Self-assembly of Si particles toward IR-active metamaterial

Megan A. Parker [1], Lucien Roach[1], Raul Barbosa[2], Maria L. De Marco[1], Alexander Castro-Grijalba[1], Vasyl G. Kravets[3], Alexander N. Grigorenko[3], Sabrina Lacomme[4], Brian A. Korgel[2], Virginie Ponsinet[5], Philippe Barois[5], Mathieu Gonidec[1], Patrick Rosa[1], Glenna L. Drisko[1]

[1]CNRS, Université de Bordeaux, ICMCB, UMR 5026, 33600 Pessac (France)
[2]McKetta Department of Chemical Engineering, University of Texas at Austin, 78712 Austin TX (USA)
[3]Department of Physics and Astronomy, University of Manchester, Manchester, M13 9 PL (UK)
[4]CNRS, Université de Bordeaux, BIC, UMR 3420, 33000 Bordeaux (France)
[5]CNRS, Université de Bordeaux, Bordeaux INP, CRPP, UMR 5026, 33600 Pessac (France)

The synthesis and self-assembly of Si@SiO_xN_y core-shell particles, optically active at infrared wavelengths is reported. In a previous work we demonstrated that similar particles with reduced size (~350 nm) more efficiently supported forward light scattering, and over a broader region of the visible spectrum, than pure silicon particles.[1] Here, the scattering frequencies are shifted to the infrared, with the synthesis of larger particles (~540 nm) obtained from the use of a different silane precursor.[2] Individual particles were produced by decomposing a Si coordination complex alongside cyclohexasilane, under supercritical conditions. The bottom-up approach employed here leads to particles fulfilling the requirements for efficient light scattering: being smaller than the wavelength of incident light and large enough to support Mie resonances at optical frequencies and being monodisperse in size. The synthesis of the core@shell particles only produces a relatively small amount of material (~5 mg per batch) which heavily restricts the self-assembly techniques that can be employed to prepare a monolayer. The strategy ultimately pursued here was interfacial self-assembly within a restricted area. Particles were deposited onto an air-water interface from a 2:1 ethanol:butanol suspension and then transferred to a hydrophilic substrate. The prepared films are not completely close-packed and have a degree of disorder (c.f. a HCP monolayer). The optical properties of 2D assemblies of scatterers are studied using ellipsometry, and the results are compared to simulations.

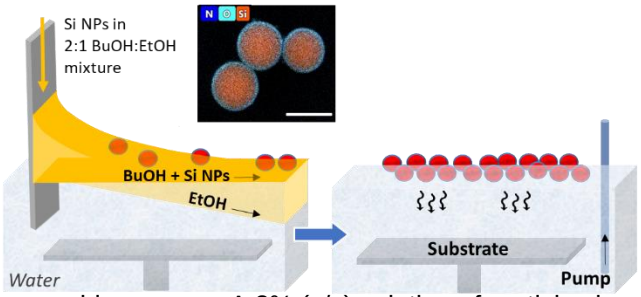

Figure 1. Schematic showing the assembly process. A 2% (v/v) solution of particles in a 2:1 ethanol:butanol mix is introduced to a reservoir of H_2O via syringe pump. The solution is delivered to the surface of the H_2O via a needle attached to a hydrophilic glass slide. The high miscibility of ethanol in water leads to this component immediately mixing with the aqueous phase, whilst the butanol – particle mixture is trapped at the surface and distributes over the H_2O surface in a thin layer. The water was then removed slowly by a peristaltic pump and the particle film lowered onto the substrate before being allowed to dry. STEM-EDX inset shows elemental mapping of particles, with scale bar representing 500 nm.

References

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[2] M. L. De Marco, S. Semlali, B. A. Korgel, P. Barois, G. L. Drisko, C. Amonier, **Angew. Chem. Int. Ed.** 2018, *57*, 4478.