

Enhanced Optical NO₂ Sensing at Room Temperature through Chemical Reaction-Mediated Plasmonic Interaction

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Summary:

Recently, the interest in plasmonic nanoparticles for sensing applications has been growing due to their ability to colorimetrically quantify gas concentrations, even by naked eye. Specifically, localized surface plasmon resonance (LSPR) results in strong light absorption and enhanced sensing specifically through chemical reaction-mediated LSPR. Here, this is leveraged for the detection of relevant levels of NO₂ at room temperature with high selectivity over significant confounders using TiO₂ nanoparticles decorated with Au. Additionally, the interaction between the Au-TiO₂ nanoparticles and NO₂ has been investigated.

Keywords: plasmonic, nanoparticle, chemical sensor, environmental monitoring, air quality

Background, Motivation and Objective

Most of the urban population is frequently exposed to air pollution, leading to severe health effects and even death [1]. Gas sensing is therefore of interest to monitor the concentration of hazardous compounds and minimize exposure. Chemoresistive nanoparticles have proven to be attractive for on-site monitoring by converting chemical information into electrical signals but lack in selectivity [2], unless enhanced with filters [3], and may require heating resulting in significant power consumption and a bulky device. Therefore, plasmonic nanoparticles are of emerging interest for optical read-out due to their high light absorption, even at room temperature, through LSPR.

The presence of an analyte can change the LSPR peak absorption caused by its refractive index, but volatile organic compounds have rather similar refractive indices [4], limiting selectivity. On top of that, high concentrations are required to obtain a detectable peak shift [5]. On the other hand, through chemical reaction-mediated LSPR, high sensitivity and selectivity can be achieved [6] as shown with Ag/AgO_x-TiO₂ nano-hybrids to detect concentrations as low as 5 parts-per-billion (ppb) of formaldehyde with high selectivity (e.g., 600 against ethanol).

Here, TiO₂ nanoparticles are decorated with plasmonic Au clusters through synthesis by flame spray pyrolysis (FSP). These materials are used for relevant ppb-levels detection of NO₂ and have shown high selectivity towards a variety of confounders such as ketones, aldehydes, alcohols and more, all at room temperature and

50% relative humidity (RH). Additionally, the interaction between NO₂ and the sensing material has been investigated

Description of the New Method or System

The synthesis of the Au-decorated TiO₂ nanoparticles was achieved by FSP [7]. A precursor was prepared by first mixing gold(III) acetate (Thermo Scientific, 99.9%) with acetic acid (Fluka, 99.8%) and stirred overnight. Separately, titanium(IV) isopropoxide was dissolved in a 1:1 (v/v) mixture of acetonitrile (Merck, 99.8%) and 2-ethylhexanoic acid (Merck, 99%), and stirred overnight as well. The final precursor solution consisted of 20 vol% acetic acid and had a metal content of 0.5 M.

Particles were then collected from a water-cooled glass fiber filter positioned at 57 cm above the burner. The sensing performance was evaluated using a Cary 5000 spectrophotometer equipped with a Praying Mantis and a high temperature reaction chamber (Harrick Scientific). The following gases were tested: NO₂, NO, ethanol, benzene, NH₃, toluene, methanol, isoprene, acetone, CO₂, H₂, formaldehyde, N₂O, CO, and H₂S. In addition to the sensing performance, X-ray photoelectron spectroscopy (XPS) was used before and after NO₂ exposure to get insights into the sensing mechanisms.

Results

The optimal composition of Au and TiO₂ nanoparticles were exposed to varying concentrations of NO₂ at room temperature to assess the sensing performance (Fig. 1). The performance was characterized by a shift of the LSPR

absorption peak upon exposure to the gas. This shift is explained by a change in the electron density of the plasmonic Au clusters, with a red-shift indicating a reduction of the electron density through chemical interactions. At 500 ppb, a high response of ~15 nm was achieved at room temperature and 50% RH. Even at 25 ppb NO₂, a response of ~3 nm was obtained, considerably higher than previous works.

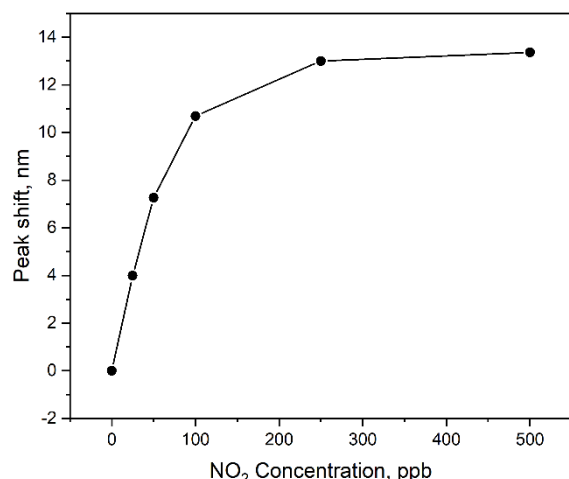


Fig. 1 Plasmonic Au peak shift as a function of NO₂ concentration, error bars represent variation between 3 samples.

The selectivity (Fig. 2) was assessed by exposing the particles to a variety of gases consisting of ketones, aldehydes, alcohols, and more, all at 500 ppb at room temperature and 50% RH. The highest response at 15 nm was obtained for NO₂, followed by NO with a shift of 1 nm, showing promising selectivity. The particles have additionally been exposed to much higher concentrations of CO, CO₂, and ethanol, up to 250 ppm under realistic conditions of 50% RH and at room temperature. There, the highest response was obtained for ethanol with a shift of 0.67 nm at 250 ppm, significantly lower than for NO₂ at 500 ppb.

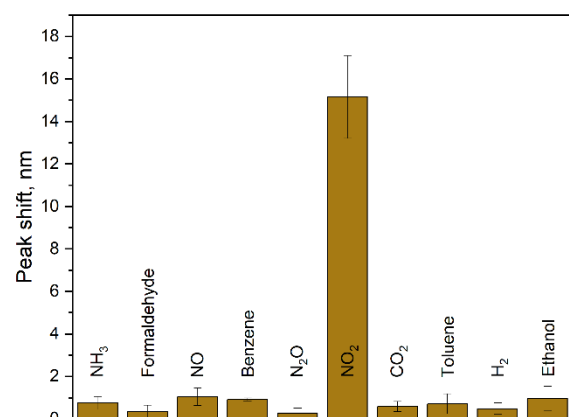


Fig. 2 Selectivity comparison at 500 ppb between NO₂ and a variety of confounders, at room temperature and 50% RH.

The particles have additionally been characterized by XPS before and after exposure to NO₂, showing a significant increase in Au⁺ and a decrease in Ti suboxides, indicating reduction in electron density on the Au clusters and the oxidation of the Ti support material. This decrease in electron density of Au is consistent with the observed red-shift upon exposure to NO₂ and corroborates, together with the oxidation of the Ti support, the theorized sensing mechanism for NO₂ sensing.

Fig. 3 Selectivity comparison of 500 ppb NO₂ to 5, 50, and 250 ppm of CO₂, ethanol, and CO.

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