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High figure of merit hydrogen sensor using multipolar plasmon resonance modes

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ABSTRACT

Fabrication of long Au nanorods (AuNRs) has resulted in the appearance of higher order plasmon resonance modes, or multipoles, in the absorbance spectrum that can be monitored as a function of time and gas exposure. Due to the proximity of the multipolar mode to the transverse dipole mode of the AuNRs, both modes were monitored as the sample was exposed to hydrogen in an air background. These results were also compared to a shorter AuNR sample where the longitudinal dipole peak position matched the multipolar peak position. Polarization dependence of the higher order resonance as well as boundary element method (BEM) simulations confirm that the mode order is n = 3. Due to the 36% decrease in linewidth of the multipolar peak compared to the dipole, the figure of merit (FoM) of the multipolar resonance is calculated to be 22% higher than the longitudinal dipole resonance for the shown gas sensing results and is promising for high temperature gas sensing applications.

1. Introduction

High temperature combustion environments are in need of accurate and highly sensitive gas detection methods for real-time monitoring of emission gases. Sensitive sensing paradigms such as Fourier Transform Infrared Spectroscopy (FTIR) and Differential Optical Absorption Spectroscopy (DOAS) have been used to monitor emissions of jet turbines in ground-based approaches [1]. However, cost-effective, in situ monitoring is preferred for monitoring of in-flight emissions as well as emissions from ground-based turbines and other combustion related infrastructure. Improved monitoring of emission gases through a real-time feedback mechanism could result in improved combustion efficiency and also enable compliance with stringent environmental regulations [2–4].

Some of the technologies that are commonly used for gas sensing include electrochemical sensors [5], acoustic-wave sensors [6], and optical sensors such as photonic crystals [7] and plasmonic sensors. The design of plasmonic based sensors can take advantage of shape alteration methods to modify rods such that extinction is increased and multipolar resonances are suppressed [8]. While this achieves increased extinction to enable better sensitivity, it limits the multivariable aspects of the sensor design and thus selectivity design criteria may not be achieved. Therefore, a balance with regards to the plasmonic materials choice and its functionality must be taken into account.

In recent years, there has been substantial progress in detecting gases such as H_2, CO, CO_2, NO_x gases and others at high temperatures [9–13]. An optical sensing method for detecting these gases has advantages that include minimal electromagnetic interferences and the potential for multiplexed detection schemes. Plasmonic sensors have been well studied by many research groups and the materials that are typically used are known to be thermally stable, sensitive, selective, and show promise for integration into high temperature combustion environments [14–17]. The results detailed in this work illustrate a pathway to improved gas response in plasmonic sensors at high temperatures, which increases the number of plasmonic signatures that can be monitored and serve as beacons for chemical changes in harsh environments. Specifically, higher order plasmonic resonances in large nanoparticles have been exploited to achieve a narrow plasmonic response and for the first time, demonstrate high temperature gas sensing with these higher order modes.

Plasmonic sensors are based on the principle of surface plasmon resonance which is the oscillation of conduction electrons upon excitation with incident electromagnetic radiation. The resulting oscillation enhances absorption and scattering cross-sections and is also affected by changes in the metal's free electron density and the surrounding dielectric environment. When dealing with nanoparticles, the resonant behavior is confined to the particle surface and is known as a localized surface plasmon resonance (LSPR). Much

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of the work on plasmonic sensors in the literature thus far has focused on monitoring the most intense plasmon peak, the dipolar resonance, and its changes to different gas/dielectric environments [14,18–20]. While plasmon resonances with higher order have been used for refractive index sensing of glycerine at room temperature [21], there have been no reports of using higher order resonances for gas sensing. The current work will show that not only are higher order resonances in gold nanorods (AuNRs) capable of gas sensing at 500 °C but they exhibit an increased figure-of-merit (FoM) over a longitudinal dipole at the same resonant wavelength which could have significant impact on multivariate analysis and distributed combustion sensor networks [22].

For a dipolar resonance established in a sufficiently small nanoparticle, the conduction electrons are excited homogenously across the entire surface of a particle. This is the dominant resonance mode at small particle sizes and can be described using the quasistatic approximation. Usually at particle sizes less than 100 nm, the quasistatic approximation gives reasonably accurate results compared to what is observed experimentally [23]. With larger particle sizes, the ratio of the particle size to wavelength becomes larger and the same wavelength of light can no longer polarize the particle uniformly, therefore making the quasistatic approximation invalid. The field retardation effect thus established in the particle leads to higher order resonances often referred to as multipolar resonances [24,25]. Due to the phase retardation that occurs in such particles, additional regions of field enhancement are present along the rod length with longitudinal polarization. This is not observed in shorter particles that have uniform polarization of the particle electron cloud. The multipole mode order can therefore be identified by both polarization dependence and electric field distribution around the particle [26]. Monitoring of additional resonance peaks could lead to improved multivariate analysis and multiplexed detection schemes [27]. There have been theoretical reports about the properties of multipolar resonances [28–30], though to date there have been no reports of using these modes for high temperature gas sensing applications.

2. Materials and methods

AuNR samples with dimensions of 255 × 60 nm (aspect ratio = 4.25) and 110 × 60 nm (aspect ratio = 1.83) have been fabricated with an electron beam lithography process. A 65 nm base layer of Yttria-Stabilized Zirconia (YSZ) base was deposited on a cleaned quartz substrate and then annealed. PMMA photoresist was spincoated onto the YSZ base layer and baked at 180 °C. Electron beam lithography was used to pattern rods with the stated dimensions followed by electron beam evaporation of titanium (to serve as an adhesion layer) and gold. The leftover photoresist was stripped with acetone. A YSZ capping layer of 50 nm was then deposited on top of the AuNRs followed by annealing the samples in a step-wise process using temperatures of 300, 400, 500, 600 °C. It has been shown previously that capping layers prepared in this way improve the thermal stability of AuNR-YSZ samples [11].

Gas sensing was performed at a sample temperature of 500 °C by mounting the sample inside a quartz flow tube within a furnace. Unpolarized white light was used to excite the resonance modes present in the two samples. The samples were exposed to 200, 500, 1000, 5000, and 10,000 ppm H_2 in air and the exposure time for each concentration was 40 min. This set of concentrations were tested a total of three times per sample to demonstrate repeatability. The peak positions were extracted using a Lorentzian fit. A baseline drift correction procedure was used to renormalize the absorbance curve to 550 nm, an optically unchanging wavelength, in order to minimize drift over the course of the experiment.

Theoretical simulations of the AuNR-YSZ system were performed with a MATLAB Toolbox, MNPBEM [31]. This toolbox relies on a boundary element method which formulates surface integral equations that can be solved at the particle boundaries. Both the 255 × 60 nm and 110 × 60 nm AuNR samples were simulated in a YSZ medium with constant refractive index of 1.8. The dielectric function for gold tabulated by Johnson et al. was used for these simulations [32]. Both x- and y-polarized light was used to simulate absorbance spectra over the indicated wavelength range. Electric field maps were generated by exciting the two samples at the peak positions found from the absorbance spectra.

3. Results and discussion

3.1. Observation of higher order resonance modes

Representative eSEM images of the patterned rods used for the current study are shown in Fig. 1a and c. As shown in Fig. 1b, the longitudinal dipole mode of the 255 × 60 nm AuNR sample used in the current study lies at 1740 nm, though in the visible region there are two additional modes present which are suspected to be a transverse dipole (630 nm) as well as a higher order mode (825 nm).

The 110 × 60 nm patterned rods display a transverse and longitudinal dipole mode at 618 and 822 nm, respectively (Fig. 1d). The shorter AuNR sample shows no additional peaks besides the expected longitudinal and transverse dipole. Overlap of the peak wavelength for the longitudinal dipole in the 110 × 60 nm sample with the higher order mode in the 255 × 60 nm sample is required to compare analyte gas responses and figure-of-merits of the different resonances. The sensing properties of different types of resonances must be compared at the same resonant wavelength due to the refractive index sensitivity differences that would be present if compared at different wavelengths [26].

Due to the characteristic polarization dependence of higher order resonances [26], polarization measurements have been acquired on the 255 × 60 nm AuNR sample to identify the two modes in the visible region (Fig. 2).

In Fig. 2, the transverse dipole is characterized by the peak at 630 nm and has its maximum absorbance with polarization along the short axis of the rod. The peak appearing at 825 nm has its maximum absorbance with polarization parallel to the rod, which is the same dependence as the longitudinal dipole peak. Based on the findings by Yong et al. [26], a resonance with this polarization dependence is suspected to be a hexapole resonance with n = 3. Even-ordered resonances have a zero net dipole moment and coupled with their symmetry properties will not appear in standard absorption spectroscopy experiments with an incident light source perpendicular to the sample [24,25]. However, even-ordered resonances can be observed by tilting the sample so that the incident excitation angle is not 90° or through excitation with an evanescent wave or through near field coupling [24,28]. Since light is incident perpendicular to the NRs for this current study, a quadrupole mode (n = 2) will not be observed. The n = 3 assignment for the peak at 825 nm is also consistent with the work by Davis et al. [28], where simulation of the optical properties of a gold nanorod with a length of 230 nm was completed. The results predicted that excitation of the third order mode will occur at ~660 nm. However, this simulation was done for shorter gold nanorods in water (refractive index = 1.33), while in this current study the medium for the 255 nm long rods was yttria-stabilized zirconia, which has a refractive index that can range from 1.8 to 2.1 depending on deposition methods [33]. Thus the increased length and the refractive index would shift the multipolar mode to longer wavelengths, which is consistent to what has been observed.