SERS induced by Au/ZnO plasmonic nanorods coupled to Au nanoparticles

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Abstract. We study the surface enhanced Raman scattering of Methylene Blue (MB) dye molecules induced by 3D array of “hot spots” made of vertical Au/ZnO core-shell nanorods coupled to self-assembled plasmonic Au nanoparticles. SERS substrates based on array of nanorods coupled to nanoparticles show much better performance compared with bare Au/ZnO nanorods. The hybrid 3D SERS substrate perfectly resolve Raman spectra of MB molecules chemisorbed from solutions with analyte concentrations of $\sim$10$^{-7}$ M even upon washing of a sample i.e. when only chemisorbed molecules were remained. Raman signal enhancement results from the superposition of two effects, namely, the ability of a plasmonic coupled system to enhance the Raman scattering via local field enhancement and from the large 3D surface which provides more adsorption sites compared with traditional 2D surfaces.

1. Introduction
Urgent request for detection of ultralow concentrations of chemical and biological molecular species using surface enhanced Raman scattering (SERS) induced by plasmonic nanoobjects has stimulated rapid development of new approaches to design efficient concentrators of the electric field at nanoscale. Suspensions of nanoparticles including core-shells [1] with strong plasmon coupling provide unique possibilities to in vivo biological and medical techniques. Meanwhile in vitro methods need efficient substrates with large amount of “hot spots” on the surface. Variety of 2D surfaces of plasmonic coupled nanobjects such as bowtie antennas [2] were prepared by expensive e-beam lithography method. A number of more cost-efficient self-assembling methods were also demonstrated. Namely, nanoparticle chains [3], particle multilayer stacks of monolayers of isolated [4] and plasmonic coupled nanoparticles [5] were designed for these purposes. Nanoengineering of substrates based on 3D architecture concept is capable to boost the sensitivity of SERS technique even further. A superior efficiency of some 3D SERS substrates was demonstrated recently [6, 7]. Indeed, 3D nanoobjects such as arrays of vertical nanorods of several microns length with large surface area do provide several orders of magnitude more adsorption sites compared with 2D surfaces.
Plasmoic nanorods in contrast to nanoparticles have the preferential direction which results in additional resonances corresponding to dipole, quadrupole, octopole and other modes of higher multipolarity [8,9]. Particle-like or “absorbing” nanorods with size much smaller than the wavelength of incident light show maximal local field enhancement at the wavelength of a dipole resonance and minor enhancement at multipolar modes. With increasing the rods length-to-diameter aspect ratio the resonances show red shift. For instance, the major dipole resonance of a rod of 40 nm diameter is shifted from ~700 to 1800 nm when its length is increased from 120 to 480 nm [10]. Corresponding near field enhancement coefficient averaged over the surface area is increased from ~300 to 870 for the dipole mode. For larger nanorods the input of scattering to extinction becomes considerable and it should be taken into account when 3D SERS substrates are designed.

We report a robust CVD and PLD based method to prepare SERS substrates with 3D array of “hot spots” made of oriented Au/ZnO core-shell nanorod arrays coupled with self-assembled plasmonic Au nanoparticles, in which Raman signal enhancement results from a superposition of two effects, namely, the ability of a plasmonic coupled system to enhance the Raman scattering and the larger 3D surface with more adsorption sites compared to 2D surfaces.

2. Experimental

2.1. Text in figures

Vertically oriented arrays of Au/ZnO nanorods with plasmonic shells are prepared by using the following procedure. First, ~40 nm ZnO buffer layer is deposited on the SiO₂ substrate by PLD method at 500°C in oxygen ambient at pressure of 2*10⁻² mbar. Then, a thin Au film of a thickness which is slightly exceeding the percolation threshold is deposited by PLD method for 800-1000 laser shots using procedure described elsewhere [10]. Au film is annealed at 500 C for 1 hour to prepare an array of well separated Au nanoparticle catalysts. An array of highly oriented ZnO nanorods shown in Figure 1a is prepared by catbothermal CVD method at the temperature of 1000°C as described elsewhere [11]. Next, ZnO nanorods are covered by thin Au continuous ~30 nm film using PLD for 1500 laser shots. The prepared Au/ZnO nanorods are covered by ~5-10 nm chitosan based polymer layer. Finally, Au nanolparticles are deposited for 500 laser shots in argon [10, 12]. In all PLD procedures the KrF laser was focused on rotating target to give a fluence of ~2 J/cm².

![Figure 1(a, b). (a) SEM image; (b) and schematics of Au-particles/spacer/Au/ZnO-rods structure.](image)

2.2. Optical transmission characterization and SERS measurements

Optical transmittance was studied by using UV/Vis Spectrophotometer Agilent Technologies HP-8453. Surface enhanced Raman scattering (SERS) of dye molecules induced by Au/ZnO nanorod arrays was studied for Methylene Blue (MB) molecules dissolved in water at concentrations of 10⁻⁶ - 10⁻⁷ M/l. The molecules were excited by 632.8 nm HeNe laser light and spectra were recorded using
Renishaw inVia Reflex Raman spectrometer with spectral resolution better than 1 cm⁻¹. The samples were excited by light of HeNe laser with power density less than ~5.4×10⁵ W/cm² using ×50 long focal distance objective (NA=0.5). Raman scattering was collected in the backward direction.

3. Results and discussion

Optical transmission spectra of bare Au/ZnO nanorods and rods covered by ultrathin dielectric spacer and Au nanoparticles are shown in Figure 2. The ZnO buffer layer used for deposition of Au/ZnO nanorods shows ~80% transmission at photon energies larger than ~400 nm and a characteristic ZnO absorption edge near 365 nm. Upon the deposition of the Au/ZnO nanorods the optical transmission is gradually reduced and does not exceed ~4% in the range of 400-1000 nm. The extinction spectra of bare Au/ZnO nanorods reveal broad plasmon bands in visible/near IR range. As the plasmonic nanorods have size comparable with the wavelength of incident light the input of scattering to extinction spectra is significant. Upon the deposition of polymer spacer and Au nanoparticles the absorption is further decreased to be smaller than 1%.

![Figure 2](image_url)

**Figure 2.** Optical transmission spectra of bare Au/ZnO core-shell nanorods (black) and Au particles/polymer spacer/Au/ZnO structures (red).

The following measurement protocol was applied for the SERS measurements. Solutions of Methylene Blue in bi-distilled water were used to characterize the performance of the SERS substrate. Upon the 5 min incubation in tested solution the sample was well washed in water and dried. Thus, only chemisorbed molecules could remain on the surface. At used analyte concentrations of 10⁻⁶ -10⁻⁸ M no Raman signal of MB molecules was detected on reference sample free of nanostructures after the washing, whereas the samples with nanorods reveal well resolved spectra of MB.
Figure 3. SERS response of Methylene Blue dye molecules adsorbed on the surface of bare Au/ZnO core-shell nanorods recorded at MB concentrations of $10^{-6}$ and $10^{-7}$ M. Smaller features of spectra are shown in the inset.

The fluorescence from molecules adsorbed on nanorods is gradually quenched whereas the Raman spectra are enhanced. Using the substrates with bare Au/ZnO plasmonic nanorods we could detect well resolved spectra at MB concentration of $\sim 10^{-6}$ M and poorly resolved spectra at $\sim 10^{-7}$ M as shown in Figure 3. Upon the deposition of Au nanoparticles onto polymer/Au/ZnO nanorods the SERS sensitivity is gradually enhanced compared with as prepared nanorods. At MB concentrations of $\sim 10^{-7}$ M perfectly resolved spectra were observed as shown in Figure 4 even after SERS substrates thorough washing in bi-distilled water.

Figure 4. SERS response of Methylene Blue dye molecules adsorbed on the surface of bare Au/ZnO core-shell nanorods and Au particles/polymer spacer/Au/ZnO structures recorded at concentrations of $10^{-6}$ and $10^{-7}$ M.
4. Conclusions
SERS substrates based on array of Au/ZnO plasmonic nanorods coupled to Au nanoparticles show much better performance compared with bare Au/ZnO nanorods. The hybrid 3D SERS substrate perfectly resolve Raman spectra of MB molecules chemisorbed from solutions with analyte concentrations of ~10^{-7} M even upon washing of a substrate. The SERS substrate performance is expected to be one or two orders of magnitude higher if one would use more common measurement protocol in which the droplet of analyte is dried on the substrates surface, i.e. when all the deposited molecules make input to SERS signal.

5. Acknowledgments
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