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Optical properties of hydrothermally synthesised and thermally annealed ZnO/ZnO₂ composites

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ZnO/ZnO₂ composites grown by hydrothermal synthesis at low temperature (180 °C) and thermally annealed at 300 °C were fully analysed by morphological, structural and optical techniques. X-ray diffraction patterns (XRD) and Raman spectroscopy clearly evidences the presence of both crystalline phases in the ZnO/ZnO₂ sample. The differential scanning calorimetry analysis and thermogravimetric profiles indicate an exothermic event with a peak temperature ca. 225 °C, which is accompanied by a 8.5 % weight loss, being attributed to the crystallization of ZnO from ZnO₂. Upon a thermal annealing treatment at 300 °C in the ZnO₂ phase was completely converted into ZnO as measured by XRD and Raman spectroscopy. Photoluminescence investigations reveal that the emission is dominated by a broad band recombination in both samples, which are due to the overlapping of different emitting centres, and that the peak position of the PL emission is dependent on the excitation density. The ZnO/ZnO₂ sample exhibits a widening of the bandgap when compared to the one only containing ZnO, likely related with the presence of the additional ZnO₂ phase and suggesting a bandgap energy of 3.42 eV for this compound. Surface analysis revealed that sample exhibits a surface area of 90 m²/g, which decreases to 30 m²/g after the thermal annealing and the full conversion into ZnO. This difference in the surface area showed a particular relevance in the stability of the measured optical properties. Particularly, the intensity of the photoluminescence signal was seen to be higher in the ZnO/ZnO₂ sample and strongly dependent on the measurement atmosphere, highlighting their potential to be employed in the fabrication of optical-based sensing systems for environmental applications, namely in gas sensors.

1. Introduction

The pollution of the environment as a result of the strong industrialisation that has been conducted in recent decades constitutes one of the major problems worldwide, whose effects on the health and prosperity of populations can be extremely harmful, as well as jeopardizing the sustainability of the planet^{1,2}. As so, the development of nanostructured materials able to detect the presence of harmful elements, and even to quantify their concentration, is gaining considerable attention in the research community³⁻⁶, due to properties like high surface-to-volume ratio and surface reactivity, promoting greater sensitivity and selectivity to the envisioned targets, as well as the possibility of their rapid detection. Among the various nanomaterials explored, semiconductor oxides, such as zinc oxide (ZnO) and its composites, have acquired a fundamental role^{3-5,7-12}. This material is one of the most investigated wide bandgap semiconductors for several technological and scientific fields, not only in sensing applications, but also including electronics, optoelectronics, biomedical devices, among others¹³⁻²¹. Moreover, ZnO has a low production cost and can

be obtained by various techniques and with different morphologies. This wide range of nanostructures gives them different functional behaviours. One of the most explored features of ZnO is its intense photoluminescence (PL), even at room temperature (RT)²¹⁻²³. With a direct bandgap of ca. 3.3 eV at RT and a free exciton (FX) binding energy of 60 meV, the PL properties of this oxide host are widely known^{22,24-33}. Typically, at cryogenic temperatures and with above bandgap excitation, the ZnO luminescence is characterised by the presence of FX, donor bound excitons (D⁰X) and surface related recombination in the ultraviolet region, followed at lower energies by visible broad bands in green (GL), yellow (YL) and red (RL) spectral range^{22,24,26-30,32,34-37}. Such general behaviour can be easily observed in bulk, thin films and nanostructures, with the corresponding PL changes mainly associated with the different ZnO growth/synthesis parameters and/or to the decrease in the material dimensionality, and thus a higher contribution of the surface characteristics to the PL output. Indeed, in the case of the nanostructures, some of these optical features have been attributed to the presence of surface-related defects, as is the case of the GL^{36,38,39}. As these defects are located at the surface of the material, they are prone to be strongly influenced by the material's surroundings, namely to the chemical species that composed the atmosphere, and so can be used to monitor ambient changes. For instance, species like O₂ or OH tend to act as acceptors on the ZnO surface, and thus can trap negative charges at the surface states and affecting the carrier density in that region^{40,41}. Changes in the charge density at the surface of the semiconductors may induce the formation of a built-in electrical field

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and a charge depletion region, which consequently affect the recombination processes and the luminescence outcome. Therefore, one can take advantage of such phenomena to produce luminescence-based sensors. In fact, gases as H_2 , O_2 or NO_2 were already successfully detected via the PL signal of ZnO nanostructures^{42–44}. It was observed that the RT PL features were sensitive to the presence and content of the analyzed gases, avoiding the problems typically associated with high operating temperatures⁴³. For instance, Bismuto *et al.*⁴² demonstrated that ZnO and SnO_2 nanobelts were effective in the detection of NO_2 species at RT by the quenching of their PL signal in the presence of the probed gas. This was particularly evidenced in the case of ZnO, where the PL intensity was seen to decrease by more than 25 % by the introduction of 5 ppm of NO_2 .

On the other hand, the optical properties and possible applications of zinc peroxide (ZnO_2) and its composites with ZnO are much less known and only scarce studies are found in the literature, most with results obtained from the RT PL analysis^{45,46}. ZnO_2 is also considered a wide bandgap semiconductor, however its reported experimental bandgap energy varies considerably among different studies, with values ranging from 3.6 eV to 4.5 eV^{47,48}. Density functional theory calculations indicate that ZnO_2 is an indirect bandgap material with bandgap energy of 2.3 eV⁴⁷ and hybrid functional methods predicted a value of ca. 4.0 eV⁴⁹. At RT, (and depending on the excitation energy), the emission of nano ZnO_2 was previously studied, revealing the presence of structureless broad bands peaked in the ultraviolet (ca. 400 nm)⁴⁵ or green spectral regions (ca. 530 nm)⁵⁰. However, to the best of our knowledge, low temperature studies are scarce or even inexistent in the literature. Regarding the ZnO/ ZnO_2 composite, previous studies⁵¹ revealed enhanced photocatalytic activity when compared with ZnO by itself. The produced composite was seen to be comprised by ZnO crystallites bonded with ZnO_2 granules at their surface, which interfacial regions were pointed out as responsible for the observed enhancement. Besides, such composites were also employed in conductometric gas sensors towards the detection of CH_4 , H_2S and CO⁵², demonstrating improved selectivity and sensitivity at a fairly low operating temperature (~130 °C). This work aims to investigate the optical properties of hydrothermally grown ZnO/ ZnO_2 composites and their conversion into ZnO upon thermal annealing. The PL features of the present samples were recorded as a function of temperature (from 14 K to RT) and excitation density. Additionally, PL excitation (PLE) and time resolved PL (TRPL) measurements were carried out at RT, providing information on the excitation mechanisms involved on the recombination processes and their lifetimes. The analysis of the photoluminescence stability reveals that the emission outcome is strongly sensitive to the used environment, namely for the ZnO/ ZnO_2 composite, which exhibits higher specific area. Indeed, as the reactions with the environment constituents (e.g. gases) that may lead to sensing phenomena take place mainly at the surface of the nanomaterials, a high specific area is strongly desired. Therefore, the data allow us to conclude that the composite structure grown at low temperatures may be used as environment optical read out sensing system, with remote interrogation (via photon excitation), which can be advantageous in harsh environments where the typical sensors, which need on site electrical contacts, cannot be used. Hence, the here reported work aims to contribute to the knowledge of the

fundamental properties of these materials, since it is vital and should be the first step towards further developing of sensing applications.

2. Experimental Details

ZnO/ ZnO_2 powders were prepared by hydrothermal synthesis. In a typical procedure, appropriate amounts of zinc sulfate ($ZnSO_4(H_2O)_7$, Sigma Aldrich), sodium hydroxide (NaOH, LABCHEM) and hydrogen peroxide (H_2O_2 - Carlo Erba) are mixed with deionized water, under magnetic stirring for 2 hours. The obtained solution is poured into a teflon lined stainless steel autoclave, which is then transferred into an oven at 180 °C where it is maintained for 1 h. After that period, the autoclave is cooled down to RT, being the precipitated powders collected and centrifuged (Beckman LB-M Ultracentrifuge) with deionised water at 3000 rpm for 15 min. The centrifugation process is repeated 4 times and then the powder particles are dried overnight at 80 °C. The ZnO/ ZnO_2 dried particles were also submitted to a post-synthesis thermal annealing treatment in air at 300 °C during 2 h. The annealing temperature was chosen based on the thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis.

The crystalline phase composition of the both ZnO/ ZnO_2 and annealed powder particles at 300 °C was assessed by X-ray diffraction (XRD) analysis (PANalytical X'Pert PRO) with $CuK\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$), within the 2θ range of 20 to 80°. Their morphological characteristics were evaluated by scanning and transmission electronic microscopy (STEM/SEM Hitachi HD-2700 with field emission and SEM Hitachi SU-70 with Schottky emission). For STEM analysis, the samples were prepared by dispersing a small amount of particles in ethanol, under ultrasonic stirring. The suspension was then dropped onto a carbon-coated copper grid, and the solvent allowed to completely evaporate before observation. For SEM analysis, the powders were scattered over a carbon tape and then observed. The specific surface area (SSA) of the obtained particles was determined by N_2 adsorption using a micromeritics – Gemini 2370 V5 equipment. The samples were thoroughly degassed at 120 °C for 24 h before nitrogen adsorption. The SSA was determined based on the multipoint Brunauer-Emmett-Teller (BET) isotherm. The thermal behaviour of the ZnO/ ZnO_2 sample was characterized by thermogravimetric analysis and differential scanning calorimetry. TG experiments were conducted on a Setaram instrument (Setsys Evolution 1750 analyser) from RT to 500 °C with the heating rate 10 °C/min and under air atmosphere. DSC was carried out in a Power Compensation Perkin Elmer instrument (Diamond DSC) calibrated with In and Pb standards and using hermetically sealed stainless steel pans under a heating rate of 10 °C/min and N_2 atmosphere.

The samples optical characterisation was assessed by Raman spectroscopy, steady-state PL, PL excitation (PLE) and time resolved photoluminescence (TRPL) spectroscopies. Raman, PLE, TRPL and excitation density-dependent PL were carried out at RT. Raman spectra were measured on a Horiba Jobin Yvon HR800 spectrometer equipped with a 600 grooves/mm grating, using the 442 nm line from a He-Cd laser (Kimmon IK Series). The experiments were conducted focusing the laser beam with an objective of $\times 50$ magnification. Temperature dependent (from 14 K to RT) PL studies were performed in both samples. The 325 nm/3.8 eV He-Cd laser line (power density $I_0 < 0.6 \text{ W/cm}^2$) and a 450 W Xe lamp coupled to a monochromator were used as excitation sources. The PL signal was measured using two systems: the emitted light was i) dispersed by a

SPEX 1704 monochromator (1 m, 1200 grooves/mm) and detected with a cooled Hamamatsu R928 photomultiplier when excited with the laser, and ii) a Fluorolog-3 Horiba Scientific set-up was used when the samples were excited with the Xe lamp. The latter has a double additive grating (Gemini 180) monochromator (1200 grooves/mm and 2×180 mm) in the excitation and a triple grating (iHR550) spectrometer in the emission (1200 grooves/mm and 550 mm). Additionally, RT PLE measurements were also conducted in the same Fluorolog-3 system, as well as TRPL. TRPL spectra were acquired using a pulsed Xe lamp (operating at up to 25 Hz) coupled to the same monochromator and with the excitation fixed at 325 nm. The full-width at half-maximum of each lamp pulse is 3 μ s, so that lamp interference during acquisition of decay curves is minimised. The measurement conditions were set to a sample window (duration of signal acquisition) of 10 ms, with 20 ms of time per flash (reciprocal of the repetition rate of the lamp pulses) and a flash count (number of lamp pulses contributing to each data point) of 200. Several time delays after flash were employed from 0.05 to 5 ms.

3. Results and Discussion

3.1. Structural and morphological analysis

Figure 1 (a) shows the XRD pattern of the ZnO/ZnO₂ powder particles after the synthesis process, where it is possible to identify the presence of two crystalline phases, which are assigned to the hexagonal modified wurtzite crystalline phase of ZnO (space group $P6_3mc$), in accordance with the JCPDS No. 04-006-2543 card, and to the cubic pyrite structure of ZnO₂ (space group $Pa\bar{3}$) in accordance with JCPDS No. 01-077-2414 card.

Figure 2 allows comparing the DSC and TG results in the temperature interval ranging from RT up to 300 °C (no significant changes were observed beyond 300 °C). The TG curve shows that the initial temperature increase up to 100 °C, originates a weight loss (ΔW) of $\sim 4\%$, which may be associated to the elimination of H₂O adsorbed on the as-synthesized powders. As temperature increases further the weight loss slows down and then accelerates in the temperature range between 200 and 250 °C, accounting for a $\Delta W \sim 8.5\%$; after that an almost unchanged weight is observed upon subsequent heating. The DSC curve presented in the same figure evidences an initial endothermic effect ascribed to H₂O loss and then a well-defined exothermic peak in the temperature range where the steep weight loss of 8.5 % is found. This exothermic event with a peak temperature of ~ 225 °C accompanied by a weight loss is attributed to the crystallization of ZnO from ZnO₂ upon oxygen loss. This crystallization temperature range is in line with that reported for ZnO₂ synthesised at RT using zinc acetate as precursor⁵³. Taking into consideration that the conversion of ZnO₂ to ZnO implies an oxygen weight loss of 16.4 %, it is even possible to estimate that 55 w% of the initial powder mixture is ZnO₂. The present results also suggest that for temperatures above 275 °C the samples are expected to be fully converted into ZnO. Figure 1 (b) shows the XRD pattern of the sample annealed at 300 °C. As observed, only the patterns associated with the ZnO wurtzite phase are depicted, confirming that under such annealing treatment the ZnO₂ cubic phase is fully converted into wurtzite ZnO.

The calculated lattice parameters for ZnO correspond to $a = b = 3.24$ Å and $c = 5.20$ Å, matching the ones typically reported in literature, $a = b = 3.2496$ Å and $c = 5.2042$ Å^{26,54}. In the case of the ZnO₂, the calculated lattice parameter corresponds to 4.88 Å, which is close to the reported value of 4.874 Å⁴⁷. In both cases, the position of the diffraction peaks agreed with the ones theoretically predicted, indicating that strain effects can be discarded in the nanostructures.

Figure 1 – X-ray diffraction patterns of the (a) ZnO/ZnO₂ composite and (b) the annealed sample. The corresponding diffraction plans of the pyrite (grey) and wurtzite (black) structures are indexed.

Figure 3 shows the STEM and SEM micrographs of the composite and annealed samples, respectively. The STEM image of the ZnO/ZnO₂ composite (Figure 3 (a)) reveals uniform nanosized particles with diameters typically lower than 6 nm, where a few particles/agglomerates with larger dimensions (lower than 30 nm) can be distinguished. Regarding the sample annealed at 300 °C, nanometric particles are still observed, although having an average diameter around 30 nm and presenting strong aggregation among them, as revealed by Figure 3 (b). The SSA of both the ZnO/ZnO₂ composite and annealed samples were estimated based on BET measurements as 90 m²/g and 30 m²/g, respectively. Assuming that the annealed particles are spherically shaped with an average diameter of 30 nm and considering a relative density of 5.61 for ZnO,

a SSA value of $39.2 \text{ m}^2/\text{g}$ can be estimated, which agrees reasonably with the value determined experimentally ($30 \text{ m}^2/\text{g}$). It is hypothesised that the smaller particles (lower than 6 nm) observed in Figure 3 (a) belong to ZnO_2 , while the larger particles correspond to ZnO . Upon thermal annealing in air, the very small ZnO_2 nanoparticles aggregate and may act as precursors for further $\text{ZnO}_2 \rightarrow \text{ZnO}$ crystal phase conversion, leading to the formation of the larger particles observed in Figure 3 (b).

Figure 2 – DSC and TG profiles of the as-synthesised powder particles.

Figure 3 – STEM micrograph of the (a) ZnO/ZnO_2 composite and (b) SEM micrograph of the ZnO sample.

The crystalline structure of the samples was further investigated by Raman spectroscopy, as shown in Figure 4. The spectra were acquired in distinct spots of the sample evidencing that a homogeneous distribution of the identified crystalline phases occurs in the probed regions. All the analysed samples presented the typical vibrational modes of the wurtzite ZnO structure^{55,56}. For ZnO , and according to group theory, six active Raman modes are expected to be observed at the Γ point of the Brillouin zone. Indeed, a decomposition into irreducible representation results in the following Raman active optical phonons $\Gamma = A_1 + E_1 + 2E_2$ ^{30,55,56}.

Figure 4– RT Raman spectra of the (a) ZnO/ZnO_2 composite and (b) annealed sample containing only the wurtzite ZnO phase.

Besides the ZnO vibrational modes, the composite sample exhibited additional resonances assigned to the crystalline phase of ZnO_2 . For a pyrite structure, five active Raman modes are expected to be observed at $\vec{k} = \vec{0}$, corresponding to the following decomposition into the irreducible representation $\Gamma = A_g + E_g + 3T_g$ ^{57–59}. In single-phase ZnO_2 nanostructures, three vibrational modes have been identified by Raman spectroscopy peaked ca. 414 cm^{-1} , 474 cm^{-1} , 839 cm^{-1} ^{45,50}. In the here studied ZnO/ZnO_2 composites, a strong resonance at 840 cm^{-1} is clearly resolved independently of the probed zone, corroborating the presence of this crystalline phase, as measured by XRD. The low frequency modes are overlapped with the ones of ZnO , therefore they could not be clearly distinguished. In both samples, the peak positions of the vibrational modes are in well

agreement (within the experimental error) with the ones reported for unstrained structures, also in line with the XRD measurements.

3.2. Optical characterisation

The RT PL and PLE spectra of the ZnO/ZnO₂ composite and annealed samples are shown in Figure 5 (a) and (b), respectively. By exciting the samples with 325 nm/3.8 eV and under low excitation density conditions (by using a Xe lamp coupled to a monochromator), both samples evidence a broad emission band with similar spectral shape, covering a wide spectral range on the visible region. The emission is mainly peaked in the yellow spectral region at ca. 570 nm. Analogous structureless emission bands have been previously reported for ZnO bulk and nanostructures grown by different techniques²². However, its defect signature is still a matter of controversy on the literature^{22,26,29,30,32,33,36,39,60–62}. Intrinsic (V_O, O_{Zn}, O_i, V_{Zn}, Zn_i) and surface defects, as well as impurities (*e.g.* Cu), are among the most debated species to explain the observed broad bands^{22,26,29,30,32,36,39,60} when the ZnO host is excited with above bandgap photon energy, as is the case of the here studied single phase ZnO sample. On the other hand, in pure single-phase ZnO₂ nanocrystals, Bai *et al.*⁴⁵ and Feng *et al.*⁵⁰ reported broad emission bands at RT peaked at ca. 400 nm and ca. 530 nm by exciting the samples with 300 nm/4.1 eV and 325 nm/3.8 eV photons, respectively. The latter corresponds to the same excitation energy used in the present work, and in the here studied composites the observed emission is red shifted when compared to the ones reported for the mentioned ZnO₂ structures. The similarity of the spectral shape and peak position in both analysed samples suggests that the observed RT emission mainly arises from the ZnO or from similar intrinsic and/or surface states in ZnO₂. Additionally, both the PL bandwidth and its asymmetry indicate that the observed recombination results from an overlap of emitting centres rather than a unique optically active defect, as will be discussed in more detail latter on. Indeed, both ZnO, ZnO₂ and the interface between the two materials or even a higher contribution from the surface defects due to the higher surface-to-volume ratio in the composites can play a role in the observed visible emission of the composite sample.

In order to identify the preferential population mechanisms of the emitting broad band, PLE measurements were carried out by monitoring the emission at the band maxima of both samples. The PLE spectra clearly reveal noticeable differences between them. For the single-phase ZnO sample (Figure 5 (b)), the emission is preferentially populated by photons with energy equal or higher than the ZnO bandgap (ca. 3.3 eV at RT²⁶). On the other hand, for the composite a remarked high-energy shift of ~120 meV is identified for the maxima of the excitation band (Figure 5 (a)). High energy shifts of the ZnO bandgap are usually observed in highly doped samples (carrier concentrations ca. 10¹⁹–10²⁰ cm⁻³) due to the Burstein-Moss effect^{30,63,64}. However, for the composite sample it is unlikely that the high excitation energy band could be related with such effect.

Figure 5 – RT PL/PLE spectra of the (a) ZnO/ZnO₂ and (b) ZnO single-phase samples. The dip in the PL spectra at ca. 620 nm corresponds to an artefact of the detection system.

By comparing the PLE spectra of both samples, a noticed shoulder is observed for the ZnO/ZnO₂ composite in the expected ZnO bandgap region at 3.3 eV (Figure 5 (a)). This indicates that the structureless emission in the composite is populated both by the ZnO bandgap and by a high-energy excitation band peaked at 362 nm/3.42 eV, which is likely due to the ZnO₂ contribution. As aforementioned, the ZnO₂ bandgap is expected to be wider^{47,48} than the one of the ZnO and therefore, we cannot exclude that the 3.42 eV band could be related with the ZnO₂ bandgap energy. The kinetic process of the broad band recombination was found to be sample dependent, as shown in Figure 6. With low excitation density (continuous and pulsed Xe lamp), and by exciting the samples with an energy of 3.8 eV, the comparison between the steady-state PL and TRPL spectra taken after a delay of 50 μ s and with a time window of 10 ms reveals slight differences between the composite and annealed samples. For the ZnO/ZnO₂ composite, the emission band is peaked at the same position than the one measured under steady-state conditions and with increased time delays the PL intensity is seen to decrease by more than 1/e after 0.5 ms, indicating a decay time in the range of hundreds of μ s. For the ZnO heat-treated sample, the emission is slightly red shifted compared with the one observed under steady-state conditions. Moreover, a longer emission lifetime was assessed, with an intensity reduction to more than 1/e after 5 ms, which is one order of magnitude higher than the previous observed one, evidencing a lifetime in the range of a few ms.

No further shifts on the peak position of the broad band were detected with increasing delays. The distinct kinetic processes associated with the large bandwidth of the emission bands corroborate the assumption that the observed emission results from overlapped emitting centres, having different contributions for the overall luminescence depending on the sample, which leads to changes in the global emission maxima. Actually, the radiative lifetime of the high energy component of the broad band was found to be faster for the composite, while such component is almost absent for the thermal annealed sample.

Figure 6 – (a) Comparison of the steady-state PL and TRPL spectra obtained with ~ 3.8 eV excitation under the conditions described in the experimental section. RT TRPL spectra of the (b) ZnO/ZnO₂ composite and (c) ZnO samples with increasing time delays.

Besides the information acquired by TRPL, excitation density-dependent PL studies can provide additional evidence on the optical active centres present in the samples^{37,62}. For such purpose, the 325 nm/3.8 eV line of a continuous wave He-Cd laser was used as

excitation source, together with a set of neutral density filters in order to reduce the excitation density. The measured PL spectra are shown in Figure 7. By using the same excitation energy and increasing the excitation density (from lamp to laser), evident spectral modifications appear in the ZnO/ZnO₂ composite and the annealed samples. In both cases, the relative intensity of the high/low energy components of the broad band was found to be particularly sensitive to the rise in the excitation density, with an obvious ratio decrease with increased excitation density. Such behaviour was found to be more pronounced for the annealed sample, where a noticed red shift of the emission maxima was identified. Decreasing the excitation density up to 10% of the laser power only leads to a slightly shift of the band maxima to higher energies, without reaching the peak position observed in the spectra obtained under lamp excitation, since even lower excitation density is expected in the case of the Xe lamp. Moreover, using the same excitation conditions in both samples, one can clearly see that the peak position of the broad band is peaked ca. 600 nm for the ZnO/ZnO₂ composite and ca. 700 nm after the thermal annealing, revealing that the concentration of the defects that originate the wide structureless luminescence features is different in the two samples. As mentioned above, broad emission bands in the green, yellow and red spectral regions have been typically assigned to the recombination of intrinsic defects in ZnO, as well as the existence of surface adsorbate species^{36,39}. The later are likely to be present in these samples due to their synthesis method. Indeed, the YL is frequently observed in samples produced by the hydrothermal method and has been associated with surface capping by zinc hydroxide^{60,65,66}, thus the yellow emission may originate from OH species adsorbed at ZnO surface and/or to the presence of Zn(OH)₂, instead of arising from bulk defects⁶⁶. In fact, the intensity of broad luminescence bands in this spectral region, also identified on ZnO micro and nanostructures synthesised in hydrothermal conditions, was seen to degrade with increasing exposure to laser irradiation, as well as on the measuring environment, clearly pointing out to the involvement of surface mediated processes which are reduced or dissociate upon irradiation⁶⁷. Conversely, the red luminescence has been associated with the presence of one of the charged states of V_{Zn} (-1/-2)^{68–70}. In fact, previous works by Djurišić^{39,66} showed that hydrothermally produced ZnO samples that exhibited the YL, only kept the red component after annealing at temperatures above 200 °C for different atmospheres (air, forming gas, argon, nitrogen), which suggested that indeed surface groups were in the origin of the YL, being desorbed upon annealing. Since, in their works, the orange-red emission was enhanced after annealing treatment in oxygen rich conditions, its association with defects related to excess oxygen was pointed out. Therefore, the predominance of the YL in ZnO/ZnO₂ composite can be related to such surface groups present after the synthesis and promoted by the high surface area of this sample (90 m²/g vs 30 m²/g for the annealed sample). Likewise, the increase in the relative intensity of the orange-red emission may also be accounted by the thermal treatment performed in air, enhancing the presence of excess oxygen related defects.

The stability of the overall emission (at RT) for the ZnO/ZnO₂ composite and annealed samples was also evaluated in this case by placing the samples in air and vacuum ($\sim 10^{-2}$ mbar), under the same excitation and detection conditions, as displayed in

Figure 8. The influence of the measurement environment was evidenced by the strong decrease in the overall broad band PL intensity when the samples were placed in vacuum, being this change more pronounced in the case of the ZnO/ZnO₂ composite.

Vacuum environment is expected to remove adsorbed OH and/or other oxygen-containing species from the surface of the samples. Assuming that such defects are present in higher concentration in the nanostructures with higher aspect ratio (ZnO/ZnO₂), as mentioned previously, when such samples are placed in vacuum conditions the removal of the adsorbates leads to a strong decrease in the luminescence intensity, since one is removing/reducing the centres that give rise to YL.

Figure 7 – RT excitation density dependent PL spectra for the (a) ZnO/ZnO₂ composite and (b) single-phase ZnO samples.

After placing again the samples in air, the intensity of the PL signal was seen to progressively increase up to the initial value (after less than 30 min of air exposure), showing that the observed effect is reversible. Such phenomenon can be related to the re-adsorption of the oxygen-containing species present in air, thus promoting again the presence of the YL. This behaviour clearly indicates the influence of the surface-related phenomena mediating the luminescence outcome, which is more prominent for the composite, in accordance

with the measured higher specific surface area (90 m²/g). Moreover, it highlights the high surface reactivity of that sample, which can be extremely advantageous for sensing application, namely in the fabrication of gas sensing devices. For the case of the ZnO sample, the ultraviolet emission, the so-called near band edge (NBE) recombination, could also be identified at RT and evidenced a stable PL intensity independently of the environment conditions, while the intensity of the broad visible band also decreased under vacuum condition. Nevertheless, the observed reduction was slightly less than in the previous case (ratio of 2.4 vs 3.4 for the ZnO/ZnO₂ composites).

Figure 8 – RT PL obtained with 325 nm/3.8 eV laser line excitation when the samples were placed in air and vacuum: (a) ZnO/ZnO₂ composite and (b) ZnO sample.

The RT peak position of this NBE recombination arises at ca. 385 nm/3.22 eV, shifted ~60 meV to lower energies when compared with the expected ZnO FX recombination at this temperature²², suggesting that the defect that originates the RT NBE is of a different nature, as will be explained in more detail later on.

In order to get a deeper insight on the mechanisms involved in the different luminescence processes, the samples were cooled down to 14 K and the temperature was further increased up to RT, as shown in Figure 9. For the ZnO/ZnO₂ composite, the temperature-

dependent PL spectra depicted an abnormal behaviour, revealing an overall intensity decrease of the signal from 14 K to 70 K, and then a further increase from 90 K to 110 K, with a subsequent decrease up to RT. Moreover, the peak position of the band was seen to shift depending on the measurement temperature. Such behaviour corroborates the assumption that the broad band is an overlap of different recombination channels, whose contribution to the overall spectra and thus relative intensity, changes with the measurement temperature due to different thermal quenching processes occurring for the different optical centres. For the ZnO sample, the overall intensity progressively decreases with increasing temperature, as more commonly observed^{34,67}. Nevertheless, a shift of the band maxima with increasing temperatures towards lower wavelength was clearly noticed, also pointing to the presence of multiple recombination channels. Similar overlapped recombination bands and shifts in the peak positions were previously reported by Tam and co-workers for hydrothermally grown ZnO nanorods⁶⁰.

At 14 K it was possible to identify the NBE recombination in both samples, as depicted in the inset of Figure 9 (e) and in the enlarged spectra shown in Figure 9 (f). Typically, in this spectral region and at this temperature, the luminescence of high optical quality ZnO samples arises from the recombination of FX and D⁰X, assisted by the LO phonon replicas of these transitions. Moreover, other types of recombination paths, namely two electron satellite (TES) transitions, can also be observed in this spectral region^{22,26,71,72}. Additionally, a line at 3.31 eV and their LO phonon replicas seems to be a common feature in ZnO samples, especially in the case of micro and nanostructures presenting high surface area^{22,37,73–75}. For instance, this was the case of microrods and tetrapods grown by laser-assisted flow deposition^{37,76,77} and flame transport synthesis^{62,78}. In the work reported by Rodrigues *et al.*³⁷, the authors successfully proven that such emission is due to the existence of surface-related states in ZnO. This hypothesis was suggested by analysing the role of surface passivation under different plasma treatments on the NBE luminescence, observing that with the appropriate plasma treatment conditions this recombination could be reduced and even suppressed. By comparing the 14 K PL of the here studied samples with the previously reported results³⁷, as displayed in Figure 9 (f), one can identify that, for the case of the as-synthesised ZnO/ZnO₂ composite, only small shoulders are seen at the energies expected for the D⁰X and 3.31 eV line, overlapped with a broad band peaked

at ca. 405 nm (see inset in Figure 9 (e)). Recently, Parmar *et al.*⁷⁰ associated a similar recombination band to the presence of the V_{Zn} (0/-1) in ZnO. On the other hand, the emission exhibits a spectral shape similar to the one previously detected by Bai *et al.*⁴⁵ in single phase ZnO₂. Hence, such hypothesis cannot be ruled out. For the ZnO sample, the FX and D⁰X transitions appear also as small shoulders in the spectra, with the PL signal in this spectral region being dominated by a line peaked at 375 nm/3.31 eV, followed by a minor line at lower energy, separated by an energy close to the LO phonon frequency, ~ 72 meV. These two transitions are overlapped with a broad band peaked at ~ 390 nm, slight shifted when compared with the composite. Since no secondary ZnO₂ phase is present in this case, its origin is most likely related with the presence of the V_{Zn} (0/-1), as suggested above. Nevertheless, the existence of other recombination centres contributing for the broadening of the emission observed in this spectral region cannot be disregarded.

Taking into account the comparison evidenced on Figure 9 (f) and the literature reports regarding the association of the 3.31 eV to surface-related defects^{37,75,76,78,79} in samples with a high SSA, it seems fair to assume that a similar origin is accountable in the here reported ZnO structures. Inspection of the temperature dependent PL measurements proves that this is the transition that rules the NBE emission at RT. Therefore, from the assessed spectroscopic measurements, one can infer that most recombination processes in the ZnO sample are associated with surface-related defects and to the presence of the two charge states of V_{Zn}, assuming that the red and UV-centred bands are related with such electronic levels, as reported in the literature^{68–70}. In the case of the composite sample, the same phenomena should be present, together with an additional contribution from the ZnO₂ phase. As most of the PL signal is supposed to originate from the surface, the higher PL intensity for the latter is likely to be associated to the higher surface area exhibited in that case. If one is envisaging to use the PL signal as transducer mechanism for sensing events, a higher intensity of the signal is important, in order to be able to probe changes in the PL outcome with a good signal-to-noise ratio. Hence, as highlighted above regarding the behaviour under air vs vacuum conditions, the ZnO/ZnO₂ composite sample seems to be the most suitable to further proceed with gas sensing tests.

Figure 9 – Temperature-dependent PL spectra obtained with 325 nm/3.8 eV laser line excitation: (a) and (b) ZnO/ZnO₂ composite; (c) and (d) ZnO sample. (e) Comparison of the 14 K and RT PL spectra of both samples. (f) Enlarged high-energy region: comparison of the 14 K PL spectra for the composite (red line), ZnO annealed sample (black line), microrods grown by laser-assisted flow deposition (from references ^{37,76}, blue line) and bulk sample (from Eagle-Picher, magenta line).

Conclusions

ZnO/ZnO₂ composites were grown by hydrothermal synthesis at 180 °C and then thermal annealed in air at 300 °C. The samples were fully analysed by morphological, structural and optical techniques. In the first case, the two crystalline phases of ZnO and ZnO₂ were clearly identified, while the annealed sample was seen to be fully converted into ZnO. Such conversion process was also supported by the thermogravimetric and differential scanning calorimetry profiles of the studied composite, for which the exothermic event with a peak temperature of ~ 225 °C accompanied by a weight loss was attributed to the crystallization of ZnO from ZnO₂ upon oxygen loss. In addition, an estimate that 55 w% of the initial powder mixture is ZnO₂ was done.

The annealing was seen to promote the aggregation of the very small ZnO₂ particles with high surface energy while accelerating the ZnO₂ → ZnO crystal phase conversion. Likewise, specific surface areas of 90 m²/g and 30 m²/g were estimated for the ZnO/ZnO₂ composite and annealed samples, respectively, evidencing the higher surface area provided by the smaller nanoparticles.

Photoluminescence investigations revealed that the emission is dominated by a broad band recombination in the visible spectral region for both cases, most likely associated with an overlapping of several emitting centres. Under low excitation density conditions, the emission peaks in the green/yellow spectral region and the presence of OH surface adsorbates were pointed as a possible contribution for such band. Higher excitation conditions seem to promote the dissociation of such surface groups and the band shift towards higher wavelengths. PLE measurements allowed to identify that the broad emission is mainly populated via photons with energy equal or above the bandgap of ZnO. In the case of the composite, an additional broad excitation band was observed, in line with the widening of the bandgap expected due to the presence of the ZnO₂ phase, suggesting a bandgap energy of 3.42 eV for this oxide. The analysis of the photoluminescence stability under air and vacuum atmospheres showed that the emission outcome is strongly sensitive to the used environment, with a more pronounced effect on the composite sample, which exhibits higher specific area. Therefore, the present data allow us to conclude that the ZnO/ZnO₂ sample display interesting prospects to be applied as an environment optical read out sensing system.

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