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Title: Nanostructured biosilica exoskeletons functionalized by gold nanoparticles as SERS-active materials

Abstract:

Natural nanostructured materials play an important role in various applications and can be readily used to produce the advanced composites. One of the promising natural objects is diatom algae, whose cellular material is enclosed in a hierarchically structured, highly porous silica cell wall, prompting scientists to exploit its structure and properties to the fullest. In this contribution, we fabricated by an innovative method based on combination of layer-by-layer assembly and freezing-induced loading technique gold-coated diatom biosilica exoskeletons that can be exploited as effective supports for surface enhanced Raman spectroscopy (SERS) [1]. Using this approach, we obtained different degrees of coverage of porous diatomite with gold nanoparticles, as confirmed by scanning and transmission electron microscopy and energy dispersive X-ray spectroscopy. The photoacoustic imaging was used as an *in situ* method for characterizing the degree of modification of the biosilica surface with gold nanoparticles. The collected photoacoustic signal increased with increasing number of deposition cycles up to three, which was in good agreement with the extinction spectra. Such hybrids were found to be good SERS substrates, enhancing the spontaneous Raman scattering of Rhodamine 6G by a factor of  $6 \times 10^3$ , which is likely the result of the optimized spatial distribution of gold nanoparticles over the biosilica. Therefore, hybrid materials based on diatomite functionalized with gold nanoparticles using a layer-by-layer technology in combination with a freezing-induced loading method can be utilized as a low-cost and easy to fabricate SERS platform.

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[1] Julijana Cvjetinovic, Anastasiia A. Merdalimova, Maria A. Kirsanova, Pavel A. Somov, Daniil V. Nozdriukhin, Alexey I. Salimon, Alexander M. Korsunsky and Dmitry A. Gorin, A SERS platform based on diatomite modified by gold nanoparticles using a combination of layer-by-layer assembly and a freezing-induced loading method. Phys. Chem. Chem. Phys., 2022,24, 8901-8912