

Supporting Information

#S.I.1. Phase-interrogation GC-SPR technology

Since grating-coupling SPR (GC-SPR) sensitivity (about 50-150°/RIU) is of the same order of magnitude of Kretschmann geometry²⁷, recent works showed that GC-SPR sensitivity can be increased up to one order of magnitude by controlling the azimuthal orientation of the corrugated surface²⁸. The symmetry breaking induced by the azimuth rotation makes p-polarization no longer the most effective for SPP excitation so that the optimal incident polarization must be tuned in order to optimize SPP excitation. Starting from these considerations we demonstrated the possibility of fixing the light incidence wavelength and angle, the grating azimuthal orientation and geometrical parameters so that a polarization interrogation could be performed. This approach has led to the realization of a compact and portable SPR detection system which is schematized in **Fig. SI.1**.

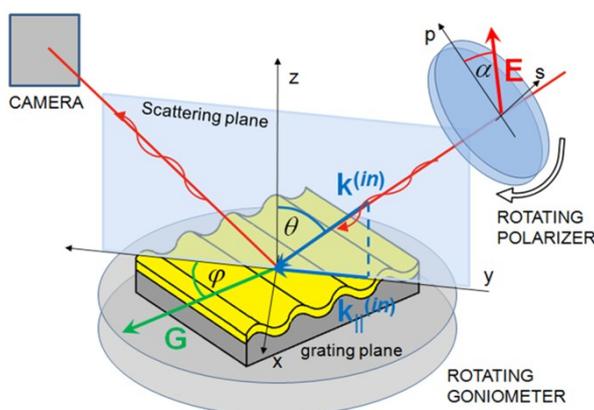


Fig. SI.1 Phase-interrogation SPR detection scheme. The plasmonic substrate is mounted onto a rotating goniometer allowing the azimuthal control of the grating plane. A fixed-wavelength laser beam, after passing through a polarizer, is reflected by the nanostructured surface and reaches a CCD camera. During the polarization-modulation analysis, polar and azimuthal angles (\mathcal{G}, φ) are kept fixed in correspondence of the plasmonic resonance and a polarization scan of the angle α is performed.

At a given azimuthal rotation φ supporting SPP excitation, two distinct dips in reflectivity appear in correspondence of resonance polar angles \mathcal{G}_m given by

$$\mathcal{G}_m = \arcsin \left(\frac{\lambda}{\Lambda} \cos \varphi m \sqrt{\frac{n^2 \varepsilon_M}{n^2 + \varepsilon_M} - \left(\frac{\lambda}{\Lambda} \sin \varphi \right)^2} \right) \quad \text{Eq. (1)}$$

where λ is the illuminating wavelength, Λ is the grating period, ε_M is the permittivity of the metallic layer and n is the refractive index of the dielectric medium. After rearranging Eq. (1) we get the following expression for the resonance azimuth (φ_{res}) as a function of the polar angle \mathcal{G} :

$$\varphi_{res} = \arccos \left(\frac{A^2 + S^2 + \sin^2 \mathcal{G}}{2A \sin \mathcal{G}} \right) \quad \text{Eq. (2)}$$

where $A = \lambda/\Lambda$ and $S^2 = \frac{n^2 \varepsilon_M}{n^2 + \varepsilon_M}$. At the resonance condition, the minimum of reflectivity R_{\min} exhibits a harmonic dependence on the incident polarization α with a periodicity of 180°:

$$R_{\min} = f_0 - f_1 \cos(2\alpha + \alpha_0) \quad \text{Eq. (3)}$$

where f_0 , f_1 and α_0 are fitting parameters that depend on the incidence angles, incident wavelength and on the optical properties of the stack. By assuming that only the electric field component lying on the grating symmetry plane is effective for SPP excitation²⁸, an analytical expression for the optimal polarization α_{opt} as a function of the resonance azimuth angle φ_{res} and the polar angle \mathcal{G} (p-polarization: $\alpha = 0^\circ$) is obtained:

$$\tan \alpha_{opt} = \tan \varphi_{res} \cos \mathcal{G} \quad \text{Eq. (4)}$$

If the grating surface is functionalized, the effective refractive index n_{eff} of the dielectric medium changes and the resonance condition is different in term of both φ_{res} and α_{res} so that, upon keeping \mathcal{G} , λ and φ fixed a shift $\Delta\alpha$ is observed. Monitoring $\Delta\alpha$ as a function of time the evaluation of binding events occurring onto the plasmonic surface is performed.

#S.I.2. Numerical simulations

Rigorous coupled-wave analysis (RCWA) was implemented in order to compute the optical response of a digital gold grating over a LiNbO₃ substrate. The digital grating, duty cycle 0.5, is assumed to grow on a 100-nm thick gold layer deposited over a 10-nm chromium adhesion film. For fixed grating pitch $\Lambda=400$ nm, reflectivity was computed as a function of the incidence polar angle θ and for increasing values of the grating amplitude from 10 to 50 nm (figure #.a). Simulations were performed in water environment (refractive index $n=1.33$) for incident wavelength $\lambda = 635$ nm at p -polarization (TM mode). As figure # shows, there exists an optimal grating depth close to 35 nm which maximizes plasmonic coupling and therefore minimizes the reflectivity minimum at resonance. A truncation order $N=40$ was chosen for Fourier series expansions during RCWA numerical routines.

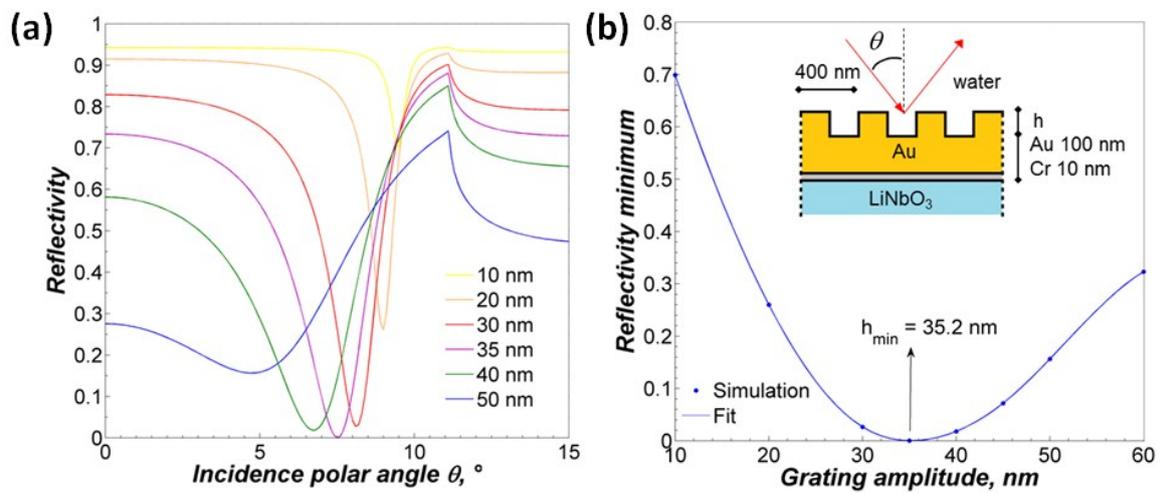


Fig. SI.2 Numerical simulations results. (a) Reflectivity curves for angular interrogation in the range 0°-15°, step 0.1° for different grating amplitudes in the set {10, 20, 30, 35, 40, 50} nm. (b) Reflectivity minimum as a function of grating amplitude, simulation points and fit curve. Inset graph: scheme of the grating stack.

#S.I.3. SPR sensor calibration

Since changes in the dielectric temperature induce changes in SPR response²⁸, a sensor calibration as a function of temperature and SAW generation was performed in the presence of buffers adopted for sensing experiments, i.e. milliQ water and 10mM PBS. Sensor response curves are shown as a function of time upon SAW application and heating in **Fig. SI.3**. A SPR response lower than 0.05 was obtained, an output significantly lower than the one typically resulting in our SPR system for avidin/biotin assay^{19,22}.

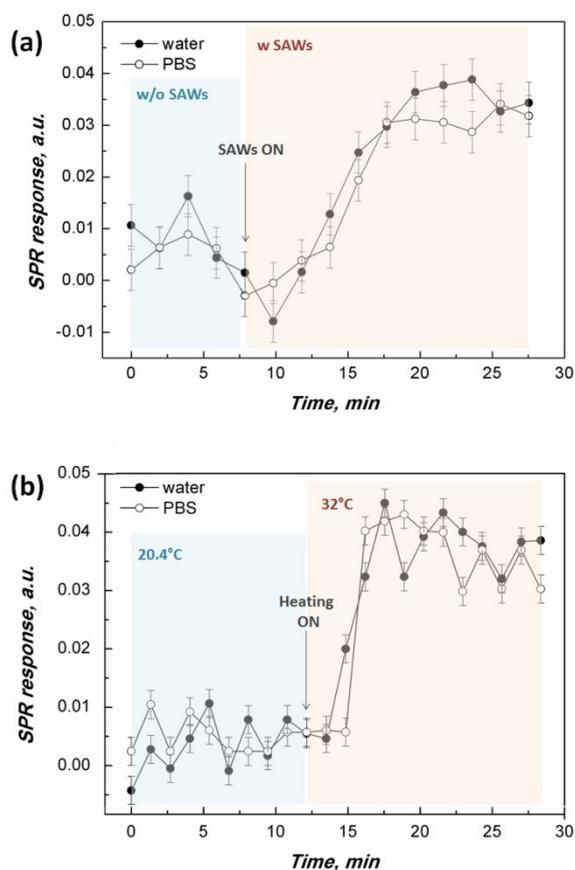


Fig. SI.3 Sensor response rough data upon SAW application and heating ($\Delta T=11.6^\circ\text{C}$); α 0-180°, step 2°, step time 0.5 s, scan time 1 s. After SAW generation a SPR response $< 0.05^\circ$ was detected for both milliQ water and 10mM PBS (a). Upon sample heating a SPR response $< 0.05^\circ$ was detected for both milliQ water and 10mM PBS (b).