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*Processes, products  
and services*

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Project: PLATFORMS: PLASmonic  
nano-Textured materials and architectures  
FOR enhanced Molecular Sensing - Strategic  
project of Padova University

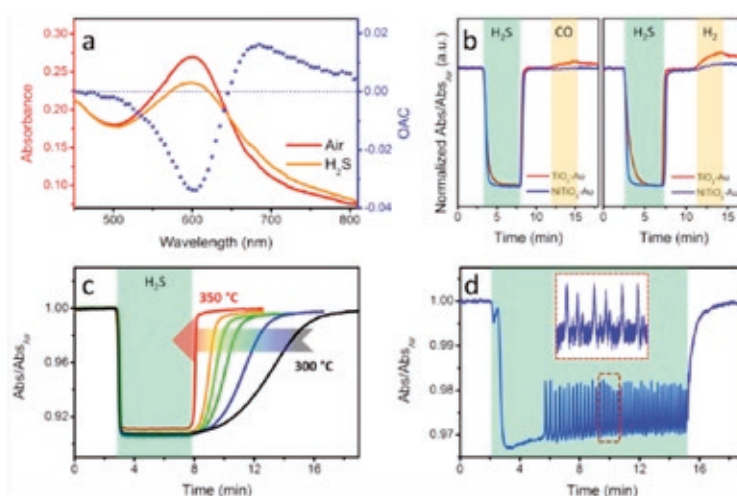
Investigation conducted in collaboration  
with Prof. Paul Mulvaney at Melbourne  
University, Prof. Giovanni Mattei and  
Prof Gaetano Granozzi at Padova University

Main research topics:

- Nanoparticles and nanopowders for functional applications.
- Functional and structural thin coatings via wet chemistry.
- Ceramic based nanocomposites.
- Nanostructured materials for gas sensors

## Surface plasmon based optical gas sensors for environmental monitoring

Plasmonic gas sensors are optical sensors that use localized surface plasmons or extended surface plasmons as transducing platform. Materials that possess a negative real and a small positive imaginary dielectric constant (like metals) are capable of supporting a surface plasmon resonance (SPR). This resonance is a coherent oscillation of the surface conduction electrons excited by an electromagnetic radiation. Surface plasmons are very sensitive to dielectric variations of the environment or to electron exchange, and these effects have been exploited for the realization of very sensitive and selective gas sensors. We developed nanomaterials for H<sub>2</sub> and also for toxic gas like CO or volatile organic compounds. Recently we developed a highly selective hydrogen sulphide (H<sub>2</sub>S) sensor based on the optical monitoring of the SPR variation of Au nanoparticles (NPs) dispersed within a NiTiO<sub>3</sub> sol-gel matrix. The sol-gel matrix provides a porous network that allows the gas molecules to penetrate and reach the reactive sites, while Au NPs are responsible for the strong optical signal in the visible range associated with their SPR peak. Interestingly, Au-free samples are not able to optically detect H<sub>2</sub>S; however, the NiTiO<sub>3</sub> matrix has been proven able to successfully decompose H<sub>2</sub>S into sulfur oxides (SO<sub>x</sub>), with a yield comparable to NiTiO<sub>3</sub>-Au composites. This evidence suggests an active role of the oxide matrix in reacting with the target gas, while Au NPs act as optical probes enabling optical detection. As shown in Fig. 1a, a strong variation in absorption around the Au SPR peak is observed after exposure to H<sub>2</sub>S: the Au SPR peak is broadened and damped in the presence of H<sub>2</sub>S, due to a direct electronic interaction between sulfur and the free electrons at the surface of Au NPs. Minimal or no cross sensitivity towards interfering gases such as CO and H<sub>2</sub> has been proved, especially after a careful selection of the operative wavelength used for the time-resolved tests (Fig. 1b). Such materials demonstrated very high sensitivity to H<sub>2</sub>S with detection limits below 10 ppm at operative temperatures between 300 and 350 °C, and very fast response times, of the order of 10–20 s (Fig. 1c). We discovered also an interesting oscillatory behavior when our nanocomposites are exposed to H<sub>2</sub>S: a reversible, highly regular change in optical absorption is found to happen when specific samples were exposed to H<sub>2</sub>S (Fig. 1d).



**Figure 1.** (a) Optical absorption spectra of a NiTiO<sub>3</sub>-Au film exposed to air and to 100 ppm H<sub>2</sub>S at 350 °C. The blue dotted plot (right vertical axis) shows the variation in absorbance as a function of the wavelength. (b) Time resolved tests for a NiTiO<sub>3</sub>-Au film showing the better response to H<sub>2</sub>S (100 ppm) and the absence of cross sensitivity to CO (1%) and H<sub>2</sub> (1%) when compared to TiO<sub>2</sub>-Au film (T=350 °C, λ=605 nm). (c) Time resolved tests for a NiTiO<sub>3</sub>-Au film exposed to 100 ppm H<sub>2</sub>S showing the variation in recovery times as a function of the operating temperature (λ=605 nm). (d) Oscillatory behavior of a NiTiO<sub>3</sub>-Au film exposed to 100 ppm H<sub>2</sub>S (T=350 °C, λ=590nm). The inset shows a zoomed view of a few oscillations.