# A Study about Surface Chemical-Physics Mechanisms Occurring for Interacting Metal Nanostructures with gas $NO_2$

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## ABSTRACT

Zinc nanostructures synthesized with different morphologies from the same evaporation/condensation technique are studied with concern to surface reactivity to $NO_2$ by Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS) at variable temperatures. Synthesis of nanopowders is obtained, according to previous work, by gas flow thermal evaporation at 540 °C of bulk Zn grains. Two types of Zn powders are fabricated and characterized by SEM, TEM, XRD in experiments. The first one is constituted by grains (≈10 µm) originated by the stratification of smaller aggregates (≈200 nm) and isolated primary particles (≈50 nm) born in the gas flow. The second one is constituted mainly by hollow Zn nanofibers with external and internal diameter about 100 and 60 nm. Comparison is made between the nanostructured powders with respect to commercial Zn standard dust. The Zn hollow nanofibers when exposed to $NO_2$ are found to exhibit dramatic reactivity, which is not observed either in the case of clustered aggregate zinc or of commercial Zn dust powder.

***Keywords***: chemical sensors, nanofibers, surface science, DRIFTS, CVD

## 1 INTRODUCTION

Transition element and relative oxides are used as nanostructured materials for gas-sensing manufacturing, owing to the properties of selectivity and sensitivity to different pollutants, hydrogen, humidity and ammonia. Common applications can be listed for Palladium, Platinum and TiO2, CuO, to cite a few. In particular, Zinc oxide is attractive material in that it exhibits a number of interesting features for instance it is classified as a wide-band-gap semiconductor (3.3 eV) with property of transparency in the visible region, piezoelectricity, photoluminescence. Possible applications include phosphor in flat panel displays and design of light emitting diodes when used as a substrate of gallium nitride (GaN) owing to the fact that ZnO does match very well the GaN lattice, expecially in its thin film form [1].

In previous paper by our group [2] we reported the receipt to fabricate hollow Zinc nanofiber by a evaporation-condensation route followed by deposition of metal vapour on quartz substrate.

The generation of nanocrystalline zinc nanostructures by thermal evaporation was also reported in the past. Yumoto et al [3] fabricated Zn crystals with metal bars as raw material. Recknagle et al [4] performed evaporation of zinc in partial vacuum environment followed by condensation of metal vapours by supersonic jet expansion.

$NO_2$ is one of the ever-present pollutants because it is generated both in the case of combustion of both hydrocarbons and hydrogen. Potentially it is responsible of formation of acid rains. It is harmful for human health at very low concentrations. For instance, Italian legislation fixed $NO_2$ concentration in urban environment at 0.1 ppm (alarm level) and 0.2 ppm (attention level).

For the reasons above it is attractive for scientists to speculate about the applicability of fabrication of low-cost sensors of nitrogen di-oxide for application to pollutant detection- In previous work [5] we demonstrated the feasility of sub-ppm $NO_2$ sensors made of Zn/ZnO material. In particular, we compared, at parity of chemical composition, the performance of powders with different morphological and structural properties at variable temperature, from room temperature (RT) to about 100 °C.

The aim of this communication is to represent an investigation about the physics-chemistry mechanisms involved in such dramatic effects. Apparently the Zn powders do differ in their surface-to-volume ratios. On this basis, we performed a series of experiment involving the surface of such materials with Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS).

## 2 EXPERIMENTS

Nanostructured powders are synthesized according to a gas-phase route described in detail in previous works [2,6]. Aerosol particles are collected for XRD analysis on high-efficiency quartz fiber filters. For characterization at SEM and TEM, Zn nanoparticles are deposited, by a thermal precipitator and a vacuum impactor, on optical glasses 18×18 mm (Menzel-Glaser) and 3 mm/400 mesh carbon-

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coated copper grids (Agar Scientific), respectively. Zinc fibers are collected as a skein of sponge-like material at the exit of the expansion nozzle after run times typically of one hour. Scanning Electron Microscope is LEICA Cambridge 360 Field Emission SEM. X-Ray Diffraction (XRD) measurements, discussed elsewhere [6] are carried out on a PW1710 Philips rotating anode X-ray diffractometer.
Commercial Zinc dust powder used for comparison in XRD analysis is obtained by Fluka Chemical and used as received. DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra are recorded on a Digilab FTS-60 equipped with a KBr beamsplitter and a MCT detector operating between 400 and 4000 $cm^{-1}$, using an Harrick reaction chamber with KBr windows, and an Harrick DRA-2C1 diffuse reflectance accessory. Spectra are measured in Kubelka-Munk (K-M) units. Backgrounds are recorded by using dry KBr powder. All the samples are treated according to the following procedure: *a*) Calcination under $O_2$ (30%)/He flow (10 mL/min) at 200°C for 1 h (heating rate 5°C/min). *b*) Cooling down to RT in He flow (10 mL/min). *c*) Replacement of He flow with a $NO_2$ (1000 ppm vol ca.)/He flow (10 mL/min). *d*) Heating-up to 300°C at 10°C/min rate, holding the temperature for 6 min at Room Temperature (RT), 50, 100, 150, 200, 250, 300°C. DRIFT spectra are recorded 2 min after the reaching of the plateau temperature. *e*) cooling-down in $NO_2$/He flow. After cooling at RT, a comparative spectra are recorded for each sample to check with the spectra at the beginning of the heating treatment.

## 3 RESULTS AND DISCUSSION

Gas sensing properties are studied for standard Zn dust powder (not shown) and for Zn stratified nanoparticle aggregates (Fig. 1 top) and Zn hollow nanofibers (Fig. 1, middle and bottom).
Fig. 2 shows the DRIFTS spectra of stratified nanoparticle aggregates, synthesized by evaporation-condensation scheme [2] at $T_{evap}$=540 °C when exposed to the $NO_2$/He flux at different test temperatures (RT to 300°C). A doublet located at 1628 and 1600 $cm^{-1}$ is visible in all the temperature range investigated, thus decreasing at the increase of temperature, which could be ascribed to R and P branches of $NO_2$ free (gas).A broad band located at 1300 $cm^{-1}$ is evident in low (< 250°C) temperature spectra and decreases raising the temperature disappearing almost completely at 300°C. Around 1500 $cm^{-1}$ another band very broad and feeble seems to be present. The analysis of bands evolution of Fig. 4 is complicated by the fact that, at increasing the temperature, a negative feature is observable between 1550 and 1300 $cm^{-1}$. Thus, the two peaks at 1300 and 1500 $cm^{-1}$ could be ascribed to two vibrational modes of mono- or bidentate $NO_3^-$ species [7] adsorbed on the ZnO thin film surface formed on the Zn surface, even if for a definitive attribution the presence of eventual absorption bands in the 970-1040 $cm^{-1}$ region (not observable in our experiments) should be checked. At the increase of temperature the band at 1300 $cm^{-1}$ first grows till 150°C. Thereafter, it becomes less pronounced and it almost disappears at 300°C. The band is restored by cooling down the sample at RT in $NO_2$/He flow.

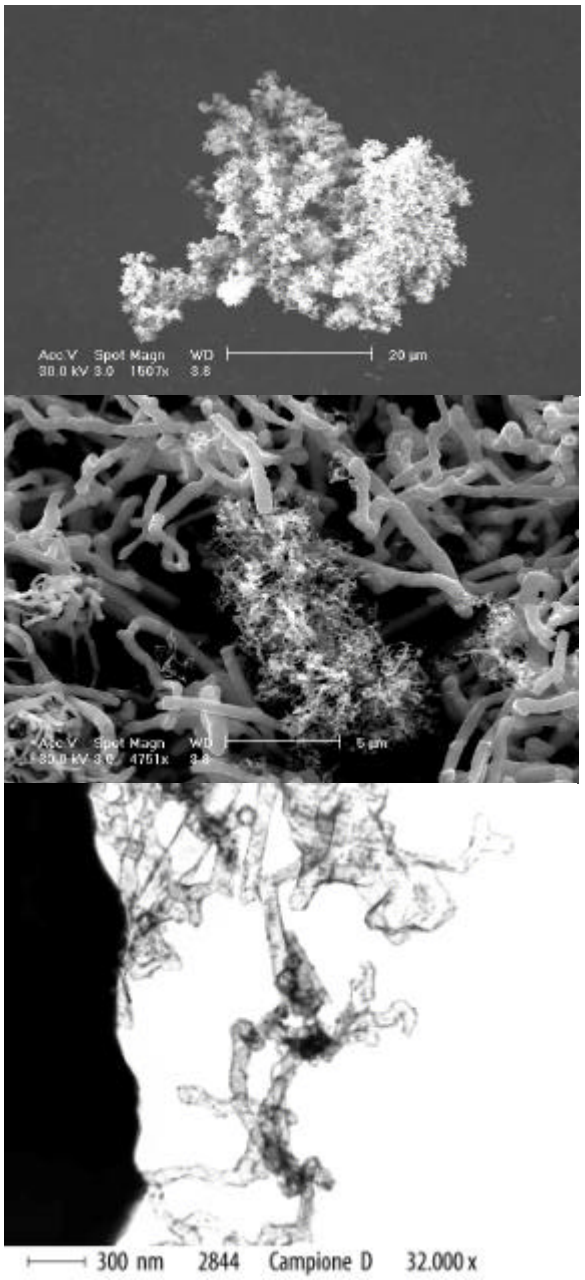


Figure 1: Top) Stratified Zn aggregates synthesized by evaporation at 560°C of bulk Zn grains and deposition of Zn vapors ; Middle) SEM image of a sponge of hollow Zn fibers lying between nested thick nanorods, as obtained by metal vapors deposition in the same experiment of Top); Bottom) TEM micrograph of hollow nano fibers.

Fig. 3 are the DRIFT spectra of Zn hollow nanofibers grown by the deposition within the quartz reactor orifice [2] of metallic zinc vapors obtained at $T_{evap}$=540°C. The


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differences of amplitude (about one order magnitude) of the IR absorption bands between Zn aggregates and Zn nanofibers is probably due to the different amount of diffused IR radiation emerging from the sample resulting from different packing of sample cup and/or different nanostructure (micro-crystalline aggregates vs. mono-crystalline rods [2]).

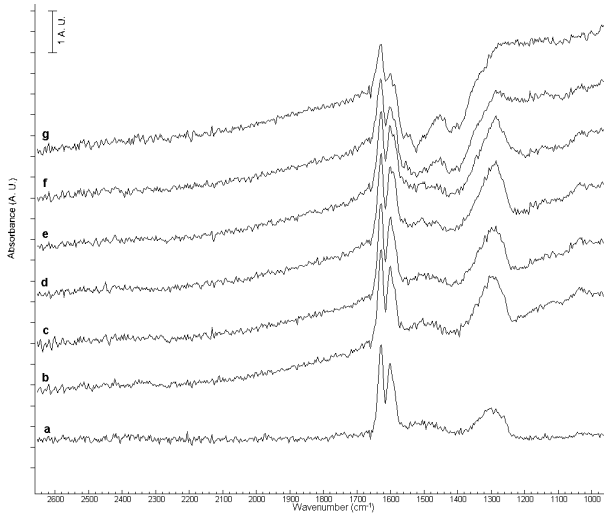


Figure 2: DRIFT spectra (background subtracted) of stratified aggregates exposed t $NO_2$/He with cauliflower-like morphology, relatively to wavenumbers 860-2640 $cm^{-1}$ at increasing temperatures. a) RT; b) 50°C; c) 100°C; d) 150°C; e) 200°C; f) 250°C; g) 300°C.

Comparative analysis of spectra in the case of aggregates and hollow nanofibers shows dramatic differences.
In the case nanofibers (Fig. 2), we note that at RT no bands attributable to adsorbed species are observed. Only the doublet located at 1600 – 1628 $cm^{-1}$, due to $NO_2$ (gas) free is present. The presence of $NO_2$ feebly adsorbed on $Zn^{2+}$ sites can not be excluded since the IR adsorption of such species fall in the 1642-1605 $cm^{-1}$ range that is masked by gas phase $NO_2$ adsorption. At increasing the temperature from RT to 300 °C, the $NO_2$ doublet disappears and a broader shoulder between about 1900 and 1500 $cm^{-1}$ grows up. At the mean time also a relatively narrow peak located at 2500 $cm^{-1}$ appears. Contemporarily a new, complex spectral feature does appear between 1400 and 1200 $cm^{-1}$.
Fig. 4 shows the DRIFT spectra obtained for commercial bulk Zinc dust. At RT the spectra are markedly different with respect to those of Zn aggregates and hollow fibers. The 1600 – 1628 $cm^{-1}$ doublet of $NO_2^-$ gas absorption is observed also in this case, but three intense bands located at 1510, 1315 and 1023 $cm^{-1}$ are visible, which are increasing with the time of contact with $NO_2$. These bands can be attributed to adsorbed bidentate nitrates $NO_3^-$ [6]. At increasing the temperature from RT to 300°C, these 1510, 1315, 1023 $cm^{-1}$ absorption bands exhibit an initial growth till 100°C, followed by a progressive depression, which can be interpreted as the process of thermal decomposition of adsorbed nitrates. In the meanwhile a negative feature located at 1650 1760 $cm^{-1}$ develops. After cooling down to RT the sample in $NO_2$/He flow all the bands grow up again.

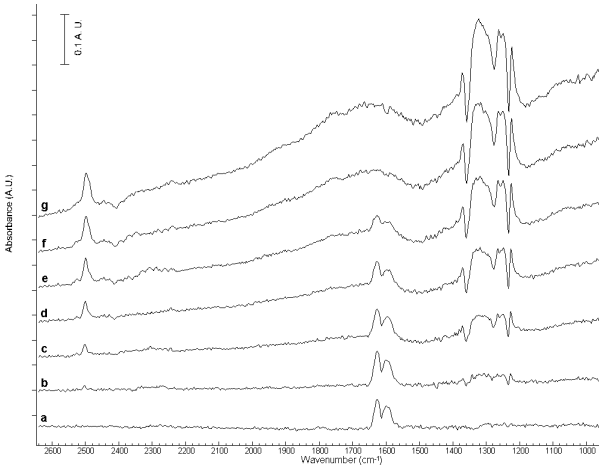


Figure 3: DRIFT spectra (background subtracted) of hollow nanofibers exposed t $NO_2$/He at 860-2640 $cm^{-1}$. a) RT; b) 50°C; c) 100°C; d) 150°C; e) 200°C; f) 250°C; g) 300°C.

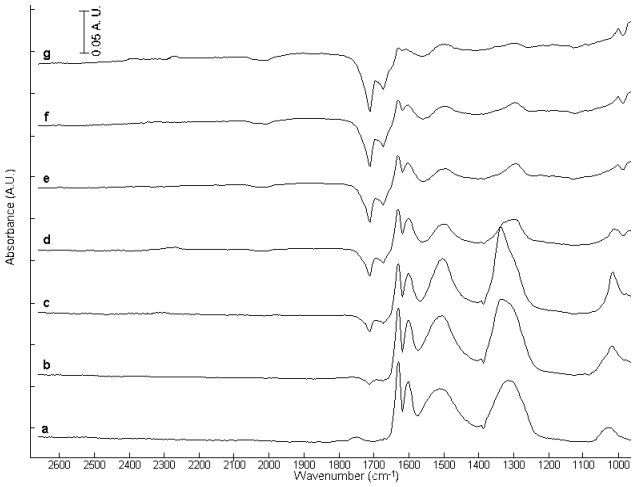


Figure 4: DRIFT spectra (background subtracted) of standard bulk Zn dust exposed t $NO_2$/He at 860-2640 $cm^{-1}$. a) RT; b) 50°C; c) 100°C; d) 150°C; e) 200°C; f) 250°C; g) 300°C.

An interpretative scheme for surface reactions yielding nitrites and nitrates has been reported previously [6,8]. Our previous experimental work on current response measurements [5] by Zn nanopowders constituted of nanofibers and nanoparticle aggregates exposed to $NO_2$ revealed relative abundance of conductive electrons in the case of nanofibers at room temperature. Similarly to present work, also in the previous study the samples were pre-treated, by exposure to humid synthetic air for 24 h at 200 °C. In particular, the current response of nanofibers at RT, 50%RH and 0.4 ppm $NO_2$ resulted almost 1 and 4 order of magnitudes higher with respect to nanoparticle aggregate and standard Zn powders, respectively. The essential point is that, even at low temperature, a thin film of ZnO is

probably formed soon on the sample powders. The current response of the nanofibers samples decreases at the increasing temperature from RT to 150 °C.

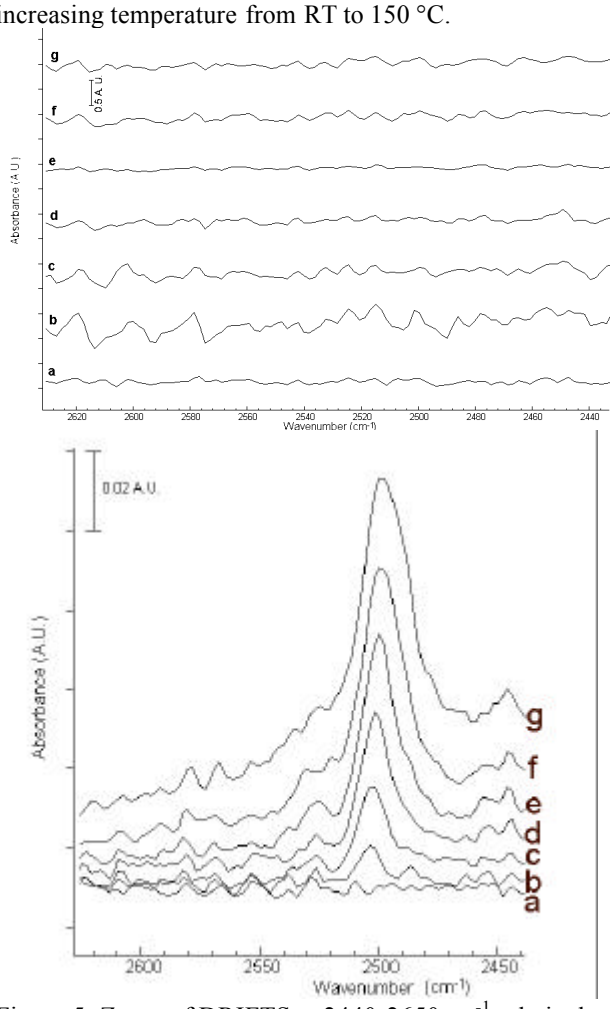


Figure 5: Zoom of DRIFTS at 2440-2650 $cm^{-1}$ relatively to (Top) stratified Zn aggregates, (Bottom) hollow nanofibers.

A supplementary mechanism can be advocated to justify the previous experimental results [5]. Kase et al [9] proposed a particular process of NO chemisorption by the formation of the so-called *pseudo-oxygen defects.* Again the mechanism is cited according to the presumable formation of a thin film of ZnO on the surface of nanofiber and nanoparticle aggregates samples. It may describe the observed changes of electrical conductivity for an n-type semiconductor, which undergo contemporary NO chemisorption. In our case we propose at RT a similar mechanism occurring for $NO_2$ at ZnO film interface of nanopowders leading to adsorbed $NO_3^-$ and releasing of conductive electrons from the surface oxygen defects. This process, according to the cited paper [9] is most probable to occur at RT and thwarted at higher temperatures at which nitrates are not stable.

Figs. 5 shows the DRIFT difference spectra of cluster versus nanofiber samples at 2440 to 2630 $cm^{-1}$. When compared with spectra about 1500 to 1800 $cm^{-1}$, we observe that, at increasing temperatures, the nanofibers spectra exhibit the rising of a narrow peak at 2500 $cm^{-1}$ and, contemporarily, the progressive smoothing and disappearing of the doublet at 1600-1628 $cm^{-1}$, thus indicating probable consumption due to further oxidation of Zn to ZnO and/or desorption of $NO_2$ at increasing temperatures from RT to 200 °C. The 2500 $cm^{-1}$ band in Fig. 5-bottom (nanofibers) may be attributed according to the literature [10] to the presence of adsorbed polymeric species of type $(N_xO_y)_z$ . A structural peculiarity of the hollow fibers, which should be accounted for in the discussion of surface reactivity effects, is the huge surface area with respect to the other samples. According to a discussion reported alsewhere [6] the ratio between the specific surface ($cm^2/g$) of hollow nanofiber with respect to Zn standard powder can result higher than 300 and the ratio between the specific surface ($cm^2/g$) of hollow nanofibers with respect to stratified aggregates powder will be about 40 and 160 for clusters of 10 and 5 μm, respectively.

## 4 CONCLUSIONS

Zinc powders constituted by nanoparticles aggregates and hollow nanofibers have been studied with respect to $NO_2$ reactivity by DRIFT spectroscopy and compared with bulk Zn dust available in commerce. DRIFT spectra of zinc aggregates and standard dust show the formation of nitrates ($NO_3^-$) and nitrites ($NO_2^-$) adsorbed species, that are stable at RT, decompose as the temperature increases, and can be again formed at RT after their decomposition. Zinc nanofibers, external and internal diameters about 100, 60 nm, do exhibit a peculiar reactivity with respect to test gas $NO_2$. DRIFT spectra , are characterized by two distinctive absorption bands at 2500 $cm^{-1}$ and 1600-1628 $cm^{-1}$, which are observed to grow up and fall off at correlated rates, respectively, when temperature is increased from RT to 300°C This feature is not at all observed in the case of the other samples. This peculiarity can be explained as nanoscale effect related to the much higher specific surface ($cm^2/g$) and/or to a confinement effect of hollow nanofibers with respect to Zn aggregates and commercial Zn standard.

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