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Reducing gases and VOCs optical sensing using surface plasmon spectroscopy of porous TiO_2–Au colloidal films

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ABSTRACT

Colloidal solutions of Au and TiO_2 nanoparticles are prepared and deposited as nanocrystal inks for the fabrication of porous thin films to be used as optical gas sensor. The introduction of Au nanoparticles within the anatase 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. Different thermal treatments, Au dimensions and concentrations are investigated and optimized in order to tailor films microstructure and their sensing properties. The nanocomposites show reversible change in optical absorption/reflection when exposed to reducing gasses (H_2, CO) at 300 °C operative temperature or when exposed to volatile organic compounds (alcohols) at room temperature.

1. 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). Semiconductive metal oxides have been widely used as active sensing materials for gaseous species recognition, even if traditionally they have been implemented within conductometric sensing platforms, following the pioneering work on tin oxide by Taguchi [1]. 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 [2,3]. Moreover, if the metal NPs show LSPR peaks in the visible range (like Au or Ag), the nanocomposites can show selectivity properties towards interfering gases [4–6]. In fact, the environment surrounding Au NPs (namely the dielectric constant or the electron concentration of the oxide matrix, for example) will be modified differently by different gas species; furthermore, specific chemical reactions can occur at the surface of Au NPs; these events will affect the LSPR bands in different ways – increase/decrease in intensity, blue/red shift, narrowing/broadening, etc. – leading to a diverse variation of the optical properties according to the analysis wavelength [7,8]. Surface plasmon spectroscopy using Au NPs as optical probes has been recently proved to be a powerful tool to monitor chemical reactions and detect gaseous species [9], even in biological environments [10], and to provide an effective way to recognize environmental pollutants [11].

We have synthesized TiO_2 porous film containing Au NPs with different sizes and concentrations using colloidal techniques. The wet chemistry approach for the synthesis of nanocomposite films is a growing topic in materials science, because of its simplicity and versatility, permitting the deposition of materials with several techniques like spin coating, spraying, ink-jet printing. In addition, synthesizing the different materials with colloidal techniques and preparing concentrated solutions of the active NPs (nanocrystal inks), allows the deposition of low temperature crystalline films without the need of thermal treatment, making this approach suitable for easy and cheap fabrication of active coatings even on delicate substrates like plastic or paper.

The synthesized Au colloids have been purified, protected with a proper surface ligand and concentrated, obtaining ethanolic stock solutions directly miscible with the methanolic anatase suspension and these nanocrystal inks have been deposited via spin coating, obtaining high quality nanocomposite coatings. These films have been tested as optical gas sensor for the recognition of CO and H_2 or for volatile organic compounds (VOC). The effect of Au concentration and size on the gas sensing properties has been studied.

2. Experimental

Au NPs of about 13 nm in diameter (hereafter called Au13) were synthesized in water with the Turkevich method as described

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in [12]: briefly, 12 mL of 1% trisodium citrate aqueous solution was added to a 200 mL boiling solution of 0.5 mM $HAuCl_4$ and let it boil for 15 min. After cooling down to room temperature, 10.000 g/mol average molecular weight poly(N-vinylpyrrolidone) (PVP) was dissolved in water and mixed with aqueous gold colloids according to the ratio gPVP/molAu = 1000. After 2 h Au NPs solution was concentrated in a rotary evaporator, precipitated with acetone, centrifuged at 4000 rpm for 5 min and re-dispersed in ethanol with concentration up to 40 mM in atomic gold.

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 [13]. Briefly, a solution containing 18 mg $HAuCl_4$ in 3 mL methanol was added to a methanolic solution of PVP (75 mg in 38 mL) under stirring. After 30 min, a separately prepared solution composed of 8 mg $NaBH_4$ dissolved in 3 mL methanol is quickly injected under strong stirring, and the resulting brownish solution is let stir for additional 30 min. The methanol is then removed by mean of rotary evaporation, and the sediment is redispersed in water; the particles are then precipitated with excess acetone, centrifuged at 4000 rpm for 5 min, and redispersed in ethanol leading to 30 mM concentrated stock solutions.

TiO_2 anatase colloids of about 4 nm in diameter were synthesized according to [14]. In a typical synthesis, 3 g of titanium isopropoxide was added dropwise to a previously prepared solution consisting in 1.78 g of hydrochloric acid, 7.18 mL of methanol and 1.24 mL of water. The solution was stirred at ambient temperature for 1 h and subsequently heated to 70 °C for 4 h Particles were then precipitated with excess acetone and centrifuged at 4000 rpm for 2 min. The obtained precipitate was dispersed in minimum amount of methanol obtaining a clear colloidal sol of anatase NPs.

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 SiO_2 glass substrates between 2000 and 4000 rpm and annealed up to 400 °C in air; details are reported elsewhere [12].

Optical absorption spectra of samples were measured in the 250–900 nm range using a Jasco V-570 standard spectrophotometer. Transmission electron microscopy (TEM) analysis of nanoparticles deposited on carbon-coated copper grids was performed with a Philips CM20 STEM. Films were characterized by X-ray diffraction (XRD) by using a Philips diffractometer equipped with glancing-incidence X-ray optics. The analysis was performed at 0.5° incidence using Cu-Kα Ni filtered radiation at 30 kV and 40 mA. Surface morphology of the samples was investigated with a FEI Nova i600 dual beam scanning electron microscope (SEM). Transmittance at normal incidence and ellipsometry quantities Ψ and Δ have been measured using a J.A. Woollam V-VASE Spectroscopic Ellipsometer in vertical configuration, at three different angles of incidence (50°, 60° and 70°) in the wavelength range 300–1500 nm. Optical constants n and k and film thickness have been evaluated from Ψ, Δ and transmittance data using WVASE32 ellipsometric data analysis software, fitting the experimental data with Cauchy dispersion, Gaussian and Tauc–Lorentz oscillators for non absorbing region, Au SPR peak and UV absorption edge, respectively. 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 H_2 and CO with different concentrations ranging from 10 ppm to 1% (v/v) using dry air as carrier. A description of the experimental setup has been described previously [12,15]. Samples annealed at 100 °C have been tested as ethanol sensors at room temperature in reflection mode using dry nitrogen as carrier as described in [16].

3. Results and discussion

3.1. Optical and morphological characterization

Colloidal syntheses enable a great control on NPs size, shape, and 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 therefore they are compatible with the methanolic TiO_2 colloidal solution.

Characterization of Au NPs is reported in Fig. 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. The different optical properties are also evident from the color of the colloidal solution as reported in the insets of Fig. 1c: Au13 NPs colloidal solution is bright red colored, while Au3 solution is brownish. 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 [17,18], 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. Au NPs of both sizes show clear diffraction peaks typical of cubic gold (JCPDS No. 040714), confirming the crystallinity of the colloids; a difference in the peaks broadening can be detected, as a consequence of the different size of the nanocrystals. Using the Scherrer relationship and fitting the experimental profiles with Lorentzian functions, the crystallites size has been estimated to be 7.1 ± 3.1 nm and 2.9 ± 0.5 nm for Au13 and Au3, respectively. So we can assume Au3 NPs as nearly monocrystalline, while Au13 are possibly polycrystalline.

These colloidal solutions have been purified by means of precipitation and redispersion processes, concentrated up to 40 mM and then mixed with the TiO_2 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. Fig. 2 shows the optical and morphological characterization of the films stabilized at 100 °C. The characterization of the films annealed at high temperatures in terms of optical properties, structure, morphology and NPs evolution with annealing temperature has been published elsewhere [12].

Upon transfer inside the anatase matrix, 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, as can be seen from Fig. 2a and b. 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 (see below). The LSPR frequency does not change with Au concentration, while a clear increase in absorption with Au loading can be observed (Fig. 2a). Moreover the optical properties of the film containing both Au13 and Au3 NPs are exactly the combination of the optical properties of the films containing separately Au3 and Au13 NPs, as can be observed in Fig. 2b. The optical characterization confirmed that no aggregation or reaction is occurring between Au NPs when transferred from ethanol to the TiO_2 matrix. Moreover, the thickness of these films is rather independent on Au concentration (all thickness values are around 100 nm, with maximum 10 nm deviation, measured with