Photonic Crystal Fibers with Nanoscale Functionalized Air Holes as Robust Chemical and Biological Sensors

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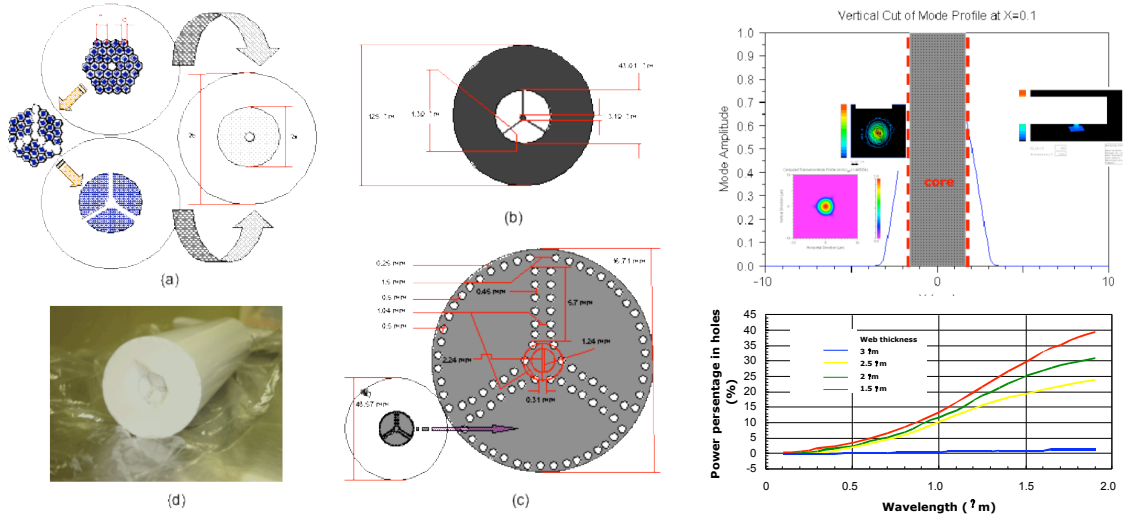
This project aims to integrate surface-enhanced Raman scattering (SERS) with the emerging photonic crystal fiber (PCF) technology to develop a powerful SERS/PCF platform for ultra-trace chemical and biological sensing and molecular fingerprinting. The premise of such platform rests on the strong mode-field overlap with the analyte over the entire PCF length as well as on the advantage that SERS offers. Key to realizing SERS/PCF is controlled immobilization of SERS-active Ag or Au nanoparticles inside the axially-aligned air channels in silica PCF with air cladding microstructure optimized for sensing applications. To this end, we have focused on the following task areas: (1) fabrication of PCF guided by simulation; (2) theoretical modeling of evanescent field interaction with metallic nanoparticles on waveguide structure; (3) molecular- and nano-scale modification of air channels in PCF; and (4) evaluation of sensing capability of the resultant SERS/PCF platform. The ultimate goal of this project is to establish the strategy and science base leading to a unique and robust technique for chem/bio detection and identification in the ppb-ppt range in gas or liquid phase.

We have designed and fabricated a PCF preform with steering-wheel structure by sol-gel method optimized for sensing use (Fig. 1(A)). Our theoretical simulation has indicated that the PCF possesses low loss and high evanescent field overlap with surrounding air channels, among other properties (Fig. 1(B)).



(A) (B)

Figure 1. (A) Design of PCF with steering-wheel structure: (a) evaluation of PCF with three rings of hole and with holes suspended in air into effective step index model; (b) cross-section of designed PCF with geometrical parameters; (c) cross-section of PCF preform with scaling pattern; (d) photo of fabricated PCF preform with steering-wheel structure by sol-gel method. (B) Top - Intensity distribution of guided mode in the core and the cladding of the PCF with steering-wheel structure design simulated using MODE Solver. Insets, the far field pattern of PCF and 3-D power profile of fundamental mode in the PCF; Bottom - Power percentage in air channels with different web thickness.

We have formulated the basis of proper integral Raman spectroscopy (PIRS) with the unique self-consistent system of equations. Our approach takes into account all possible light scattering and coupling mechanisms. PIRS is realized when the non-coherent gain of Raman signal from target analyte in the evanescent field exceeds all losses of Raman signal in PCF. We have estimated the attenuation coefficient of the probing mode propagating in solid-core PCF with Ag nanoparticles randomly immobilized in PCF air channels. Rapid increase in both absorption and radiative losses (Fig. 2) suggests using the small nanoparticles with radii 10-20 nm for a nanoparticle coverage density of 1/_m^2 on a 2 _m-diameter silica waveguide core at λ_0=785 nm. Our calculation also indicates that that resonance between the mode and localized surface plasmons excited on nanoparticles is undesirable due to loss increase by a factor of 400. Our numerical results can be directly applied to any nanoparticle coverage density by linear scaling. Reduced coverage density thus permits use of larger nanoparticle radii. The calculated power losses will allow estimation of the Raman-shifted signal gain coefficient (due to electromagnetic or chemical SERS) to realize the SERS/PCF platform.

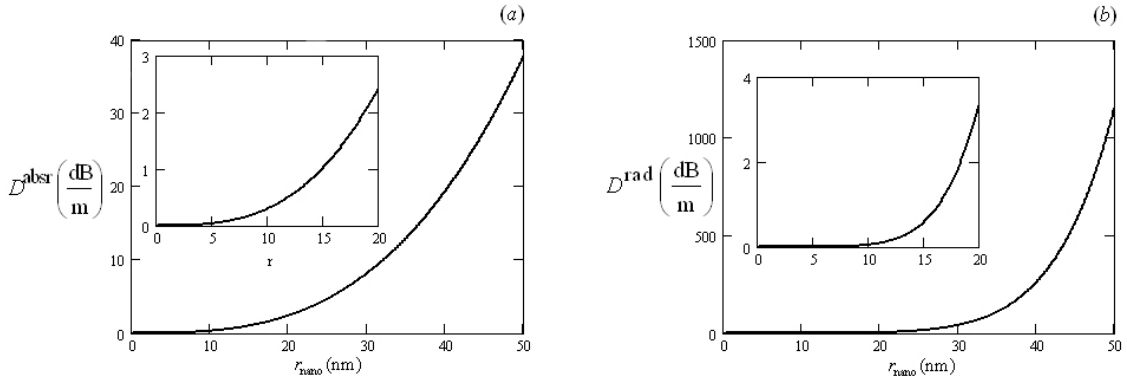
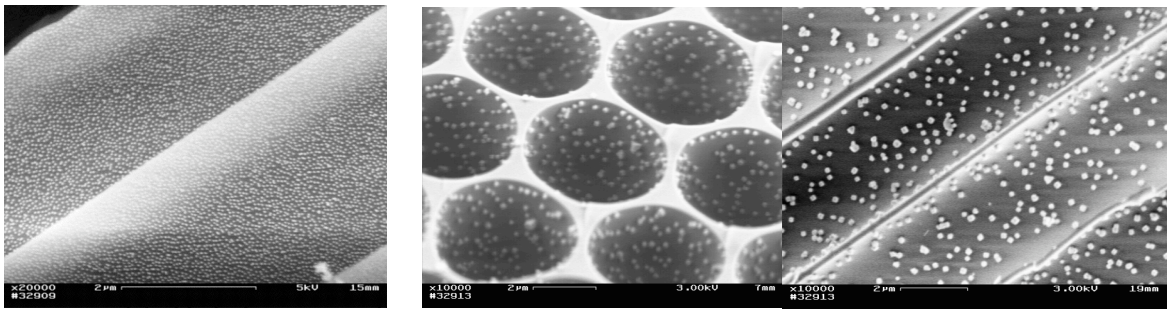


Figure 2. Size-dependent power-damping coefficients due to (A) electromagnetic energy absorption in Ag nanoparticles and (B) radiative scattering by Ag nanoparticles (1Ag particle/_m^2, d=2 _m, λ_0=785 nm).

We have developed and continue to refine the surface modification and synthesis approaches towards strong binding of SERS-active Ag or Au nanoparticles in PCF air channels. Two principal routes have been explored to immobilize the nanoparticles with self-assembled polyelectrolyte monolayer as an adhesion layer. One is based on the use of preformed nanoparticles in colloidal solutions via conventional citrate reduction (Fig. 3(A)) and the other on nanoparticles formed in-situ inside the reagent-filled air channels through reduction of metal salts by (N-(2-hydroxyethyl) piperazine-N'-2-ethanesulfonic (HEPES) acid. Planar glass substrates decorated with Ag nanoparticles under about the sample coverage density using these two methods have been shown to exhibit very similar SERS activity when measured using 1 nm rhodamine 6G (R6G) solution. The former method is suited mainly for immobilization of spherical nanoparticles in PCF air channels due to microfluidic flow constraints. The latter method, on the other hand, which was discovered by us serendipitously, is applicable to nanoparticles of any size and shape. As significantly, the charge state of the resultant nanoparticles can be either positive or negative, depending on solution pH either before or after nanoparticle formation. The polyampholytic nature of the nanoparticles thus allows one to tailor

the surface charge to suit the detection of either a cationic or anionic analyte in an aqueous solution.



(A) (B)

Figure 3. Axial or radial SEM micrograph of metallic nanoparticles immobilized on the surface of PCF air channels: (A) using Au colloidal solution and (B) through in-situ reduction of 1mM $AgNO_3$ and 1mM HEPES at pH 3.

Work is in progress in fiber drawing and optical characterization; expanded simulation of evanescent field-nanoparticle interaction and its interplay between nanoparticle size, coverage density, and light wavelength; experimental control of nanoparticle size and coverage density. We are on track to achieving SERS/PCF sensing platform through simulation-guided fiber design and fabrication, reproducible immobilization of highly SERS-active Ag or Au nanoparticles with the size and coverage parameters established by theoretical modeling. We have made significant progress in understanding the fundamentals of the light-nanoparticle interactions in PCF, the nucleation and growth of in-situ reduced metal nanoparticles, and the immobilization of the nanoparticles using self-assembled polyelectrolyte monolayer.

From education and outreach points of view, we have involved three undergraduate students as part of their summer research experiences. Two doctoral students and one and one-third postdoctoral scientists are funded by the NIRT grant pursing the afore-described theoretical and experimental studies. Research results have been included in undergraduate and graduate classes as case studies in nanotechnology. Three papers are in print and seven presentations have been given at professional meetings or as invited seminars (two of which abroad). We have established collaborative relationship with the US Army Edgewood Chemical Biological Center. We have also started to partner with ORC, Southampton University, UK, a world leader in PCF design and fabrication. We organized and chaired SPIE's first Conference on Photonic Crystals and Photonic Crystal Fibers for Sensing Applications at Optic East 05, Oct. 23-26, Boston, MA.

References

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