Nanofabrication of gold-nanoparticle-linked sea-sponges on ZnO nanowires using hydrothermal synthesis and its use as 3D surface-enhanced Raman bio-sensing substrates

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We have fabricated nanoscale sea sponges on zinc oxide (ZnO) nanowires (NW) by linking gold (Au) nanoparticles (NP) in a novel and simple 2-step hydrothermal synthesis and demonstrated its use as a three-dimensional (3D) surface-enhanced Raman spectroscopy (SERS) substrate. Fabrication repeatability is excellent, and the substrate can detect benzene thiol (BT) molecules down to the 100nM concentration, with the enhancement factor of $10^9$. Currently, we are pursuing optical and physical parametric studies to optimize the NW/NP geometries and spatial distribution for detecting glucose and insulin.

To fabricate the substrates, we prepared three solutions: (1) ZnO-textured seed solution (5-mM zinc acetate dihydrate in ethanol); (2) ZnO-NW precursor (a mixture of 25-mM zinc nitrate hydrate, 25-mM hexamethylenetetramine, and 6-mM polyethyleneimine in DI water); and (3) Au-NP precursor (a mixture of 1-mM sodium tetrachloroaurate (III) dihydrate, 0.4-$\mu$M sodium citrate dihydrate in DI water, and 0.1-M sodium hydroxide solution). To grow ZnO-NWs, we applied a ZnO-textured seed solution on Si substrates and anneal at 350 °C for 0.5 hours. The substrates are then immersed in the ZnO-NW precursor solution at 95 °C for 2.5, 5.0 and 7.5 hours. Then, to create Au-NP sea sponges, we immersed the substrates in the Au-NP precursor solution at 90 °C for 0.5, 1, 1.5 and 2 hours.

In our scanning electron microscope analysis, ZnO-NWs were perpendicularly and uniformly synthesized on a Si wafer. Using the synthesis times of 2.5, 5.0 and 7.5 hours produced the NWs of 1.5, 2.8 and 3.4 $\mu$m in length, respectively. The diameter of the NWs remained constant at ~50 nm in all three cases. The area densities of Au NPs in sea sponges were 0.5×10⁶ and 5×10⁶ $\mu$m² for 0.5 hours and 1 hour, respectively. Au-NP coating beyond 1 hour resulted in density saturation, and the atomic ratio of Au to ZnO stayed constant at 10 % in the energy dispersive X-ray analysis.

To test the fabricated substrates for SERS use, we incubated the substrates in 1mM BT solution for 1 hour. The Raman intensity increased with the Au-NP density, yet the intensities remained independent of the NW lengths because all the NWs, including 1.5-$\mu$m NWs, were long enough to provide sufficient absorption for SERS effect. Next, to test the detection limit, the substrates with 3.4-$\mu$m NWs and 5×10⁶ NPs/$\mu$m² were incubated in BT solutions (concentration levels: 100 nM - 1 mM in 5 increments) for 1 hour. The minimum detection limit of the substrate was 100 nM.

SERS has been widely researched in chemical and biological sensing applications, and various nanofabrication methods have been explored. However, a simpler fabrication approach to produce spatially uniform and repeatable SERS substrates is still desired. In this work, we show that our 3D SERS substrates produced using the straightforward hydrothermal synthesis can provide a wafer-scale uniform SERS substrate with significantly increased SERS hot spots for biomedical detection.