COMMUNICATION

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ADVANCED MATERIALS

Hydrogels

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Hydrogel Interferometry for Ultrasensitive and Highly Selective Chemical Detection

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Relevance to the group

- This paper shows a new and different kind of approach towards sensing.
- Claims to provide an universal platform for sensing for varied chemicals.
- Reflectance spectroscopy can be alternative to look into in absence of luminescent or electrically conducting sensing material.

Optical Reflectance Spectroscopy

A reflectance spectrum is obtained by the collection and analysis of surface-reflected electromagnetic radiation as a function of frequency (v,. usually in wavenumbers, cm - 1) or wavelength (A,, usually in nanometers, nm).

Concept of Interferometry in the field of sensing

The basis of interferometry lies in the splitting and recombining of an initial coherent light. As a result of light splitting, part of the original light interacts with the measurand and incurs a phase difference with respect to the rest of the light. As a result, when the light is recombined, an interference pattern is observed. A phase shifting of the interference pattern is obtained when the measurand is changed and is the principle underlying interferometry-based sensors.

Ref: Sensors and Actuators B 202 (2014) 185–193

Introduction

- An approach for chemical detection of exceptionally high sensitivity and selectivity through the synergy of chemistry, mechanics, and optics.

- A hydrogel interferometer consists of a reflective substrate coated with a single thin film of hydrogel.

- The polymer network of the hydrogel provides a scaffold to carry a large number of ligands specific to the analyte (ligand-to-polymer mass ratio = 1:5).

- The thickness of the hydrogel is comparable to the wavelength of visible light (≈300 nm at dry state and ≈1000 nm at hydrated state).

- When a drop of analyte-containing solution is applied on the surface of the hydrogel, the analyte diffuses into the hydrogel, causing a cascade of signal transduction, involving chemical reaction, mechanical deformation, and optical detection (C→M→O).

- free copper ions in ocean should be critically maintained between picoM and femtoM (10^{-12} and 10^{-15} M) to be micronutrients for organisms, however, the stateof-the-art sensitivity of, for example, copper ion detection is 10^{-4}–10^{-10} M, and that of horse radish protease detection is 10^{-4}–10^{-7} M.(USEPA standard is $2x10^{-5}$M in drinking water for Cu^{2+})

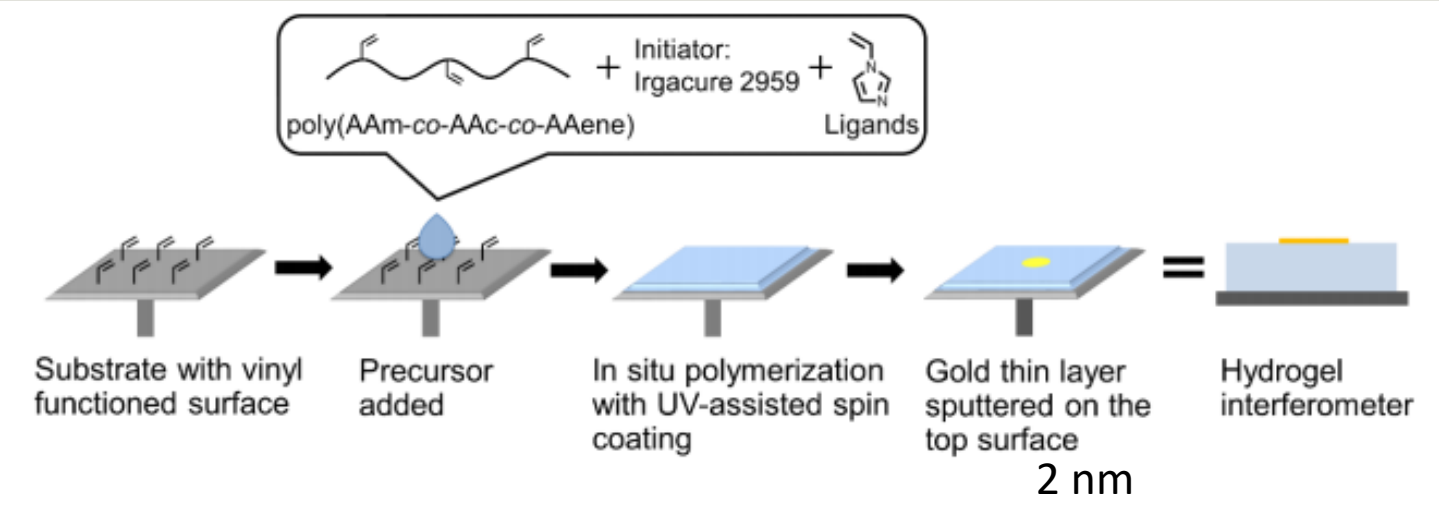
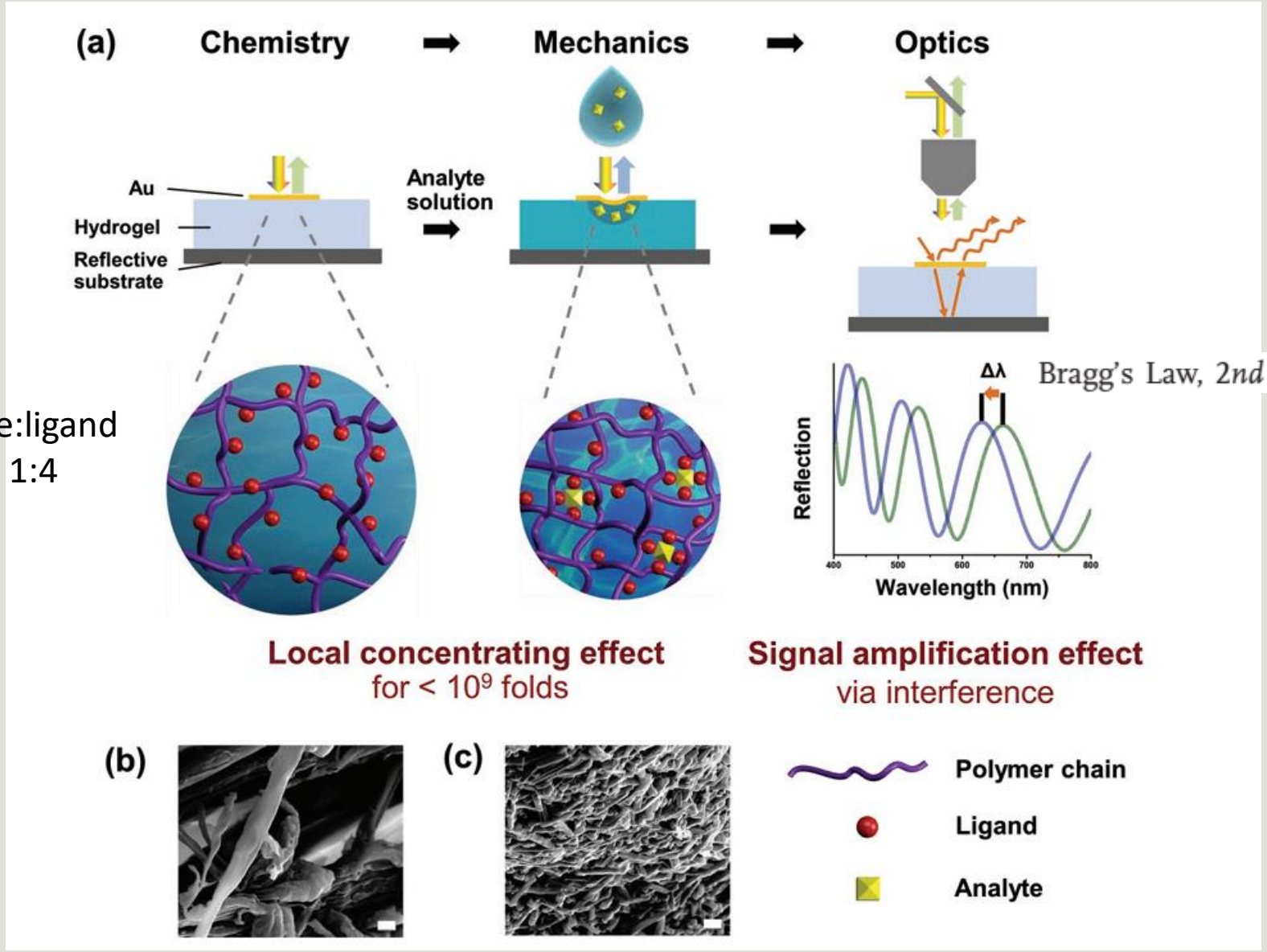


Figure S5. *Fabrication process of the Cu^{2+} ions sensor.*

Optical measurement

- The sensor was first dried on hot plate for the hydrogel film to reach the same thickness for each measurement
- 10 µL solution was added on the surface of the sensor (for glycoprotein detection, the solutions with different concentrations of proteins
- the hydrogel sensor is incubated for 30 min for complete diffusion and binding reaction
- After using a piece of cover glass to cover the sensor, the sensor was transferred and placed on the stage of the microscope (Leica DM5000) with light illuminating vertically from the top or the bottom.
- The reflected light was collected by a UV-Vis spectrometer



Analyte:ligand ratio is 1:4

Figure 1. a) Sensing mechanism of the hydrogel interferometer platform: the complete chemical-mechanical-optical signal transduction process. b,c) The SEM images of hydrogel before (b) and after (c) adding Cu^{2+} ions into it. The scale bar is 1 μm.

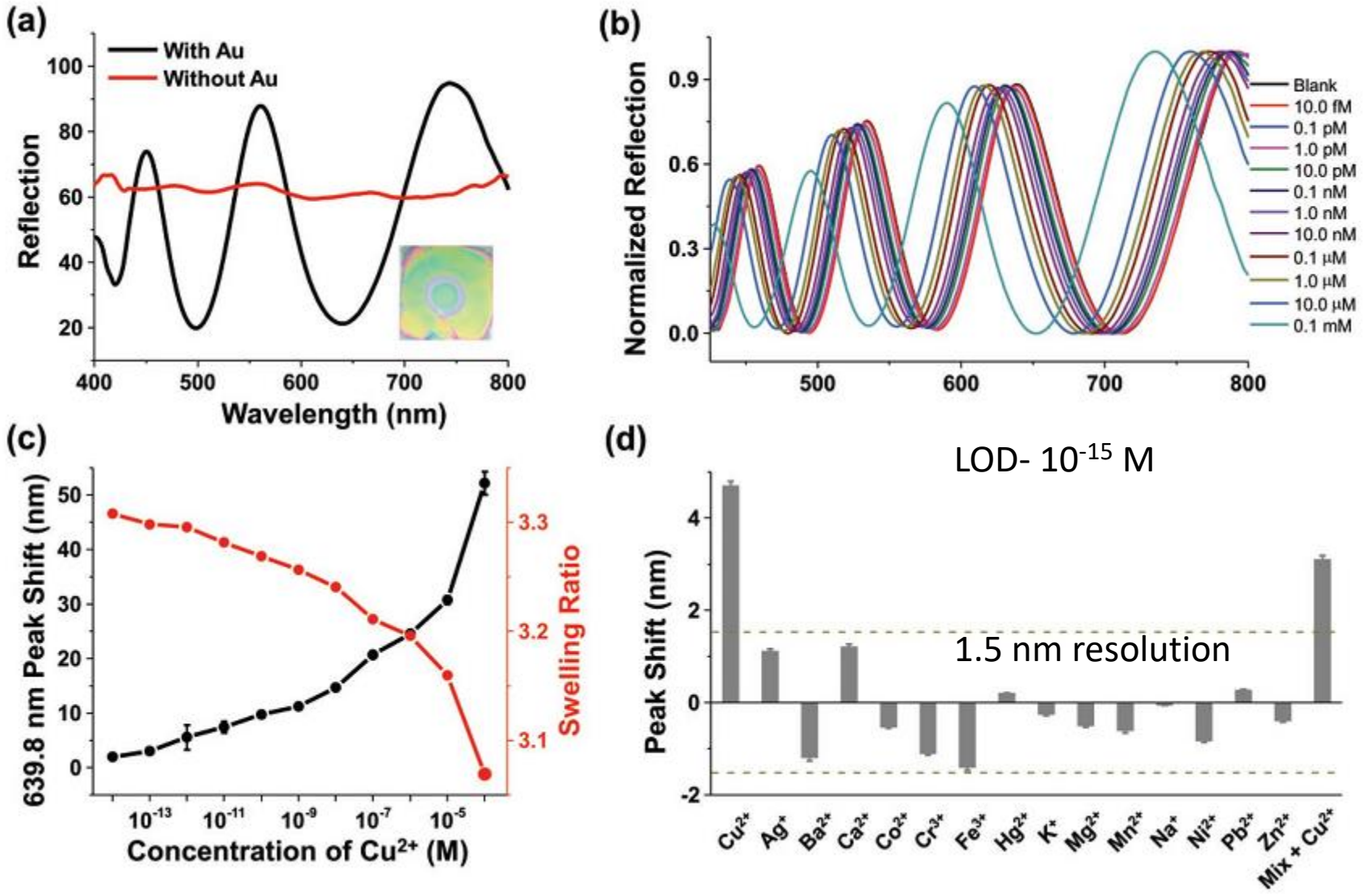


Figure 2. High sensitivity and selectivity of the Cu^{2+} sensor. a) Reflective spectra of the Cu^{2+} sensor with and without the sputtered gold film on the surface. b) The complete reflective spectra of the sensor with different concentrations of Cu^{2+}. The curves for blank solution and 10.0 fM overlap due to the small peak shift. c) The reflective peak shift and the swelling ratio measured as a function of the concentration of Cu^{2+} at the wavelength of 639.8 nm. d) Reflective peak shifts at 458.7 nm induced by Cu^{2+} of 10^{-11} M and 14 different metal ions of 10^{-9} M, as well as a mixture of them. The dash lines represent the resolution of the spectrometer (1.5 nm). All error bars indicate the standard deviation of three parallel experiments.

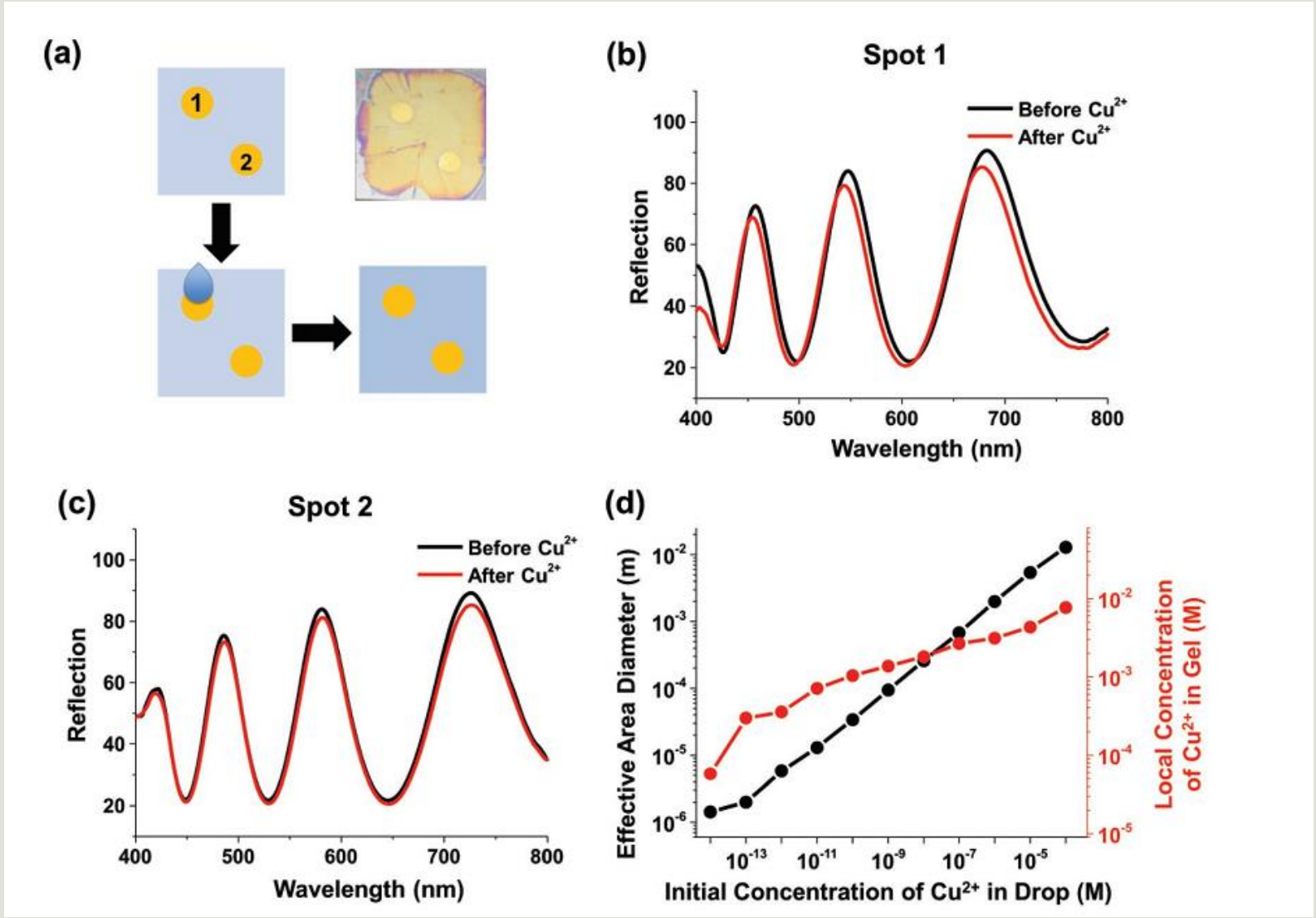


Figure 3. The localized binding of Cu^{2+} in the sensor and small effective area. a) The experimental setup for verifying the localized binding. The distance between Spot 1 and Spot 2 is about 5.0 mm. b,c) The reflective spectra before and after applying 10 µL of Cu^{2+} with 10^{-11} M is recorded as in Spot 1 (b) and Spot 2 (c). d) The estimated diameter of the effective area of binding and the local concentration of Cu^{2+} within the effective area.

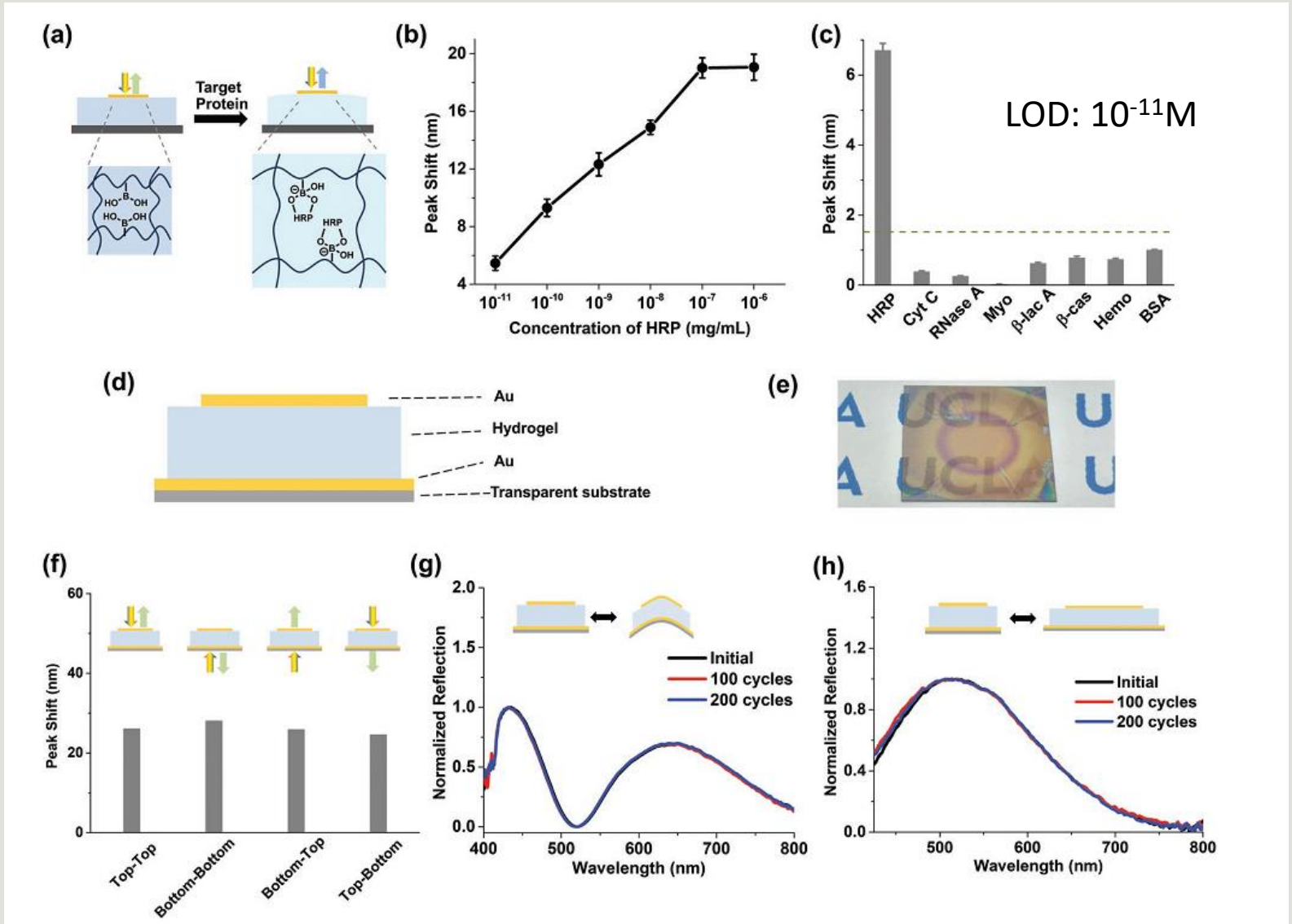


Figure 4. Generality of the sensing platform. a) The detection mechanism of the glycoprotein-specific sensor. b) Reflective peak shift at the wavelength of 601.0 nm as a function of the concentration of HRP (from 10^{-11} to 10^{-6} mg mL^{-1}). c) Reflection peak shifts at the wavelength of 452.0 nm of 10^{-10} mg mL^{-1} HRP compared to 10^{-8} mg mL^{-1} of seven other different proteins. The dash line represents the resolution of the spectrometer (1.5 nm). d) The configuration of the hydrogel sensor on transparent substrates. e) The photo of the hydrogel sensor on glass substrate. f) Reflective peak shifts of the hydrogel sensor on glass substrate induced by Cu^{2+} from different projecting–detecting directions including top–top, bottom–bottom, bottom–top, and top–bottom. g) Reflective spectra of the hydrogel sensor on PET substrate before and after cycles of bending. h) Reflective spectra of the hydrogel sensor on PDMS substrate before and after cycles of stretching. All error bars indicate the standard deviation of three parallel experiments.

Summary

- The general sensing platform based on hydrogel interferometer that exhibits remarkable high performance takes advantage of coupling two attributes: optical interference and responsive hydrogels.

- Overall, this unique hydrogel interferometer-based sensing platform adopts a highly efficient chemo-mechano-optical signal transduction that enables fM-level sensitivity on a sub-μm^3 sensing active region.

- In addition, a hydrogel can be functionalized to become responsive to different environmental cues, by linking specific functional groups or monomers to its polymer chains, which provides an analyte specific matrix.

- A universal physical principle based on hydrogel interferometry sensor that can effectively enhance the chemical detection sensitivity for several orders of magnitude, by remarkable local concentrating effect (10^9 times) and large signal amplification in a chemo-mechano-optical signal transduction.

Thank you