

Extended Abstract

Optical Gas Sensors Based on Localised Surface Plasmon Resonance [†]

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Gas species recognition through fully optical devices is currently a raising trend over the well-established conductometric approach, as it opens new possibilities especially for *in situ* recognition of flammable and/or toxic species such as CO, H₂ NO₂ or volatile organic compounds (VOC).

Au nanoparticles (NPs) dispersed in an oxide matrix represent an effective design for a gas sensor's active material owing to their catalytic and localized surface plasmon resonance (LSPR) properties. Noble metal NPs can exhibit catalytic properties and hence modify the chemical interactions between the oxide surface and the target analyte, thereby improving the sensing process. Moreover, if the metal NPs show a LSPR peak in the visible range (like Au), the nanocomposites can be used as selective optical gas sensors. The variation in the dielectric constant around the LSPR peaks will differ for different gas species, leading to a diverse variation in the optical properties at different wavelengths.

TiO₂ thin films with embedded Au and/or Pt NPs have been obtained by synthesizing high-quality metal and metal oxide colloids and directly spinning a nanocrystalline ink made of colloidal solutions on glass substrates. These TiO₂-Au samples showed fast and reversible changes in optical absorption when exposed to H₂ and CO species at 200°–350 °C, with high sensitivities. More impressively, TiO₂-Au-Pt films showed room-temperature response to H₂ and VOC.

Thin films composed of Au NPs dispersed inside a TiO₂-NiO mixed oxide matrix were obtained spin coating a sol-gel solution on a glass substrate and subsequently thermal annealing. These samples show high response to H₂S down to few ppm and almost no interference in response is observed during simultaneous exposure to CO or H₂. For mechanistic studies, experimental evidence using reaction product analysis and thin film surface characterization suggests a direct catalytic oxidation of H₂S over the Au-TiO₂-NiO nanocomposite film.

More recently, we demonstrate the application of ZnO doped with gallium (GZO), aluminum (AZO) and silicon (SZO) nanocrystals as novel plasmonic sensors for the detection of hazardous gases. GZO, AZO and SZO nanocrystals are obtained by non-aqueous colloidal heat-up synthesis with high transparency in the visible range and strong LSPR in the near IR range, tunable with dopant concentration (up to 20% mol nominal). Thanks to the strong sensitivity of the LSPR to chemical and electrical changes occurring at the surface of the nanocrystals, such optical features can be used to detect the presence of toxic gases. By monitoring the changes in the dopant-induced plasmon resonance in the near infrared, we demonstrate that GZO, AZO and SZO thin films prepared depositing an assembly of highly doped ZnO colloids are able to optically detect both oxidizing and reducing gases at mild (<100 °C) operating temperatures.



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