Silicon nanowire aqueous liquid crystal formation and processing into macromaterials

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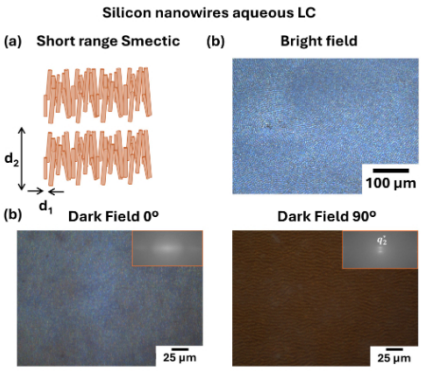
Nanowires are elongated inorganic crystalline objects whose shape and nanoscale size in one dimension give them a wealth of properties distinct from their bulk analogues[1,2]. For silicon nanowires (SiNWs), these include size-dependent optical absorption and Mie scattering, tolerance to electrochemical alloying for energy storage. In many instances, the challenge is in translating single-nanowire properties to the macroscopic scale. In particular, it is of interest to study the formation of ordered fluid phases with nanowires and their use for controlled assembly into networks. This strategy could enable formation of new macromaterials with extreme anisotropy and bulk properties beyond the envelope of their monolithic analogues.
We report for the first time the formation of liquid-crystal (LC) dispersions of SiNWs and their assembly into macroscopic fibres[3]. SiNWs are synthesized by Floating catalyst chemical vapour deposition (FCCVD), enabling gram per day synthesis of these one-dimensional nanomaterials. These nanowires exhibit high crystallinity, log-normal length (~2.5 μm) and diameter (~40 nm) distributions, and aspect ratios of 50–100[1,2]. In concentrated aqueous media, the nanowires behave as charged rigid rods, spontaneously forming LC domains. The concentration phase diagram shows isotropic–biphasic and biphasic–nematic transitions at 1.2 and 2.1 vol.%, respectively. Followed by the emergence of short-range-ordered smectic phase at 4.5 vol.%. Remarkably, smectic ordering persists despite the broad aspect-ratio polydispersity, contrary to predictions based on hard-rod steric interactions[4]. This behavior is attributed to electrostatic interactions, with the effective nanowire diameter governed by the Debye length, leading to a narrowing of the effective size distribution. Aligned domains exhibit anisotropic resonant Mie scattering and strong polarised Raman feature. Harnessing this spontaneous order, we assemble continuous macroscopic fibres that are flexible and remarkably tough, with a specific fracture of energy of 2.1 J g^{-1}, approximately 150× that of monolithic silicon.

Keywords:
Silicon nanowires, lyotropic liquid crystal, smectic phase, fibre



Silicon nanowires 4.5 vol.% aqueous dispersion characterization: (a) Schematic of the smectic phase, (b) Bright light optical micrograph in reflection of the dispersion, revealing smectic structure, (c) Optical dark field micrographs show strong light scattering for different polarization directions

References:

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