Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Parylene-Mediated Plasmonic-Photonic Hybrid Fiber-Optic Sensor and its Instrumentation for Miniaturized and Self-Referenced Biosensing

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1. Details of the PPR sensor fabrication process.

Multimode optical fibers (NA = 0.22) with diameters of 1.0 and 1.1 mm for the core and cladding, respectively, were used in this work. The fibers were cut into 10-cm-long sections, and the jacket on both ends was stripped about 2.0 cm. To employ the optical fiber tips as the sensing area, the two end faces of the fiber were first polished with 9μm, 3μm, 1μm, 0.2μm, 0.02μm grit emery papers. Subsequently, the flattened fiber tips were cleaned with acetone, ethanol, and deionized (DI) water, and then treated with oxygen plasma for hydroxylation

For the photonic cavity, to ensure the morphology was controllable, uniform, and reproducible, an attractive material, parylene-C (PAC), was adopted in this work. As depicted in Figure 2, the PAC CVD process involved three main steps. The powder-like PAC dimer was first vaporized at 175 °C in a vacuum. The evaporated dimer was then pyrolyzed to radical PAC monomers at 690 °C. Finally, the monomeric PAC vapor entered the room-temperature deposition chamber, where it polymerized on all the exposed optical fiber surfaces. In this process, a low pressure (~15 mTorr) should be adopted to obtain a slow deposition rate, thereby a high-quality coating of PAC.

Further, to efficiently prepare the plasmonic nanostructures, AuNPs were immobilized onto the PAC cavity by the self-assembly strategy. To obtain well-dispersed AuNPs on the PAC cavity, an optimized self-assembly strategy based on the block copolymer PS-b-P4VP was adopted in this work. As depicted in Figure 2, the principle of the block copolymer assisted self-assembly was dependent on the interaction of PAC-P4VP-AuNPs. In fabrication, the PAC-coated optical fiber endfaces were first treated with oxygen plasma for hydroxylation, and then dipped in 0.05 mg/ml solutions of PS-b-P4VP in THF for 15 min. In this process, as a result of the noncovalent bonding with the -OH groups on PAC surfaces, the block copolymer PS-b-P4VP was anchored to the photonic cavity and formed a uniform monolayer. After washing the fibers with THF to remove unbound PS-b-P4VP, the endfaces were then dipped into the AuNP solution (0.5 mg/ml) for 2 h. In this state, due to electrostatic interactions between the negatively charged AuNPs and protonated P4VP, the AuNPs were adsorbed onto the PAC surface, thereby forming the plasmonic-photonic hybrid structure with the PAC cavity. Finally, the obtained PPR fiber-optic sensors were rinsed with DI water and dried in a vacuum for use. Compared with silane agents assisted self-assembly, the assembled AuNPs with assistance of copolymer were surrounded by PS, which was repulsive to water. As a result,

the PS segments prevented the formation of a water film and limited the capillary force between AuNPs during drying, thus inhibiting the aggregation of AuNPs.

2. Schematic diagram of the functionalization and biomolecule detection process.

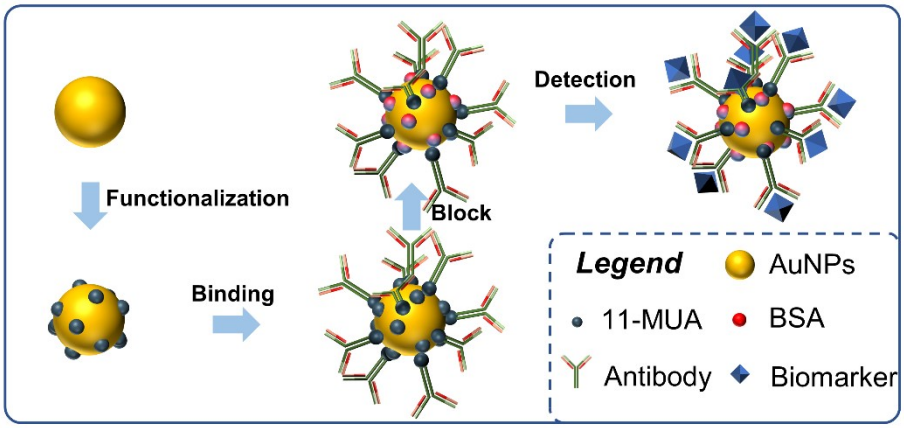

Figure S1. Schematic diagram of the functionalization and biomolecule detection process based on the miniaturized system.

3. Relationship between the RI sensitivities and the cavity thickness.

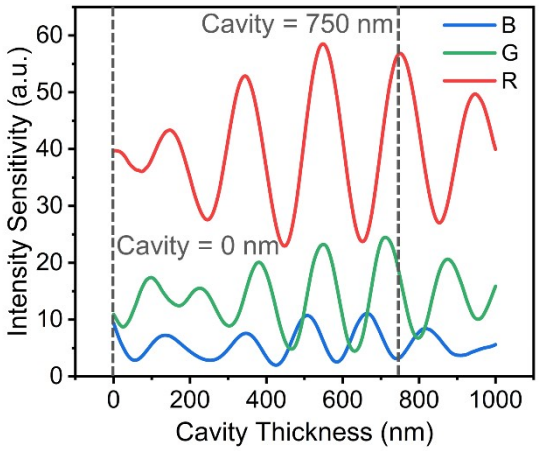

Figure S2. Relationship between the RI sensitivities of the RGB channels and the cavity thickness.

3. Characterization of the PAC cavity on the fiber tip.

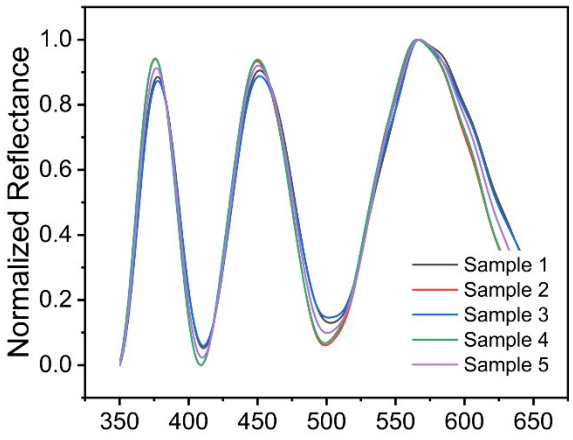

Figure S3. Reflectance spectra of the five PAC cavities on different optical fiber tips, showing good consistency of the PAC deposition process.