

Au Nanoparticles Dispersed Inside Porous TiO₂ Thin Films: High Performance Optical Gas Sensors Through Localized Surface Plasmon Resonance Monitoring

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Abstract:

Colloidal solutions of Au and TiO₂ nanoparticles are prepared and used as nanocrystal inks for the fabrication of porous thin films to be used as optical gas sensor. The introduction of Au nanoparticles in the TiO₂ matrix affects the reactions mechanism improving the sensing process, moreover the Au Surface Plasmon Resonance peak can be used for the realization of a gas sensor with tunable sensitivity. The effect of thermal treatment, Au dimension and concentration is analyzed in order to tailor films microstructure and their sensing properties. The nanocomposites showed reversible change in optical absorption/reflection when exposed to reducing gasses (H₂, CO) at 300 °C operative temperature or when exposed to volatile organic compounds (alcohols) at room temperature.

Key words: colloidal synthesis, noble metals, anatase, nanocomposites, nanocrystal inks.

Introduction

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 or volatile organic compounds (VOC). Noble metal nanoparticles (NPs) dispersed inside a porous semiconductive matrix constitute an effective design for a gas sensor's active material, thanks to their catalytic and localized surface plasmon resonance (LSPR) properties. In fact, metal NPs can show catalytic properties and therefore modify the chemical interactions between the oxide surface and the target analyte, improving the sensing process [1]. Moreover, if the metal NPs show LSPR peak in the visible range (like Au), the nanocomposites can be used as selective optical gas sensor [2]. In fact, the variation of the dielectric constant around Au will differ for different gas species; moreover, specific chemical reactions can occur at the surface of Au NPs; these events will affect the LSPR bands in different ways leading to a diverse variation of the optical properties at different wavelengths. We have synthesized TiO₂ porous film containing Au NPs with different size using colloidal techniques. The films have been tested as optical gas sensor for the recognition of CO and H₂ or for volatile organic compounds

(VOC). The effect of Au concentration and size on gas sensing properties has been studied.

Experimental

Au NPs of about 13 nm in diameter (hereafter called Au13) were synthesized in water with the Turkevich method as described in [3]. Poly(N-vinylpyrrolidone) (PVP)-capped Au NPs of about 3 nm in size (hereafter called Au3) were synthesized by reducing gold ions in methanol with sodium borohydride adapting a previously published procedure [4]. TiO₂anatase colloids of about 4 nm in diameter were synthesized according to the procedure presented by Antonello *et al.* [5] Films with different Au NPs concentration (up to 5% molar) and size were deposited by spin coating a mixture of Au and anatase colloids on SiO₂ glass substrates and annealed up to 400 °C in air; details are reported elsewhere [3]. Optical absorption measurements have been carried out with a Jasco V-570 spectrophotometer. Transmission Electron Microscopy (TEM) analysis of nanoparticles deposited on carbon-coated copper grids were performed with a Philips CM20 STEM. The nanostructured films annealed at 400 °C have been subjected to optical gas sensing tests in transmission at operative temperatures (OT) between 250 °C and 350 °C and they were exposed to H₂ and CO with different concentrations ranging from 10 ppm to 1% v/v. a description of the

experimental setup has been described previously [3] Samples annealed at 100 °C have been tested as VOCs sensors at room temperature in reflection mode as described in [6].

Results and Discussion

Colloidal syntheses enable a great control on NPs size, shape, size distribution. Moreover by selecting proper solvents and capping agents, it is possible to mix different colloidal solutions avoiding aggregation of the NPs: in this way, high quality thin films can be deposited from these nanocrystal inks with easy and cheap techniques (spin coating, drop casting, ink-jet printing). PVP-capped Au NPs are highly soluble in polar solvents such as alcohols, and so compatible with the methanolic TiO₂ colloidal solution.

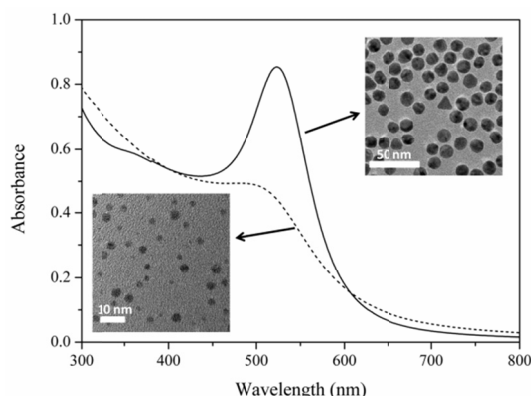


Fig. 1. Absorption spectra of Au13 (straight line) and Au3 (dotted line) NPs in ethanol. The insets show the TEM images for Au13 (top right angle) and Au3 (bottom left angle) NPs.

Optical absorption spectra and respective TEM images of PVP-capped Au NPs in ethanol are reported in Figure 1. It is clear that Au13 NPs are highly monodisperse (the average diameter is 12.9 ± 0.9 nm, standard deviation less than 7%) and they show a sharp and intense LSPR peak centered around 520 nm; on the contrary, Au3 NPs are slightly polydisperse (average size is 2.7 ± 0.6 nm, standard deviation around 20%) and they show a blue shifted and less intense plasmon band. We selected these two sizes to investigate the relationship between optical properties and catalytic activity of Au NPs: it is known that very small Au NPs (usually less than 5 nm) show catalytic properties [7], but their plasmon band is not very intense; on the contrary, Au colloids with diameter in the 10-20 nm range show a clear LSPR peak, but their catalytic behavior is assumed to be greatly reduced. These colloidal solutions have been purified by means of precipitation and redispersion processes, concentrated up to 40mM and then mixed with the TiO₂ NPs

suspensions and directly used to prepare thin films by spin coating, as described in the experimental section. The thickness of the films is in the 40-100 nm range according to deposition parameters and annealing temperature. The deposited films show high porosity, even after the thermal annealing performed in order to remove organic compounds and stabilize the films. The porosity has been evaluated from the refractive index measurements performed with spectroscopic ellipsometry as described in [2,3], and it is found to be around 35% for the samples annealed at 100°C (the refractive index of the oxide matrix at 600 nm is about 1.93) and about 20% for the samples annealed at 400° C, as a consequence of the thermally induced densification (matrix refractive index around 2.2 at 600nm). The optical properties of Au NPs are maintained in the nanocomposite films, but a red shift of the LSPR peak is observed in all samples, compared to the colloidal solution. This effect is due to the higher refractive index – if compared with ethanol – of the anatase matrix Au NPs are in contact with, as confirmed by ellipsometry measurements.

CO and H₂ sensor.

All Au-doped samples give a response to both gases, with a typical behavior of gold doped semiconductor thin films [8,9], that has a wavelength dependence of optical sensitivity, allowing to tune the sensor response. Samples without Au did not give any appreciable optical response, highlighting a pivotal role of Au NPs optical properties. Figure 2a shows the optical spectra collected in air and during 1% CO flowing for a film annealed at 400 °C and containing Au13 NPs; the Optical Absorbance Change (OAC, defined as $Abs_{Gas} - Abs_{Air}$) for the same film for 1% H₂ and 1% CO exposure is also reported. The Au LSPR peak during gas exposure undergoes a blue-shift, due to the interaction between reducing gases and n-type TiO₂ semiconductive matrix. As a consequence of this shift, an absolute maximum and minimum can be determined in the OAC plot, allowing to tune the sensor response by means of wavelength modulation. Samples annealed at 400 °C have been tested as CO and hydrogen sensor to evaluate the effect of size and concentration of Au NPs in the sensing performances. As can be seen from Figure 2b, there is a different effect in the intensity and wavelength dependence of the response according to type and concentration of Au NPs when the samples are exposed to hydrogen: comparing high (4%) and low (1%) Au13 amount, it can be seen that the wavelength positions of OAC absolute maximum and

minimum are almost the same, and only the intensity of the response is rather different, being higher in the sample containing 4% Au.

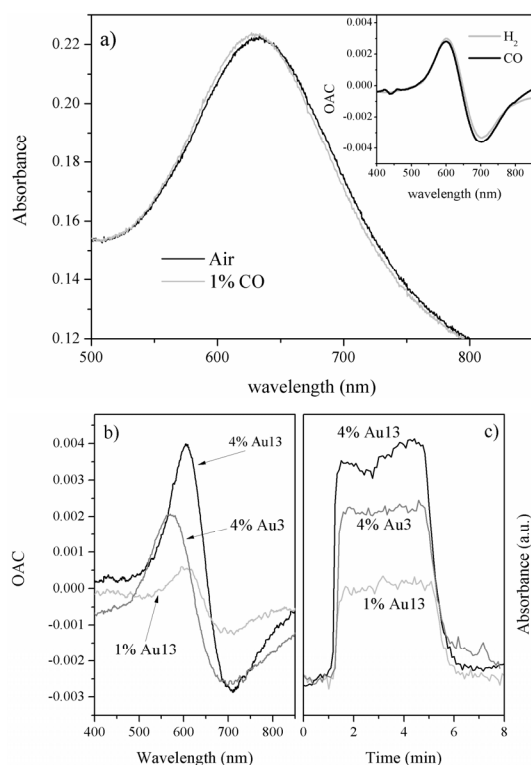


Fig. 2. a) Absorption spectra of a $\text{TiO}_2\text{-Au13}$ film annealed at 400 °C measured in air (black line) and during exposure to 1% v/v CO (grey line) at OT=300 °C. The inset shows the OAC plot of the same film after exposure to 1% v/v CO (black line) and H_2 (grey line) at OT=300 °C. b) OAC of films containing different concentration of Au3 and Au13 NPs after exposure to 1% v/v H_2 at 300 °C OT. c) Dynamic response for the same $\text{TiO}_2\text{-Au}$ films when exposed to one air-1% H_2 -air cycle at 300 °C OT.

These results highlight the role of Au NPs as optical probes, since Au free sample did not give any detectable results, while Au containing samples showed a response intensity proportional to Au amount. Similar results are observed also for CO exposure. As far as samples containing Au3 NPs are concerned, they show as well a wavelength dependent behavior, with the OAC plot slightly blue shifted as expected from the LSPR peak position, but the intensity of the response is smaller (see Figure 2b), as a consequence of the difference in the LSPR peak intensity between Au13 and Au3 NPs discussed previously. This effect was expected as well, but the introduction of small Au colloids was intended to be beneficial to the reaction kinetics, thanks to the catalytic properties of small Au clusters.

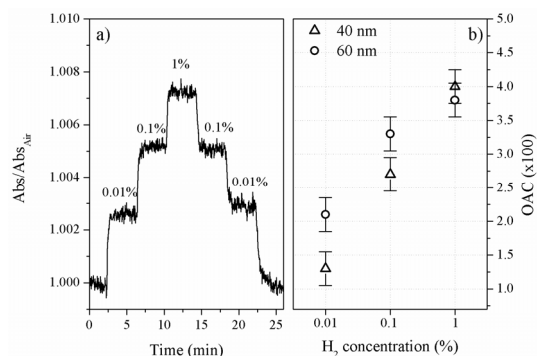


Fig. 3. a) Dynamic response of a $\text{TiO}_2\text{-Au13}$ sample annealed at 400 °C, tested at 585 nm and 300 °C OT, during exposure to different H_2 concentrations expressed volume percent. b) Sensitivity plot for two $\text{TiO}_2\text{-Au13}$ samples with 5% Au NPs with different thickness.

Time resolved measurements have been performed at 300 °C OT at the wavelengths corresponding to absolute maximum and minimum of the OAC curves. A clear and reversible response has been recognized in all the tested samples, with very fast transient times as shown in Figure 2c. The response times (calculated as the times needed to reach 90% of the optical variation following the target gas insertion in the test cell) for all samples are in the 10-30 seconds range for both hydrogen and CO, while the recovery times (times needed to recover 90% of the baseline level) are slightly longer, about 50-60 seconds for hydrogen and 120-150 seconds for CO. We did not observe any improvement in the transient times when TiO_2 films were loaded with Au3 NPs, so a greater catalytic effect of small Au NPs with respect to bigger ones towards reducing gases adsorption and/or decomposition was not observed in this study. Tests at different target gas concentrations show that the intensity of the response is proportional to the gas concentration, as can be clearly seen on Figure 3a; these films can be easily detect 100 ppm H_2 even at very low thickness (see Figure 3b). In addition, the baseline level is fully recovered in all the tests, resulting in great reproducibility of the sensing results.

VOC sensor.

Samples annealed at 100 °C have been tested as VOC sensors at room temperature. The annealing at 100 °C was performed to remove residual solvents and stabilize the films, and this thermal treatment is compatible with several temperature sensitive substrates like polymers, SPR devices and so on. The synthesis of crystalline colloids enables to lower the post processing temperature of the deposited films, allowing to widen the range of

application of these materials. The samples exposed to ethanol vapors show a clear and reversible signal again with a wavelength dependent response, as already experienced for reducing gases detection. In fact, according to the test wavelength, an increase (Fig. 4a) or a decrease (Fig. 4b) in reflection is observed. In addition, a clear increase in the intensity of the response with increasing the Au amount has been detected (Fig. 4c), confirming the key role of Au NPs as optical probes for the target analyte detection, since again Au-free samples did not show any detectable optical variation during ethanol exposure.

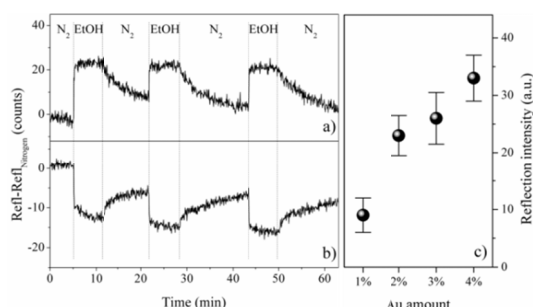


Fig. 4 Dynamic response of a $\text{TiO}_2\text{-Au}_{13}$ film under exposure to multiple nitrogen-ethanol (180 ppm) cycles at 368 nm (a) and 449 nm (b) at room temperature. c) Intensity of the response for $\text{TiO}_2\text{-Au}_{13}$ films as a function of Au amount.

Again, no beneficial effects of the incorporation of small Au NPs have been detected, neither in the response intensity nor in the transient times. So a clear catalytic effect of very small Au cluster is not observed for ethanol detection either, but rather a major role is played by the optical properties of Au NPs, giving better results in terms of response intensity when the LSPR peak is sharp and definite. It is worth noticing that the response times are extremely fast for a sensor operating at room temperature, in the range of 15-20 seconds, while the recovery times are substantially longer. This might be due to the slow desorption process of ethanol from the sensing film at room temperature; this behavior can be improved by increasing the operative temperature or adding catalysts.

Conclusion

TiO_2 and Au nanocrystals have been prepared with colloidal techniques and directly used for active films deposition. The nanocomposites show clear and reversible optical variations when exposed to reducing gases and VOCs, with a wavelength dependent behavior. High sensitivity of the active layers has been proved.

Acknowledgements

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