Supporting Information for:

Fast and All-Optical Hydrogen Sensor Based on Gold-Coated Optical Fiber Functionalized with Metal-Organic Framework Layer

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Experimental details

Preparation of ADT-COOH

To a solution of p-TsOH (1.425 g, 7.5 mmol) in acetic acid (12 mL), tert-butyl nitrite was slowly added (0.9 mL, 7.5 mmol). Next, 4-aminobenzoic acid (0.685 g, 5 mmol) was added in 4 steps to the reaction mixture over 1 min. The mixture was stirred for 30–40 min until TLC indicated the complete consumption of the amine (hexane/ether 1:1). After completion, the reaction mixture was precipitated by adding diethyl ether (200 mL). The precipitate was washed with diethyl ether, filtered under reduced pressure and dried under vacuum.

Preparation of IRMOF-20 mother liquid and surface assisted growth of IRMOF-20. Preparation of IRMOF-20 modified surface was carried out according to [45] with slight modifications. Thieno[3,2-b]thiophene-2,5-dicarboxylic acid (0.075 g, 0.33 mmol) and zinc nitrate tetrahydrate (0.3 g, 1.1 mmol) were dissolved in 10 mL of N,N-diethylformamide with stirring in a mouth glass jar. The jar was tightly capped and placed in a 100 °C oven for 18 h to yield cubic crystals. After cooling down to room temperature, the suspension was centrifugated for 3 h (7700rpm) and mother liquid was used for further surface-assisted MOF growth.

The residual powder was rinsed with DMF, the product was immersed in chloroform for 1 d, washed 3 times by chloroform and dried under vacuum at room temperature. The resulting powder was used for comparative analysis.

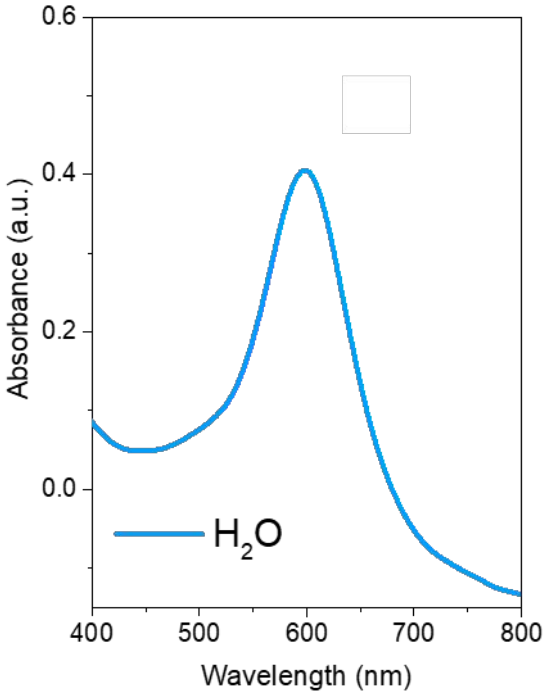

Fig. S1

Control measurements of plasmon absorption band appearance (before grafting of IRMOF-20 layer): UV-Vis spectrum of gold-coated optic fiber in the underwater conditions (the light transmission at air was used as a spectral background).

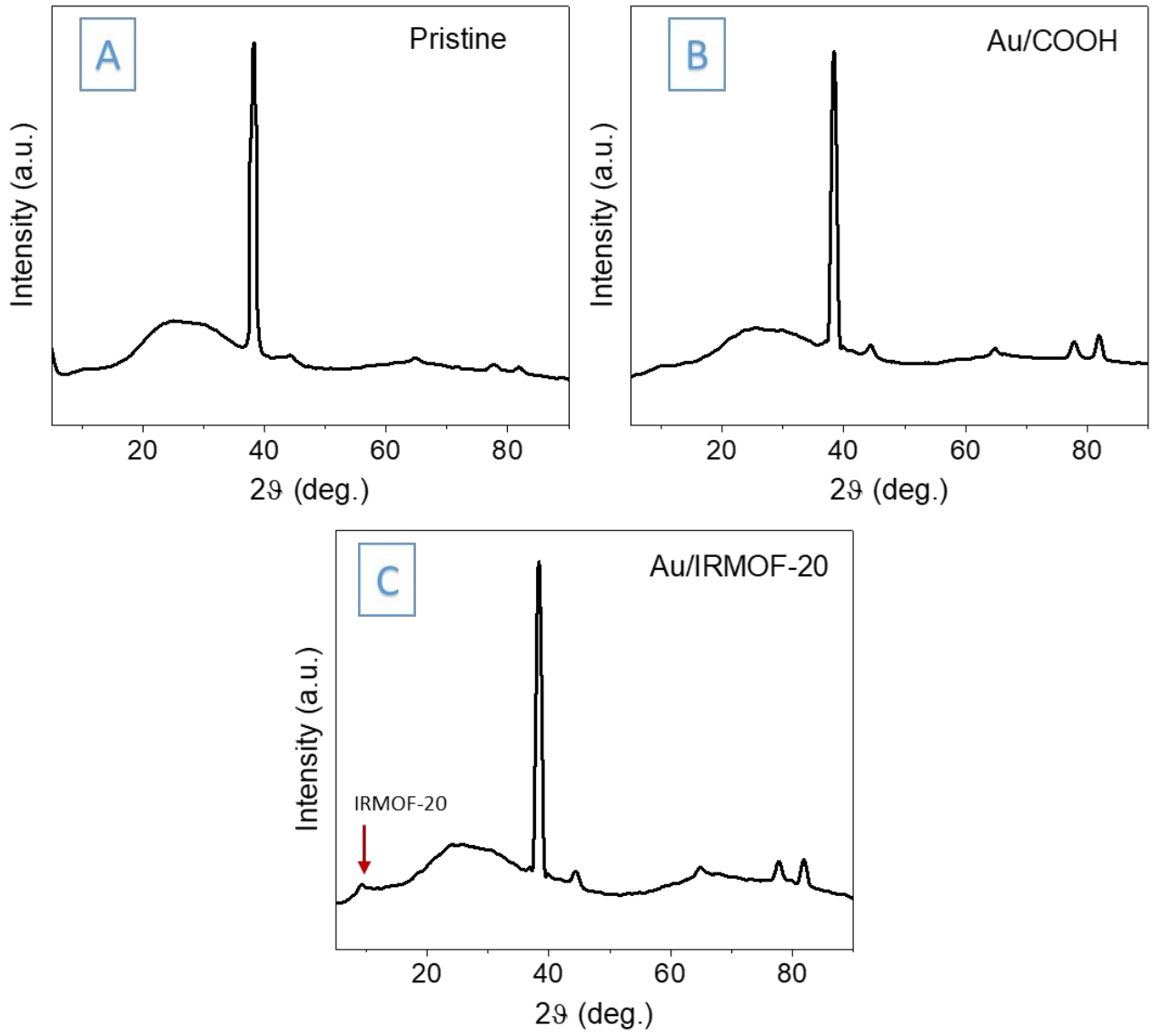

Fig. S2

Control measuremnments and XRD proof of the crystalic nature of surface grown IRMOF-20 layer: XRD-diffractograms of pristine thin gold film (A), thin gold film grafted by ADT-COOH (B), and thin gold film decorated with thin IRMOF-20 layer, according the used experimental procedure (C). The more informative IRMOF XRD peak, corresponding to "large" crystallographic parameter (arising from IRMOF-20) is designated by array in the part C.

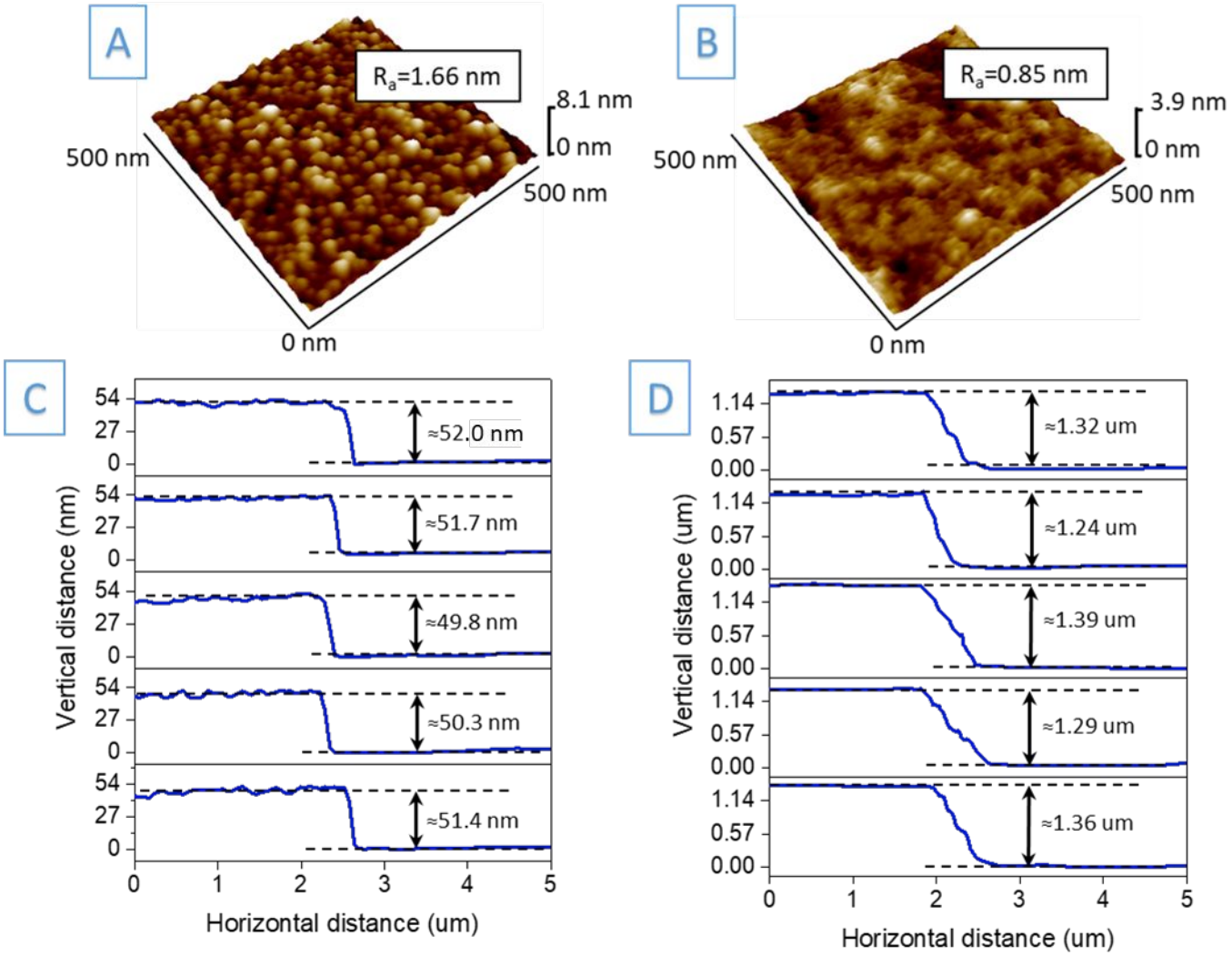

Fig. S3

AFM images of plasmon-active surface of the optical fiber after gold deposition (A) and subsequent IRMOF-20 grafting (B). AFM scratch tests, demonstrated the thickness of the gold layer (C) and the gold layer grafted with IRMOF-20 (D).

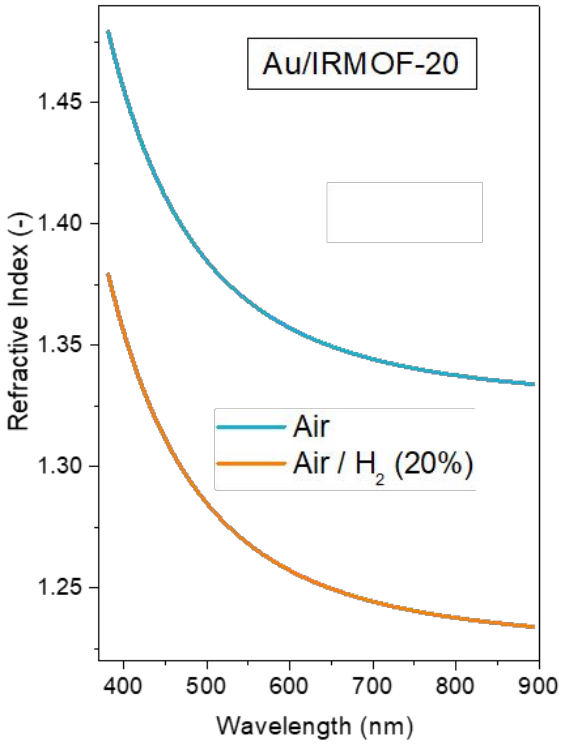

Fig. S4

Control ellipsometry measurements: wavelength dispersion of IRMOF-20 refractive index (real part) measured at air or in the hydrogen/air mixture.

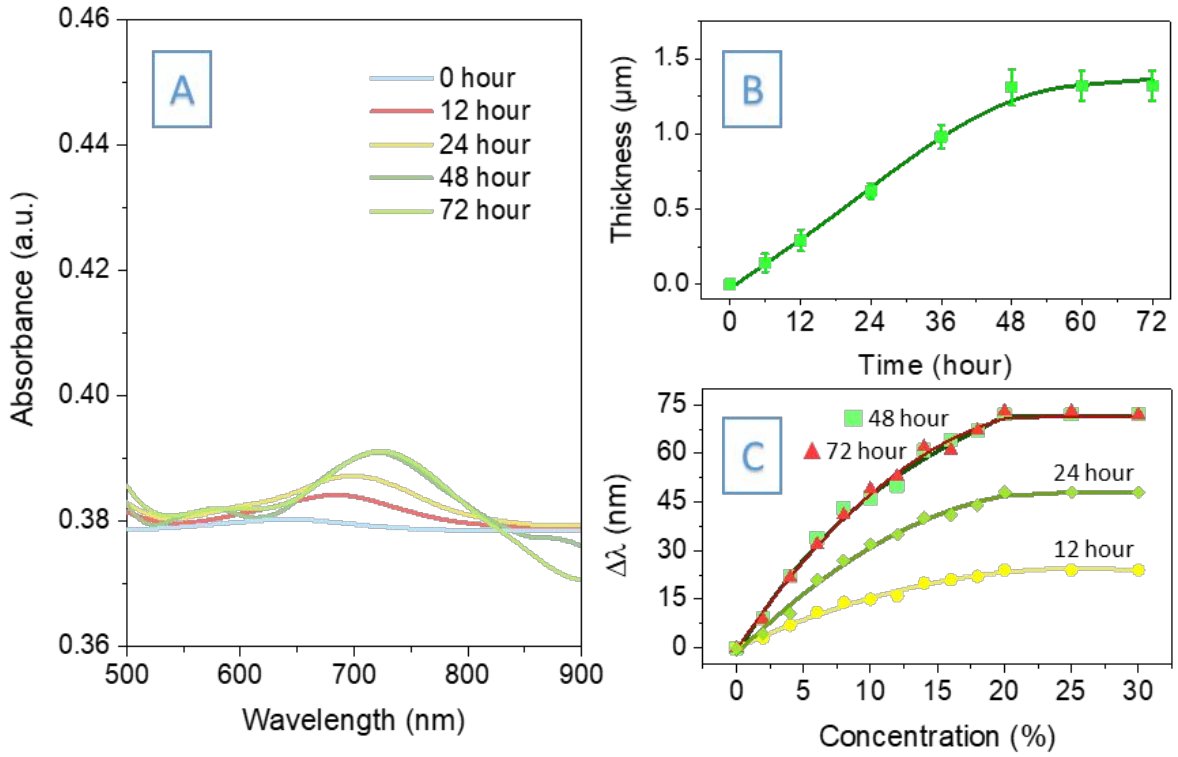

Fig. S5

(A) - UV-Vis absorption spectra, measured after different times of IRMOF-20 surface assisted grown, (B) – dependency of IRMOF-20 thickness on the time of grown, (C) – shift of plasmon absorption band due to hydrogen presence as a function of IRMOF-20 time of grown.

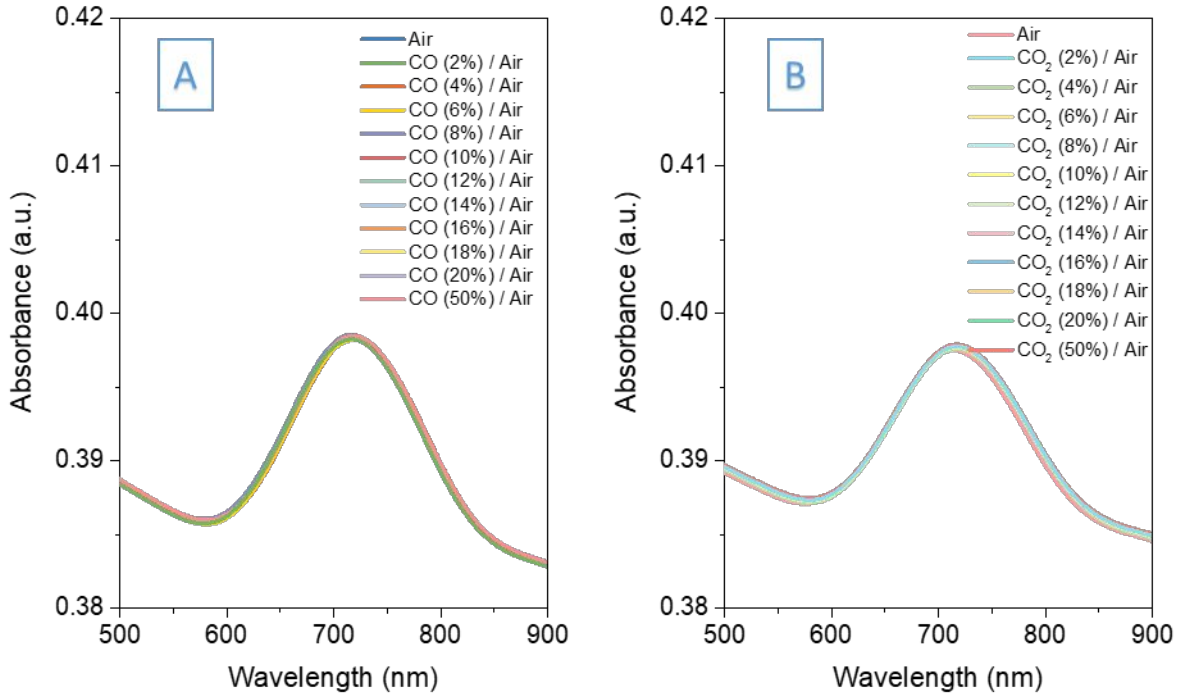

Fig. S6

Spectral position of plasmon absorption band of proposed optical fiber sensor as a function of the increased concentration of CO_2 (A) or presence of different CO concentrations (B) in the air.