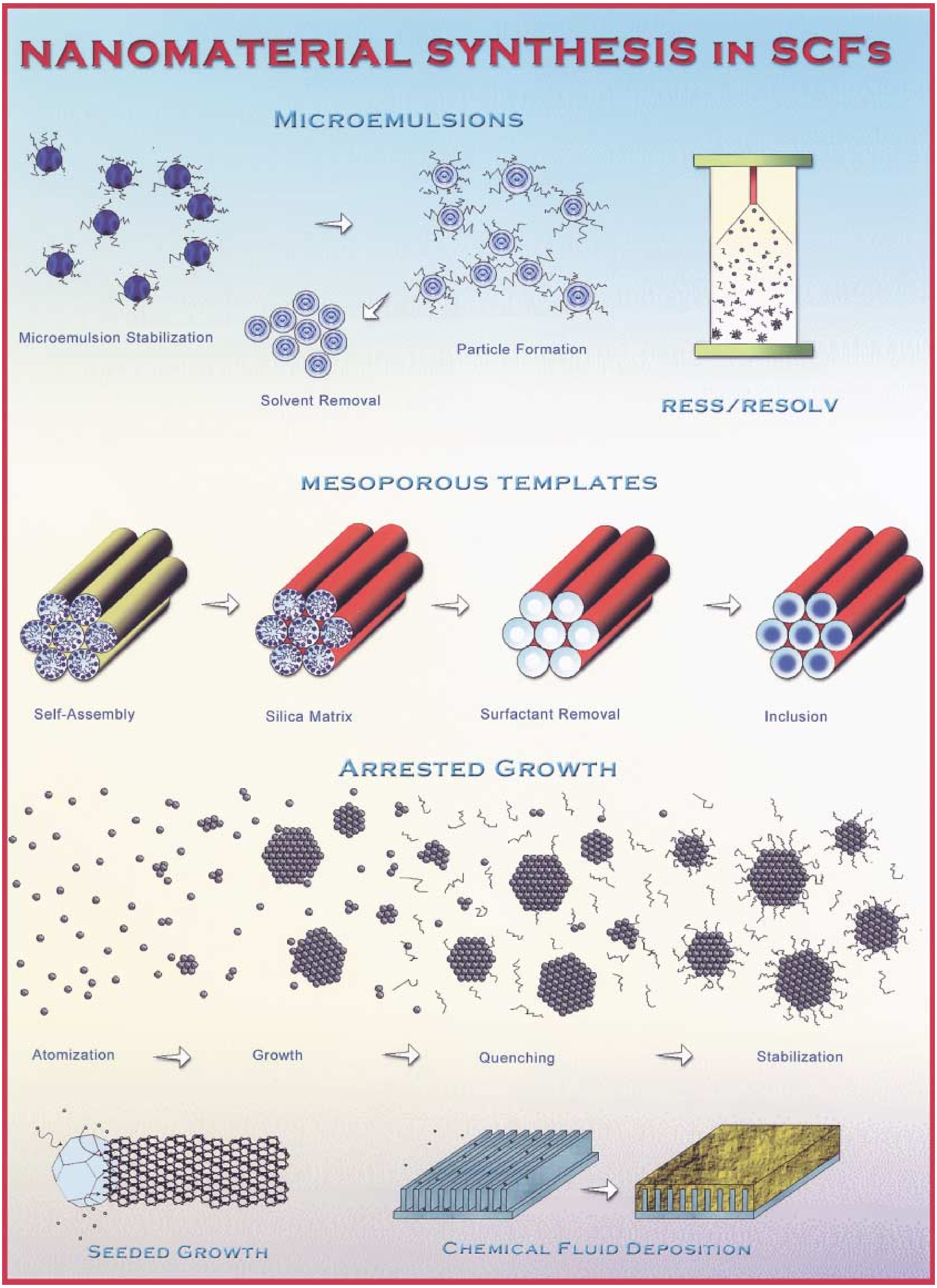

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Supercritical Fluid Synthesis of Metal and Semiconductor Nanomaterials

Justin D. Holmes,* Daniel M. Lyons, and Kirk J. Ziegler[a]

Abstract: In the near future physical and economic constraints are expected to limit the continued miniaturisation of electronic and optical devices using current "top-down" lithography-based methods. Consequently, nonlithographic methods for synthesising and organising materials on the nanometre scale are required. In response to these technological needs a number of research groups are developing new supercritical fluids methodologies to synthesise and self-assemble "building blocks" of nanomaterials, from the "bottom-up", into structurally complex device architectures. This concept paper highlights some of the recent advances in the synthesis of metal and semiconductor nanoparticles and nanowires by using supercritical fluids. In addition, we describe an efficient supercritical fluid approach for constructing ordered arrays of metal and semiconductor nanowires within mesoporous silica templates.

Keywords: mesoporous materials · nanostructures · nanowires · supercritical fluids ·

Introduction

Many technologies, including electronics, separation science and coatings will be enhanced by the ability to control the structure of materials on a nanometre-length scale. The ability to pack high densities of memory storage and processing circuitry into specific nanoscale arrays, and to utilise the unique transport properties associated with these architectures, is expected to lead to future generations of computer processors with device sizes many times smaller and faster than current silicon-based processors. However, both physical constraints and economics are expected to limit continued miniaturisation of electronic and optical devices by using current "top-down" lithography-based methods.[1] Consequently, alternative nonlithographic methodologies for constructing the smallest mesoscopic features of an integrated circuit will soon be needed. One promising nonlithographic strategy for creating mesoscopic architectures is the use of supercritical fluids (SCFs) to synthesise and assemble materials from precursor "building blocks" into structurally complex mesoscopic architectures.

A key aspect of nanotechnology is that quantum confinement effects evident in low-dimensional materials can give rise to unique and unusual optical, electronic and catalytic properties.[2] In particular, with many semiconductor materials there is a strong correlation between their optical properties and their size. As the size of a semiconductor is reduced the electronic excitations in the material shift to higher energies, and the oscillator strength is concentrated into just a few discrete transitions. These basic phenomena of quantum confinement arise as a result of changes in the density of electronic states as is shown in Figure 1. Excellent examples of size-dependent discrete optical transitions exist for clusters of direct band-gap semiconductors, such as CdSe[2, 3] and InAs.[4] These unique size-dependent properties may afford innovative electronic, optical and sensor applications. For example, the discovery of visible luminescence from nanocrystalline silicon has led to an explosion of interest in this material for potential opto-electronic applications.

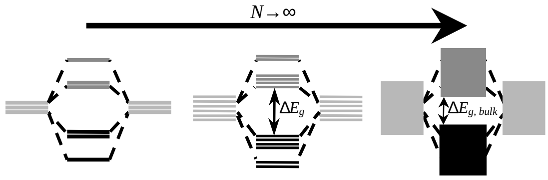

Figure 1. Simplified molecular orbital energy levels for a homonuclear species without hybridisation. Energy levels for the orbitals of a two-atom model to a bulk semiconductor as the number of atoms (N) increase to infinity. Note the intermediate stage at which the energy-level degeneracy has not completely formed the bulk band structures. This loss of the energy-level degeneracy relative to the bulk material is quantum confinement and results in discrete energy levels and a band gap energy (ΔE_g) that is dependent on the number of atoms.

Materials Synthesis using Supercritical Fluids

A supercritical fluid (SCF) is a compound, mixture or element above its critical pressure (p_c) and critical temperature (T_c), but below the pressure required to condense it to a solid.

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Many of the physical properties of SCFs vary with density. As seen in Figure 2, small changes in pressure or temperature can cause large variations in the density of a SCF between gas- and liquidlike values, for example, between 0.2–0.9 g cm^{-3}.

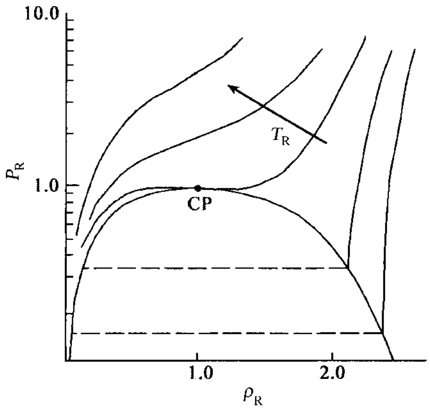

Figure 2. Pressure–density phase diagram of a pure substance. The envelope denotes the two-phase region in which both a liquid and vapour phase exist. CP denotes the critical point of the fluid at which the distinction between a vapour and a liquid disappears resulting in a continuous fluid.

Hence conducting reactions in SCFs affords opportunities to manipulate the reaction environment, for example, viscosity, diffusivity and surface tension, through the control of pressure and temperature to enhance solubilities of reactants and products and to eliminate transport restrictions on reaction rates. Hence SCFs provide a tunable medium for reaction and separation processes.[5] In particular, supercritical CO_2 (sc-CO_2) has attracted much attention as an alternative to organic solvents as it is nontoxic and nonflammable. Since SCFs offer great chemical flexibility and synthetic tunability, they have recently been utilised in the synthesis of nanocrystalline materials. The ability to control the mass-transfer properties of an SCF is particularly important for the nucleation and growth of crystals or films.[6, 7] Complete reviews on the use of SCFs in the synthesis of polymers and inorganic materials are offered elsewhere.[8, 9] Here, we will concentrate on the key developments in the synthesis of metal and semiconductor materials within SCFs for electronic and optoelectronic applications.

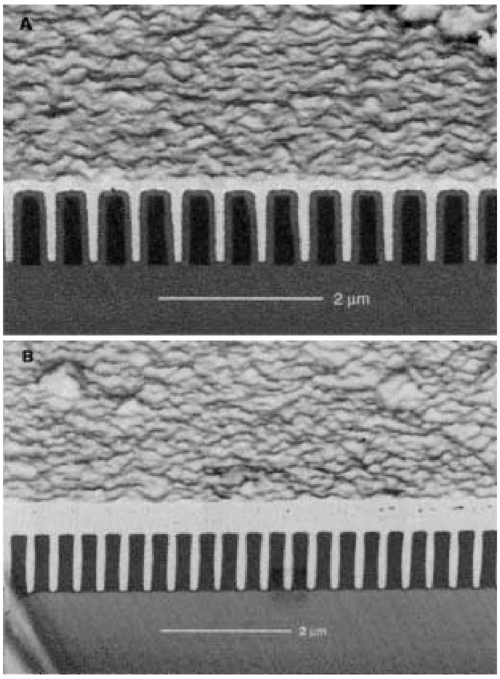

Figure 3. SEM micrograph of copper films deposited by chemical fluid deposition onto a) a Pd-seeded and b) a bare silicon wafer. Reproduced with permission from *Science* **2001**, *294*, 141. Copyright 2001 American Association for the Advancement of Science.

Nanoparticle synthesis: One of the first successful applications of SCFs in the synthesis of metal and semiconductor nanoscale materials was demonstrated by Watkins and co-workers,[6, 7, 10, 11] who produced uniform metallic thin films, ~100–200 nm thick, by a chemical fluid deposition (CFD) method (see Figure 3). Using CO_2-soluble organometallic precursors, in the temperature range 60–80 °C, they synthesised metallic films with lower contamination levels than those produced by conventional chemical vapour deposition (CVD) techniques. While demonstrating the advantages of SCFs in materials synthesis, these films did not exhibit quantum confinement effects that could possibly be exploited in future nanodevices. However, quantum confinement effects have been observed in nanoparticles synthesised from water-in-CO_2(w/c) microemulsions.[12–15] Ji et al.[12] and Holmes et al.[13] were the first to utilise w/c microemulsion droplets as "nanorectors" to synthesise metal and semiconductor nanoparticles, while Cason et al.[16–18] used water-in-ethane microemulsions to form copper nanoparticles. Even though the size and morphology of the nanoparticles formed within these microemulsion systems can readily be controlled, it is difficult to collect the as-prepared nanoparticles owing to their aggregation and coalescence upon removal of the SCF. Preparing nonaggregated nanoparticles from a SCF can be achieved by coating the particles in a protective layer, which binds to their surfaces, quenches particle growth and provides a steric barrier to aggregation. Such a method has been successfully demonstrated by Shah et al., who used perfluorooctanethiol as a capping ligand in the synthesis of several metal nanocrystals in sc-CO_2, including silver, iridium and platinum.[19] To overcome the problem of coalescence, other researchers have focused on the impregnation of nanoparticles into polymers by using SCFs.[20] Sun et al. have utilised expansion processes, such as RESS (rapid expansion of supercritical solution)[21, 22] and RESOLV (rapid expansion of a supercritical solution into a liquid solvent),[23, 24] to obtain polymer-protected nanoparticles resistant to coalescence. Whilst these low-temperature methods for generating nanoparticles offer high quality and reliable approaches for synthesising "soft" metals they lack the high temperatures required to form crystalline materials for many other metal and semiconductor nanomaterials, for example, silicon.[1]

Until recently, high-temperature SCF approaches for producing nanoscale materials have mostly been conducted in near-critical or supercritical water (SCW).[25–33] Specifically, Arai and co-workers have shown that metal nitrates can be decomposed to form a wide variety of metal oxide crystals in SCW.[25–28] Poliakoff and co-workers also demonstrated that metal–organic precursors can be used to obtain metal oxide nanocrystals through a similar mechanism.[29–33] Both of these research groups have reported their ability to control the oxidation state of metal nanoparticles formed through the addition of reductants or oxidants into the reaction chamber during particle growth.[27, 32] Whilst the particle size, morphology and oxidation state of metal nanoparticles produced in SCW can be readily controlled, collecting the as-prepared particles is more problematic owing to particle agglomeration and coalescence. However, recently Ziegler et al.[34] have overcome the problem of agglomeration and coalescence of nanoparticles synthesised in SCW. This group added alkanethiol ligands into their SCW reaction chamber during the formation of copper nanoparticles. Due to the low dielectric constant of water above its critical point, the alkanethiol ligands were fully miscible in the supercritical phase and acted as a stabilising ligand preventing aggregation of the nanoparticles. These nanoparticles could then be removed from the SCW reaction chamber and redispersed in organic solvents at room temperature (Figure 4).

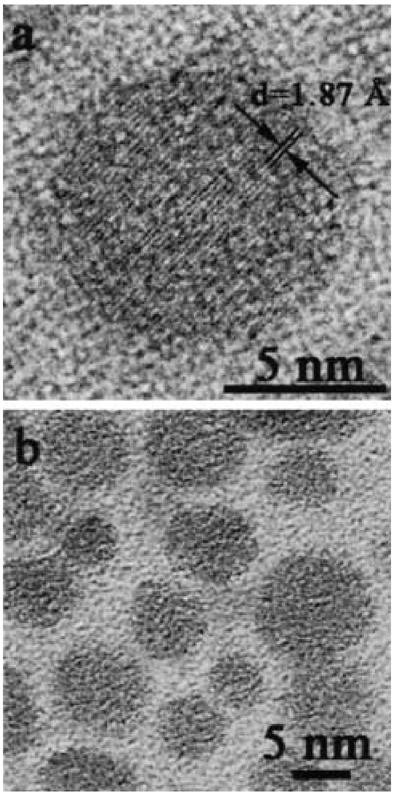

Figure 4. a) High-resolution and b) low-resolution TEM images of 1-hexanethiol stabilised copper nanoparticles synthesised in SCW. Reproduced with permission from *J. Am. Chem. Soc.* **2001**, *123*, 7797. Copyright 2001 American Chemical Society.

SCW, however, is not conducive to the synthesis of many materials and often results in the formation of unwanted metal hydroxides or metal oxides.[25] The use of other SCFs at high temperature has not received much attention to date,[8, 35] but may offer the possibility to synthesise materials, such as silicon, for which traditional methods have met with limited success.[36] Combining the benefits of high temperatures used in aerosol methods and the highly successful use of wet chemical arrested-growth procedures for producing nanoparticles, a new wet chemical approach for producing silicon nanocrystals has recently been described by Holmes et al.[37] By using octanol as a capping ligand in sc-hexane, silicon nanoparticles were synthesised which exhibited significant size-dependent optical properties due to quantum confinement effects. Additionally, the smallest nanocrystals produced, 15 Å in diameter, exhibit previously unobserved discrete optical transitions.

Nanotube and nanowire synthesis: While nanowires and nanotubes have existed in nature for billions of years,[38] the synthesis and manipulation of atoms in the laboratory in a controlled way to form such materials remains a challenge. Carbon nanotubes have recently been the focus of a significant amount of research due to their mechanical strength, chemical inertness and electronic properties. Recently, researchers have demonstrated the ability to synthesise multiwalled carbon nanotubes from a variety of precursors in SCW[39–41] and in sc-CO_2[42] by using lower temperatures than many conventional approaches. However, the random formation of either metal or semiconducting nanotubes[43] renders the response of nanodevices based on these building blocks random as well. Metal or semiconductor nanowire building blocks, however, offer the distinct advantage that these nanowires have sizes and electronic properties that can be controlled in a predictable manner during their synthesis.

One of the most successful approaches for producing nanowires is based on the vapour-liquid-solid (VLS) growth process described nearly 40 years ago by Wagner and Ellis.[44, 45] In this process liquid gold droplets on a substrate surface were used as seeds for Si nanowire growth. The silicon precursor, in the gas phase, was introduced into the reaction chamber where it dissolved into the gold droplet to form a Au:Si alloy. Upon saturation silicon was expelled from the gold droplets in the form of a whisker. The diameter of these silicon whiskers, or nanowires, typically mirrored the diameter of the liquid droplets from which they were grown (~100 nm). In 1998, Morales and Lieber[46] used an adaptation of this method to generate silicon nanowires with a mean diameter of ~20 nm. In their procedure silicon nanowires were grown in the gas phase from gold nanocrystals produced through laser ablation. The problem with laser ablation methods, however, is the broad size distribution of the nanoparticles produced upon ablation and, hence, the diameters of nanowires grown from them.

Building upon their success in synthesising silicon nanocrystals in sc-hexane, Holmes et al.[47] adapted the VLS method described above to obtain monodisperse silicon nanowires. In their method monodispersed alkanethiol-capped gold nanocrystals, 2.5 nm in diameter, were used as seeds to direct one-dimensional Si crystallisation in supercritical hexane. Additionally, the crystal structure of the nanowires produced using this supercritical fluid-liquid-solid growth process could be controlled by changing the reaction pressure. At a pressure of 270 bar, silicon nanowires grow preferentially along the $\langle 110\rangle$ direction and along the $\langle 100\rangle$ plane at pressures of 200 bar (Figure 5). Both these supercritical[48] and laser ablation[49–53] approaches have since been extended to other semiconductors. One inherent problem with these approaches, however, is the formation of entangled meshes of nanowires. While Lieber and co-workers[54] have made significant progress in manipulating these nanowire meshes into useful configurations for potential electronic devices, other researchers[55–68] have focused on forming nanowires in predefined architectures allowing easier processing and integration into functioning devices.

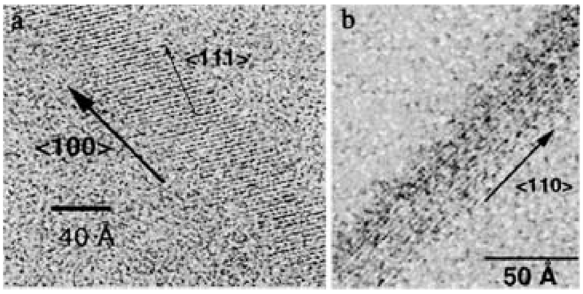

Figure 5. Pressure-dependent growth of silicon nanowires synthesised in supercritical hexane at a) $P = 200$ bar and b) $P = 270$ bar. Reproduced with permission from *Science* **2000**, *287*, 1471. Copyright 2000 American Association for the Advancement of Science.

Inclusion of mesoporous templates: Nanometre-wide channels of anodic aluminium oxide films,[55, 56] polycarbonate track etched membranes[57] and nanochannel array glasses[58] have previously been used as templates for nanowires of conductive polymers,[59] metals[57, 60] and semiconductors.[55, 56, 61] While these templating methods are useful, forming an ordered array of nanoscale channels is difficult, and the channel dimensions are usually too large to engineer nanowires that exhibit quantum confinement effects. Mesoporous materials,[69] however, have unidirectional pores with diameters in the range 2 – 15 nm and offer a convenient route to forming ordered arrays of nanowires.

Mesoporous solids have previously been exploited as templates for semiconductor materials formed from the gas phase with moderate success.[70] In particular, Leon et al.[63] reported the partial filling of MCM-41 mesoporous silica with germanium wires by using vapour-phase epitaxy. In a similar approach, Dag et al.[62] employed CVD to deposit silicon nanocrystals within the pores of hexagonal mesoporous films. These gas-phase methods have met with some success, but the high temperatures (ca. 800 °C) or extensive reaction times (ca. 48 h) required for successful nucleation and growth of nanowire arrays makes these techniques both costly and time-consuming.[62, 63] Furthermore, these methods have been unable to achieve complete filling of the pores with nanowires or nanoparticles. The relatively high diffusion coefficients, higher precursor solubility and reduced surface tension of high-temperature SCFs, however, results in almost complete inclusion of the mesoporous materials with nanowires.

Investigations in our laboratory have focused on preparing ultra high-density three-dimensional arrays of metal and semiconductor nanowires within the pores of mesoporous silica hosts.[64–68] The supercritical fluid inclusion-phase technique developed in the group has proved successful not only in allowing a range of stable nanowire-matrix composites to be reproducibly synthesised, but it is also extremely fast, efficient and cost effective. Typically, reactions are completed within 15 – 30 minutes compared to other techniques that may require days. In addition, using simple liquid-phase precursors offers a relatively safer preparation method to many CVD approaches.

Characterisation of these nanowire/silica host matrix composites has shown that the SCF inclusion-phase method is an efficient alternative to gas- or liquid-phase inclusion techniques. Prior to nanowire guest inclusion, transmission electron microscopy (TEM) of the mesoporous silica matrix reveals an open hexagonal open-pore framework (Figure 6a). After nanowire inclusion, crystalline nanowires are easily witnessed within the mesopores by TEM (Figure 6b). Further evidence of inclusion can be seen from low-angle X-ray diffraction (XRD), adsorption techniques and solid-state NMR spectroscopy. All of these investigative techniques have provided a clear indication of the success of the SCF inclusion-phase technique as a method for creating hierarchical materials on the nanoscale.

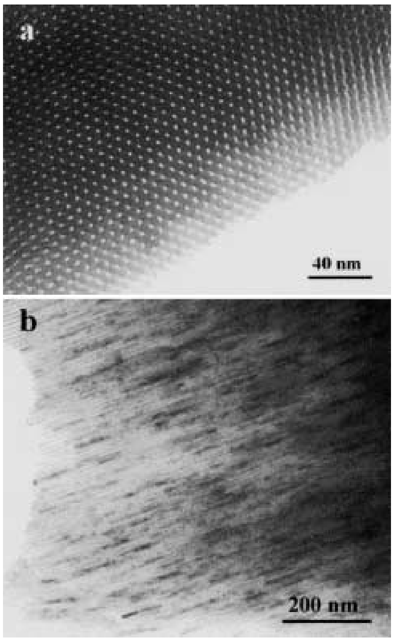

Figure 6. TEM micrographs of a) a calcined mesoporous silica framework prior to nanowire inclusion (front view) and b) after loading half of the mesopores with germanium nanorods/nanowires (side view).

Furthermore, we have discovered that silicon nanowires prepared within mesoporous matrices exhibit high-intensity ultraviolet (UV) and visible photoluminescence (PL). Bulk silicon is an indirect band-gap semiconductor that traditionally exhibits very weak PL. However, as the size and dimensionality of silicon is decreased, quantum confinement effects become pronounced resulting in electronic characteristics that are different from the bulk material.[71, 72] We have recently discovered an ability to manipulate the UV PL[67] of these encased silicon nanowires (Figure 7) by controlling the pore size of the silica matrix and, hence, diameter of the silicon nanowires grown within them.[73] UV PL in silicon has previously been ascribed to electron excitation followed by electron-hole pair recombination at oxygen defect centres in silica. However, simple electron-hole recombination in silica can not explain the variation in the UV PL emission wavelength of the silica–silicon composite materials as the silicon nanowire diameter changes. We have argued that this UV PL arises due to intrinsic strain within the nanowires and have observed that as the curvature or strain of the nanowires increases, the UV PL emission maximum is shifted to higher energies. This control over the UV PL demonstrates the ability to manipulate optical properties in semiconductor nanowires through strain-induced effects; this could be a new parameter in the design of three-dimensional optical devices.

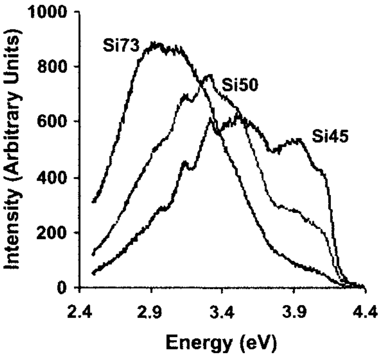

Figure 7. Ultraviolet photoluminescence emission spectra for silicon nanowires embedded in a mesoporous silica matrix and dispersed in anhydrous hexane (excitation energy of 4.92 eV). PL emission maxima were observed at 2.93 eV, 3.3 eV and 3.49 eV for nanowires with 73 Å (Si73), 50 Å (Si50) and 45 Å (Si45) diameters, respectively. Reproduced with permission from *Nano Lett.* **2002**, *2*, 811. Copyright 2002 American Chemical Society.

The great advantage of this SCF inclusion technique is that it may be easily applied to a range of other semiconductor and metallic nanowires including germanium, copper, cobalt, iron oxide and nickel.[64–68] In addition, not only can elemental nanowires be synthesised within porous materials, but also doped or alloyed nanowires may be formed; this is a source of further investigation within our laboratories. The ability to create elemental, doped and alloyed nanowires within porous materials will make supercritical methodologies one of the techniques of choice in emerging fabrication technologies.

Conclusion

Limitations with current lithographic technology have motivated the search for a technique that allows nanoparticle and nanowire synthesis, with a high level of control, that is cost-effective, reproducible and easily integrated with existing technologies. To date, no general method for synthesising defect-free nanoparticles or nanowires has been established. Since SCFs enable great chemical flexibility and synthetic tunability they have begun to attract attention in the production of highly controlled solution-phase and templated nanomaterials. These unique solvents offer several advantages over conventional solvents in the synthesis of materials such as low surface tension, low viscosity and high diffusivity, which may be beneficial for the construction of nanoscale building blocks. The use of SCFs in the formation of ordered arrays of nanowires within mesoporous phases allows nearly complete inclusion of mesoporous matrices with nanomaterials due to the high penetrating power of SCFs into the mesopores. In addition, SCF inclusion techniques may be easily applied to a range of other semiconductor and metallic nanowires making it a viable technique for emerging fabrication technologies.

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