Lab-on-Fiber Optrodes Integrated with Smart Cavities

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Abstract A multi-responsive microgel film sandwiched between two gold layers is directly integrated on the tip of an optical fiber to form a multifunctional device able to work as an effective sensor for detecting low-molecular weight biomolecules, as well as a fiber-coupled nano-opto-mechanical-actuator triggered by light through thermo-plasmonics effects.

Keywords Lab-on-Fiber Technology · Plasmonics · Thermo-plasmonics · Microgels · Biosensing · Nano-Opto-Mechanical-Actuation

1 Introduction

The development of the Lab-on-fiber (LOF) technology has conferred to optical fibers new functionalities, thanks to the improvement of nanofabrication techniques that are allowing the effective exploitation of the nanoscale optical physics [1]. The possibility of integrating resonant nanostructures onto the tip of a standard optical fiber has led to the realization of advanced micro-sized devices, which are finding application especially in bio-chemical sensing field [2]. When properly functionalized, the nanostructures can immobilize target molecules, allowing their interaction with light localizations, thus providing signals (typically wavelength shifts of spectral features)

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related to the molecules concentration. In this framework, we have recently demonstrated that multi-responsive 'smart' materials can offer the potentiality for further boosting the performances of LOF biosensors, thanks to their unique capability of changing their characteristics in response to external stimuli [3]. More specifically, we have successfully integrated onto a nanostructured optical fiber tip functionalized microgels (MGs), i.e. colloidal hydrogels particles with radius ranging from few tens of nanometers up to micrometers, able to undergo reversible conformational size changes induced by external physical or chemical stimuli [4, 5]. Such variations can interact with the electromagnetic field localizations strongly tuning the resonant modes, thus giving rise to a huge amplification of the optical signal. Moreover, the MGs integration also offers the possibility of tailoring the probe response in terms of limit of detection and response time [3]. With the aim of exploiting all the degrees of freedom offered by MGs, we propose a new device consisting of a MGs film sandwiched between two gold layers in such a way to form a cavity whose length is modulated by the MGs swelling dynamics. In one configuration of this device, the bottom gold layer is patterned in such a way to excite plasmonic modes. We demonstrate that the combination of the optically resonant effects and MGs properties confers to the Cavity-enhanced LOF device the unique ability to work as a sensor for detecting small molecules with an enhanced sensitivity, as well as a nano-opto-mechanical-actuator triggered by light, setting the stage for the development of multifunctional, reconfigurable optical fiber optrodes.

2 Fabrication and Characterization

The device essentially consists of a MGs film sandwiched between two gold layers and integrated onto the tip of a standard single mode optical fiber (the schematic is shown in Fig. 1a). The gold layer deposited onto the fiber tip has a thickness of 30 nm and is patterned with a square lattice of holes of period 700 nm and radius

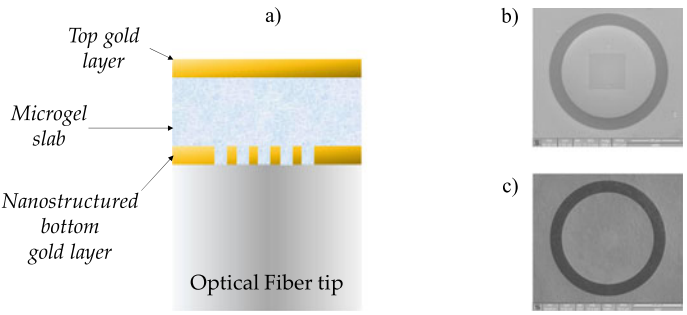

Fig. 1 Schematic of the Cavity-Enhanced LOF device (**a**). SEM image (top view) of the probes realized with 'small' (**b**) and 'large' (**c**) MGs respectively

210 nm; this allows to excite plasmonic modes in the wavelength range of single mode optical fibers [6].

In our previous works we demonstrated that such a cavity can operate with two opposite spectral behaviors, occurring for cavity thicknesses smaller and larger than ~200 nm, which corresponds to the evanescent tail of the plasmonic resonance [7, 8]. These two regimens can be set during the fabrication step by properly choosing the MGs size, and through a careful control of the MGs deposition procedure, based on dip coating technique, optimized in our previous works [9, 10]. Therefore, we realized two different probes starting from MGs of different size, i.e. 'small' MGs (radius between ~100 nm and ~240 nm) and 'large' MGs (radius between ~190 nm and ~400 nm). Specifically, the 'small' MGs set was deposited onto the fiber tip covered by a 30 nm thick, patterned gold layer. The plasmonic nanostructure was fabricated via a focused ion beam milling process. The 'large' MGs set was instead deposited on an unpatterned gold layer of 12 nm. The two devices were then processed by depositing a 12 nm thick gold layer to form a cavity. Finally, the top mirror was patterned with a circular 5 μm width trench (external radius of 50 μm) centered in correspondence of the fiber core for ensuring a rapid and uniform MGs slab wetting. The top views of the fabricated samples are shown in Fig. 1b ('small' MGs) and 1c ('large MGs').

The two probes were placed in a temperature-controlled cuvette heated by a Peltier cells system, and characterized by exploiting the MGs thermo-responsivity for inducing the swelling dynamics, according with Dynamic Light Scattering (DLS) measurements of the MGs radius shown in Fig. 2a. The acquired spectral evolution as a function of the solution temperature is shown in Fig. 2b, c. The pseudo-color plots clearly show two opposite trends. Specifically, the cavity probe realized with 'small' MGs shows a red-shift of a reflection spectrum dip of 75.6 nm (dashed blue curve of Fig. 2b) induced by a temperature increase of 42 °C. This behavior is given by the excitation of a hybridized plasmonic mode between the two gold layers [11] that shifts towards higher wavelength in response to MGs slab shrinking induced by temperature (according with the MGs size variations shown in Fig. 2a). The probe realized with 'large' MGs shows different reflection spectral dips that blue-shifts in response to the same temperature increase. In this second case the spectral dips are given by interferometric Fabry–Perot effects occurring between the two gold layers

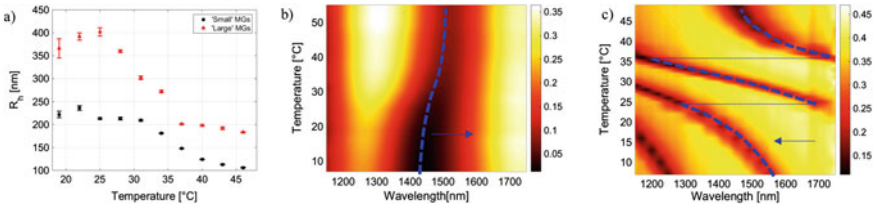

Fig. 2 MGs radius as a function of temperature (**a**). Reflection spectra evolution as a function of solution temperature pertaining to the probe realized with 'small' (**b**) and 'large' (**c**) MGs. The insets show the measured spectra at three different temperatures

[5]. By cumulating the shifts of different spectral dips, as shown by dashed blue curve in Fig. 2c, we measured an impressive total shift of 1067 nm.

3 Light-Controlled LOF Actuators

The MGs thermo-responsivity combined with the plasmonic nature of the resonant modes can add new functionalities to optical fiber probes realized with the LOF technology. The gold nanostructure integrated onto the fiber tip, in fact, works as an effective local heater, whose temperature can be controlled by the input optical power, by exploiting the thermo-plasmonic effect, i.e. the local overheating caused by the light absorption [12, 13]. The light absorption by the gold film is in fact strongly enhanced by the field localization caused by the excitation of plasmonic modes. The pseudo-color plot of Fig. 3a shows the numerically evaluated absorption spectra for different MGs slab thicknesses.

In Fig. 3b we report the integral of each spectrum normalized to the integral value obtained with the standard 'open' device. It is evident that a strong absorption enhancing occurs in correspondence of a thickness of ~150 nm, i.e. when the hybridized mode is excited. By exploiting the thermo-plasmonic effect, it is thus possible to induce the MGs slab swelling/shrinking dynamics. A modulation of the input optical power, in fact, allows to control of the local overheating, and thus for the actuation of the top gold layer position. In order to demonstrate this principle, we acquired the reflection spectra of the patterned probe (realized with 'small' MGs), in correspondence of different values of the optical input power (in the range 2 μW–1 mW). During this experiment, the solution temperature was kept constant by using the Peltier cells based system mentioned above. Specifically, the same test was repeated for a solution temperature equal to 6 °C, 21° and 45°, at pH4. The plot of Fig. 4a shows the reflection spectral dip wavelength as a function of the input power level, for the three different solution temperatures. These results essentially demonstrate

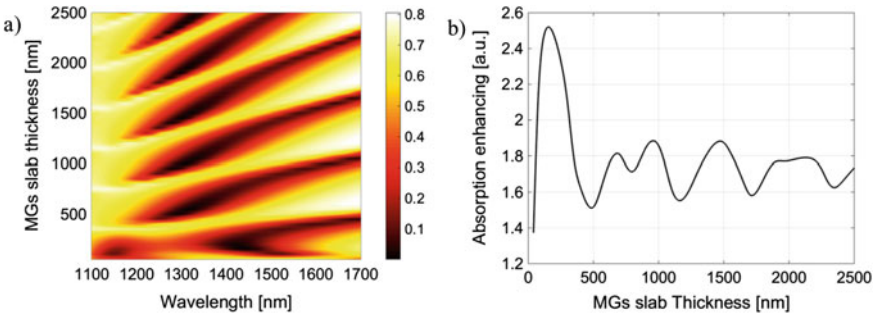

Fig. 3 (**a**) Numerically evaluated absorption spectra evolution as a function of MGs layer thickness. (**b**) Integral absorption enhancing evaluated with respect to the standard 'open' device

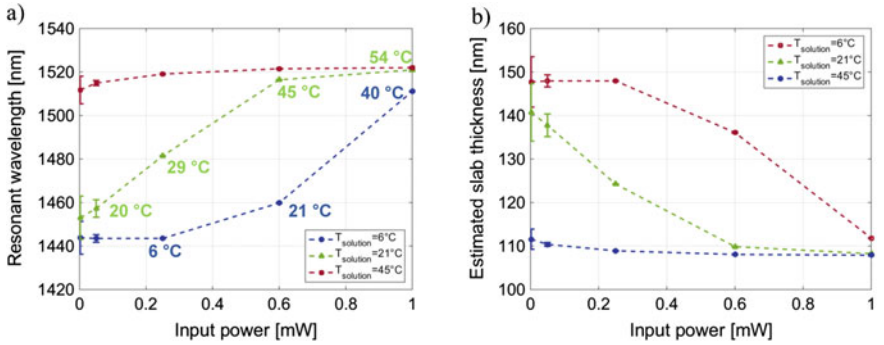

Fig. 4 Wavelength shift (**a**) and estimated slab thickness (**b**) as a function of the input optical power

that by increasing the input optical power it is possible to induce the same wavelength red-shift observed by changing the bulk temperature solution (Fig. 2b).

The entity of the resonant shift clearly depends on buffer solution temperature, and is maximum at 6 °C, i.e. when the MGs are completely swollen. On contrary, the wavelength shifts measured at 45 °C, is negligible since MGs are already collapsed. By correlating the results of Fig. 4a and 2b, we estimated the temperature of the fiber tip as a function of the input power (cf. values reported in Fig. 4a). It is important to remark that the results shown in Fig. 2b were obtained by using a low input optical power (5 μW) in order to avoid any overheating effect. We found that the estimated temperature achieved on the fiber tip linearly increases as a function of the input power, with a slope of about 45 °C/mW. Then, to evaluate the cavity thickness variations induced by the input optical power, a numerical fitting process was implemented by taking into account the inverse relation between the RI and the thickness of the MGs slab. More specifically, the MGs slab was modeled as a uniform layer whose RI (n_{slab}) is given by the Eq. (1), as a function of the MGs slab thickness (h_{slab}), according with the model described in our previous works [14, 15],

$$n_{slab} = (n_p - n_s)K\frac{L}{h_{slab}} + n_s \tag{1}$$

where n_p and n_s are respectively the RI of the NIPAM (1.47) and solution (1.33), L is the number of MGs layer (set equal to 2 according with the number of immersions during the dip coating procedure) and K is a constant depending on the MGs particle profile in dry state, measured by means of an Atomic Force Microscopy (cf. [15] for more details). The results of our analysis are shown in Fig. 4b. Coherently with the wavelength shift, the maximum cavity thickness excursion (36 nm, from 148 to 112 nm) was achieved at low temperature (6 °C). At 21 °C the estimated thickness variation range is 32 nm, (i.e. from 140 to 108 nm), while at 45 °C the actuation was negligible.

4 Sensitivity Enhanced Biosensors

When MGs slab is properly functionalized to respond to molecules binding events, the induced swelling/shrinking dynamics can be exploited to detect target molecules dissolved in a buffer solution, obtaining a wavelength shift that is correlated to the molecules concentration. For evaluating the capability of the Cavity-Enhanced LOF probe to detect molecules, we tested the sample working in the Fabry–Perot like regime, in order to take advantage from the huge shift observed during the preliminary thermal characterization. In the wake of our previous work, the MGs slab was functionalized with amino phenyl boronic acid (APBA) in order to make the probe sensitive to glucose molecules, chosen as benchmark for small molecules detection. The glucose assay was carried out by placing the fiber probe in a carbonate buffer solution (700 μL, pH9) whose temperature was fixed at 20 °C, containing glucose molecules at different concentrations (between 0.16 μM and 16 mM). After the insertion we monitored the reflection spectra evolution; at the end of the measurement of each concentration, the probe was regenerated in water solution for 1 h under stirring, and tested in the new concentration.

At glucose concentrations of 160 μM, 1.6 mM, and 16 mM, respectively, the sensorgram (i.e. the wavelength shifts of the reflection spectrum dip as a function of time) reached steady-state values of 58.9 nm, 242.7 nm and 1043.1 nm. These results are shown in Fig. 5a. Similarly to the above described thermal characterization, the shift obtained with the higher concentration was estimated by cumulating the single shifts of different reflection dips. Negligible wavelength shifts were instead measured for concentrations up to 16 μM. For demonstrating the enhanced sensitivity we deposited the same MGs set on a patterned device, without realizing the top gold layer. This standard MGs-assisted LOF probe (the same studied in our previous work [3]) responded to the same glucose concentrations with a blue-shift that does not exceed ~16 nm (Fig. 5b).

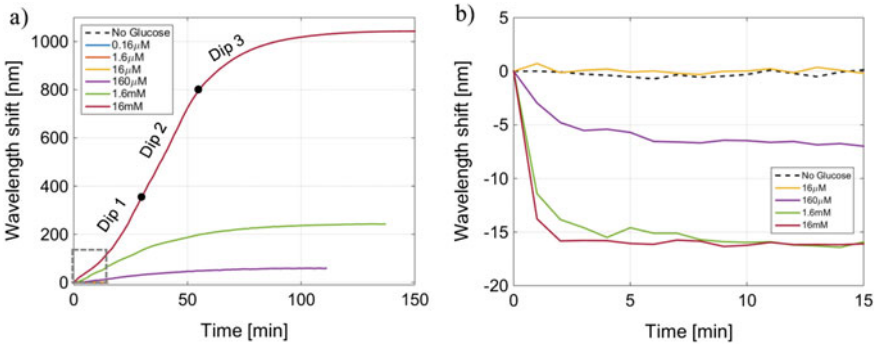

Fig. 5 Biosensing experiment: sensorgram for different glucose concentrations for Cavity-Enhanced LOF probe (**a**) and 'standard' open device (**b**)

5 Conclusion

In conclusion, in this work we reported on an advanced multi-responsive LOF device arising from the integration onto an optical fiber tip of a swelling cavity composed by a MGs slab placed between two gold layers. The probe is reconfigurable for different applications, depending on the MGs characteristics and on the electromagnetic phenomena exploited as well. By combining the thermo-plasmonic effect with the MGs thermo-responsivity we successfully demonstrated the capability of inducing changes of the top membrane position by modulating the input optical power in mW range. These results pave the way to the development of active light-triggered nano-actuators completely integrated onto the fiber tip. Moreover, by properly functionalizing the MGs slab, we demonstrated an enhanced sensitivity for small molecule detection up to a factor 65 with respect to a standard 'open' MGs assisted-LOF probe. Overall, the discussed results enables to achieve significant improvements in terms of performances and functionalities of LOF probes opening new avenues for the development of advanced, multifunctional, reconfigurable and tunable fiber optic devices.

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