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Optical fiber-based polymer micro-cantilever for chemical sensing: A through-fiber fabrication scheme

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Abstract

Fiber optics offer an emerging platform for chemical and biological sensors, when engineered with appropriate materials. However, the large aspect ratio makes the optical fiber a rather challenging substrate for standard microfabrication techniques. In this work, the cleaved end of an optical fiber is used as a fabrication platform for cantilever sensors based on functional polymers. The through-fiber fabrication process is triggered by photo-initiated free radical polymerization and results in a high aspect ratio polymer beam in a single step. The dynamic mode application of these cantilevers is first demonstrated in air. These cantilevers are then tuned for sensing applications, including humidity and chemical sensing based on molecularly imprinted polymers.

Micro(nano)electromechanical systems (M(N)EMS) such as single clamped cantilevers have become over the years standards for bio and chemical sensing. Indeed, operated in dynamic mode, these devices can be used as label-free, sensitive mass sensors with a resolution down to single molecule and particle recognition reached under very controlled conditions (e.g. high vacuum, cryogenic temperature).¹ The majority of M(N)EMS sensors are based on silicon and associated complex micro/nano-machining techniques. M(N)EMS based on polymers offer an interesting alternative, since their chemical properties can be easily tuned towards the desired application.² Polymer M(N)EMS can be processed by a large variety of fabrication techniques, ranging from modern techniques for rapid prototyping such as 3D-printing or two-photon stereolithography,^{3,4} to mass-manufacturing methods such as injection molding.⁵ Compared to silicon M(N)EMS, polymer micro and nanosystems can be processed by means of bottom-up approaches, greatly simplifying their fabrication, as well as enabling the introduction of breakthrough concepts, in particular, when photopatterned. In this context, fiber optics, that are nowadays state of the art technology for modern telecommunication, are also an interesting tool for metrology, including physical and chemical sensors.^{6,7} Especially physical sensors such as fiber Bragg gratings (FBG) and fiber optic gyroscopes (FOG) are nowadays well established in academia and for industrial applications.^{8,9} For chemical sensing a suitable receptor element needs to be attached to the optical fiber.^{7,10} Often polymers are chosen as recognition element for proof of concept studies of new read-out schemes since this class of material is more accessible for microfabrication techniques than complex (bio-) macromolecules.¹¹⁻¹³ On the other hand, macromolecules such as antibodies, nucleotide chains, or aptamers give access to selective target recognition.¹⁴⁻¹⁶ An interesting and simple method for the fabrication of a fiber-based opto-chemical sensor using fluorescence was introduced by Ton et al.¹⁷ A molecularly imprinted polymer (MIP) tip was synthesized in one step at the end of an optical fiber by a through-fiber fabrication process.¹⁸ However, despite their exceptional sensitivity, fluorescence sensors are somehow limited towards intrinsically

fluorescent analytes, labeling techniques, or complex MIP systems where certain analytes can trigger fluorescence.

In this work, we present the development of a new fabrication strategy for polymer microcantilever sensors based on fiber optics. Free-standing polymer beams are directly synthesized at the end of a cleaved optical telecommunication fiber by photo-induced free-radical polymerization and applied as mechanical resonators. After having demonstrated the suitable dynamic operation of the resulting polymer tips, two sensing applications are presented in this work. In a first application, the beam is functionalized with a hydrophilic polymer with a low cross-linking density for the online monitoring of humidity in air. In a second application a MIP targeting the antibiotic enrofloxacin is grafted on the cantilever by a unique post-polymerization process, which enables the selective and sensitive detection of this low molecular weight analyte.

The polymer cantilevers at the end of a cleaved optical fiber are generated in a single step and in a cleanroom-free environment, as an extension of the fiber core by a through-fiber fabrication technique⁷ as shown in **Figure 1** A-C. Therefore, UV-light is guided through an SMF-28 optical telecommunication fiber with an 8 μm core and polymerizes a monomer solution that is placed between the surface of the cleaved optical fiber and a substrate by radical photopolymerization. The resulting bottom-up fabricated cantilever, with a cylindrical shape of 10 μm in diameter, is generated within seconds by a self-guiding effect of the polymerized material. This effect was experimentally and analytically described by Hocine and co-workers and is based on a refractive index change of the polymerized material.¹⁹ The polymerization at the end of the optical fiber core creates a small section with a higher refractive index than the surrounding monomer environment and can be seen as an extension of the core in which the light is guided. The small size of the polymerized area is confined by

the exposure intensity and the core diameter, whereas the length (from 30 μm to 200 μm) of the beams is controlled by a micrometer positioner and defined by the distance of the substrate surface and the cleaved optical fiber.

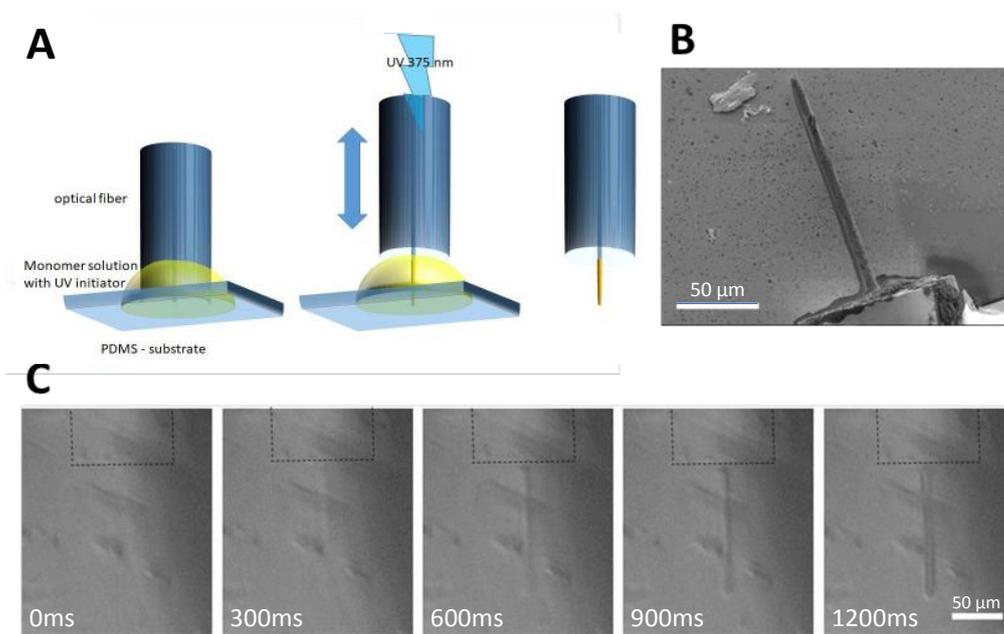


Figure 1. (A) Schematic view of the fabrication process of an end-of-the-fiber polymer beam. An optical telecommunication fiber is brought into a polymerizable precursor solution. After adjusting the distance between substrate and the end of the optical fiber, UV-light is guided through the core and polymerizes a free standing polymer beam of controlled length at the extremity of the optical fiber. (B) SEM image of a through-fiber fabricated polymer cantilever. (C) Polymerization propagation of a cantilever beam tip.

To first demonstrate the dynamic mechanical operation of the through-fiber fabricated polymer micro-cantilever, the latter is fixed on a piezo driven lead zirconate titanate (PZT) actuator and its resonant frequency is recorded with a laser-Doppler vibrometer (**Figure 2 A**). As shown in **Figure 2 A**, the resonance spectra of the through-fiber photopolymerized polymer beams can be easily obtained. Also the length dependence of the resonant frequency confirms the expected dynamic mechanical behavior of the polymer tips (**Figure 2 B**). The $1/L^2$ linear dependence validates the proposed scheme for the well-controlled fabrication of polymer micro-cantilevers. The associated quality factors are around 22 (**Figure 2 C**), which is in agreement with values found in literature for polymer-based microcantilevers.^{20,21}

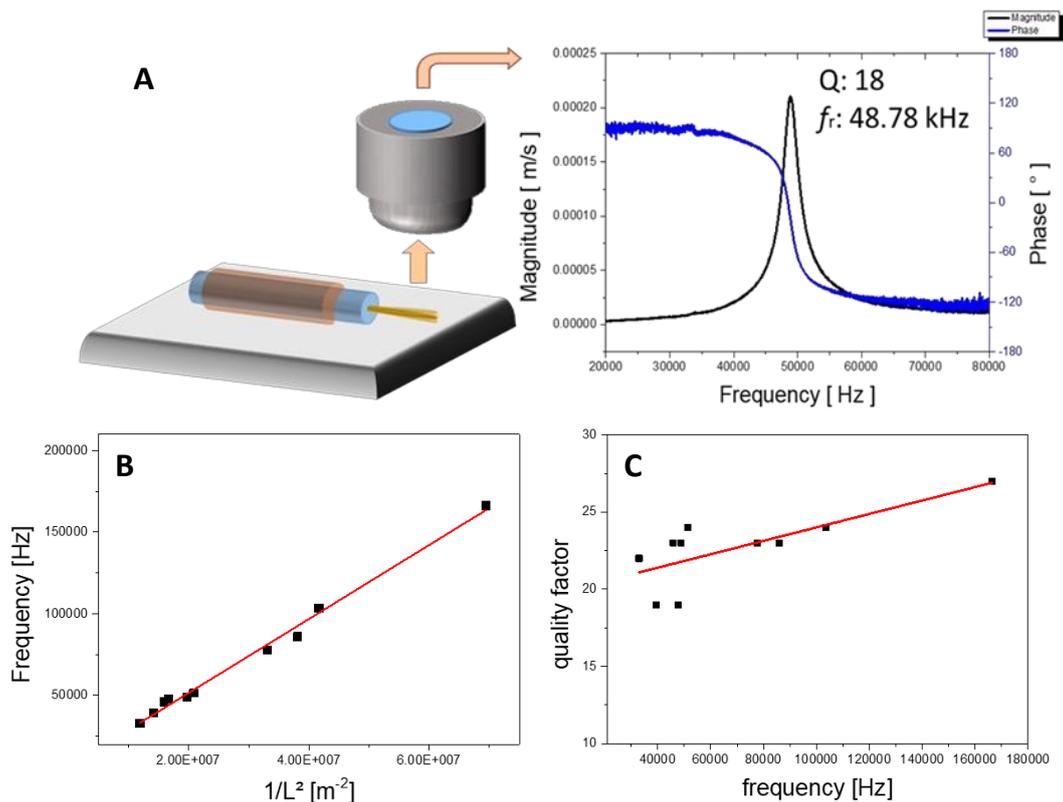


Figure 2. (A) Schematic view of the optical read-out of a through-fiber fabricated cantilever fixed to a piezoelectric actuator with an example of a recorded frequency spectrum of a polyPETIA cantilever of 100 μm in length. (B) Evolution of the resonance frequency of through-fiber fabricated micro-cantilevers with their length. (C) Evolution of the quality factor of through-fiber fabricated micro-cantilevers with associated resonance frequency.

In a first application example, a core-shell cantilever for humidity sensing is presented in order to demonstrate the feasibility of tuning the properties of the polymer beam for a specific sensing application. In an initial step, a hydrophobic core tip made from trimethylolpropane trimethacrylate (TRIM) is synthesized through the fiber in the presence of the non-polar solvent toluene. The solvent toluene helps to solubilize the photoinitiator bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide and enhances the hydrophobic properties of the core. In a second step, a hydrogel shell is synthesized through re-initiation with a pre-polymer mixture consisting of 2-hydroxyethyl-methacrylate (HEMA) and the cross-linker ethylene glycol dimethacrylate (EGDMA). The relative dynamic response of the core-shell cantilever towards a change of the relative humidity from 20 to 60 % is with 3.4 % significantly higher than the response of the unfunctionalized control cantilever (1.4 %) (**Figure 3 A**) and highlights the strength of the tailor-made cantilever sensors based on polymers. **Figure 3 B**

presents the real-time evolution of the frequency shift of a typical hydrogel core-shell cantilever towards different relative humidity levels. The displayed sensor resonates at 45.5 kHz (at 20 % relative humidity) and shows a maximum frequency shift of more than -1500 Hz for an increase of the relative humidity from 20 to 60 %. After each change in humidity, the atmosphere was re-adjusted to 20% humidity to verify the reversibility of the sensor response. No shift in baseline signal is observed. Also, the repeatability of the core-shell humidity sensors is showed in Figure S1. The values obtained for each repeated cycle are almost identical, showing that the humidity uptake of the sensors is reversible and thus, that they can be used for multiple sensing operations. Finally, the plateau frequency, plotted versus the relative humidity change, shows a linear dependence (Figure 3 C). A large sensitivity of $-836 \text{ ppm}/\%_{\text{RH}}$ is obtained experimentally. This value is one of the largest sensitivity values reported in literature for comparable systems.^{22,23}

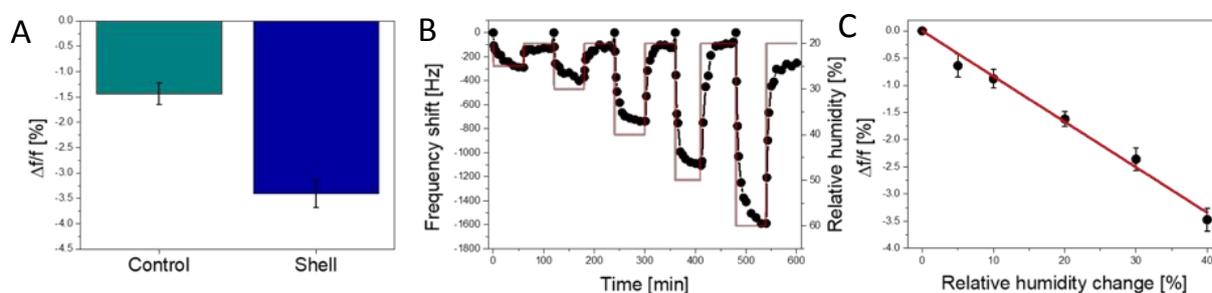


Figure 3. (A) Cantilever response towards a humidity change from 20 % to 60 % (error bars represent the standard error of the mean for $n = 5$); (B) Online measurements of the resonant frequency shift for increasing levels of humidity; (C) endpoint values of the relative humidity change as a function of the resonant frequency shift (error bars represent the standard error of the mean for $n = 3$)

Another interesting proof-of-concept application of the proposed through-fiber fabricated cantilever is the use as a specific chemical sensor in the liquid phase based on MIPs. These biomimetic polymers are capable of selective target recognition comparable with natural antibodies. This is achieved by polymerizing cross-linker monomers and functional monomers around a template molecule. After template extraction an imprinted cavity is left in the polymer matrix with functionalities that selectively bind the analyte of interest. In many applications where MIPs are structured on the micro/nano scale, new formulations of the

functional polymer have to be developed to meet the requirements of the fabrication method.^{3,26-28} In most cases a trifunctional cross-linker such as PETIA or TRIM is employed for the structural integrity of the polymer. Such MIPs have been described in several works and were used by Fuchs et al. for the microfabrication of a diffraction grating.^{26,27} This approach would have allowed in our case the through-fiber synthesis of a cantilever in one step from MIP precursors only. However, we have developed a more versatile core-shell approach to MIP-MEMS chemical sensors, for the selective recognition of the antibiotic enrofloxacin. Fabrication of a core-shell structure presents unique advantages over the bulk fabrication method. Indeed, Ton et al. demonstrated that binding kinetics are faster for core-shell structures, since diffusion distances to the binding sites of the MIP are shorter.¹⁷ Furthermore, this approach allows to fabricate MIPs using also bifunctional cross-linkers such as EGDMA or DVB. This is a big step towards a versatile sensor concept that can be applied to the huge library of already existing MIPs and where the cantilever transducer core can be generic based on a standard protocol.

The MIP targeting the antibiotic enrofloxacin²⁹⁻³¹ is used here since the intrinsic fluorescent properties of this analyte can be used for reference binding assays (see supporting information, Figure S2). Furthermore, the successful fabrication of the MIP-based core-shell polymer beam is easy to visualize, as shown in **Figure 4 A**. The MIP based core-shell cantilevers are fabricated in a two-step approach with a structural polyPETIA mechanical core and a through-fiber photo-polymerized MIP shell around it.

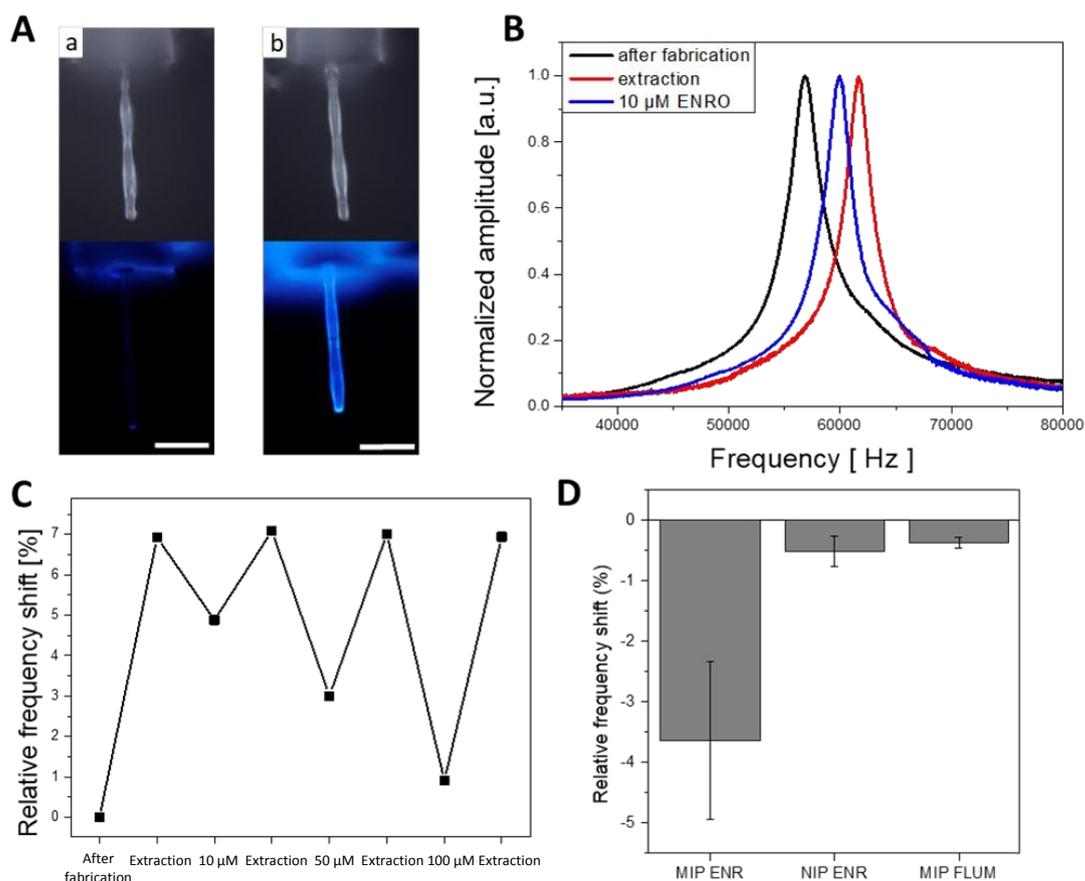


Figure 4. (A) a) Bright-field and fluorescence microscope images of a polymer cantilever before MIP shell grafting, and b) after MIP shell photo-polymerization; (B) Recorded resonant frequencies in vacuum after fabrication (black); after template extraction (red) and after binding in 10 μM enrofloxacin in acetonitrile (blue); (C) dynamic response of the MIP core-shell cantilevers after multiple extraction and rebinding cycles (enrofloxacin concentrations 10 μM , 50 μM and 100 μM in acetonitrile); (D) relative frequency shift of MIP and NIP cantilevers towards 50 μM enrofloxacin in acetonitrile, MIP response towards 50 μM flumequine in acetonitrile (error bars represent standard error of the mean, $n=5$).

For the gravimetric binding studies, they were carried out by the dip and dry method. After extraction of the template molecule with acetic acid / ethanol (1:10) the MIP core-shell cantilevers were thoroughly rinsed with acetonitrile and dried. A significant increase of the resonant frequency was observed (Figure 4B), as well as a decrease by approximately 80 % of the fluorescence intensity of the initial value (**Figure S2**). Figure 4B shows resonance spectra of a MIP cantilever after fabrication, after template extraction and after incubation in 10 μM of enrofloxacin, respectively. The decrease of the resonance frequency after incubation proves the uptake of the analyte into the binding sites. After incubation for 2 hours in 10 μM , 50 μM and 100 μM of enrofloxacin in acetonitrile solutions (with a preliminary immersion into

acetonitrile to ensure that no solvent effect e.g. swelling of the polymer, is observed), resonance spectra were acquired and analyzed. The decrease of the resonance frequency showed a mass dependence on the analyte concentration (Figure 4C), confirmed by fluorescence analysis (Figure S2). Also, cantilevers were used for several cycles and showed a repeatable concentration dependent response towards the analyte enrofloxacin. Binding specificity of the fabricated MIP cantilevers was evaluated using a chemically identical non-imprinted control polymer (NIP), and by incubating the sensors in 50 μ M flumequine, a structural analogue (Figure 4D). The frequency shift was much smaller for flumequine than for enrofloxacin, indicating that the MIP specifically targets enrofloxacin. Also, a low frequency variation was measured on the NIP control after incubation in 50 μ M enrofloxacin, showing again the specific detection of analyte by the MIP cantilevers. These results are in good agreement with earlier reports on MIPs targeting enrofloxacin.^{3,30}

MIPs have already been introduced in the 1990s as a receptor layer for mass sensors, using a quartz crystal microbalance (QCM).^{24,25} More recently a microcantilever sensor fully based on MIPs was fabricated by a shadow masking technique, proving the potential of label-free polymer microcantilever chemical sensors.² In the latter work, a multi-step fabrication process was proposed, without the possibility of integrating transduction schemes. Concerning enrofloxacin, photoluminescence remains the main detection scheme, with exceptional sensitivities.^{29,31,32} In this context, the through-fiber fabricated MIP core-shell cantilevers presented here are simple to fabricate, in a single step, and show label-free, specific and sensitive low molecular weight analyte detection, a challenge for mass sensors operating in standard environmental conditions.

In conclusion, we have developed a versatile and simple strategy for the fabrication of polymer microcantilever chemical sensors based on a through optical fiber fabrication concept. The devices can be generated within seconds at the end of an optical

telecommunication fiber and allow easily the addition of functional polymer layers, such as hydrogels and MIPs. After having demonstrated the dynamic mode operation of the cantilevers, a first proof-of-concept application for sensing in the gas phase has been demonstrated. Cantilevers were decorated with a hydrogel, enabling the sensitive and real-time monitoring of the relative humidity in air. In a second proof-of-concept application, the cantilevers were tested in liquid for the specific and sensitive binding of the antibiotic enrofloxacin by decorating them with a MIP shell. More generally, the use of an optical fiber not only offers an interesting fabrication platform for cantilever sensors but might be an interesting tool for the read-out, as it was proven in a study by Frazao et al, where a through-fiber fabricated polymer tip was used as a Fabry-Perot cavity for refractive index measurements.³³

Experimental Section

Polymer samples: For the humidity sensing application, the core polymer was made from trimethylpropane trimethacrylate (TRIM), mixed with 50%_{wt} toluene and 1%_{mol} (of polymerizable groups) of the initiator bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide. The shell was made from a mixture of ethylene glycol dimethacrylate (EGDMA) (0.03 mmol) and 2-hydroxyethyl methacrylate (HEMA) (1 mmol) with 1 %_{mol} (of polymerizable groups) bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, mixed with 50 %_{wt} of water.

For the enrofloxacin MIP experiments the core was fabricated from PETIA mixed with 50%_{wt} toluene and 1%_{mol} (of polymerizable groups) initiator bis(2,4,6-trimethyl-benzoyl)-phenylphosphineoxide. For the MIP shell the template enrofloxacin (0.05 mmol) was mixed in a small vial with the functional monomers MAA (0.2 mmol) and HEMA (0.2 mmol) in 130%_{wt} (mass of monomer mixture) anhydrous acetonitrile. After the template was completely dissolved, the cross-linker ethylene glycol dimethacrylate (1 mmol) was added together with 1%_{mol} (of polymerizable groups) initiator bis(2,4,6-

trimethylbenzoyl)-phenylphosphineoxide. The sample was degassed with argon for 5 minutes and sealed before use. All chemical were purchased from Merck.

Through-fiber cantilever fabrication: A 375 nm UV laser source (Oxxius lbx-375-70-CSB-PP, controlled by a mechanical shutter) was coupled into an optical fiber with an 8 μm core (SMF-28-J9 by Thorlabs). The cleaved end of the fiber was carefully dipped into a droplet of the pre-polymer mixture and the length of the cantilever (defined by the distance between the cleaved fiber surface and the surface of the support on which the droplet was placed) was adjusted between 100 μm and 200 μm with a micropositioner.

After polymerization, the cantilever tip was dipped into ethanol and unreacted monomers were washed away. For the humidity sensing experiments the core-shell was fabricated by dipping the polyTRIM core into the pre-polymer solution. A shell was polymerized around with an exposure intensity of 50 μW . The process was monitored by a camera and stopped after a visible shell was polymerized on the cantilever.

For the cantilever sensor based on the MIP targeting enrofloxacin the core-shell was fabricated from the MIP precursors in the same way as described before. In a final step the fabricated structures were fixed with SU-8 on a glass support.

Dynamic characterization: For vibrational analysis of cantilever structures, the glass slides with the through-fiber fabricated cantilevers on top were fixed on a piezo driven lead zirconate titanate (PZT) actuator (purchased from PI) with double-sided adhesive tape. Frequency spectra were recorded with a laser Doppler vibrometer (Polytec MSA 500) and the first out-of-plane flexural mode was analyzed for the sensing applications.

Humidity sensing: For humidity sensing the cantilever samples were placed in an environmental chamber (purchased from Surface Measurement Systems). The temperature was fixed at 21°C and the humidity level controlled over a range of 20% and 80%. Each cycle started after the signal stabilized at a relative humidity level of 20% and each cycle was recorded for 1 hour.

MIP sensing: Measurements of MIP structures were carried out in a custom-made vacuum chamber. Each resonant frequency measurement was carried out after the signal stabilized (minimum 4 hours). MIP binding tests were carried out by the dip and dry method. The resonant frequencies of the structures were analyzed before template extraction, after template extraction (over-night washing in acetic acid / ethanol (1:10) and 3 times rinsing for 1 hour in acetonitrile), and after analyte binding (10 μ M, 50 μ M and 100 μ M enrofloxacin in anhydrous acetonitrile for 2h). For selectivity studies a binding test with 50 μ M flumequine in anhydrous acetonitrile was carried out.

Supporting Information Available:

The following files are available free of charge: SI v1.docx. The supporting information shows the repeatability of the sensors towards several cycles of humidity, as well as the control fluorescence response of the sensors for Enrofloxacin detection.

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