Plasmonic Doppler Gratings for Hydrogen Sensing and Coking Detection

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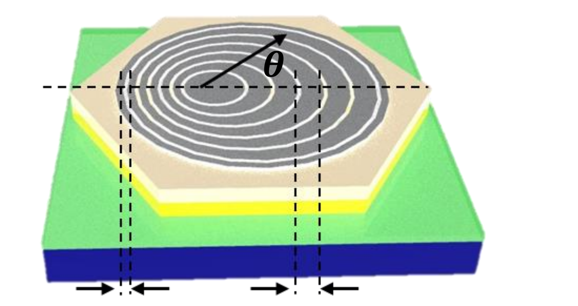
Introduction

Plasmonic Doppler grating (PDG) is a designed platform which offers a continuous azimuthal angle-dependent lattice momentum for photon-plasmon coupling. The center and span of the working frequency are fully designable for the optimal performance in sensing applications. In this work, we demonstrate the capability of PDG for hydrogen (H_2) sensing and coking detection.

❖ Design principle of the PDG sensing platform



$P(180^o) = \Delta r - d \quad P(0^o) = \Delta r + d$

λ_0 : wavelength of incident light , α : incident angle
m : resonant order , ε_m : metal permittivity
n_i : refractive index of the medium of incident light
n_d : refractive index of the medium surrounding the grating

Trajectories of n^{th} circular slits

$$[x - n \cdot d]^2 + y^2 = (n \cdot \Delta r)^2$$

d: Ring center shift Δr: Radius increment

Azimuthal angle-dependent periodicity

$$P(\theta) = \pm d \cos\theta + \sqrt{(d^2 \cos 2\theta + 2\Delta r^2 - d^2)/2}$$

Momentum matching condition

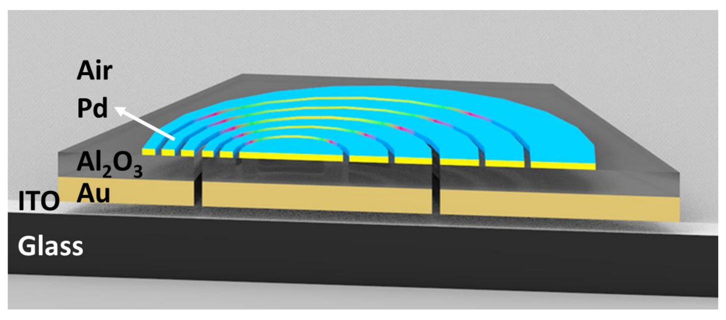
$$\frac{2\pi}{\lambda_0} n_i \sin\alpha + \frac{2m\pi}{P(\theta)} = \frac{2\pi}{\lambda_0}\sqrt{\frac{\varepsilon_m \cdot n_d^2}{\varepsilon_m + n_d^2}}$$

Advantages of PDG sensor:

- ✓ **Designable spectral window**
- ✓ **Spectrometer-free**
- ✓ **Single-color spectroscopic analysis**
- ✓ **Compatible with microfluidic channel**

MIM-PDG for H_2 sensing

H_2 sensing : Pd → PdH



Disadvantages of Pd-based optical sensors

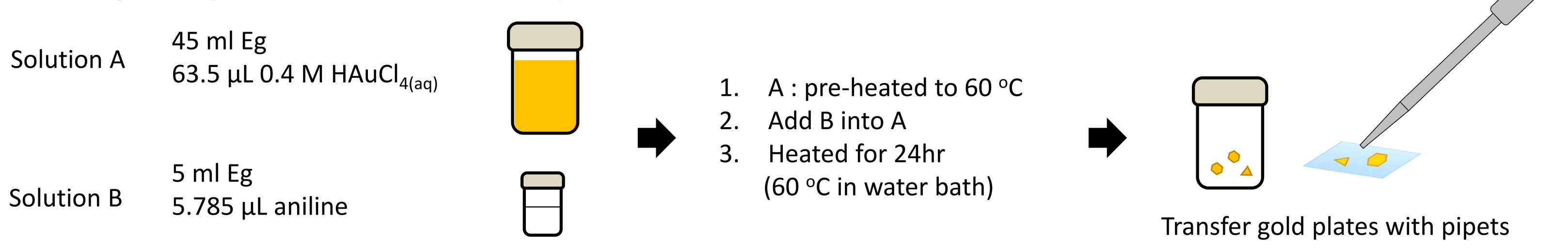
- X Non-designable spectral window
- X Small spectral shift
- X Requirements of spectrometer
- X Requirements of broadband light source

Metal-insulator-metal (MIM) PDG sensors

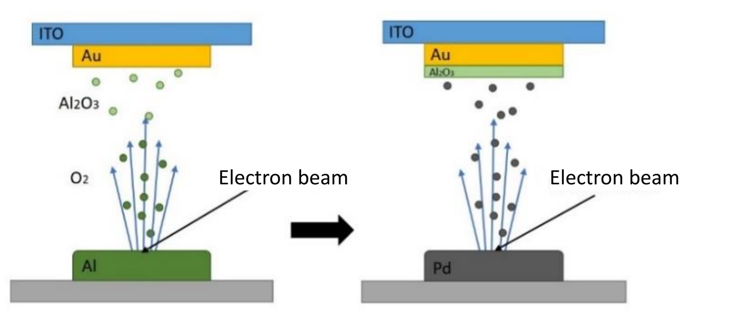
- ✓ Advantages of PDG
- ✓ Enhanced optical signal by the MIM structure (perfect absorber)

❖ MIM-PDG fabrication

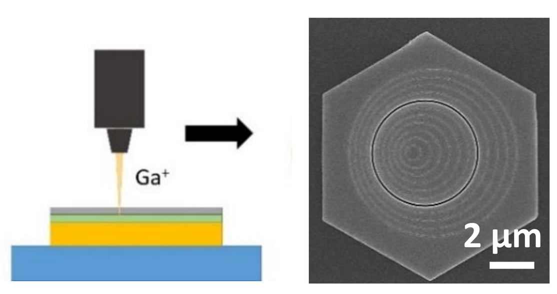
(a) Single crystalline Au flakes synthesis



(b) Pd & Al_2O_3 layer evaporation



(c) FIB milling



❖ H_2 sensing by MIM-PDG

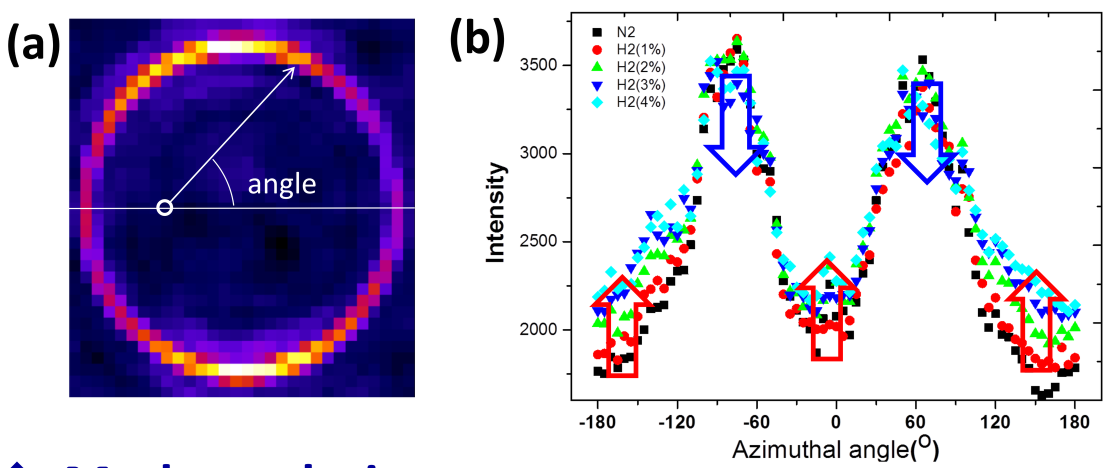


Figure 1 (a) Transmission intensity distribution after adsorption of 4 % H_2 (b) Azimuthal angle-dependent transmission intensity profile after adsorption of H_2 from 0 % to 4 %.

❖ Mode analysis

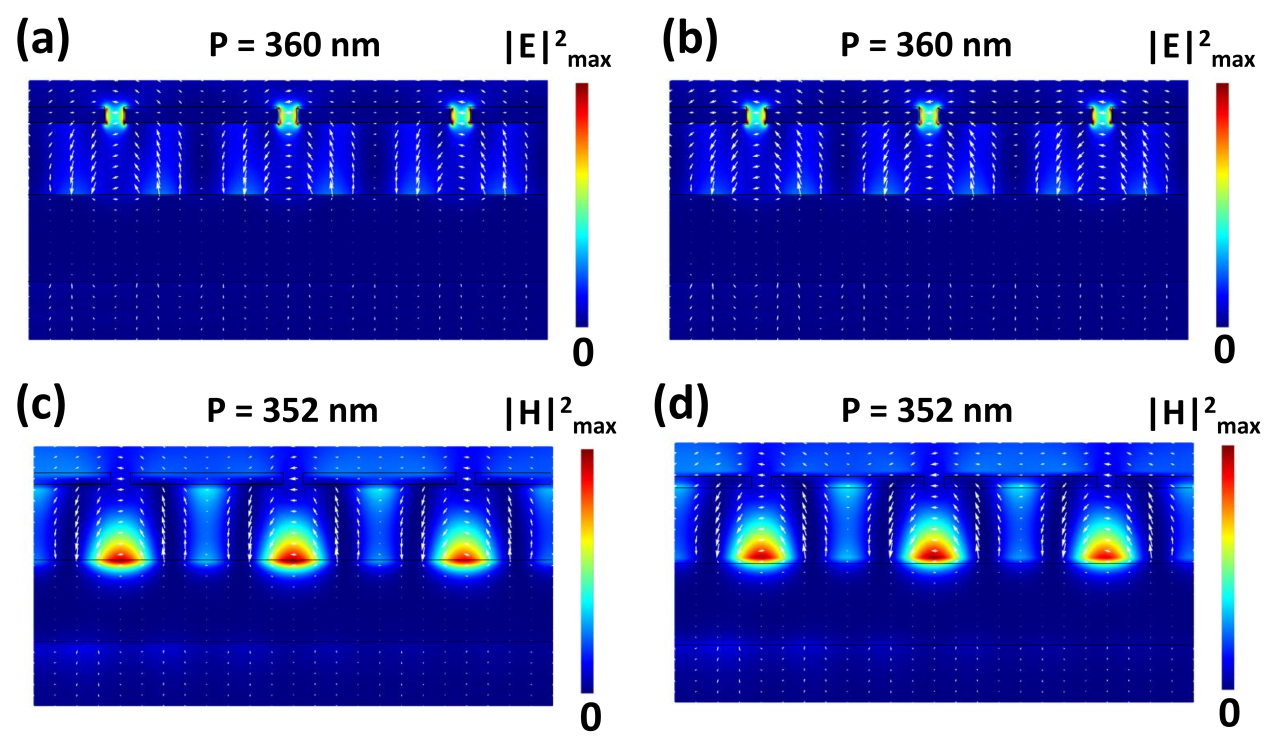


Figure 2 Electric field intensity ($|E|^2$) and electric field (E_x+E_y) distribution of the MIM-PDG structure at grating mode (a) before and (b) after H_2 adsorption. $|E|^2$ and E_x+E_y at MIM mode (c) before and (d) after H_2 adsorption. The direction of the electric field has also been shown with arrows.

❖ Data fitting by using Fano resonance model

Fano resonance model

$$\sigma_a(\omega) = \frac{\left(\frac{\omega^2 - \omega_a^2}{2W_a\omega_a} + q\right)^2 + b}{\left(\frac{\omega^2 - \omega_a^2}{2W_a\omega_a}\right)^2 + 1} \quad (1)$$

$$\sigma_s(\omega) = \frac{a^2}{\left(\frac{\omega^2 - \omega_s^2}{2W_s\omega_s}\right)^2 + 1} \quad (2)$$

$$\sigma_t(\omega) = \sigma_a(\omega)\sigma_s(\omega) \quad (3)$$

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	Simulation			Experiment		
	Pd	PdH		Pd	PdH	
Amplitude (a)	0,077	0,062	-	52,36	41,72	-
MIM mode (ω_a)	351,06	351,64		351,9	352,43	
MIM mode width (W_a)	18,47	25,14		34,82	42,37	
Grating mode (ω_s)	360,40	360,41		360,19	360,2	
Grating mode width (W_s)	49,27	74,25		51,23	98,75	
Modulation damping parameter (b)	2,85	3,33	+	0,92	1,37	+
Fano coupling factor (q)	-0,042	-0,031	-	-0,181	-0,179	-

Table 1 Parameters obtained by fitting with equation (3)

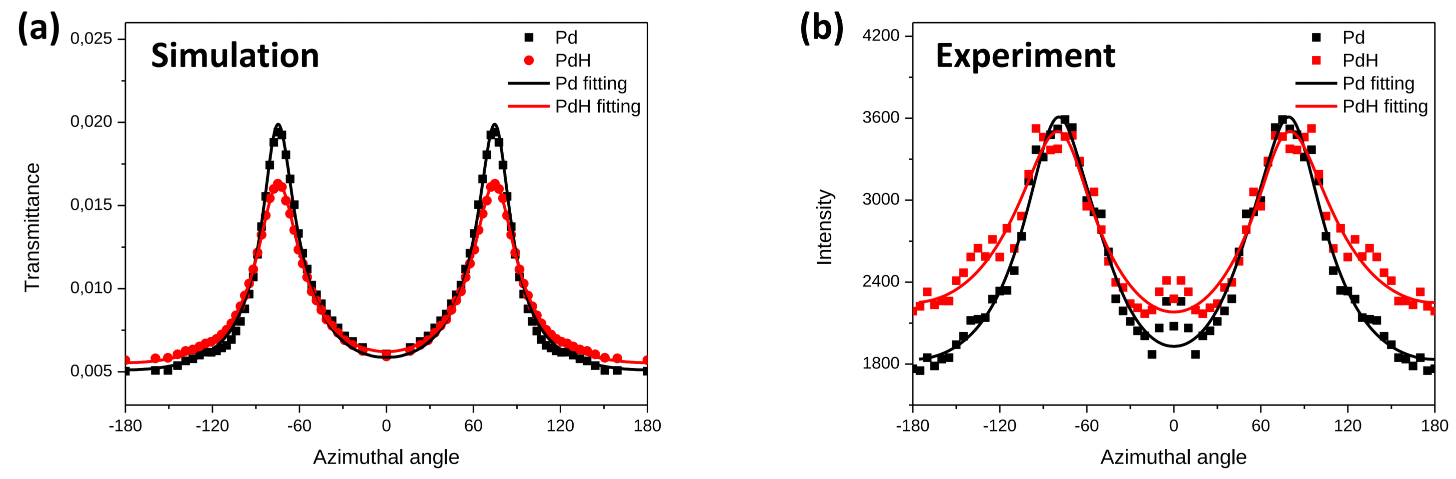
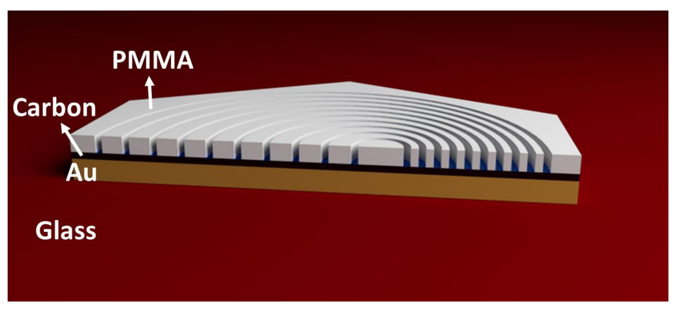


Figure 3 (a) Simulation of transmission intensity profile (dot) at different azimuthal angles before and after adsorption of 4% H_2. (b) Transmission intensity profile (dot) on MIM-PDG before and after H_2 adsorption. The transmission profile is fitted (solid line) by using the Fano resonance model.

DL-PDG for coking detection

Coking detection : 0 nm to 25 nm carbon



Catalyst deactivation due to coke (carbon) formation

- X An important technological and economic problem in petroleum refining and in the petrochemical industry
- X No method that can quantitatively analyze the thickness of carbon layer

Dielectric-loaded (DL) PDG sensors

- ✓ Advantages of PDG
- ✓ Quantitative optical analysis

❖ Coking detection by DL-PDG

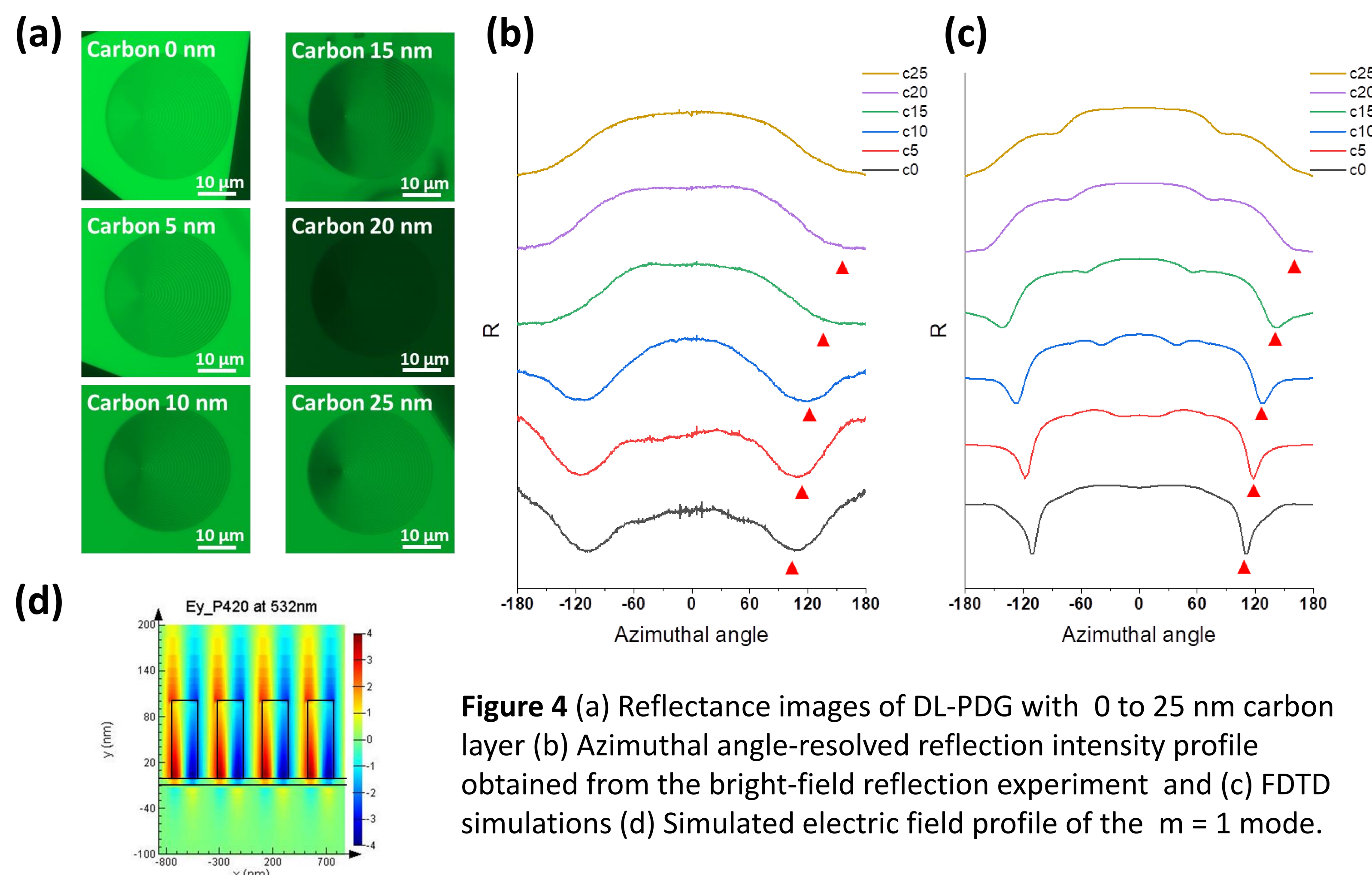


Figure 4 (a) Reflectance images of DL-PDG with 0 to 25 nm carbon layer (b) Azimuthal angle-resolved reflection intensity profile obtained from the bright-field reflection experiment and (c) FDTD simulations (d) Simulated electric field profile of the m = 1 mode.

Summary

1. The designed H_2 sensor based on MIM-PDG platform can realize spectrometer-free and single-color spectroscopic analysis with designable spectral window.
2. Upon absorption of H_2, Pd change to PdH. This leads to the change of Fano resonance from the coupling of grating mode and MIM mode. As a result, the azimuthal angle-dependent transmission intensity profile changes. The intensity profile fits very well with the Fano resonance model.
3. An optical coking detector is realized by using DL-PDG. The azimuthal angle-dependent color distribution of the bright-field reflectance images varies according to the carbon thickness on metal surface. The dynamic range of the carbon thickness that our DL-PDG can detect is from 0 to 20 nm.