Supplementary material: Resonant Raman scattering from silicon nanoparticles enhanced by magnetic response

Pavel A. Dmitriev,[†] Denis G. Baranov,[‡] Valentin A. Milichko,[†] Sergey V. Makarov,[†] Ivan S. Mukhin,[†,¶] Anton K. Samusev,[†] Alexander E. Krasnok,[*,†] Pavel A. Belov,[†] and Yuri S. Kivshar[†,§]

†*Laboratory of Nanophotonics and Metamaterials, ITMO University, St. Petersburg 197101, Russia*

‡*Moscow Institute of Physics and Technology, Dolgoprudny 141700, Russia*

¶*Laboratory of Renewable Energy Sources, St. Petersburg Academic University, St. Petersburg 194021, Russia*

§*Nonlinear Physics Centre, Australian National University, Canberra ACT 2601, Australia*

E-mail: krasnokfiz@mail.ru

Optical measurements from a single nanoparticle

All of the optical characterization (Raman and elastic scattering) is carried out on a multifuncational confocal setup (Fig. S1).[1] Silicon nanoparticles are found in the video camera placed in the image plane of our optical scheme. The collecting volume of the measured signal is determined by numerical apertures (NA=0.7 or NA=0.9) of used objectives and confocal pinhole diameter (50 μm). Such parameters allowed to measure all optical signals from a single nanoparticle, when inter-particle distance is larger than $\approx 1\mu$m.

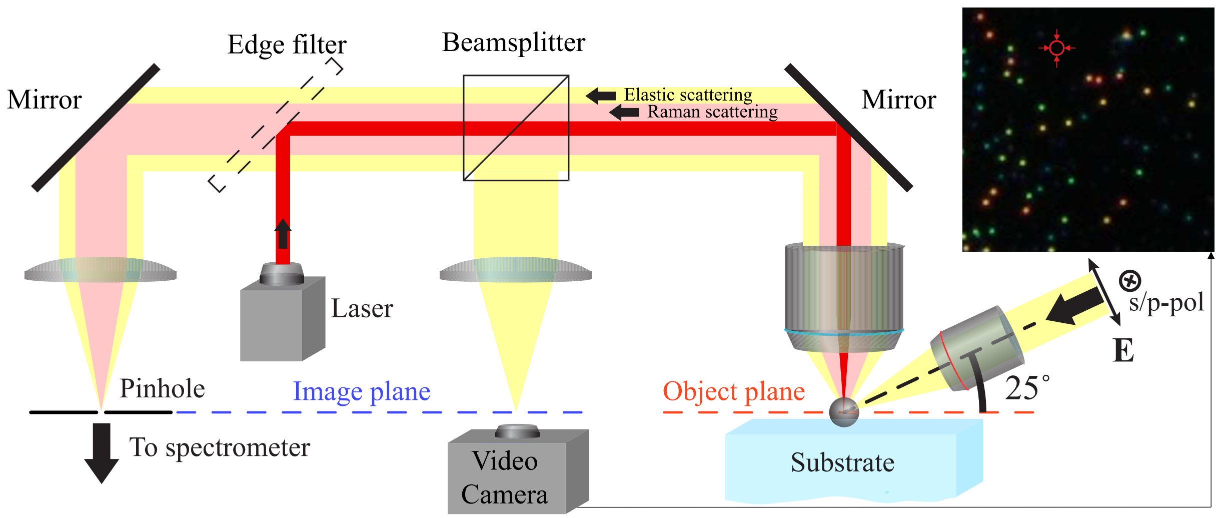

Figure S1: A schematic illustration of multifunctional experimental setup for Raman scattering and dark-field optical microscopy.

Determination of the nanoparticle diameter

Resonant optical properties of silicon nanoparticles are known to be sensitive to their shape,[2] crystallinity,[2,3] to the substrate[4] and to the thickness of native oxide layer,[2,5] which is always present on silicon surface.[6]

In this work, the shape of the particles has been controlled using SEM measurements, while the diameter of silicon core has been extracted from dark-field spectroscopy experiments.

The crystalline phase of silicon nanoparticles fabricated using laser-induced forward transfer technique has been recently confirmed by means of the combination of Raman spectroscopy and electron diffraction measurements.[3]

In order to analyze the influence of native silicon oxide layer on the optical properties of the studied nanoparticles, we have carried out additional experimental measurements and numerical simulations. First, to estimate the thickness of the layer, we have characterized typical silicon nanoparticle using transmission electron microscopy (TEM), see Fig. S2a. Our measurements confirm that nanoparticles are coated with less than 5-nm-thick silica layer, which is in good agreement with previously reported results.[2,5]

To analyze the influence of the oxide layer on the resonant properties of nanoparticles, we have simulated total scattering cross section spectra of a crystalline silicon nanoparticle ($D = 150$ nm) surrounded by silica shells with different thicknesses, see Fig. S2b. For the sake of simplicity, the simulations have been carried out using Mie theory.[7] Our results confirm that in the case of fixed silicon core diameter appearance of additional 5-nm-thick silica layer leads to red spectral shifts of both electric and magnetic dipole resonances of the nanoparticle as small as ≈ 4.2 nm and ≈ 2.5 nm, respectively.

The influence of different substrates has been analyzed in Ref.[4] The authors have demonstrated that both electric and magnetic dipole resonances of crystalline silicon nanoparticle placed on the fused silica substrate exhibit small red spectral shifts with respect to the resonances of the nanoparticle in free space. In the case of nanoparticle with the diameter of $D = 130$ nm these shifts are as small as ≈ 3.5 nm and ≈ 0.5 nm, respectively.

Therefore, the spectral shift of the nanoparticle's magnetic dipole resonance is practically insensitive to both the substrate and the native silica layer. This allows to conclude that the diameter of silicon core of the nanoparticle can be precisely extracted from the spectral position of magnetic dipole resonance in the dark-field spectroscopy measurements compared to the simulations based on Mie theory.

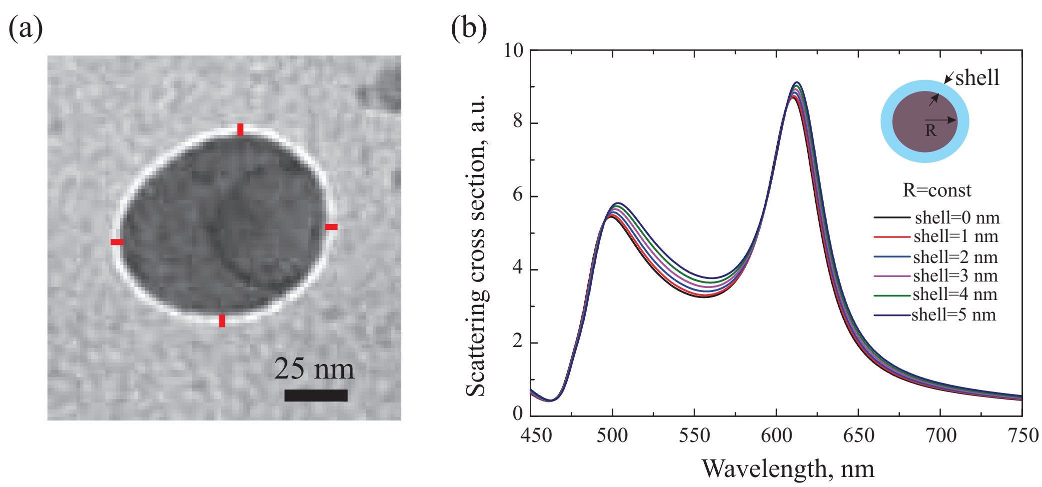

Figure S2: (a) TEM image of the typical silicon nanoparticle fabricated using laser-induced forward transfer technique. Red lines represent 5 nm. (b) Total scattering cross sections of silicon nanoparticle ($R = 75\ nm$) coated with silica layers with different thicknesses.

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