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CO optical sensing properties of nanocrystalline ZnO–Au films: Effect of doping with transition metal ions

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ABSTRACT

Zinc oxide nanocrystals, pure and doped with transition metal ions, have been synthesized using colloidal techniques; after purification and concentration protocols, the ZnO solutions are mixed with monodisperse Au colloidal suspensions and used for thin film depositions. The effect of the dopant ions on the structural, morphological and optical properties of the as-synthesized colloids as well as the nanocomposite thin films has been analyzed and discussed. The dopant presence has been found to affect the CO optical sensing properties of the nanocomposite ZnO–Au films: compared to pure ZnO, an increase in sensitivity up to 80% and 55% has been detected for Co-doped and Mn-doped ZnO respectively, while Ni-doped ZnO films show only minor improvements. This observation has been ascribed to the multiple oxidation states of cobalt and manganese ions that can facilitate electron transfer between the target gas and semiconductive oxide matrix, and also to the lower surface concentration of Ni ions inside ZnO crystals, as compared to Co and Mn. A fast and reversible response after repeated CO exposures has been detected for all tested samples, and a linear response intensity with the order of magnitude of CO concentration has been observed in the 10–10,000 ppm range, with a lower detection limit of 1–2 ppm.

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1. Introduction

The need for high quality and low temperature active materials has increased substantially in recent years, especially for printable electronic devices [1], and for sensing applications that require delicate and temperature-sensitive substrates, e.g. surface plasmon resonance (SPR) substrates where the Au or Ag layer is deposited over a polymeric diffraction grating [2]. Wet chemical syntheses of inorganic colloidal nanoparticles (NPs) of the active materials represent a useful tool to obtain low-temperature, crystalline materials dispersed in an appropriate solvent that can be directly deposited with a variety of techniques (spinning, dipping, casting, spraying, and ink-jet printing) on the desired substrates. Since the as-deposited material is crystalline, the thermal treatment of the film can be dedicated to obtain the desired final properties, for example to promote sintering, or to remove organic templating agents increasing the porosity. Moreover, the colloidal approach allows an accurate control on the size, the shape and other physical and chemical properties of the synthesized nanocrystals, all key parameters for materials to be used in sensing and catalysis.

Zinc oxide is one of the most investigated materials: its wide direct band gap (3.36 eV at 25 °C [3]) and its high transmittance in the visible and near infrared range make ZnO an interesting material for a wide range of applications, especially in optoelectronic devices like sensors, transistors, solar cells, light emitting diodes (LEDs), transparent conducting electrodes and smart windows coatings [4–9].

In this paper we report the synthesis of colloidal ZnO NPs, pure and doped with transition metal ions, and their use as starting materials to deposit nanocrystalline ZnO–Au thin films. The effect of the ion doping has been evaluated with structural, optical and electronic characterization, and it has been exploited to increase the sensing performances for optical CO detection. An enhancement in the optical response, together with an almost ideal step-like dynamic behavior has been observed. The developed procedure could be used for the realization of nanocrystalline inks for high quality printable sensing materials on a variety of different substrates.

2. Material and methods

The synthetic procedure employed here for the synthesis of ZnO and doped-ZnO NPs is adapted from the work presented by Gamelin and coworkers [10]: briefly, 500 mg of zinc acetate

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dihydrate are dissolved in 22.5 mL dimethyl sulfoxide; separately, 750 mg tetramethylammonium hydroxide (TMAH) are dissolved in 7.5 mL ethanol. The TMAH solution is added dropwise (about 2 mL/min) to the zinc solution under vigorous stirring at room temperature; after 10 min the solution is heated at 50 °C for 1 h to promote Ostwald ripening of the particles. To prepare ZnO NPs doped with 2.5% metal ions, it is sufficient to substitute 12.5 mg of the Zn precursor with the respective amount of the dopant precursor, keeping the total Zn + dopant molarity constant. The ZnO doping was performed with manganese (from manganese acetate tetrahydrate), nickel (from nickel acetate tetrahydrate) and cobalt (from cobalt acetate tetrahydrate). After 1 h at 50 °C, the solutions were cooled down to room temperature, precipitated with the minimum amount (about 3:1 in volume) of methyl ethyl ketone, centrifuged at 1500 rpm for 5 min and redispersed in ethanol to a final nominal concentration of 0.8 M in molar zinc or Zn + dopant.

Gold colloids were prepared according to the Turkevich method [11,12] by reducing HAuCl₄ with trisodium citrate in water. Briefly, 12 mL of 1% trisodium citrate aqueous solution was added to a 200 mL boiling solution of 0.5 mM HAuCl₄. After the solution turned a red-wine colour, it was stirred at boiling point for an additional 15 min and then was cooled down to room temperature; 10,000 g/mol average molecular weight poly(N-vinylpyrrolidone) (PVP) was dissolved in water to yield a 50 g/L concentration, and then this solution was mixed with aqueous gold colloids under constant stirring according to the ratio gPVP/molAu = 1000. After 2 h the solution was concentrated in a rotary evaporator and Au NPs were precipitated with acetone, centrifuged at 4000 rpm for 5 min and re-dispersed in ethanol leading to a 30 mM concentrated solution.

The solutions for the film depositions were prepared by mixing the ethanolic suspension of ZnO NPs and PVP-capped Au NPs leading to a final Au:Zn molar ratio of about 0.06. Au free samples were also prepared for comparison purposes, by substituting the Au colloidal solution amount with pure ethanol. All the samples were deposited by spin coating with a multilayer procedure: solutions were spun at 2500 rpm for 30 s on either SiO₂ or Si substrates, and the films were stabilized at 400 °C for 5 min on a hot plate. This procedure was repeated 4 times, and the last annealing was performed at 500 °C for 1 h in a muffle furnace.

The crystalline phases of the thin films were characterized by X-ray diffraction (XRD) by using a Philips PW1710 diffractometer equipped with grazing incidence X-ray optics. The analyses were performed at 0.5° incidence, using CuK α Ni filtered radiation at 30 kV and 40 mA. The mean crystallite diameter has been evaluated using the Scherrer equation performing a Lorentzian fit of the most intense diffraction peaks. Transmission electron microscopy (TEM) analysis of nanoparticles deposited on colloidal solutions deposited on carbon-coated copper grids were performed with a Philips CM20 STEM system operating at 200 kV. UV–vis absorption spectra of colloidal solutions and thin films were taken using a JASCO V-570 standard spectrometer. Ellipsometry measurements were carried out on a J.A. Woollam V-VASE Spectroscopic Ellipsometer in vertical configuration, at two different angles of incidence (60° and 70°). The surface composition of thin films was analyzed by X-ray photoelectron spectroscopy (XPS) using a modified VG ESCALAB MK II (Vacuum generators, Hastings, England) where a twin (Mg/Al) anode X-ray source, a sputter gun, and a hemispherical electrostatic analyzer with a five channel detector are mounted. The XPS data reported were obtained using Mg-K α radiation (1253.6 eV) as the excitation source. The charging effect has been compensated by referencing all the binding energies (BEs) to the C 1s peak at 284.8 eV. Photoemission spectra have been obtained at room temperature using normal emission geometry. Before taking XPS measurements, the samples were degassed overnight under UHV (pressure lower than 10^{−8} mbar). In order to

Fig. 1. XRD patterns of ZnO and doped-ZnO NPs (doping level is 2.5%) heated at 50 °C for 1 h; the theoretical diffraction lines for wurtzite crystalline phase are indicated at the bottom.

Table 1

Crystallite size of ZnO and doped-ZnO NPs (doping level is 2.5%) heated at 50 °C for 1 h evaluated with the Scherrer equation using the FWHM of the five diffraction peaks detected for each sample (see Fig. 1).

Sample	Crystallites size (nm)
ZnO	7.6 ± 0.5
ZnO:Co	5.8 ± 0.7
ZnO:Ni	5.7 ± 0.4
ZnO:Mn	5.0 ± 0.5

derive the chemical composition of the films, the theoretical photoemission cross sections by Yeh and Lindau have been used [13], while the electron inelastic mean free path has been calculated with the TPP2 algorithm [14]. Atomic force microscopy (AFM) height profiles were recorded using a NT-MDT Solver Pro instrument in tapping mode. The surface structure of the nanocomposite films has been investigated with an xT Nova NanoLab scanning electron microscopy (SEM). Optical gas sensing tests were performed by making optical absorbance/transmittance measurements over the wavelength range 400 nm < λ < 800 nm with sample films mounted on a heater inside a custom-built gas flow cell coupled with a Varian Cary1E spectrophotometer. Thin films were exposed to four different concentrations (10 ppm, 100 ppm, 1000 ppm and 10,000 ppm, i.e. 1% v/v) of CO, all balanced in dry air, at a flow rate of about 0.4 L/min. Tests were performed at an operating temperature (OT) of 300 °C. The substrate size was approximately 1 cm × 2 cm and the incident spectrophotometer beam was normal to the film surface and covering a 6 mm × 1.5 mm section area.

3. Results and discussion

Zinc oxide NPs synthesized with this method present the wurtzite crystalline structure, with a mean crystallite dimension ranging from 3 to 10 nm depending on the synthetic parameters.

Since the freshly prepared NPs are found to continuously grow for several hours at room temperature due to Ostwald ripening, it was decided to perform a mild heating at 50 °C for 1 h after the TMAH addition in order to accelerate this process and obtain stable colloidal solutions. XRD patterns of ZnO and doped-ZnO NPs after the annealing procedure are reported in Fig. 1. Typical diffraction peaks for wurtzite ZnO (JCPDS no. 36-1451) are clearly detected in all samples, but a difference in peak broadening can be observed, with the crystallite size of doped NPs being significantly smaller compared to undoped ones (see Table 1). Moreover ZnO:Mn

Fig. 2. TEM images of (a) pure ZnO colloids and (b) Au colloids.

nanocrystals have the lower crystallite size, and this is maintained also in the thin films deposited from these solutions and heated at 500 °C (see below).

This effect has been ascribed to the difference in size between Zn^{2+} and dopant ions: since these dopants are substitutional to zinc in the ZnO lattice structure [10,15,16], the doped crystallites grow mechanically stressed. Thence, extended growth of the crystals is expected to be energetically unfavorable since the variation in lattice energy is not balanced by the reduction in the surface/volume ratio.

Fig. 2 shows TEM images of as-synthesized ZnO and Au NPs: almost spherical ZnO nanocrystals with an average diameter ranging from 4 to 7 nm can be seen in Fig. 2a, in good agreement with the XRD evaluation, suggesting that the NPs are mainly monocrystalline; despite the low contrast of ZnO, some lattice planes can be seen, confirming the crystalline wurtzite phase. Monodisperse (standard deviation about 7%) spherical Au colloids of 13 nm in diameter can be easily seen in Fig. 2b: some faceting and some triangular shapes can be detected, quite common phenomena for Au NPs synthesized with the citrate reduction method.

From UV–vis absorption spectra of the ZnO colloidal solutions reported in Fig. 3, it is possible to see the sharp UV absorption onset of ZnO nanocrystals at about 350–360 nm. For doped ZnO

the onset is blue shifted, as highlighted in the inset (a) of Fig. 3. This is due to the dopant effect in reducing the particle size that in turn leads to higher energies associated to the optical band gap, due to the quantum confinement effect. In fact it has been confirmed that the size dependence of ZnO electronic properties can be present for crystals size up to 7 nm [17], in agreement with that evaluated both from XRD and TEM. The three distinctive absorption bands in the green–red range that can be seen in the inset (b) of Fig. 3 are ascribed to the d–d adsorption levels of divalent Co^{2+} ions in tetrahedral coordination [18], in this particular case in the tetraoxo cation coordination environment of wurtzite [19,20], consistent with a Co^{2+} substitutional site.

Ethanollic suspensions of Au and ZnO NPs are mixed together and directly used for film deposition, as described in Section 2. All the characterizations presented in the following, if not differently specified, refer to Au-containing films annealed at 500 °C, since no significant difference in structural, morphological and optical properties of ZnO films is detected when Au NPs are embedded inside the oxide matrix (except the expected presence of the Au diffraction and plasmon peaks).

The XRD patterns of the synthesized films are shown in Fig. 4: both Au (JCPDS no. 04-0784) and ZnO (JCPDS no. 36-1451) diffraction peaks are clearly evident, and a big difference in the FWHM of ZnO peaks compared to the as synthesized NPs can be seen

Fig. 3. UV–vis absorption spectra of ethanolic suspension of ZnO colloids. The insets show (a) the effect of the dopants on the UV absorption onset of ZnO and (b) the distinctive Co^{2+} ion absorption bands.

Fig. 4. XRD patterns of ZnO and doped-ZnO thin films containing Au NPs annealed at 500 °C; the theoretical diffraction lines for wurtzite (straight lines) and Au (dashed lines) crystalline phases are indicated at the bottom.

Table 2

Crystallite size of ZnO and doped-ZnO thin films containing Au NPs annealed at 500 °C for 1 h evaluated with the Scherrer equation using the FWHM of the five ZnO diffraction peaks detected for each sample (see Fig. 4).

Sample	ZnO crystallite size (nm)
ZnO	19.5 ± 0.7
ZnO:Ni	19.0 ± 0.6
ZnO:Co	15.8 ± 0.6
ZnO:Mn	10.7 ± 0.4

Table 3

Surface stoichiometries of the ZnO and doped-ZnO thin films containing Au NPs annealed at 500 °C derived from the XPS data reported in Figs. 5 and 6.

Atomic composition	ZnO	ZnO:Ni	ZnO:Co	ZnO:Mn
Zn	48.5	47.0	47.6	42.8
O	49.0	50.6	49.0	51.4
Au	2.5	2.0	2.4	2.9
M ²⁺ dopant	–	0.4	1.0	2.9

(compare with Fig. 1). This is due to crystal growth promoted by high temperature annealing. The average diameter of the ZnO crystallites is between 11 and 20 nm according to the type of dopant, as shown in Table 2.

Again, the influence of the dopant is to reduce or almost prevent the temperature-driven ZnO crystallite growth, even if this effect is much more evident for Mn compared to the other ions.

Besides the already discussed difference in dopant size, a possible explanation of this behavior can be ascribed also to different oxidation states of the cations: while Zn and Ni ions exist mainly in the +2 oxidation state, Co and Mn present multiple oxidation states (+2 and +3 the more common, but Mn can be also found in compounds with higher oxidation states). The presence of an ion with a different oxidation state, higher than Zn²⁺, would lead to a substantial amount of negatively charged Zn vacancies, inducing a higher extent of mechanical stress in the lattice, inhibiting the crystallite growth. Considering that samples doped with Co and Mn show the smallest crystallite sizes, while the effect of Ni in reducing the crystallite size is not so pronounced after the 500 °C annealing, the different oxidation state of the dopant ions could be an explanation of the difference in crystal growth. Even if Co²⁺ absorption bands are only detected in the corresponding optical spectra, a minor contribution from Co³⁺ species cannot be excluded. Actually, ZnO crystals doped with several ions, including Fe and Co, have been prepared and analyzed by XANES [16]: the presence of both Fe²⁺ and Fe³⁺ species has been demonstrated, while in the case of Co the majority of the ions are divalent, even if a broadening at shorter lengths of peak profiles of the radial distribution functions has been ascribed to the effect of Co³⁺ species.

As expected, Au diffraction peaks are not evidently affected by the type of ZnO NPs, and they do not undergo any relevant change in shape, indicating good stability of Au NPs inside these oxide matrices, as observed also in the past for TiO₂-based nanocomposites [21].

In order to evaluate the successful incorporation of dopant ions inside the ZnO films and to evaluate their oxidation state, XPS analysis was carried out. As far as the ZnO matrix and the Au NPs are concerned, the XPS results are quite homogeneous in all the examined samples: the photoemission spectra of the Zn 2p and Au 4f core levels do not show significant changes in all the samples (see Fig. 5) and are compatible with the presence of stoichiometric zinc oxide and metal Au NPs, respectively. In Table 3 the elemental surface stoichiometries of the different films are reported: the amount of Au found in the different samples is only slightly varying ranging from 2.9% in the Mn doped sample to 2.0% in the case of the Ni doped one. However, it can be seen that large differences can be observed

Table 4

Thickness and surface roughness for the four samples containing Au annealed at 500 °C evaluated from AFM images.

Sample	Thickness (nm)	Surface roughness (nm)
ZnO	92.3 ± 2.8	3.4
ZnO:Co	67.9 ± 2.5	2.3
ZnO:Ni	78.1 ± 5.9	2.4
ZnO:Mn	67.6 ± 3.3	2.7

in the concentration of the dopant itself, which varies from 0.4% in the case of Ni to 2.9% in the case of Mn (i.e. almost one order of magnitude).

One possible explanation for this trend is surface segregation [22] of the larger dopant ions (the ionic radii scale as Mn²⁺ > Co²⁺ > Ni²⁺) induced by the strain, considering that the probing depth of XPS measurements is rather low (3–5 nm).

It is interesting to note that there is also a direct relation between the dopant surface concentration, as determined by photoemission, and the crystallite size, as determined by XRD, which is a bulk sensitive technique: the more the dopant concentration at the surface, the smaller is the crystallite size (as shown in Tables 2 and 3). Therefore it seems reasonable to interpret both compositional and structural data with a unique framework that is the amount of doping induced strain.

For the identification of the chemical states of doping cations, high resolution spectra of the corresponding 2p levels have been measured (see Fig. 6). A clear and definitive assessment of the chemical states is rather difficult since these metals are present only in trace amounts and the expected chemical shift between different oxidation states is quite small. More useful in this respect is to analyze the satellite fingerprint of the photoemission lines, which, in the case of 2p transition metals is very distinctive of the oxidation state [23]. Thus by comparing the positions and relative intensities of the main photoemission peak and satellites [24–28] it can be concluded that all the doping ions are present predominantly as divalent cations. However the low signal to noise ratio prevents excluding the possibility of the presence of small contributions from minority oxidation states.

Atomic force microscopy measurements were conducted to analyze sample morphology and evaluate thickness: Fig. 7a and Table 4 show the results of the AFM analysis. As can be seen, the surface of the samples is quite structured, due to ZnO crystalline grains; nevertheless the surface roughness is not high, being below 4 nm for all the samples, providing good optical quality and absence of scattering phenomena. Only one AFM scan has been presented here because the different samples are rather similar, and just minor differences in surface roughness have been detected. The thickness evaluated by scratching the samples and using the AFM tip to scan the edge of the lines, is in the range 70–90 nm for all the samples, but a trend in the thickness can be seen, with the pure ZnO sample being the thickest, and the Co-doped and Mn-doped samples the thinnest.

A confirmation of the surface morphology comes also from SEM: a typical micrograph of a ZnO–Au film is reported in Fig. 7b. As can be seen the surface roughness as well as the high porosity extent can be appreciated from this image.

Optical absorption spectra of the Au-containing samples are shown in Fig. 8: the UV absorption onset of ZnO is still clearly evident, and it is slightly red shifted compared to as-synthesized NPs; moreover the difference between the 4 samples is not as large as the one found for the colloidal solutions. This behavior is due to the temperature-driven crystal growth that causes the particle not to be subjected any more (or only weakly) to the quantum confinement regime, reaching the ZnO bulk band gap value. Also the Au SPR peak is easily detected, centered at about 570 nm, considerably red

Fig. 5. XPS Au 4f and Zn 2p data of ZnO and doped-ZnO thin films containing Au NPs annealed at 500 °C.

Fig. 6. XPS Co 2p, Mn 2p and Ni 2p data of doped-ZnO thin films containing Au NPs annealed at 500 °C.

shifted compared to the Au SPR peak for the as-synthesized colloids in ethanol recorded at 523 nm. This is due to the difference in refractive index between ethanol and the nanocrystalline zinc oxide films, the latter being much higher than the former.

In fact, the refractive index values of the ZnO films are found to be in the 1.8–1.85 range at 600 nm, as measured with spectroscopic ellipsometry, substantially higher compared to the refractive index of ethanol at the same wavelength (1.36 [29]). By using the

effective medium approximation (EMA) models, the porosity of the films can be estimated from the comparison between the experimental refractive index, and the theoretical value for fully densified material (2.01 at 600 nm for wurtzite ZnO [30,31]): the nanocomposite film is thus modeled as an effective medium composed of dense ZnO and pores. Among the different EMA models that can be used, the Bruggemann function [32] is universally accepted and widely employed for porosity evaluation [33,34]. Table 5 shows

Fig. 7. AFM (a) and SEM (b) images of a ZnO film containing Au NPs annealed at 500 °C.

Fig. 8. Optical absorption spectra of ZnO and doped-ZnO thin films containing Au NPs annealed at 500 °C.

Table 5

Experimental refractive index at 600 nm and estimated porosity for the samples without Au annealed at 500 °C, evaluated from spectroscopic ellipsometry measurements.

Sample	Refractive index	Porosity%
ZnO	1.84	16
ZnO:Co	1.84	16
ZnO:Mn	1.80	20
ZnO:Ni	1.82	18

refractive index values at 600 nm and corresponding pores volume fractions for the four samples: as can be seen, porosity values are in the 16–20% range for all samples. The ellipsometric measurements were performed on Au-free samples in order to obtain a Cauchy dispersion of the refractive index in the visible range, because, as a consequence of the strong SPR absorption peak of Au NPs, ZnO–Au films present a perturbation of the refractive index dispersion curve. Nevertheless, in the NIR region, the refractive index values of Au-free and Au-containing samples are almost identical, suggesting that the porosity amount is only weakly affected by Au NPs presence.

Besides the already mentioned red shift of Au NPs SPR peak when the metal is embedded inside a ZnO matrix compared to ethanol, also a clear broadening and a small red shift of the Au SPR peak is detected when Au NPs are embedded inside a doped-ZnO matrix with respect to pure ZnO. This effect might be related to a difference in the electronic properties of the doped-ZnO crystals compared to the undoped ones, that can interact with the surface free electrons of Au NPs, affecting the SPR frequencies, as described by the Mie theory [35].

From the intensity of the ZnO exciton peak it is possible have some insight on the thickness of the films, as reported in the literature [36]: the undoped ZnO film is the thickest, followed in order by Ni-doped, Co-doped and Mn-doped. These data are in good agreement with the thickness estimated from AFM measurements. Since the precipitation–redispersion protocol for all the different ZnO colloidal solutions was the same, and so were the deposition parameters, this difference in thickness can be ascribed to a different precipitation threshold of the ZnO colloids according to the type of dopant, or to different solubility of these particles in the solvent/nonsolvent mixture (being also the size of the particles slightly different). This leads to a difference in nanocrystals concentration and also the viscosity of the final solution used for depositions. Moreover, also experimental variability of the spinning procedure cannot be excluded as a cause of such thickness differences, as well as a limited sintering of ZnO crystals during the annealing of the

films due to the presence of the dopants. The actual thickness of the sample has thus to be taken into consideration when comparing the gas sensing results.

These materials were tested as optical sensors for CO detection where different operating temperatures (OTs) were used, in order to identify the best operative conditions. All the samples gave low response between 25 °C and 200 °C OTs, with quite long transient times, while in the 250–350 °C range the response was easily detected, and all the tests reported in the following have been carried out at 300 °C OT. Au-free samples did not give any appreciable optical response, as already observed in the past [37], while Au-containing samples showed the typical wavelength dependent behavior of Au-doped transition metal oxides [38,39]. All samples present a blue shift of the Au SPR peak when exposed to the reducing gas, consistent with the oxidation of CO and the subsequent electron injection inside the n-type ZnO matrix, leading to the shift to higher frequencies of the plasmon band. It is reasonable that other reducing gasses like H₂ will react similarly with the ZnO matrix, while oxidizing gasses like NO₂ will cause a red shift of the SPR peak. The sensing performances were monitored using the optical absorption change parameter, defined as the difference in absorbance during target gas exposure and during air exposure ($OAC = A_{CO} - A_{air}$). Fig. 9a shows the OAC curves for the 4 prepared samples exposed to 1% CO at 300 °C OT.

The distinctive shape of the response versus wavelength curve can be seen, resulting in wavelengths where the response is maximized (about 570 nm and 670 nm, positive and negative, respectively) and wavelengths in which the sensing response is extremely low or null (below 450 nm, ~625 nm and over 800 nm), allowing to tune the material sensitivity and possibly selectivity by using wavelength modulation.

A difference in the intensity of the response can be seen comparing the four samples with undoped ZnO showing the less intense OAC maximum and minimum, despite having the highest thickness, while the Co-doped sample is the most sensitive to CO, even though the thickness is much lower than with the pure ZnO sample.

This difference in response becomes clearer when normalizing these values to the sample thickness expressed in microns, as shown in Fig. 9b. The normalization has been performed by calculating the average response of each sample and summing the absolute OAC value both at the positive and negative maximum wavelengths, and then dividing by the sample thickness as measured with AFM (thus the units are expressed in μm^{-1}). Cobalt and manganese doped samples show evidently the best sensing response, while undoped ZnO has the lower response, confirming the positive effect of doping ZnO crystals with transition metal ions. The enhancing effect of Co and Mn ions might be again related to their multiple oxidation states, that allows a variation of charge carrier concentrations, thereby improving the material performances, as shown in the literature for ZnO films doped with trivalent ions like Al³⁺ or Ga³⁺ [8,40,41], as a matter of fact Ni-doped ZnO does not show a great improvement, and according to what was discussed earlier, this might be ascribed to the main oxidation state of Ni, being the same as Zn. Moreover, as shown above, the Ni amount at the surface of ZnO crystals is rather low compared to the other dopants, and since the gas sensing mechanism includes a surface process, this may be an additional explanation to the rather low optical response of the Ni-doped ZnO nanocomposite.

Since there is no confirmation of the different oxidation state of the dopant ions, due to the accuracy provided by XPS measurements not allowing to distinguish clearly possible 3+ species, it cannot be stated unequivocally that trivalent ions are present. In any case, even assuming that all the species are in the 2+ state, the presence of cations that can exist with different oxidation states is useful in the gas sensing performance because the dopants can change their oxidation state according to the redox nature of

Fig. 9. (a) Optical absorption change plot ($\text{OAC} = A_{\text{CO}} - A_{\text{Air}}$) for ZnO and doped-ZnO thin films containing Au NPs annealed at 500 °C for 1 h. (b) Normalized OAC intensity for the four tested samples.

the atmosphere they are in contact with, facilitating the electron transfer between the gas and matrix, improving the sensing performances. For example, it is known that WO_3 crystals when exposed to hydrogen, undergo the formation of some W^{5+} species in opposition to the pristine W^{6+} ions, changing both the electrical and the optical properties of the material [42].

All ZnO doped samples show acceptable dynamic behavior after repeated exposures to different CO concentrations in air, as reported in Fig. 10: the response times are relatively fast, while the recovery times are a little longer but still satisfactory. If considering an air–1% CO–air cycle, the response times (defined as the times needed to reach 90% of the total response) for all the samples are in the 15–20 s range, while the recovery times (defined as the times needed to recover 90% of the initial baseline) are around 2–3 min. If considering lower CO concentrations instead, response times do not change significantly, while recovery times

are substantially lower. As can be seen, even though these samples are relatively thin, they are able to easily detect down to 10 ppm CO, with a linear-logarithmic relationship between intensity of the optical variation and target gas concentration, as already observed for nanocrystalline TiO_2 –Au samples prepared by our group [21].

Comparing the response intensities of the time-resolved tests, it can be seen again that samples doped with cobalt and manganese ions show the best performance, while the undoped ZnO has the lower intensity: this is a confirmation of the normalized response shown in Fig. 9b. From these dynamic tests the sensitivity and the detection limits can be evaluated. The parameter used for this evaluation is the response intensity (RI), defined as the following:

$$\text{RI} = \left| \frac{\text{OAC}}{t} \right|$$

where t is the thickness of the samples expressed in microns. Basically, the response intensity is defined as the absolute value of OAC taken at one wavelength and normalized to the sample thickness; the RI value has been defined in this way in order to take into account the difference in thickness between the four samples, and to obtain always positive values of the sensing response, since considering the OAC curves shown in Fig. 9a, there is a range of frequencies in which the OAC is negative. Measuring the RI values for two different tests for each sample, and plotting the average value versus the CO concentration (Fig. 11), a linear relationship between the response intensity and the order of magnitude of the target gas concentration can be seen, and also extrapolating the data at lower concentrations the detection limit can be estimated to be in the 1–2 ppm range. The linear fits of the experimental data shown as dashed lines confirm the linear relationship, and make the calibration curve calculation simple. The sensitivity is hence defined as the slope of the response curve versus concentration, and the Co-doped sample showed the highest sensitivity together with the highest response intensity as is also indicated for the Mn-doped sample. By defining the sensitivity S as the following:

$$S = \frac{\text{RI}}{\text{Log}([\text{CO}])}$$

where $[\text{CO}]$ is the CO concentration expressed in ppm, the S value is exactly the slope of the linear fits presented in Fig. 11.

The obtained sensitivity values – taking the horizontal axis in a logarithmic scale – are 1.6×10^{-2} , 2×10^{-2} , 2.5×10^{-2} , and

Fig. 10. Dynamic response of (a) ZnO; (b) ZnO:Ni; (c) ZnO:Co and (d) ZnO:Mn samples containing Au NPs at the wavelength corresponding to the maximum of the OAC curve (Fig. 9a) and at 300 °C OT, during exposure to different CO concentrations expressed in ppm.

Fig. 11. Sensitivity plots for CO detection for the four samples tested at the wavelength corresponding to maximum of OAC curves and at 300 °C OT. Linear fits for the four experimental sets of data are also reported.

$2.9 \times 10^{-2} \mu\text{m}^{-1} \text{ppm}^{-1}$ for undoped, Ni-doped, Mn-doped and Co-doped ZnO films, respectively. A trend is clearly identified, being Co-doped ZnO film the better, with the sensitivity almost doubled compared to pure ZnO (the actual increase is more than 80%); the highest sensitivity together with the highest response intensity makes cobalt ions the ideal dopant to enhance ZnO sensing properties. In addition, promising sensing properties have been shown also for ZnO:Mn samples (sensitivity is increased more than 55%), while only minor positive effects have been detected for Ni-doped films (sensitivity improved by 25%).

4. Conclusion

High quality nanocrystalline ZnO and transition metal ions-doped ZnO films have been prepared starting from colloidal solutions of crystalline NPs, and the incorporation of monodisperse Au NPs has also been performed. Morphological and optical characterization of both colloidal solutions and thin films confirmed the dopants presence and their effect on the crystallite sizes and on the UV absorption onset of ZnO. Optical gas sensing tests for CO detection showed a fast, reversible and linear-logarithmic response in the 10–10,000 ppm range for all the samples tested, and the positive effect of the dopants have been exploited to increase both the magnitude of the response and the sensitivity of the nanocomposites. Cobalt ions inside the ZnO lattice structure are found to increase the CO sensitivity of ZnO–Au films by more than 80%.

These nanocrystalline colloidal solutions are a promising tool for the realization of low-temperature active thin films for many applications like sensors, LEDs, transistors, and coatings in general.

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