Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

High-sensitivity and fast-response fiber-tip Fabry-Perot hydrogen sensor with suspended palladium-decorated graphene

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Theoretical analysis of the sensor's response to H_2:

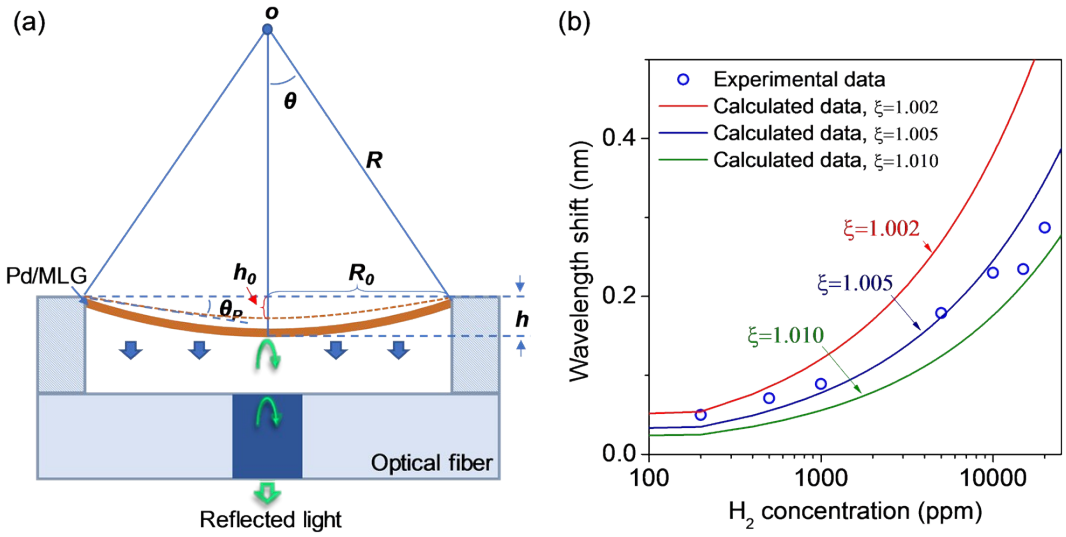

Fig. S1 (a) Schematic of the out-of-plane deflection of Pd/MLG film after H_2 adsorption. (b) The dip wavelength shift of the sensor reflection spectrum as a function of the H_2 concentration C_H.

After adsorption of H_2 molecules, the lattice of the Pd film expands and stretches the beneath multilayer graphene MLG, which deflects Pd/MLG composite film inward, as shown in Fig. S1. If the Pd/MLG composite film is considered as a thin and elastic membrane, the strain in the composite film caused by the H_2 adsorption can be described by,

$$\varepsilon_c = \frac{R\theta - R_0}{R_0} = \frac{\theta - sin\theta}{sin\theta} \tag{S1}$$

where R_0 and R are the radius and the curvature radius of the composite film, respectively. θ is the arc angle as shown in Fig. S1(a). The out-of-plane deflection of the film h is related to the arc angle θ by,

$$h = \frac{R_0}{2}\frac{sin\theta}{1 + cos\theta} \tag{S2}$$

which is derived from the basic geometric relationship of the arc-shaped composite film.

As the deflection of the Pd/MLG film induced by H_2 absorption is much less than the Pd/MLG film radius R_0, we have θ <<1. Using Taylor expansion, Eq. (S1) and (S2) can then be simplified to,

$$\varepsilon_c \approx \frac{\theta^2}{6}, \tag{S3}$$

and

$$h \approx \frac{R_0}{2}\theta. \tag{S4}$$

Based on Eq. (S3) and (S4), the deflection h is related to the strain in the film ε_c by,

$$h \approx \frac{\sqrt{6}}{2}R_0\sqrt{\varepsilon_c}. \tag{S5}$$

The strain in the composite film ε_c can be calculated by

$$\varepsilon_c = \frac{E_{Pd}t_{Pd}}{E_{Pd}t_{Pd} + E_G t_G}\varepsilon_{Pd}, \tag{S6}$$

where E_{Pd} and t_{Pd} are Young's modulus and the thickness of the Pd film, respectively, E_G and t_G are Young's modulus and the thickness of the supporting film, respectively, and the strain in the Pd film ε_{Pd} relates to the H_2 content in the Pd film C_H by [S1],

$$\varepsilon_{Pd} = 0.026 \cdot C_H . \tag{S7}$$

In the α-phase, the relationship between the H_2 partial pressure p (Torr) and C_H follows,

$$p^{1/2} = K \cdot C_H , \tag{S8}$$

where K is the Sievert's coefficient (K = 350 Torr$^{1/2}$). Combing Eq. (S5-S8) gives the relationship between the film deflection h and the H_2 partial pressure p as,

$$h \approx \frac{\sqrt{6}}{2} R_0^{\,4} \sqrt{\frac{0.026}{K} \cdot \frac{E_{Pd}t_{Pd}}{E_{Pd}t_{Pd} + E_G t_G} p} \tag{S9}$$

Once the deflection h is obtained, the wavelength shift of the reflection dip can be calculated by $\Delta\lambda = \Delta L/(\lambda L)$, where ΔL is the cavity length of the Fabry-Pérot cavity and equal to the out-of-plane deflection of the film h. The H_2 information encoded in the wavelength shift of the sensor reflection spectrum can then be read using an optical spectrum analyzer.

During the transfer of the MLG film from water to fiber-tip, it is difficult to obtain a perfectly flat film due to the water surface tension [S3]. To account for the initial deflection of the film h_0, as shown in Fig. S1(a), a weighting coefficient $\xi = 1/cos\theta_P$ is introduced and Eq. S1 can then be written as,

$$\varepsilon_c \approx \frac{R\theta - \xi R_0}{\xi R_0} = \frac{\theta - \xi sin\theta}{\xi sin\theta} \tag{S10}$$

In our experiment, t_{Pd} = 5.6 nm, E_{Pd} = 121 GPa for the Pd film [S2] and t_G = 3.1 nm, E_G =1 TPa for the MLG [S3]. The relationship between the wavelength shift (near 1550 nm) and the H_2 concentration for the sensor with a cavity length of 25 μm is numerically calculated and compared with the measured data in Fig. S1(b). A good agreement is obtained between the calculation and the experiments when the initial deflection of the composite film is considered via a weighting factor of 1.005.

Experimental setup for characterizing the sensor response to H_2:

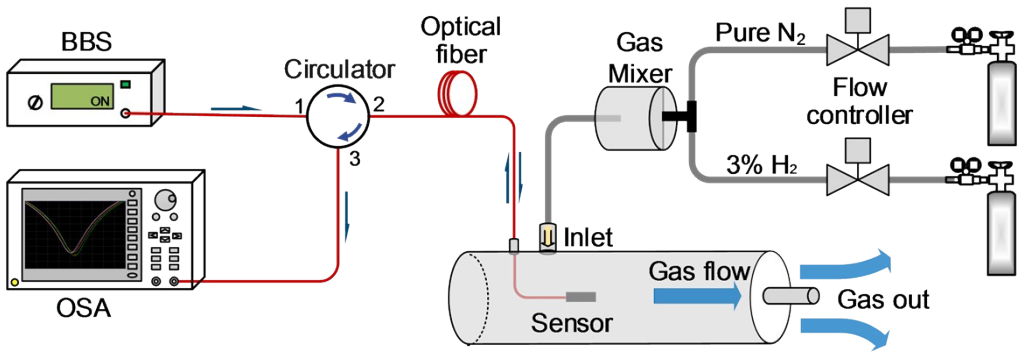

Fig. S2 Experimental setup for measuring the sensor hydrogen response. BBS: broadband source, OSA: optical spectrum analyzer.

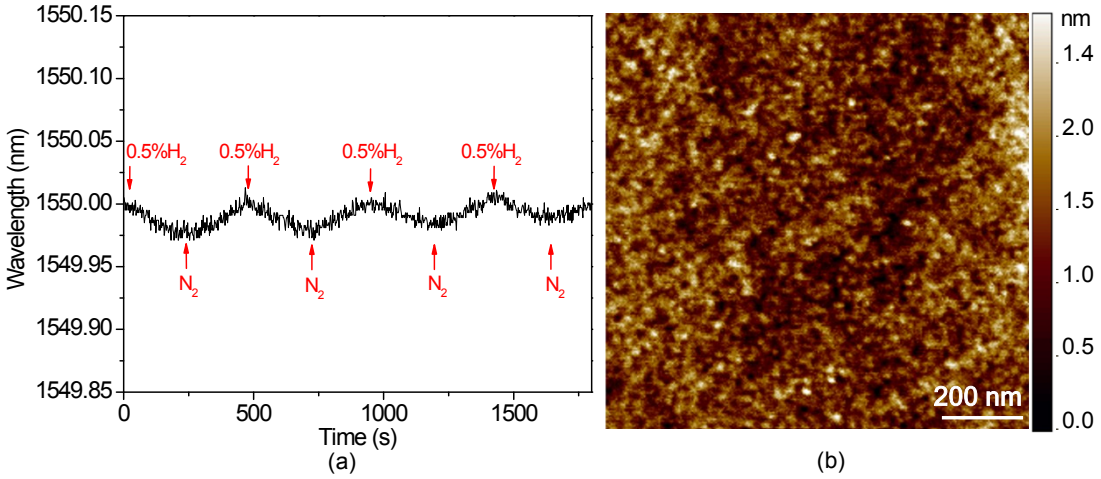

Fig. S3. (a) Temporal wavelength variation of the reflection spectrum for the sensor with ~ 3 nm thick Pd when 0.5% H_2 was applied. (b) Atomic force microscope (AFM) image of the morphology of the Pd film.

Temperature sensitivity:

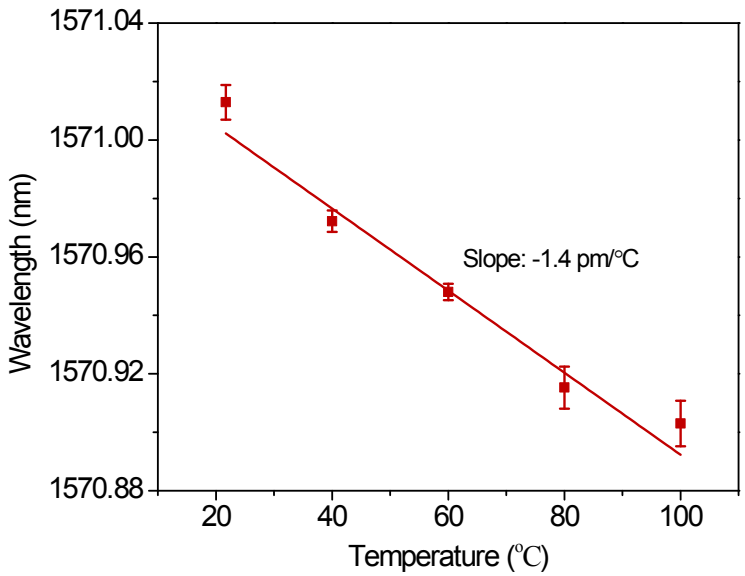

Fig. S4 Wavelength shift as a function of temperature.

To experimentally characterize the temperature sensitivity, the sensor was horizontally placed into a furnace. The heating temperature was raised in steps of 20 °C and maintained for about 10 mins at each step to make sure the temperature in the furnace had stabilized. At each temperature step, the sensor reflection spectrum was recorded. Based on the wavelength shift at different temperatures, as shown in Fig. S4, the temperature sensitivity is ~ 1.4 pm/°C.

Flow influence:

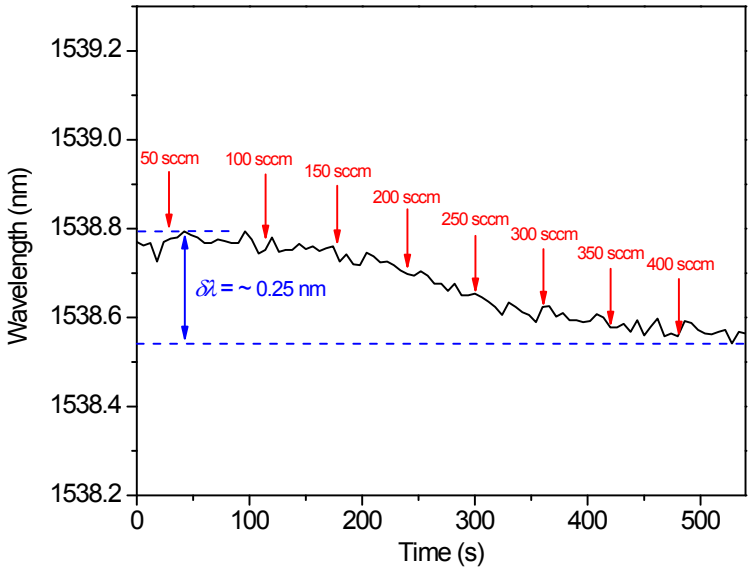

Fig. S5. Temporal wavelength evolution of the sensor reflection spectrum with increasing flow rate.

Sensor durability:

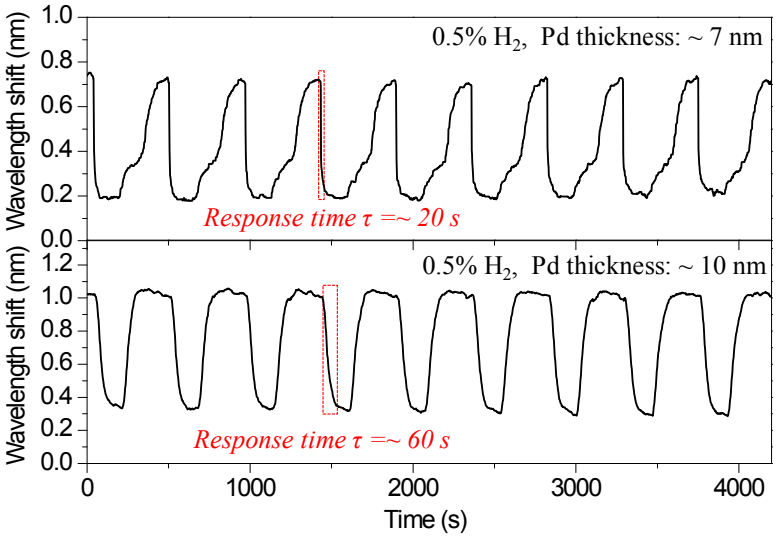

Fig. S6. Temporal response of the sensor with different thickness to cyclic H_2 of 0.5% concentration.

Reference:

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[S2] D. E. Gray, American Institute of Physics Handbook (McGraw-Hill, 1982).

[S3] C. Lee, X. Wei, J. W. Kysar and J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, Science, 2008, 321(5887), 385-388.

[S4] R. A. Barton, B. Ilic, A. M. Van Der Zande, W. S. Whitney, P. L. McEuen, J. M. Parpia and H. G. Craighead, High, Size-Dependent Quality Factor in an Array of Graphene Mechanical

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