On the mechanism of photoluminescence quenching in tin dioxide nanowires by NO$_2$ adsorption

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Abstract. The recent observation of selective photoluminescence (PL) quenching in tin dioxide (SnO$_2$) nanowires (NWs) upon adsorption of nitrogen dioxide (NO$_2$) molecules triggered much interest on possible applications of SnO$_2$ nanostructures as selective optochemical transducers for gas sensing. Understanding the peculiar gas–nanostructure interaction mechanisms lying behind this phenomenon may be of great interest in order to improve the selectivity of solid-state gas sensing devices. With this aim, we studied the luminescence features of SnO$_2$ NWs in controlled adsorption conditions by means of continuous wave- and time-resolved PL techniques. We show that, under assumption of a Langmuir-like adsorption of gas molecules on the nanostructures surface, the decrease of PL intensity is linearly proportional to surface density of adsorbed molecules, while the recombination rates of excited states are not significantly affected by the interaction with NO$_2$. These findings support a picture in which NO$_2$ molecules act as ‘static quenchers’, suppressing emitting centres of SnO$_2$ in an amount proportional to the number of adsorbed molecules. A simple model based on the above mechanism and allowing good fitting of the data is described and discussed. The possible indirect or direct role of oxygen vacancy states in SnO$_2$ luminescence is finally discussed.
1. Introduction

Tin dioxide (SnO$_2$) is a key functional material in many different applications such as transparent conducting electrodes, catalyst support, dye-based solar cells and gas sensors. Due to its large chemoresistive response (i.e. modification of electrical conductivity due to adsorbed gas species), it is nowadays considered the standard material for commercial gas sensors, whose active components consist, in most cases, of thick films of sintered SnO$_2$ nanopowders and nanograins. Nanograin sizes and surface-to-volume ratios are crucial parameters affecting the sensitivity of chemoresistive response. Thus, the development of novel sensing devices is strictly related to improvement in synthesis and deposition techniques. With this aim, metal oxide (MOX) nanostructures are very interesting in view of gas sensing applications. As a matter of fact, MOX nanostructures typically exhibit well-defined single-crystal surfaces, thermal stability and large surface areas. Moreover, due to their reduced transverse dimensions (a few tens of nanometres typically) the depletion layer induced by gas adsorption may in principle extend even over the whole nanostructure, thus enhancing the chemoresistive sensitivity. A number of low-cost ‘bottom-up’ approaches and techniques have been developed in past years for preparation of MOX nanostructures, such as pulsed laser deposition [1], arc discharge [2], chemical vapour deposition [3] and vapour phase transport [4, 5]. Different kinds of SnO$_2$ nanostructures have been synthesized and investigated in recent years (for a review on SnO$_2$ nanostructures, see the work by Batzill and Diebold [6] and references therein) and sensing devices based on variations of electrical conductivity of SnO$_2$ nanowires (NWs) operating at relatively low temperatures and exhibiting temporal response of the order of one or a few minutes have already been investigated [7]–[9].

Another route to gas sensing, alternative to the standard approaches based on chemoresistive response, is based on the modification of optical responses of a material induced by interaction with gas molecules. This approach (‘optochemical sensing’) may present a number of advantages over the traditional chemoresistive sensing. Electromagnetic waves are described by a certain number of degrees of freedom (intensity, wavelength, polarization): optochemical sensing thus allows multi-parametric detection, which is not possible in electrical sensing where only a single scalar quantity (electrical conductivity) is involved. Optical sensors do not need electrical contacts, do not suffer from electromagnetic noise and may allow optoelectronic integration. Different optical responses may be involved in optochemical sensing [10], such as reflectance, optical absorption, surface plasmon resonances or photoluminescence (PL). The approaches based on PL appear promising in the case of nanostructured SnO$_2$, as it typically exhibits strong visible PL emission peaked at photon energy...
of about 2.0 eV [1], [11]–[17]. A recent work [18] evidenced that the intensity of PL emission of SnO$_2$ NWs is quenched by exposure to low concentrations (few ppm) of nitrogen dioxide (NO$_2$). More interestingly, the PL response of SnO$_2$ NWs was found to be insensitive to large variations of relative humidity [19, 20] and to the presence of other typical pollutants such as ammonia [18], carbon monoxide [18] and methane [19]. As the scarce selectivity to different gas species is one of the major drawbacks of standard chemoresistive SnO$_2$-based gas sensors, the above described findings of a specific NO$_2$ response are very interesting. Moreover, in view of the growing concern over pollution caused by combustion emissions from industrial facilities and vehicles, the possibility of selective sensing of NO$_2$ is of great importance. Since such earlier investigations [18], no further analysis on gas-sensitive PL of SnO$_2$ NWs has been reported and a physical interpretation has still to be obtained.

With the aim of investigating this phenomenon, we analysed the PL response of SnO$_2$ NWs upon exposure to different concentrations of NO$_2$ by means of continuous wave- and time-resolved PL measurements. In view of the experimental findings, we propose a description of the phenomenon showing good agreement with the PL quenching measurements. The possible role played by oxygen vacancies (OVs) in the PL of SnO$_2$ is finally discussed briefly.

2. Experimental details

SnO$_2$ NWs were prepared by the evaporation–condensation (EC) process with a vapour–liquid–solid (VLS) growth mechanism. Such a deposition technique consists of thermally driven evaporation of bulk MOXs followed by condensation. The experimental set-up for the EC oxide deposition consists of an alumina furnace capable of achieving high temperatures, in order to activate decomposition of the oxide and to promote evaporation. Controlled pressure of an inert atmosphere and the gradient of temperature within the furnace allow condensation and nucleation of the nanostructures downstream of the gas flow. Such a peculiar thermodynamic condition promotes formation of nanosized one-dimensional (1D) structures. First, metallic platinum nano-particles were deposited by sputtering on the silicon substrate. Then the oxide powder was placed in an alumina tube inserted in a horizontal tube furnace. Evaporation took place by heating the source to 1370 °C. Mass transport was obtained using an Ar flow (75 sccm) at a pressure of $1 \times 10^4$ Pa. Furnace heating from room temperature (RT) to 1370 °C took 1.5 h approximately. During furnace heating and cooling a reverse Ar gas flow (from the substrates to the powder) was applied to avoid uncontrolled mass deposition during inappropriate conditions. Once the desired temperature was reached, the deposition process lasted for 10 min. NWs grew in a colder zone of the furnace, at a temperature between 400 and 500 °C on 3 $\times$ 3 mm$^2$ platinum-coated silicon substrates. High-resolution TEM and electron diffraction analyses show that the wires are single crystalline, with atomically sharp termination of lateral sides; the whole symmetry of the electron diffraction pattern agrees with the cassiterite tetragonal SnO$_2$ phase (P42/mnm- SG 136) [20].

Continuous wave PL (CWPL) and time-resolved PL (TRPL) measurements were performed by enclosing the analysed SnO$_2$ NWs samples inside a test chamber having a volume of 200 cm$^3$ equipped with optical quartz windows for optical analysis and gas inlet and outlet. A mass flow control provided calibrated mixing of synthetic air and test gas coming from certified bottles inside the analysis chamber. During all PL experiments the gas flow (pure dry air or mixtures of dry air and test gas) was kept constant at 0.3 l min$^{-1}$. The CWPL
Figure 1. SEM images of SnO$_2$ NWs. (a) A large area (340 × 224 µm$^2$) image of the entangled wires, while (b) and (c) show details at a higher magnification.

spectra were obtained by using a He–Cd laser (325 nm emission wavelength) as excitation source and a 320 mm focal length spectrometer coupled with a Peltier cooled CCD camera for spectral acquisition. The TRPL measurements were performed using the same analysis chamber employed for CWPL characterization, while the laser excitation was provided by frequency tripled pulses of a mode-locked Nd–YAG laser (355 nm wavelength, 25 ps time duration). The time-dependent PL signal was collected by a focusing lens system and coupled to the input slit of a streak camera. The temporal profile of the PL decay was measured at a time resolution of about 50 ps, resulting from the convolution of the response function of the streak camera and of the laser pulses duration. In both the experimental set-ups the excitation beam was split into a signal beam and a reference beam by a wedged window. The signal beam was directed onto the sample, while the reference beam was sent to the head of a UV-enhanced power meter in order to continuously monitor the laser intensity and to normalize the acquired PL spectra. All the PL spectra were corrected by the spectral response function of the acquisition set-up, which was previously measured using a certified calibration lamp.

3. Experimental results

Different SnO$_2$ NW samples were prepared by means of the procedure described in the previous section. Samples were analysed by using scanning electron microscopy (SEM). The SEM images reveal that the NWs grow in a homogeneous entanglement on a large area (figure 1(a)). NWs have high degree of crystalline quality [20, 21] and their diameter typically ranges between 30 and 150 nm. Average sizes, lengths and densities of NWs generally depend on the preparation parameters (duration of deposition, substrate temperature): it has however to be outlined that the PL spectral features (peak position, spectral profile, PL spectral width) of the NWs did not show significant dependence on the morphological parameters.

Quenching of PL spectra due to interaction with NO$_2$ is shown in figure 2, where RT CWPL spectra obtained upon exposing the sample to pure synthetic dry air or to different concentrations of NO$_2$ (expressed in parts per million, ppm) are shown. In the inset of figure 2 the PL emission peak energy and full widths at half maximum (FWHM) are also reported. It is
Figure 2. CWPL spectra of SnO$_2$ NWs obtained at different concentrations of NO$_2$ inside the test chamber. In the inset: PL peak energy and FWHM of the PL spectra as a function of NO$_2$ concentration.

Figure 3. Quenching ratio $\Phi/\Phi_0$ (A) and relative variations $\Delta \Phi/\Phi_0$ (B) of the PL yield as a function of the NO$_2$ concentrations. The dashed lines are the best-fit curves based on the Langmuir function (equation (4)).

evidenced that introduction of NO$_2$ quenches the PL spectra uniformly, i.e. the spectral shapes are not modified by interaction with the gas. It is observed that the spectra, normalized at their maximum, overlap except for a small increase (about 4%) of the FWHM (inset of figure 2). The NO$_2$ induced quenching is fully reversible to its original value once NO$_2$-free atmosphere is introduced inside the cell. In order to quantify the total PL quenching induced by gas exposure, it is useful to define a total PL yield $\Phi$ by integration of the PL spectral data over the emission wavelength interval: $\Phi = \int \phi(\lambda) \, d\lambda$, where $\phi(\lambda)$ is the measured PL spectrum normalized to the excitation laser power and to the spectral response of detection apparatus.

The quenching of PL yield induced by NO$_2$ exhibits nonlinear behaviour as a function of the quencher concentration inside the test chamber: significant variations of the PL efficiency are observed upon exposure to low concentration of NO$_2$ (few ppm) followed by saturation at increasing NO$_2$ concentration. Such behaviour is evidenced in figures 3(a) and (b), where the
quenching ratio of the PL yield and the relative response \( \Delta \Phi / \Phi_0 = (\Phi_0 - \Phi) / \Phi_0 \) are reported versus gas concentration. As evidenced by figure 3(b), a relative response of about 5% ppm is obtained at NO\(_2\) concentrations lower than 1 ppm. The dashed curves in figures 3(a) and (b) correspond to numerical fitting of the data using equation (4), as discussed in the next section.

As discussed in detail in the next section, PL quenching may result from different mechanisms. Important information on which mechanism is acting in a specific case can be obtained by studying the luminescence lifetimes and their dependence on quencher concentration. Such analysis can be performed by TRPL measurements, in which instantaneous excitation of the sample is provided by a pulsed laser source. To achieve this aim, we performed TRPL measurements at gas concentrations varying from 0 to 70 ppm by means of the experimental set-up described in the previous section.

In figure 4(a) some experimental panchromatic TRPL curves are shown in linear scale evidencing that the maxima at time \( t = 0 \) and the area under the curves decrease upon increasing NO\(_2\) concentrations, i.e. that introduction of NO\(_2\) quenches the time-resolved luminescence signal, coherently with the results obtained for stationary laser excitation. In the inset of figure 4(a) the measured quenching ratio values are reported versus NO\(_2\) concentrations (the panchromatic TRPL signal is already integrated over the emission spectrum, thus the yield \( \Phi \) is obtained by numerical integration of the signal over time). In figure 4(b) the TRPL decay curves are shown in semi-log scale, evidencing that the curves do not exhibit simple mono-exponential decay shapes. From figure 4(b) it can be noticed that TRPL curves have very similar decay slopes. In other words, once the experimental TRPL curves are normalized to unity, no large differences in decay dynamics are observed due to the interaction with changing NO\(_2\) concentrations. An example is shown in figure 4(c), where we report the two TRPL curves corresponding to the largest investigated variation of NO\(_2\) concentration (pure dry air—full squares, 70 ppm NO\(_2\) concentration—open circles). Good fittings of the TRPL curves can be obtained by a two-exponential function \( \phi(t) = A_s \exp(-t/\tau_s) + A_f \exp(-t/\tau_f) \), where \( \tau_s \) and \( \tau_f \) represent a slow and a fast lifetime, respectively. The full lines in figure 4(c) represent the best-fit curves using double exponential function and in the inset the fast and the slow decay lifetimes obtained from fits are reported versus the NO\(_2\) concentration.

In summary, to a pure phenomenological level it is observed that NO\(_2\) quenches the luminescence efficiency of SnO\(_2\) NWs with a highly sensitive response associated with low concentrations. On the other hand, it has a small effect on the recombination dynamics (TRPL temporal profile) of the electrons decaying from excited states. These results are discussed in the following section.

4. Discussion

The existing literature on PL properties of SnO\(_2\) evidences that two factors mainly affect the light emission efficiency of an SnO\(_2\) crystal: its physical size and its defect composition (and, in a relevant manner, its OV density [11]–[17], [22]). It has been observed that bulk SnO\(_2\) crystals and thin films exhibit low PL efficiency [22], while instead the PL efficiency of SnO\(_2\) nanostructures is usually large regardless of the kind of morphology. For example, relevant PL emission was observed in SnO\(_2\) nanoribbons [1], nanowhiskers [23], nanotubes [17], nanobelts
Figure 4. (A) TRPL decay signals obtained at different NO$_2$ concentrations (only some of the experimental curves are shown). Inset: measured quenching ratios (circles) and best-fit curve (full line) obtained using equation (4). (B) The TRPL data plotted on semi-log scale. Dashed line: temporal profile of the excitation laser pulse. (C) Normalized TRPL data obtained in dry air (full squares) and at 70 ppm concentration of NO$_2$ (open circles) and their best-fit curves obtained using a double-exponential function. Inset: the fast ($\tau_f$) and slow ($\tau_s$) decay lifetimes obtained from fittings of the data as a function of NO$_2$ concentration.
Figure 5. PL yield ratios $\Phi_0/\Phi$ (circles) and lifetime ratios for the slow (open squares) and fast (full squares) components of TRPL signals measured as a function of the NO$_2$ concentration.

within the bandgap have to be invoked. The key role played by OV states in such PL emission was highlighted in all cases in which the oxygen stoichiometry of a sample was intentionally altered by means of annealing under vacuum and/or under oxygen flow: it is found as a general trend that the PL efficiency is reduced (or eventually almost suppressed) as OV's are removed [14, 17, 22]. These findings evidence that a key role is played by OV states in SnO$_2$ luminescence. However, the real nature of such a role (and, thus, the nature of luminescence mechanisms) is still to be clarified in our opinion. In particular, OV states may represent both a direct or an indirect cause of luminescence: for instance, OV states lying inside the bandgap above the Fermi level may be the upper electronic levels decaying radiatively to the ground state (‘direct’ origin) or their presence may trigger other mechanisms (‘indirect’ origin) resulting in photon emission. We will further discuss this point at the end of this section.

We now consider the PL quenching phenomenon induced by adsorption of NO$_2$. In a general manner, modifications of light emission efficiency (or PL yield) of a material due to introduction of some external perturbation (e.g. gas molecules) may be due to either a change in the recombination rates or to a change in the density of excited states responsible for the radiative transitions. One can notice it by simply considering the ‘Fermi golden rule’, which states that the yield associated with a given electronic transition is related to the product of the density of excited states (whose energy distribution is reflected in the PL spectrum) times the oscillator strength of the transition (which is related to the recombination lifetimes). Reductions of PL yield may hence be due to (first case) introduction of alternative non-radiative de-excitation channels affecting the PL lifetimes or to (second case) a decrease in the number of available radiative states (‘emitting centres’) not accompanied by modifications of the decay rates (and lifetimes). We refer to these two cases as ‘dynamic quenching’ and
Common examples of dynamic quenching can be observed in fluorescence quenching of binary systems obeying the Stern–Volmer kinetics, where the PL lifetime (τ) in the presence of a quencher (whose concentration is indicated as [Q]) differs from the PL lifetime in the absence of the quencher (τ₀) according to the equality

\[
\frac{\tau_0}{\tau} = 1 + k_q [Q],
\]

where \( k_q \) represents the bimolecular reaction rate constant [26, 27]. On the other hand, the main feature of static quenching lies in the fact that the external perturbation leads to reduction of the PL yield while at the same time it does not affect the PL lifetimes. The origin of such behaviour lies in suppression of emitting centres as a consequence of interaction with the quencher. Examples can be found in the Perrin ‘hard sphere’ model [25], where the radiative excited states (‘fluorophores’) are turned off as an excimer complex is formed or as the distance between fluorophore and quencher molecule lies within a critical radius [28].

Comparisons between PL yield variations \( \Phi_0/\Phi \) and PL lifetimes variations \( \tau_0/\tau \) at different quencher concentrations thus allow to distinguish between static and dynamic behaviour. In the case of simple single-exponential decays, the two situations can be distinguished by the direct comparison of the quantities \( \Phi_0/\Phi \) and \( \tau_0/\tau \). In our case a single lifetime cannot be defined as the PL decays do not exhibit simple mono-exponential behaviour. However, the physically relevant point (eventual modifications of recombination dynamics due to the presence of NO\(_2\)) can be investigated here by simply defining phenomenological lifetimes describing the observed TRPL decay, such as for instance the slow and fast decay lifetimes determined previously. In figure 5 the values of \( \Phi_0/\Phi \) and of the lifetimes ratios \( \tau_s^{(0)}/\tau_s \) and \( \tau_f^{(0)}/\tau_f \) are reported as a function of NO\(_2\) concentration, where \( \tau_s^{(0)} \) and \( \tau_f^{(0)} \) represent the slow and fast lifetimes in the absence of the gas quencher. It is seen that the quenching and the lifetime ratios are not linearly correlated and the equality \( \Phi_0/\Phi = (\tau_0/\tau) \), characterizing a dynamic quenching process, does not hold here. We can thus conclude that the gas molecules adsorbed at the surface act as static quenchers, determining a change in the number of states acting as radiative recombination centres.

In the light of the results obtained so far, the quenching dynamics induced by NO\(_2\) and observed in figures 2 and 3 can be interpreted by means of a simple picture. According to the classical ‘two-level model’ notation, we call \( N_1 \) and \( N_0 \) the equilibrium densities of electrons (under CW pumping conditions) in the excited radiative state and recombined (ground) state, respectively and assume that \( N_1 \) depends on \( n_a \), where \( n_a \) is the surface concentration of adsorbed quencher molecules. At first approximation, in the limit of low quencher concentrations, it is reasonable to assume a first-order approximation leading to a linear dependence:

\[
N_1(n_a) = N_1^{(0)} (1 - kn_a),
\]

In the molecular fluorescence literature, the often used terms ‘static’ and ‘dynamic’ refer to the kind of interaction occurring between the excited fluorescent molecule (‘fluorophore’) and the quencher molecule during their mutual inter-diffusion process [25]. In the case of interest here (interaction between gas molecules and a solid) the concept of ‘fluorophore’ is not well defined (the light emission cannot be assigned to a molecule but only to an electron transition) and the gas–nanostructure interaction is not localized in space as in the case of bimolecular interactions. Nothwithstanding this, for the sake of clarity we will adopt the same ‘molecular’ notation and will intend as ‘static quenching’ the case in which the quencher modifies the number or the states available for radiative recombinations (the ‘fluorophores’ here). Under this scheme, changes of PL yield which are not accompanied by changes in recombination lifetimes represent the signature of a static quenching mechanism.

New Journal of Physics 10 (2008) 043013 (http://www.njp.org/)
where $N_1^{(0)}$ represents the density of radiative states in the absence of the quencher and the constant $k$ represents the relative variation of PL induced by adsorption of one quencher molecule per unit surface. The CWPL yield $\Phi$ is proportional to the product of $N_1$ and of the radiative recombination rate. For recombination rates independent of the quencher concentrations (static quenching) quencher-dependent PL yield is thus obtained as follows:

$$\Phi = \Phi_0 (1 - kn_a),$$

(2)

where $\Phi_0$ is the PL yield in the absence of quencher. In expressions (1) and (2) a linear dependence of $N_1$ and $\Phi$ as a function of $n_a$ is assumed or, equivalently, it is assumed that the quantity $k$ does not depend on gas concentration. Once the physical meaning of the constant $k$ is considered, one sees that linear expressions (1) and (2) are therefore equivalent to stating that the molecule–surface interaction potential is the same for each adsorbed molecule. This assumption (usually correct when the molecules are chemisorbed at the surface, thus allowing the molecule–molecule interaction to be neglected) is the basis of the well-known Langmuir adsorption model [29], in which the existence of a maximum finite number of surface sites which are available for surface adsorption is assumed.

In the Langmuir model the number of adsorbed gas molecules per unit surface is related to the gas partial pressure $P$ by the equation

$$n_a = n_0 \frac{bP}{1 + bP},$$

(3)

where $n_0$ is the surface density of available adsorption sites and the quantity $b$ depends on the free energy of desorption of the system [29]. We thus get:

$$\Phi = \Phi_0 \left(1 - kn_0 \frac{bP}{1 + bP}\right).$$

(4)

We notice that this expression describes the correct PL quenching behaviour observed in figure 3. In fact, equation (4) describes an almost linear dependence of the quenching ratio $\Phi/\Phi_0$ versus $P$ at low pressures ($P \ll 1/b$) followed by saturation for $P \gg 1/b$. The high sensitivity at low NO$_2$ pressures noticed in figure 3(b) can thus be interpreted as a consequence of low ‘saturation pressure’ $1/b$.

The data reported in figure 3(a) and (b) were thus fitted by using the expression $\Phi = \Phi_0[1 - abP/(1 + bP)]$, where $a = kn_0$ according to equation (4). It is observed that the experimental results are satisfactorily described by equation (4) notwithstanding the simplicity of the underlying model. From the best fit of the data of figure 4(a) the values $a = (17.6 \pm 0.6) \times 10^{-2}$ and $b = (0.25 \pm 0.06)$ ppm$^{-1}$ (corresponding to a saturation pressure $1/b$ of about $(330 \pm 80) \times 10^{-3}$ Torr) are obtained.

As a final point, we underline that the above described interpretation does not require a particular hypothesis on the real nature of the active radiative centres ($N_1$) which are statically quenched by NO$_2$ adsorption. The evidence showing a direct correlation between PL activity and oxygen stoichiometry (discussed at the beginning of the present section) and the surface-limited nature of PL quenching may for instance suggest that surface or near-surface OV states may form radiative levels inside the SnO$_2$ bandgap, thus PL activity has a direct origin. On the other hand, the hypothesis based on luminescent centres different from OV states whose formation is promoted by OVs cannot be ruled out. For instance, the effect of OVs and the static PL quenching findings may be explained also in terms of localized electron–hole pairs whose...
formation is triggered by lattice defects (as in the case of self-trapped excitons in pure SiO$_2$ [30] or SrTiO$_3$ [31]) and is inhibited by the electric field generated in the space charge layer by adsorbed oxidizing molecules (such as NO$_2$). Further investigations are needed to clarify the nature of such PL mechanisms.

5. Conclusions

We show that, in agreement with previous findings [18], the NO$_2$ PL intensity of SnO$_2$ NWs is quenched by interaction with low concentrations of NO$_2$. Such an effect, very promising in view of applications based on selective NO$_2$ optochemical detection, was investigated by us to obtain a clearer physical description. With this aim CWPL and TRPL analyses performed in controlled conditions were employed. The measured PL quenching data are well described by assuming a Langmuir-like adsorption of NO$_2$ and under such an assumption the decrease of PL intensity is linearly proportional to surface density of adsorbed molecules. TRPL measurements show small modifications of recombination rates due to introduction of NO$_2$ and such modifications are not proportional to simultaneous changes in PL intensity. The findings support a picture in which NO$_2$ molecules act as static quenchers, suppressing emitting centres of SnO$_2$ in an amount proportional to the number of adsorbed molecules. We also show that a simple model based on the above mechanism and not requiring a particular hypothesis on the real nature of the radiative centres allows good fitting of the data. The surface-limited nature of PL quenching may suggest that the surface of near-surface OV states may represent active radiative centres in SnO$_2$ NWs, while other origins for their PL activity cannot be ruled out and further investigations are needed to clarify this point. The results encourage investigations on oxygen-deficient SnO$_2$ NWs as selective optical gas sensors.

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