Supplementary Information

Hydrogen gas sensing using aluminum doped ZnO metasurface

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1. AZO NANOTUBES SENSING SYSTEM:

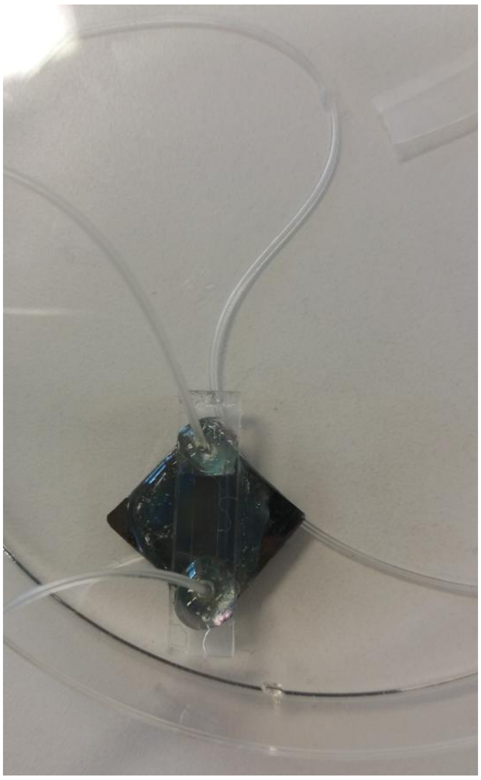

Figure S1: A picture of the AZO metasurface hydrogen gas sensor.

A picture of our hydrogen (H_2) gas sensor based on high aspect ratio highly ordered AZO nanotubes is shown in Figure S1 above. This is showing clearly how the PMMA microfluidic channel is built with proper inlets and outlets for the flow of gas mixture.

2. TE- AND TM-POLARIZED LIGHT FOR GAS SENSING - WHICH IS THE SUITABLE ONE:

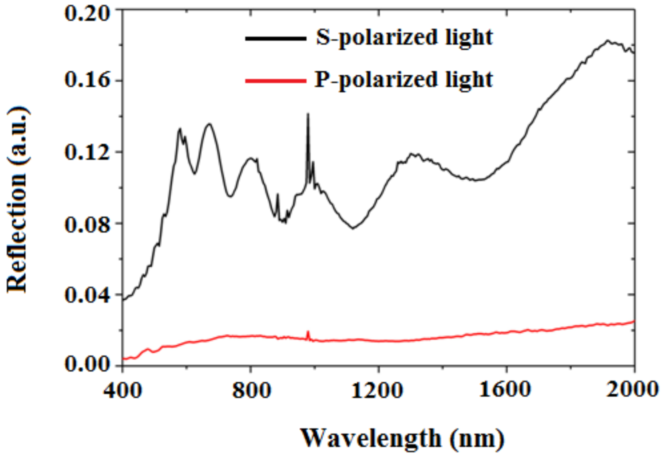

Figure S2: The reflection spectra of both TE-(S-) and TM- (P-) polarized light is shown. For AZO nanotube system we chose TE-polarized light for all the gas sensing measurements because it shows the presence of different modes that can be used for sensing.

Here in Figure S2 the reflection spectra for both TE (S-) and TM (P-) polarized light is shown. Here the measurement angle is 45°. It can be seen that the reflectance spectra of TM-polarized light shows almost no variation in absence of H_2 gas and thus this spectra will not be useful for H_2 gas sensing by monitoring any kind of mode shift. On the other hand for TE polarized light the presence of different modes can be seen in the reflectance spectra in absence of H_2 gas. Thus any kind of mode shift for TE polarized light can show the presence of the H_2 gas immediately. Thus from these measurements is can be concluded that for this sensing system the TE-polarized light is suitable for the gas sensing.

3. NUMERICALLY CALCULATED WAVELENGTH SHIFT BY AZO NANOTUBES IN PRESENCE OF HYDROGEN GAS:

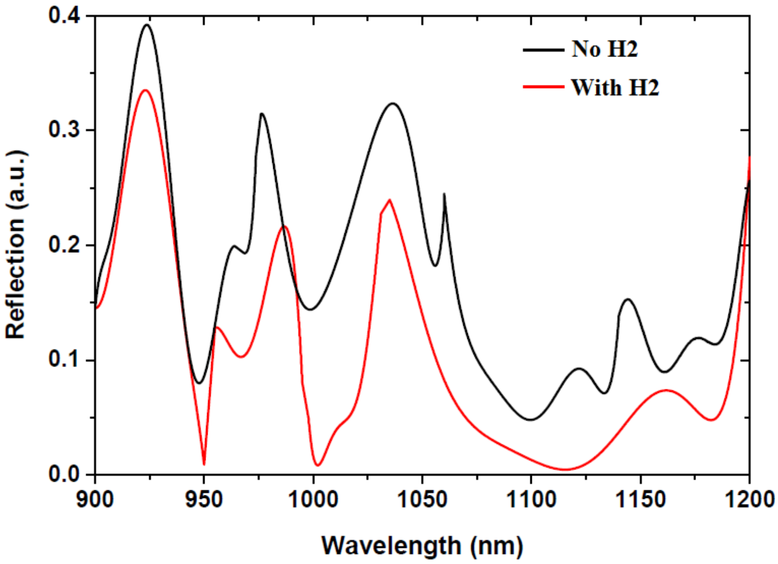

Figure S3: The reflection spectra of AZO nanotube metasurface in presence and absence of H_2 gas simulated using Comsol 5.4.

In Figure S3 reflection spectra of the AZO metasurface in absence and in presence of H_2 gas has been depicted. The results are calculated using FEM based Comsol 5.4 simulation method. Here one can notice clear mode shift in presence of H_2 gas. The 1100 reflection minima mode shifts 17 nm in presence of H_2 gas. Along with the wavelength shift, reflection minima mode intensity change of 4.8% has also been seen in this case.

4. NUMERICALLY CALCULATED WAVELENGTH SHIFT BY AZO SOLID PILLARS IN PRESENCE OF H_2 GAS:

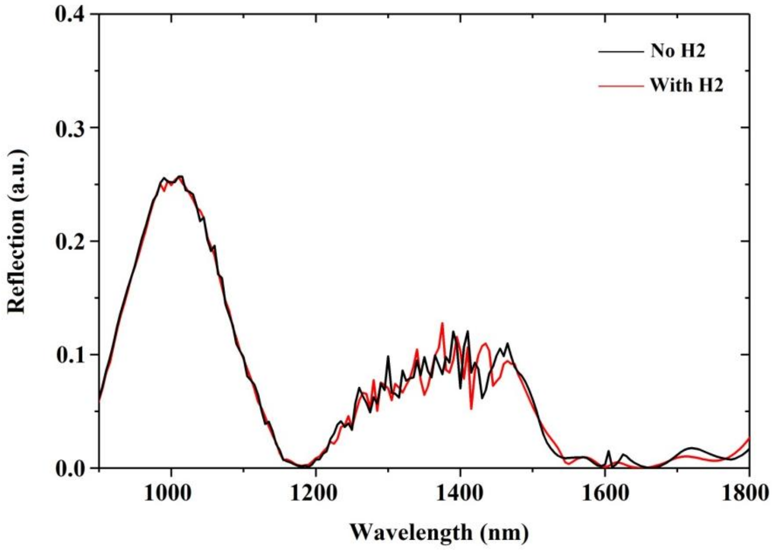

Figure S4: The reflection spectra of the metasurface made of AZO solid nanopillars in presence and absence of H_2 gas simulated using Comsol 5.4. No change in the reflectance spectra is observed here.

In Figure S4 reflection spectra of the metasurface made of AZO solid nanopillars in absence and in presence of H_2 gas has been depicted. The results are calculated using FEM based Comsol 5.4 simulation method. Here no wavelength shift has been seen in presence of H_2 gas. In contrast, for AZO nanotubes a shift in the reflectance spectra in presence of H_2 both in terms of wavelength shift and the reflectance intensity change can be easily seen in Figure S3 (experimental results also supports the theoetical study which is given in the main manuscript). This is indicating that AZO nanopillars are not suitble for this kind of optical H_2 gas sensing. The experimental results to support this theoretical claim is given in the figure (Figure S5) below. Here it is worth to mention that due to the use of the PMMA microfluidic channel during gas sensing the reflectance intensity of the sensing system decreases with respect to its performance without channel (valid for both nanotubes and solid nanopillars) which is identical to the computational scenario.

5. RESPONSE OF AZO SOLID PILLARS IN PRESENCE OF H_2 GAS (EXPERIMENTAL):

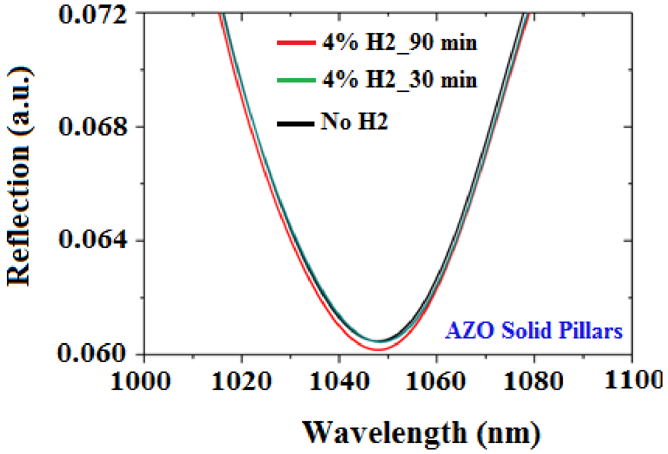

Figure S5: The response of AZO solid pillars for 4% hydrogen gas. Almost no change in the reflectance mode is observed for 4% H_2 after 90 min which indicates the incompatibility of these solid pillars for hydrogen gas sensing.

Here in Figure S5 the gas sensing response of high aspect ratio highly ordered AZO solid pillars array system is shown. After 1 hour and 30 min. of the intercalation of 4% H_2 gas in the AZO solid pillar metasurface platform no reflectance mode shift has been seen. This is indicating that the solid AZO nanopillars array system is incompatible for this type of optical H_2 gas sensing.

6. DEPENDENCE OF WAVELENGTH SHIFT ON THE MEASUREMENT ANGLE AND MODE WAVELENGTH:

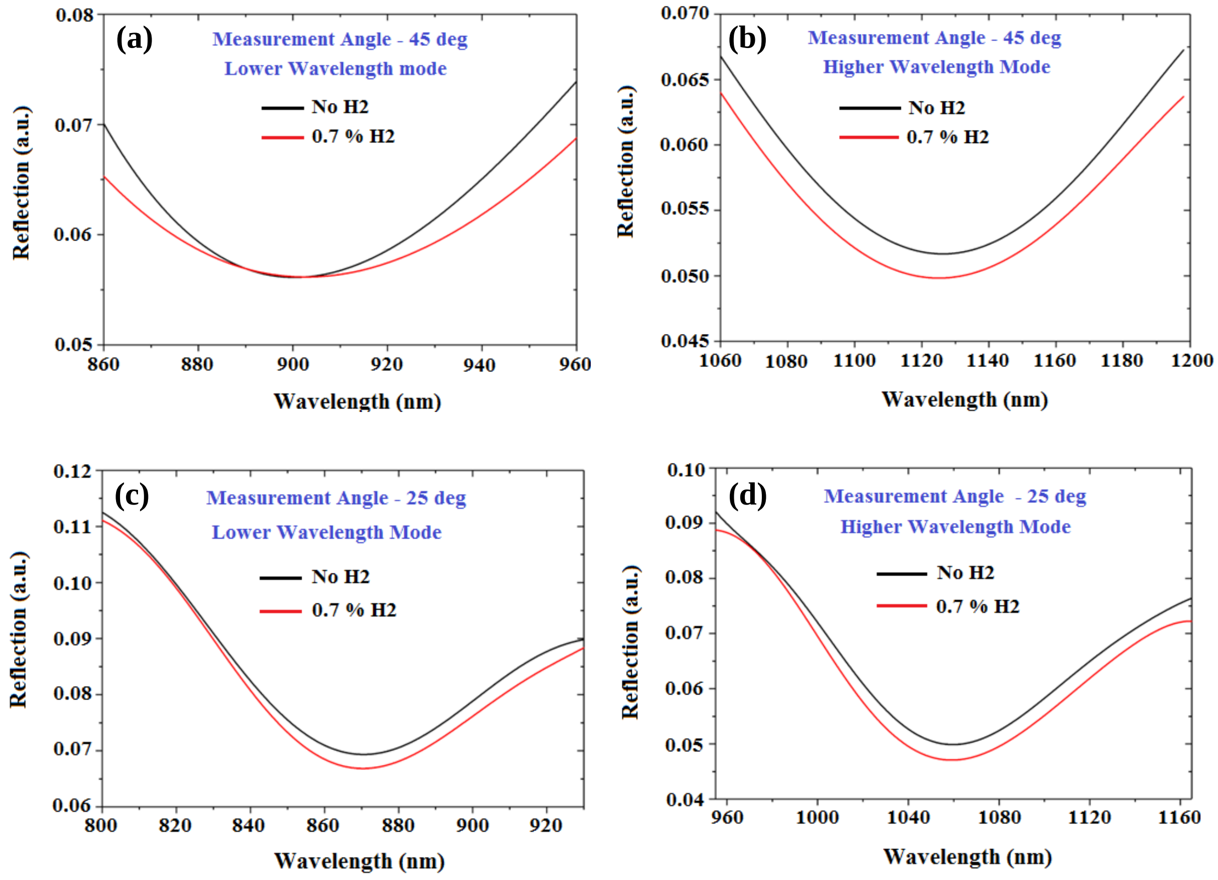

Figure S6: The response of the AZO nanotubes sensing system is shown for 0.7% H_2 gas. For all these cases, the response time is 10 min. Panel (a) describes the case for a lower wavelength mode around 900 nm when the measurement angle is 45^o. In this case no wavelength shift is seen. Panel (b) describes the case for a higher wavelength mode around 1100 nm when the measurement angle is 45^o. In this case wavelength shift as well as the reflection intensity change has been observed. Panel (c) describes the case for a lower wavelength mode when the measurement angle is 25^o. In this case variation is observed. While panel (d) describes the case for a higher wavelength mode when the measurement angle is 25^o. In this case also the wavelength shift in mode is observed.

Here in Figure S6 the response of AZO metasurface is shown in absence and in presence of H_2 gas. For all these measurements AZO sensing system interacted with 0.7% H_2 gas and the response of the system is taken considering 10 min response time. Panel (a) and (b) describe the situation for the same measurement angle of 45^o but for different wavelength mode. Here it can be seen that the higher wavelength modes are better for sensing because the mode shift is clear there. Panel (c) and (d) describes the situation for the same measurement angle of 25^o but for different wavelength mode. Here it seems that both the wavelength mode is good for sensing. If one compares the higher and lower measurement angle keeping the mode wavelength almost same then it can be seen that the lower angular measurements are good for higher sensitivity. However, for our experimental measurements we chose 45° because of several reasons as written in the manuscript.

7. PERFORMANCE OF THE AZO SENSING SYSTEM IN AIR WITH AND WITHOUT THE PMMA CHANNEL:

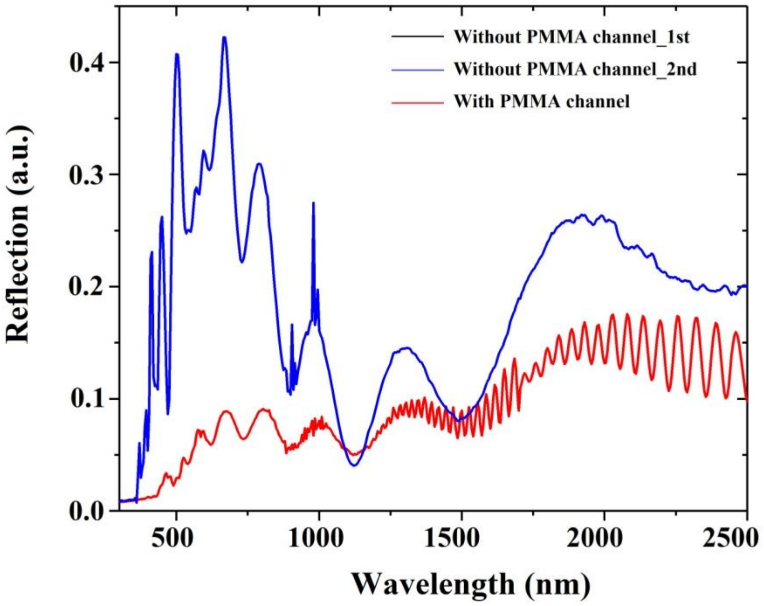

Figure S7: Reflection spectra with and without PMMA channel in air. The measurement is taken at room temperature without PMMA channel (black line, bare sensing platform) and after keeping the sample for 7 hours in air (blue line). Reflection spectra after adding the PMMA channel (red line) shows less reflection and Fabry-Perót fringes especially above 1000 nm in wavelength.

Figure S7 shows the influence of PMMA channel (cover) on the reflection spectra, as well as the stability of AZO tube sample in air. The reflection spectra without PMMA channel (bare sensing platform) at room temperature does not exhibit any change after keeping the sample for 7 hours in air, showing the stability of the sample in air at room temperature condition. After adding the PMMA channel, a significant decrease in the reflectance intensity and appearance of interference fringes can be seen but no significant wavelength shift of the characteristics modes of the AZO sensing system is observed. The decrease in reflection is due to the absorption at the by the thick PMMA channel (please see the photo of the actual sensing platform in Figure S1), which also causes the Fabry-Perót fringes especially above 1000 nm in wavelength.

8. LIMIT OF DETECTION (LOD) MEASUREMENT:

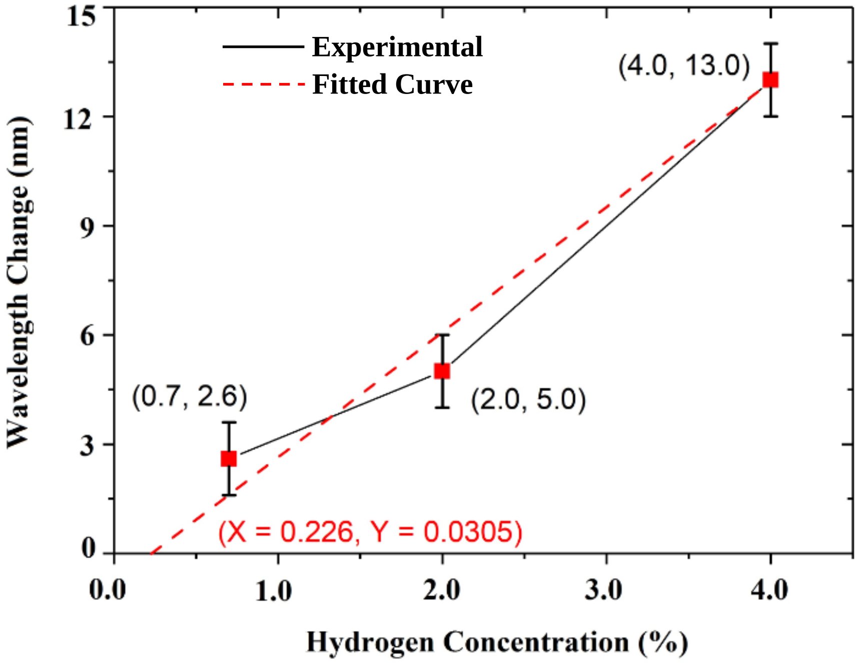

Figure S8: Wavelength change ($\Delta\lambda$) is plotted for different H_2 concentration measured during the optical H_2 gas sensing with AZO nanotubes metasurface system. This plot helps to estimate the Limit of Detection (LOD) to be 0.2% of H_2 gas considering 0.03 nm as the maximum possible resolution of our spectroscopic ellipsometer.

Here in Figure S8 the wavelength change ($\Delta\lambda$) is plotted for different H_2 concentration measured during the optical H_2 gas sensing with AZO nanotubes metasurface system. The black curve shows the experimentally measured trend of the wavelength shift of reflection minima mode observed for AZO nanotubes sensing system in presence of H_2 gas of different concentration (0.7 %, 2 %, and 4 %). The red dashed curve is the fitted curve to show the limit of detection (LOD). If one considers wavelength change as the parameter to detect the presence of H_2 gas, the LOD is estimated to be approximately 0.2% H_2 gas according to the fitted curve. Here we consider the maximum possible resolution of the used spectroscopic ellipsometer is 0.03 nm.

9. HYSTERESIS OF THE AZO SENSING SYSTEM:

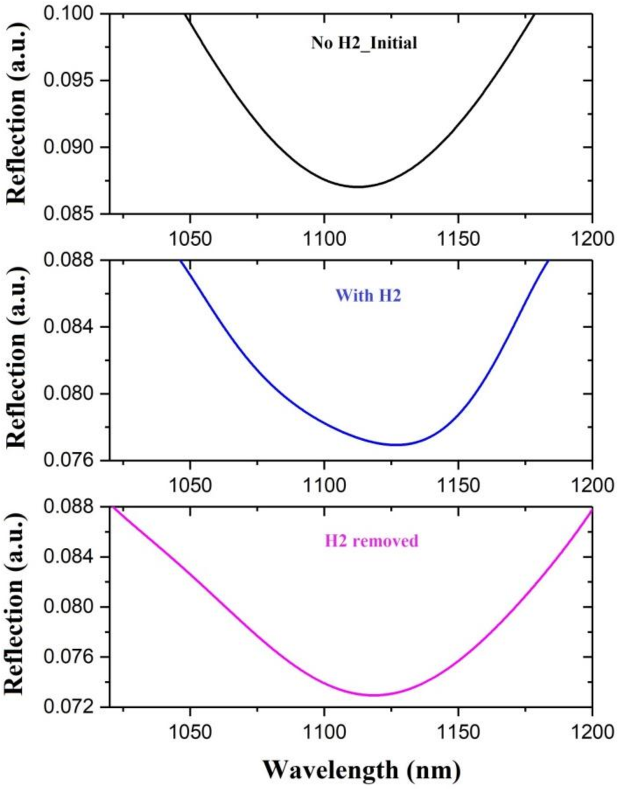

Figure S9: Reflectance spectra of AZO nanotube sensing system in different condition – before intercalation of H_2 (initial reflection mode – 1112, 0.0923), after 2 hours of H_2 gas flow (modified reflection mode – 1126, 0.0768) and after out flowing of H_2 gas by flowing in N_2 gas for 2 hours within the channel at room temperature condition (reflection mode with hysteresis – 1118, 0.073). Here 4% H_2 gas is taken. This is showing a hysteresis in the reflectance mode after flowing out of H_2 from the sensing system.

Figure S9 is showing the hysteresis of the AZO nanotube sensing platform. For this experiments TE polarized light used at 45^o incident angle. The initial reflection mode (collected in absence of H_2 gas) shifts for almost 14 nm when H_2 gas intercalates into the system (collected after 2 hours). After this gas sensing measurements H_2 gas has been flowing out of the system by flowing in the pure N_2 gas within the chamber at room temperature condition. However, the initial mode (λ – 1112 nm) could not be regained even after 2 hours of N_2 gas flow at room temperature. The new reflection mode is at 1118 nm, nearly 6 nm away from its initial mode, is the reflection mode of the system with hysteresis. Here it is worth to mention that we have done all our experiments in ambient temperature and pressure and no special treatment like applying external heat or pressure or any chemical treatment has been taken to restore its primary reflectance position.