Sub-ppm Formaldehyde Detection by \( n-n \) TiO\(_2\)@SnO\(_2\) Nanocomposites

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Abstract: Formaldehyde (HCHO) is an important indicator of indoor air quality and one of the markers for detecting lung cancer. Both medical and air quality applications require the detection of formaldehyde in the sub-ppm range. Nanocomposites SnO\(_2\)/TiO\(_2\) are promising candidates for HCHO detection, both in dark conditions and under UV illumination. Nanocomposites TiO\(_2\)@SnO\(_2\) were synthesized by ALD method using nanocrystalline SnO\(_2\) powder as a substrate for TiO\(_2\) layer growth. The microstructure and composition of the samples were characterized by ICP-MS, TEM, XRD and Raman spectroscopy methods. The active surface sites were investigated using FTIR and TPR-H\(_2\) methods. The mechanism of formaldehyde oxidation on the surface of semiconductor oxides was studied by in situ DRIFTS method. The sensor properties of nanocrystalline SnO\(_2\) and TiO\(_2\)@SnO\(_2\) nanocomposites toward formaldehyde (0.06–0.6 ppm) were studied by in situ electrical conductivity measurements in dark conditions and under periodic UV illumination at 50–300 °C. Nanocomposites TiO\(_2\)@SnO\(_2\) exhibit a higher sensor signal than SnO\(_2\) and a decrease in the optimal measurement temperature by 50 °C. This result is explained based on the model considering the formation of \( n-n \) heterocontact at the SnO\(_2\)/TiO\(_2\) interface. UV illumination leads to a decrease in sensor response compared with that obtained in dark conditions because of the photodesorption of oxygen involved in the oxidation of formaldehyde.

Keywords: formaldehyde gas sensor; sub-ppm concentration; UV light; metal-oxide nanocomposites; SnO\(_2\); TiO\(_2\)

1. Introduction

Formaldehyde, HCHO, a colorless gas with an unpleasant odor, is a toxic compound that causes, in trace concentrations of 0.1–0.5 mg/m\(^3\), serious diseases of the respiratory tract, gastrointestinal tract and eyes. Biochemical oxidation of HCHO in human body occurs with the formation of carbon dioxide and formic acid, which, with prolonged exposure, causes asthma, pulmonary edema, and cancer. Formaldehyde is widely used in the manufacturing of polymeric materials for flooring, furniture, heat and electrical insulation, artificial tissues, plastic windows, etc. In addition, a concentrated HCHO solution (formalin) is used in medicine for disinfection, and in the food industry for the preservation of fruits and vegetables. Formaldehyde is also included in some cosmetics and personal care products. A detailed description of the characteristics of formaldehyde and its effects on health can be found in Ref. [1]. According to the World Health Organization, the maximum permissible concentration of...
formaldehyde in the air of the working area is 0.5 mg/m$^3$ (0.4 ppm), in the air of the residential area is 0.125 mg/m$^3$ (0.1 ppm) [1,2].

Recently, it was proposed that formaldehyde is one of the markers for lung cancer detection using exhaled breath analysis [3–6]. The median HCOH level observed for lung cancer patients (83 ppb) is higher than that for healthy ones (48 ppb) [5]. Thus, both medical and air quality applications require the detection of formaldehyde in the sub-ppm range. Metal oxide based semiconductor gas sensor for formaldehyde detection are quite attractive since they can have sufficient sensitivity, are inexpensive and can be integrated into portable devices such as e-Nose, that could detect formaldehyde at ppb level at high humidity level (e.g., 90% RH for breath analysis) and in the presence of different interfering gases [6–8]. However, most studies consider the sensor characteristics of various semiconductor oxides in the detection of HCHO in the concentration range of 10 ppm or more [9,10]. Recent efforts are focused at the implementation of a new principle of HCHO detection under conditions of minimal thermal heating combined with illumination by a low-power UV or visible light source [11,12].

It was shown by the authors of [13–18] that under UV illumination molecules of volatile organic compounds (VOCs: acetone, acetaldehyde, ethanol, hydrocarbons) undergo photolysis on the surface of semiconductor oxides that facilitates their subsequent oxidation with chemisorbed oxygen, leading to a change in the conductivity of the semiconductor. Titanium dioxide TiO$_2$ and zinc oxide ZnO demonstrate the highest activity in the photocatalytic VOCs oxidation. A comparative study on UV light activated porous TiO$_2$ and ZnO sensors demonstrated that TiO$_2$ exhibited a superior performance to ethanol and formaldehyde [19].

As a sensor material for HCHO detection TiO$_2$ with different morphology was studied: mesoporous powders [20], nanotube arrays [21], polycrystalline thick films [22], hollow microspheres [23]. In all cases, the investigations were conducted under UV illumination. The experimental study of the TiO$_2$ sensor properties in dark conditions is difficult because of the exceptionally high electrical resistance of these materials. A decrease in the resistance of TiO$_2$-based materials can be achieved by creating nanocomposites, in which TiO$_2$ plays the role of a photocatalyst/receptor, while the transport of charge carriers is effectuated by another semiconductor with more suitable electrical characteristics. Nanocomposites SnO$_2$/TiO$_2$ are promising candidates for formaldehyde detection both in dark conditions and under UV illumination. It was shown that as compared with pure SnO$_2$ and TiO$_2$, nanocomposites with different Sn/Ti ratio demonstrate higher sensor response toward triethylamine [24], ammonia [25], hydrogen [26,27], and formaldehyde [28]. Moreover, DFT calculations and experimental study presented by the authors of [29] revealed that these nanocomposites have higher photocatalytic activity in UV-light initiated degradation of RB5 and RhB dyes. However, the role of each component in the formation of the sensor signal when detecting formaldehyde in dark conditions and under UV illumination is not clear.

In this paper, we compare the sensor properties of nanocrystalline SnO$_2$ and TiO$_2$@SnO$_2$ nanocomposites when detecting formaldehyde in the sub-ppm range in dark conditions and under periodic UV illumination in the temperature range of 50–300 °C.

2. Materials and Methods

2.1. Materials Synthesis

Nanocrystalline SnO$_2$ was prepared by the precipitation method. Aqueous ammonia solution (25%) was added dropwise to 0.3 M solution of tin (IV) chloride pentahydrate (SnCl$_4$·5H$_2$O, 98%, Sigma-Aldrich) under vigorous stirring until pH = 7 [30,31]. The synthesis was carried out at room temperature. The obtained α-stannic acid gel was separated by centrifugation at 3500 rpm for 3 minutes, repeatedly washed with deionized water and then with 0.01 M NH$_4$NO$_3$ solution. AgNO$_3$ test was used to confirm the negative reaction to chloride ions. The resulting gel was dried in air at 50 °C for 24 h, then obtained β-stannic acid xerogel was ground in an agate mortar and annealed in
air at 300 °C for 24 h. According to transmission electron microscopy data [30,31] the SnO₂ powder consists of a rounded shape, agglomerated nanoparticles of 3–8 nm in diameter.

Nanocomposites TiO₂@SnO₂ were synthesized by atomic layer deposition (ALD) method. Titanium (IV) isopropoxide (Ti(OCH(CH₃)₂)₄, TTIP) and H₂O used as precursors, were introduced consequently into the growth reactor containing SnO₂ nanocrystals to avoid premature interaction. The ALD parameters: temperature and pressure were set to 150 °C and 0.1 torr, respectively. TTIP and H₂O were kept in bubblers at 40 °C and 24 °C, respectively. The typical ALD cycle included the following stages: 1 s for TTIP dosing, 10 s for N₂ purging, 0.2 s for H₂O dosing, and 25 s for N₂ purging. The ALD cycles were repeated for 500, 1000 and 2000 times, respectively, producing TiO₂@SnO₂ nanocomposites with increasing Ti/Sn ratio. After ALD synthesis the nanocomposites were annealed in air at 500 °C for 1 h to remove organic residues and ensure TiO₂ crystallization. To obtain an adequate reference sample, nanocrystalline SnO₂, which was not subjected to ALD treatment, was additionally annealed in air at 500 °C for 24 h.

2.2. Materials Characterization

Chemical composition ([(Ti]}/[(Ti]+[Sn]), mol%) of TiO₂@SnO₂ nanocomposites was determined by X-ray fluorescent analysis (XRF) performed on M1 Mistral spectrometer (Bruker, Billerica, MA, USA) with the beam energy of 50 keV. The diameter of the analyzed area was 1.0 mm, the signal accumulation time 2 min.

The microstructure of the synthesized products was studied by high resolution transmission electron microscopy (FE-TEM, JEOI JEM-2100F, JEOI Ltd., Tokyo, Japan).

The phase composition of TiO₂@SnO₂ nanocomposites was characterized using powder X-ray diffraction (XRD) and Raman spectroscopy. The XRD patterns were collected by DRON-4 diffractometer (Burevestnik, Moscow, Russia) using monochromatic Cu Kα radiation (λ = 1.5406 Å). The survey was carried out in the range of 2θ = 10°−80° with a step of 0.1° at scanning rate of 0.5°/min. The crystallite size \( d_{XRD} \) of SnO₂ and TiₓOᵧ phases was calculated from the broadening of the most intense XRD peaks using Scherer equation. WinXPow (STOE and Cie GmbH, Darmstadt, Germany) software was used for phase and full profile analysis, DSH software (laboratory made) was used for crystallite size calculations. The crystalline phases were determined using structural parameters of SnO₂ cassiterite (ICDD 41-1445), TiO₂ anatase (ICDD 21-1272) and TiO₂ brookite (ICDD 75-1582). Raman spectra were recorded by a Renishaw InVia multichannel spectrometer (Renishaw plc., Gloucestershire, UK) using an argon laser with a wavelength of 514 nm as the radiation source. The laser beam was focused on the sample using a microscope objective (magnification × 50) so that the analyzed area was approximately 100 μm². The spectra were recorded in air at room temperature in the range of 100–900 cm⁻¹ with a step of 1 cm⁻¹ (data was collected for each point for 10 s).

The nature of chemical groups presenting in obtained samples was investigated using the FT-IR spectroscopy. The IR spectra were recorded using a Perkin–Elmer Spectrum One Fourier Transform Infrared (FT-IR) spectrometer (Perkin Elmer Inc., Waltham, MA, USA) in the range of 4000–400 cm⁻¹ with a step of 1 cm⁻¹ in the transmission mode. For this the TiO₂@SnO₂ powders (0.3–0.5 mg) were ground with 50 mg of dried (350 °C, 2 h) KBr (FT-IR grade, Sigma-Aldrich, Saint Louis, MO, USA) and pressed into tablets. DRIFT spectra were collected in situ using the DiffusIR annex and heated flow chamber HC900 (Pike Technologies, Fitchburg, WI, USA) sealed by ZnSe windows. DRIFT spectra were registered in the range 4000–1000 cm⁻¹ at 4 cm⁻¹ resolution with an accumulation of 30 scans. Powders (50 mg) were placed in alumina crucibles (5 mm diameter). Gas mixture containing 100 ppm of HCHO in dry air was used for the investigations.

The investigations of SnO₂ reference sample and TiO₂@SnO₂ nanocomposites by the method of thermo-programmed reduction with hydrogen (TPR-H₂) was effectuated on Chemisorb 2750 (Micrometeritics, Norcross, GA, USA) in a quartz reactor using 10% H₂/Ar gas mixture (50 mL/min) under the heating to 900 °C at a heating rate of 10 K/min.
Specially designed micro-hotplates were used to investigate gas sensor properties. The micro-hotplates consist of dielectric substrate (Al₂O₃) with dimensions of 0.9 × 0.9 × 0.15 mm, which provides a small temperature gradient between the heater and the sensitive layer. Substrate is covered with Pt electrodes on the top side for resistance measurements and Pt heater on the back side, which is protected by an insulating layer of dielectric paste. Electrodes and heater are made using Pt-based paste by screen printing method (Figure 1). The powders of nanocrystalline oxides were mixed with a vehicle (α-terpineol in ethanol) and deposited in the form of thick films over dielectric substrate to cover the electrodes. Thick films were sintered at 300 °C for 10 hours in air to remove the organic binder. The method used allows us to obtain the coatings which are continuous and uniform over the entire substrate with the thickness about 1 μm [30] and with the value of resistance in air at 300 °C, differing by no more than 10%. The current–voltage (I-V) characteristics of the sensors measured using Potentiostat P-8-NANO (Elins, Zelenograd, Russia) are shown in Figure 1c. All the samples exhibited linear I-V curves both for positive and negative applied bias voltages up to +2V and −2V, respectively.

![Micro-hotplate scheme](image)

**Figure 1.** Micro-hotplate scheme: (a) front side; (b) back side; (c) Current–voltage (I-V) characteristics of the sensors.

The schematic illustration of sensor measurements setup is shown in Figure 2. The DC conductivity was measured in situ using electronic module (10) providing control of sensor heating and high-precision measurement of the resistance of the sensitive layer. The sensors were placed into a Teflon airtight and light-tight flow chamber (3) connected to a computer-controlled (5) gas delivery system with electronic mass-flow controllers (8). The measurements were carried out under a controlled constant flux of 100 mL/min in the temperature range of 300–50 °C with a step of 50 °C, in the dark conditions and under periodic UV illumination. Miniature UV LED (4) (10 mW/cm², λ_max = 365 nm) located at a distance of 4 cm above the sensors was used as an illumination source. The power of the LED was effectuated using DC power supply (1). The illumination of the sensors was carried out in a pulsed mode with the period 2 min “on”–2 min “off”. An automatic cyclic relay (2) periodically opened and closed the circuit, allowing measurements to be made with periodic illumination. The sensor properties of SnO₂ reference sample and TiO₂@SnO₂ nanocomposites were investigated toward formaldehyde HCHO (0.06–0.08–0.15–0.3–0.6 ppm) in air (relative humidity at 25 °C RH₂₅ = 30%). The gas mixtures containing preassigned concentration of HCHO were prepared by dilution of certified gas mixture (6) with background purified air (7). Flow through humidifier (9) was used to adjust the humidity (RH₂₅ = 30%) of gases passing through the sensor chamber. The sensor response was calculated as

\[ S = \frac{R_{\text{air}}}{R_{\text{gas}}} \]

where \( R_{\text{air}} \) is the resistance in background air, \( R_{\text{gas}} \) is the resistance in the presence of HCHO.
3. Results and Discussion

3.1. Characteristics of Nanocrystalline SnO\textsubscript{2} and TiO\textsubscript{2}@SnO\textsubscript{2} Nanocomposites

The elemental and phase composition of the samples under investigation are presented in Table 1. An increase in the number of ALD cycles led to a proportional increase in the titanium content (presented as ([Ti]/([Ti]+[Sn])) ratio, mol%) in nanocomposites.

| Sample | Number of ALD Cycles | [Ti]/([Ti]+[Sn]), mol.% | Phase Composition | d\textsubscript{XRD}, nm |
|--------|----------------------|--------------------------|-------------------|-----------------|
| SnTi-0 | 0                    | 0                        | SnO\textsubscript{2} cassiterite | 9 ± 1 |
| SnTi-1 | 500                  | 20 ± 2                   | SnO\textsubscript{2} cassiterite | 5.1 ± 0.5 |
|        |                      |                          | TiO\textsubscript{2} brookite  | 13 ± 1 |
|        |                      |                          | TiO\textsubscript{2} anatase   | n/d |
| SnTi-2 | 1000                 | 24 ± 2                   | SnO\textsubscript{2} cassiterite | 4.5 ± 0.5 |
|        |                      |                          | TiO\textsubscript{2} brookite  | 16 ± 2 |
|        |                      |                          | TiO\textsubscript{2} anatase   | n/d |
| SnTi-3 | 2000                 | 39 ± 3                   | SnO\textsubscript{2} cassiterite | 3.5 ± 0.5 |
|        |                      |                          | TiO\textsubscript{2} anatase   | 22 ± 2 |

Figure 3 shows the TEM image of SnO\textsubscript{2} powder used as a substrate in ALD synthesis confirming formation of SnO\textsubscript{2} nanocrystals with approximate size of 5–10 nm. Lattice-resolved TEM image presented in Figure 3b highlights the crystalline phase of SnO\textsubscript{2} with a plane spacing of 0.34 nm.
belonging to the (110) plane of cassiterite SnO$_2$. The lattice-resolved TEM image of SnTi-1 nanocomposite (Figure 3c) makes it possible to detect crystalline regions with interplanar distances of 0.34 and 0.29 nm, corresponding to (110) SnO$_2$ (cassiterite) and (121) TiO$_2$ (brookite), respectively.

![Figure 3. (a) TEM and (b) Lattice resolved TEM image of SnO$_2$ powder used as a substrate in ALD synthesis; (c) Lattice-resolved TEM image of Sn-Ti nanocomposite.](image)

According to the results of the XRD analysis (Figure 4), the SnO$_2$ annealed at 500 °C (equivalently to the post-synthetic annealing used for the synthesis of TiO$_2$@SnO$_2$ nanocomposites) crystallizes in a tetragonal cassiterite structure (ICDD 41-1445) with a crystallite size of 9–10 nm. Intense reflections from the cassiterite phase are observed in the diffraction patterns of all the samples. The titanium-containing phases, formed during post-synthetic annealing, change with an increase in the number of ALD cycles. The TiO$_2$ with brookite structure (ICDD 29-1360) presents in SnTi-1 and SnTi-2 nanocomposites, as evidenced by the appearance of the intense (121) diffraction peak at 2θ = 30.8°. The most intense (120) at 2θ = 25.3° and (111) 2θ = 25.7° diffraction reflections of brookite coincide with the most intense (101) diffraction reflection (2θ = 25.3°) of the TiO$_2$ anatase phase (ICDD 21-1272). Therefore, the presence of the anatase phase in these nanocomposites cannot be excluded. The intensity of diffraction peak at 2θ = 25.3° increases with increasing titanium content. In the diffraction pattern of SnTi-3 nanocomposite a new diffraction peak at 2θ = 48.1° corresponds to the (200) reflection of the anatase phase. At the same time, the diffraction peak at 2θ = 30.8° does not appear that indicates the absence of the brookite phase in this sample. The least intense and wide peaks in the ranges of 2θ = 36.5°–40.0° and 2θ = 52.6°–64.5° correspond to the superposition of the reflections of almost all of the above phases, so their deconvolution and assignment to a certain phase is a difficult task. The broadening of the SnO$_2$ reflections in the diffraction patterns of nanocomposites and overlap of intense diffraction peaks corresponding to SnO$_2$ and TiO$_2$ in SnO$_2$-TiO$_2$ (anatase) and SnO$_2$-TiO$_2$ (brookite) systems (in contrast to the TiO$_2$-ZnO [32]) do not allow us to make a positive or negative conclusion about the incorporation of Ti into the SnO$_2$ lattice.

The crystallite size of detected Sn- and Ti-containing phases depending on titanium content in the samples is presented in Table 1. The crystallite size of tin dioxide, used as a substrate for the deposition of titanium dioxide by the ALD method, is 3–4 nm [30,31]. The post-synthetic annealing at 500 °C, necessary for the removal of organic residues of the titanium precursor, leads to an increase in the size of SnO$_2$ crystallites to 9–10 nm. With an increase in the titanium content in TiO$_2$@SnO$_2$ nanocomposites, a decrease in the size of SnO$_2$ crystal grains is observed as compared with the reference sample. A similar effect was repeatedly noted for nanocomposites based on semiconductor metal oxides [33–35]. The presence of impurities on the surface of growing crystallites slows down their growth rate under isothermal annealing due to the so-called Zener pinning [36]. The maximum crystallite size of the main phase is determined by the volume fraction and the size of particles (crystalline or amorphous) segregated on the surface of growing crystallites. The deposition of TiO$_2$ layer on the surface of nanocrystalline SnO$_2$ reduces the area of SnO$_2$ intergranular contacts, that prevents recrystallization.
of SnO2 particles. The greater the thickness of the deposited TiO2 layer, the less the coarsening of SnO2 particles occurs. For the TiO2 brookite phase in SnTi-1 and SnTi-2 nanocomposites the crystallite size was estimated using the (121) reflection that does not overlap with another diffraction peaks. For the size of the crystallites of the TiO2 anatase phase, such an estimate is possible only in the case of SnTi-3 nanocomposite, in which there is no brookite phase. For the Ti-containing phases, the increase in the crystallite size is observed. Since during the ALD cycles the Ti-containing precursor has been deposited on the outer surface of SnO2 agglomerates, the sintering and coarsening of Ti-containing particles will be easier. That is why an increase in the titanium content leads to an increase in the crystallite size of the Ti-containing phases.

Figure 4. XRD patterns of nanocrystalline SnO2 and TiO2@SnO2 composites and references for SnO2 cassiterite (ICDD 41-1445), TiO2 anatase (ICDD 21-1272) and TiO2 brookite (ICDD 29-1360).

The IR spectra of nanocrystalline SnO2 and TiO2@SnO2 composites are compared in Figure 5a. In all spectra, a large broad peak in the region of 2700–3500 cm\(^{-1}\) is observed, which is related to the stretching vibrations of OH groups and a peak at 1628 cm\(^{-1}\), which is related to the deformation vibrations of adsorbed water [37,38]. The wide and intense absorption bands at 530 cm\(^{-1}\) and 620 cm\(^{-1}\) in the case of SnO2 correspond to stretching vibrations of the Sn–O and symmetric vibrations of the O–Sn–O bonds, respectively [39]. The metal–oxygen (M–O) oscillation modes for SnO2 in TiO2@SnO2 composites overlap in the range of 400–650 cm\(^{-1}\), nevertheless different components can be distinguished. All the FT-IR spectra of the composites show vibration modes at 450 and 610 cm\(^{-1}\), which can be attributed to oscillations of Ti–O–Ti and Ti–O bonds, respectively [40–42]. With an increase in the titanium content an increase in the intensity of the Ti–O oscillation modes is observed, which appears as a broadening of the M–O absorption peak in this region.

Figure 5b shows the Raman spectra of nanocrystalline SnO2 (SnTi-0) and TiO2@SnO2 composites. Raman spectrum of the SnO2 clearly shows three characteristic modes at 480.5, 631 and 772.8 cm\(^{-1}\) that correspond to the E\(_g\), A\(_{1g}\) and B\(_{2g}\) vibrational modes, respectively [43,44]. The A\(_{1g}\) and B\(_{2g}\) modes are associated with symmetric and asymmetric Sn–O stretching, respectively, orthogonally to the c axis. The translational E\(_g\) mode is related to the motion of oxygen anions along the c axis [43,44]. The B\(_{1g}\) oscillation mode appears only in the spectra of nanocrystalline SnO2 in the range of 100–184 cm\(^{-1}\) [45,46]. In the SnO2 spectrum presented in Figure 5b the band at 137 cm\(^{-1}\) is due to B\(_{1g}\) mode, the shift may be associated with the nanoparticles size effect.
J. Zuo et al. studied the size effects in SnO$_2$ nanoparticles [47]. They showed that, in addition to the characteristic vibrational modes of bulk SnO$_2$, the Raman spectrum of nanocrystalline SnO$_2$ has two additional Raman scattering bands at 358 (B$_1$) and 572 cm$^{-1}$ (B$_2$). The B$_2$ band corresponds to surface modes and is very sensitive to the changes in crystallite size for nanoscale SnO$_2$. The appearance of surface modes is associated with a small particle size of SnO$_2$ and can be due to the appearance of oscillations that are forbidden by symmetry due to the breaking of long-range order in the systems of reduced dimension. That is why a decrease in crystallite size leads to the formation of a highly defective surface layer, the contribution of which will be the highest for the materials with the smallest particle size [48]. Based on the above considerations, the wide band located at 563 cm$^{-1}$ corresponds to the surface modes associated with in-plane oxygen vacancies of the nanocrystalline cassiterite SnO$_2$ [48–50]. Consequently, the small size and surface defects of the SnO$_2$ nanoparticles may have a positive effect on the gas sensitivity of the sensor. This assumption was experimentally confirmed in by the authors of [31], where it was shown that the relative intensity of Raman surface modes $I_S/I_V$ taken as the ratio of the sum of their intensities $I_S$ to the intensity of A$_{1g}$ mode $I_V$ demonstrates the best linear correlation with gas response of SnO$_2$ nanocrystalline materials to CO.

Changes in the crystal’s local symmetry produce changes in some of the components of the polarizability tensor, even for usually forbidden vibration modes [49]. That is why the A$_{2u}$ IR active and Raman forbidden modes are found to transform into Raman active modes [48]. In this case the bands at 309 and 352 cm$^{-1}$ (E$_u$) and the band at 444 (B$_{1u}$) are related to transformation of an IR to Raman active modes.

Raman peaks observed in the spectra of TiO$_2$@SnO$_2$ composites at 145, 198, 397, 516 and 635 cm$^{-1}$ (Figure 5b), refer to the E$_g$, E$_g$, B$_{1g}$, A$_{1g}$ + B$_{1g}$ and E$_g$ modes of the anatase phase, respectively [51]. For TiO$_2$ nanoparticles the E$_g$ Raman peak is mainly caused by symmetric stretching vibration of O–Ti–O groups, B$_{1g}$ peak is caused by symmetric bending vibration of O–Ti–O and A$_{1g}$ peak is caused by antisymmetric bending vibration of O–Ti–O [52]. The presence of an intense 145 cm$^{-1}$ mode (a characteristic oscillation mode of anatase) indicates that TiO$_2$ nanocrystals have a certain degree of long-range order, while weaker and wider peaks in the high-frequency region indicate the absence of a short-range order in the anatase phase [53–55]. According to the factor group analysis, TiO$_2$ brookite phase has a total of 36 Raman active modes ($9A_{1g}$ + $9B_{1g}$ + $9B_{2g}$ + $9B_{3g}$). Raman spectra of the SnTi-1 and SnTi-2 composites show both anatase and brookite bands. In total, 4 brookite bands were readily identified, including A$_{1g}$ (255 cm$^{-1}$), B$_{3g}$ (285, 443 cm$^{-1}$), B$_{2g}$ (581 cm$^{-1}$). Also, the A$_{1g}$ (153, 194 cm$^{-1}$) and B$_{2g}$ (395 cm$^{-1}$) brookite bands may be overlapped by anatase modes, which are very close to
them [56,57]. The full assignment of the vibrational modes in the Raman spectra of nanocomposites is presented in Table 2.

Table 2. Assignment of Raman vibrational modes (cm$^{-1}$).

| SnTi-0   | SnTi-1   | SnTi-2   | SnTi-3   |
|----------|----------|----------|----------|
| 137 (B$_{1g}$, cassiterite) | 145 (E$_g$, anatase) | 145 (E$_g$, anatase) | 145 (E$_g$, anatase) |
| 309 (IR E$_{4u}$, cassiterite) | 198 (E$_g$, anatase) | 198 (E$_g$, anatase) | 198 (E$_g$, anatase) |
| 352 (IR E$_{4u}$, cassiterite) | 255 (A$_{1g}$, brookite) | 255 (A$_{1g}$, brookite) | 255 (A$_{1g}$, brookite) |
| 444 (IR B$_{1u}$, cassiterite) | 397 (B$_{1g}$, anatase) | 397 (B$_{1g}$, anatase) | 397 (B$_{1g}$, anatase) |
| 563 (surface mode) | 443 (B$_{2g}$, brookite) | 443 (B$_{2g}$, brookite) | 443 (B$_{2g}$, brookite) |
| 631 (A$_{1g}$, cassiterite) | 516 (B$_{2g}$, brookite) | 516 (B$_{2g}$, brookite) | 516 (B$_{2g}$, brookite) |
| 773 (B$_{2g}$, cassiterite) | 635 (E$_g$, anatase) | 635 (E$_g$, anatase) | 635 (E$_g$, anatase) |

Thus, the Raman spectra confirm the data obtained by the XRD method. The formation of the metastable brookite phase is observed in SnTi-1 and SnTi-2 composites. Anatase can play the role of a stabilizer for this phase [58]. A correlation among the surface enthalpies of the TiO$_2$ three polymorphs and their particle size was found by Zhang and Banfield [59]. The formation energies of anatase, brookite and rutile are sufficiently close that they can be reversed by small differences in surface energies. Zhu et al. [60] developed an empirical expression on a critical grain size of brookite, which determines the transition sequence between anatase and brookite. These transformations become noticeable with prolonged isothermal annealing at temperatures above 500 $^\circ$C. To avoid the changes in phase composition and crystallite size of nanocomposites subjected to post synthesis annealing at 500 $^\circ$C, the maximum temperature during the manufacture of sensor elements and gas sensor measurements did not exceed 300 $^\circ$C.

3.2. Gas Sensor Properties

As discussed in the review [8], depending on the operating temperature the change of the resistance of n-type semiconductor oxides when interacting with formaldehyde is due to HCHO oxidation with chemisorbed oxygen O$_{\text{ads}}^{2-}$ to HCOOH or CO$_2$:

$$\beta \cdot \text{HCHO}_{\text{gas}} + O_{\text{ads}}^{2-} = \beta \cdot \text{HCOOH}_{\text{gas}} + \alpha \cdot e^-$$  \hspace{1cm} (1)

$$\beta \cdot \text{HCHO}_{\text{gas}} + 2O_{\text{ads}}^{2-} = \beta \cdot \text{CO}_2_{\text{gas}} + \beta \cdot \text{H}_2\text{O}_{\text{gas}} + 2\alpha \cdot e^-$$  \hspace{1cm} (2)

At constant temperature and HCHO concentration, the value of the sensor response will depend on the concentration and the predominant form of chemisorbed oxygen on the surface of the semiconductor oxide.

According to the literature [20,61–64], the interaction of UV light with TiO$_2$ involves the following processes: electron-hole pairs generation (3), oxygen photodesorption (4), formation of “active” chemisorbed oxygen (5), which is able to oxidize formaldehyde even at room temperature (6)

$$h^+ + e^- \rightarrow \text{TiO}_2 \rightarrow h^+ (hv) + e^- (hv)$$  \hspace{1cm} (3)

$$h^+ (hv) + O_{\text{ads}}^{2-} \rightarrow O_{2\text{gas}}$$  \hspace{1cm} (4)

$$O_{2\text{gas}} + e^- (hv) \rightarrow O_{\text{ads}}^{2-} (hv)$$  \hspace{1cm} (5)

$$\text{HCHO}_{\text{gas}} + O_{\text{ads}}^{2-} (hv) \rightarrow \text{CO}_2_{\text{gas}} + \text{H}_2\text{O}_{\text{gas}} + e^-$$  \hspace{1cm} (6)
Under UV light, hydroxyl groups presented on the TiO$_2$ surface can also pass into the “active” form (7) and then participate in the oxidation of formaldehyde (8):

$$\text{OH}^{-} + h^+ (hv) \rightarrow \text{OH}^* (hv)$$ \hspace{1cm} (7)

$$\text{HCHO}_{(\text{gas})} + 2\cdot\text{OH}^*(hv) \rightarrow \text{CO}_2_{(\text{gas})} + \text{H}_2\text{O}_{(\text{gas})} + 2\cdot\text{H}^+ + 2\cdot\text{e}^- \hspace{1cm} (8)$$

Figure 6 demonstrates the change in the resistance of nanocomposites with the cyclic changes in the composition of the gas phase “air (15 min)”–“0.6 ppm HCHO in air (15 min)”. The measurements were carried out in the temperature range of 300–50 °C in dark conditions (Figure 6a) and under periodic UV illumination (Figure 6b). At a fixed temperature, TiO$_2$@SnO$_2$ nanocomposites have a higher resistance than unmodified SnO$_2$ (SnTi-0). UV illumination leads to reduced resistance of nanocomposites by 1.5–3 times. In all cases in the presence of HCHO, the resistance of SnO$_2$ and TiO$_2$@SnO$_2$ nanocomposites decreases due to the oxidation of formaldehyde by chemisorbed oxygen. In dark conditions, the maximum response was detected for the SnTi-0 sample. UV illumination leads to a slight decrease in the temperature of the maximum sensor signal to 150 °C. In dark conditions, the maximum response was detected for the SnTi-0 sample. UV illumination leads to a slight decrease in the temperature of the maximum sensor signal to 150 °C. Such a decrease in the sensor response can be caused by a decrease in the concentration of chemisorbed oxygen participating in the oxidation of formaldehyde by reactions (1) and (2), due to the partial desorption of oxygen from the surface of semiconductor oxides under UV light [65].

Figure 6. Resistance of the TiO$_2$@SnO$_2$ nanocomposites in the temperature range 300–50 °C under periodic change of the gas phase composition (a) in dark conditions; (b) under periodic UV ($\lambda_{\text{max}} = 365$ nm) illumination.

The obtained results allowed us to draw the temperature dependence of the sensor response $S = R_{\text{min}} / R_{\text{gas}}$ (Figure 7a). The maximum sensor response of unmodified SnO$_2$ (SnTi-0) is observed at $T = 20 °C$. The introduction of Ti-containing phases leads to a decrease in the temperature of the maximum sensor signal to 150 °C. In dark conditions, the maximum response was detected for the SnTi-2 nanocomposite. The use of UV illumination does not change the position of the maxima on the temperature dependence of the sensor response, but unexpectedly it leads to a slight decrease in the signal value in the low temperature range of 50–150 °C. Such a decrease in the sensor response can be caused by a decrease in the concentration of chemisorbed oxygen participating in the oxidation of formaldehyde by reactions (1) and (2), due to the partial desorption of oxygen from the surface of semiconductor oxides under UV light [65]. Figure 7b shows the temperature dependences of the effective photoresponse $S_{\text{ph}}$ of nanocomposites in background air calculated as $S_{\text{ph}} = R_{\text{dark}} / R_{\text{light}}$, where $R_{\text{light}}$ is the minimum resistance achieved during the sensor illumination, and $R_{\text{dark}}$ is the maximum
resistance achieved in the dark period [66]. The maximum photoresponse corresponds to a temperature range of 150–200 °C. A decrease in the \( S_{Ph} \) value with an increase in the measurement temperature up to 250–300 °C is due to the contribution of thermal oxygen desorption in dark conditions.

![Figure 7](image_url)

**Figure 7.** (a) Temperature dependencies of sensor response of the TiO\(_2@\)SnO\(_2\) nanocomposites toward 0.6 ppm HCHO in air in dark conditions (left) and under UV periodic illumination (right); (b) Temperature dependencies of effective photoresponse \( S_{Ph} \) of the TiO\(_2@\)SnO\(_2\) nanocomposites in background air.

The dynamic sensor characteristics, response time \( \tau_{90} \) and recovery time \( \tau_{90}^* \), are presented in Figure 8. Even though the absolute values of response time and recovery time are strongly dependent on the parameters of the testing system (geometry and size of the measurement cell, the method to switch the gases, the gas flow rate), they are useful to compare the dynamic sensor characteristics of materials if measurements are performed in identical conditions. With a decrease in the operating temperature, an increase in both the response and recovery times is observed. It should be noted that the sensor based on unmodified SnO\(_2\) is characterized by significantly worse dynamic characteristics than sensors based on TiO\(_2@\)SnO\(_2\) nanocomposites, which are close to each other. Such a difference may be due to a decrease in the degree of sintering of SnO\(_2\) nanoparticles in nanocomposites as compared to unmodified tin dioxide.

![Figure 8](image_url)

**Figure 8.** Temperature dependencies of response time \( \tau_{90} \) (left) and recovery time \( \tau_{90}^* \) (right) during detection of 0.6 ppm HCHO in air in dark conditions.
To clarify the mechanism of formaldehyde oxidation on the surface of semiconductor oxides, the in situ DRIFT studies have been conducted. In situ DRIFT spectra of the unmodified SnO₂ (SnTi-0) and SnTi-2 nanocomposite during HCHO adsorption at room temperature are shown in Figure 9.

![Figure 9](image_url)

**Figure 9.** In situ DRIFT spectra of the unmodified SnO₂ (SnTi-0) (a) and SnTi-2 nanocomposite (b) during HCHO adsorption at room temperature.

The bands of weakly bonded forms at 1202, 1742, 1766 and 3010 cm⁻¹ for SnTi-0 and at 1768 cm⁻¹ for SnTi-2 attributed to molecular adsorption form of HCHO with the formation of hydrogen bonds between its carbonyl oxygen and surface hydroxyl groups [67–69]. The formation of CO₂ (at 2337 and 2365 cm⁻¹) was observed on SnTi-0 after 5 min of HCHO adsorption, moreover these bands grew in intensity with the increase of the adsorption time [70]. In SnTi-2 spectra the bands at 1344 and 1592 cm⁻¹ are assigned to COO symmetric stretching and COO asymmetric stretching of formate species [71,72]. The bands located at 2838, 2890 and 2590, 2868 cm⁻¹ are assigned to CH stretching of formate species [68,73,74]. The bands at 2936 cm⁻¹ for SnTi-0 and 2930 cm⁻¹ for SnTi-2 were assigned to the characteristic peak of dioxymethylene (DOM) intermediate [71]. The other DOM bands also were identified at 1050, 1107, 1145 cm⁻¹ for SnTi-0 and 1066, 1107, 1146, 1165, 1478 cm⁻¹ for SnTi-2 [67,68].

Figure 10 shows the DRIFT spectra of the SnTi-2 nanocomposite obtained during the heating in dry air at T = 300 °C after formaldehyde adsorption at room temperature. From the results, it can be seen that the formats are intensively desorbed from the surface of the nanocomposite, as evidenced by decreasing of their characteristic vibrational modes at 1346, 1382 and 1553 cm⁻¹ [68,71,72]. However, at such a high temperature, there is an increase in the intensity of dioxymethylene species, the bands of which are at 1050, 1108 and 1450 cm⁻¹ [67,68], which indicates partially HCHO oxidation to DOM. Most likely, at T=300 °C, formaldehyde is oxidized to CO₂ and H₂O, as a result of which hydroxyl groups of water accumulate on the surface (increase in the intensity of OH bands at 3550 and 3630 cm⁻¹) and CO₂ desorption occurs (decrease in intensity at 2340 cm⁻¹); at room temperature CO₂ is accumulated on the SnTi-0 surface (Figure 9a). The assignment of IR bands for intermediates is summarized in Table 3.
At first, formaldehyde molecularly adsorbs as a whole via strong hydrogen-bonding interactions (9). Desorption of formaldehyde is in competition with the reaction between formaldehyde and co-adsorbed surface oxygen to yield formate HCOO\(^-\), which can proceed via formation of dioxyethylene H\(_2\)COO\(^-\) intermediate (10),(11) [69]. For SnTi-0 sample there are two weak bands at 2337 and 2365 cm\(^{-1}\) indicated.

**Table 3. Assignment of IR bands (cm\(^{-1}\)) for the intermediates of HCHO oxidation.**

| Sample  | Formaldehyde HCHO | DOM H\(_2\)COO\(^-\) | Formate HCOO\(^-\) | Other Bands       |
|---------|-------------------|-----------------------|--------------------|------------------|
| SnTi-0  | 1202 \(\alpha\) (CH\(_2\)) | 1050 \(\nu\) (CO) | 2838 \(\nu\) (CH) | 2337 CO\(_2\) |
|         | 1742 \(\nu\) (CO)   | 1107 \(\rho\) (CH\(_2\)) | 2890 \(\nu\) (CH) | 2365 CO\(_2\) |
|         | 1766 \(\nu\) (CO)   | 1145 \(\rho\) (CH\(_2\)) |                   |                  |
|         | 3010               | 2936 \(\delta\) (CH\(_2\)) |                   |                  |
| SnTi-2  | 1768 \(\nu\) (CO)   | 1066 \(\nu\) (CO) | 1344 \(\nu\)_\(_s\) (COO) | 2340 CO\(_2\) |
|         |                    | 1107 \(\rho\) (CH\(_2\)) | 1346 \(\nu\)_\(_s\) (COO) | 3550 \(\nu\) (OH) |
|         |                    | 1146 \(\rho\) (CH\(_2\)) | 1382 \(\delta\) (CH) | 3630 \(\nu\) (OH) |
|         |                    | 1165 \(\rho\) (CH\(_2\)) | 1553 \(\nu\)\(_{\text{gas}}\) (COO) |             |
|         |                    | 1450 \(\delta\)_\(_s\) (CH\(_2\)) | 1592 \(\nu\)\(_{\text{gas}}\) (COO) |             |
|         |                    | 1478 \(\delta\)_\(_s\) (CH\(_2\)) | 2590               |             |
|         |                    | 2930 \(\delta\) (CH\(_2\)) | 2868 \(\nu\) (CH) |             |

So, for HCHO oxidation, oxygen ions adsorbed on the surface of the nanocomposites play a key role in the generation of the surface formates. According to the results of the in situ DRIFT analysis and literature review [67–70,75,76] we propose a reaction mechanism as depicted in (9)–(12):

\[
HCHO_{\text{(gas)}} \rightarrow HCHO_{\text{(ads)}} \tag{9}
\]

\[
\beta \cdot HCHO_{\text{(ads)}} + O^\text{ads}_{\beta} \rightarrow \beta \cdot H_2COO^-_{\text{(ads)}} + (\alpha - 1) e^- \tag{10}
\]

\[
\beta \cdot H_2COO^-_{\text{(ads)}} + O^\text{ads}_{\beta} \rightarrow \beta \cdot HCOO^2^-_{\text{(ads)}} + \beta \cdot OH^\text{(ads)}_{\alpha - 1} \tag{11}
\]

\[
2\beta \cdot HCOO^2^-_{\text{(ads)}} + O^\text{ads}_{\beta} \rightarrow 2\beta \cdot CO_2 + \beta \cdot H_2O + (4\beta + a) e^- \tag{12}
\]

![In situ DRIFT spectra of the SnTi-2 nanocomposite obtained during the heating in dry air at \(T = 300 \degree C\) after formaldehyde adsorption at room temperature.](image)

**Figure 10.** In situ DRIFT spectra of the SnTi-2 nanocomposite obtained during the heating in dry air at \(T = 300 \degree C\) after formaldehyde adsorption at room temperature.
the appearance of carbon dioxide [64,77]. In this case, CO₂ and H₂O were formed as the result of oxidation of formate ions (12) of chemisorbed oxygen on semiconductor oxides [78], reaction (10) proceeds without changing the electron concentration in the conduction band of the semiconductor, that causes the absence of a sensor response at T = 50 °C (Figure 6).

The observed effect of Ti-containing phases on the sensor response of SnO₂ toward HCHO in dark conditions should be explained based on the model considering the formation of n-n heterocontact at the SnO₂/TiO₂ interface. The estimated band alignment of the SnO₂ (cassiterite) and TiO₂ (anatase) is presented on Figure 11a [24,79,80]. The available lower-energy conduction band states stimulate electron transfer to n-SnO₂ [81]. As a result, the depletion layer is formed at n-TiO₂ surface due to loss of electrons, and accumulation layer is formed at SnO₂ surface due to added electrons. In turn, an increase in the electron concentration stimulates the chemisorption of oxygen species enhancing the response formed due to reactions (1). The scheme in Figure 11a is constructed for the heterocontact SnO₂ (cassiterite)/TiO₂ (anatase), since the anatase phase is present in all nanocomposites (as it follows from the data of Raman spectroscopy). Brookite (revealed in SnTi-1 and SnTi-2 nanocomposites) is the least studied polymorph of TiO₂. However, from the data of Ref. [82] it follows that the bottom of the conduction band of brookite lies above the bottom of the conduction band of anatase. Thus, in the formation of a heterocontact SnO₂ (cassiterite)/TiO₂ (brookite), electron transfer will also occur from TiO₂ (brookite) to SnO₂, increasing the chemisorption of oxygen on its surface. An increase in the concentration of chemisorbed oxygen on the surface of nanocomposites compared with unmodified SnO₂ is confirmed by the method of thermo-programmed reduction with hydrogen (TPR-H₂). Figure 11b shows the temperature dependencies of the hydrogen consumption during the reduction of unmodified SnO₂ and SnTi-1 nanocomposite. The reduction of SnO₂ with hydrogen occurs in the temperature range of 430–800 °C, the maximum H₂ consumption is observed at T = 620 °C. The introduction of Ti-containing phases leads to a shift of the H₂ consumption towards lower temperatures 570–600 °C. Such a change in the TPR-H₂ profiles may be due to the reduction of highly dispersed Ti-containing phases. According to the reports [83–85], the reduction of TiO₂ with hydrogen occurs at T > 400 °C, the maximum H₂ consumption is observed at T = 530–650 °C, depending on the TiO₂ dispersion. Another feature of the TPR-H₂ profiles is the presence of hydrogen absorption peaks in the low-temperature range of 100–400 °C. This corresponds to the interaction of hydrogen with oxygen-containing particles (chemisorbed oxygen, hydroxyl groups, etc.) on the surface of highly dispersed semiconductor oxides. The reduction of TiO₂@SnO₂ nanocomposites is accompanied by more significant hydrogen consumption in the low-temperature region that indicates a higher concentration of oxygen-containing species on its surface. An increase in the concentration of chemisorbed oxygen on the surface of nanocomposites provides an increase in their resistance compared to unmodified SnO₂. At the same time, due to the photodesorption of chemisorbed oxygen under UV light, TiO₂@SnO₂ nanocomposites are characterized by the larger photoresponse in the background air and demonstrate a more significant decrease in the sensor response to HCHO.

Thus, we are forced to conclude that in the case of TiO₂@SnO₂ nanocomposites, the amplitude of the sensor response when detecting HCHO in the sub-ppm range is determined mainly by the SnO₂/TiO₂ interface. The role of UV light is to enhance the photodesorption of oxygen, and the processes of HCHO oxidation by photoactivated particles (reactions (6) and (8)) do not contribute to the sensor response.

The dependence of the sensor response on the HCHO concentration in air was studied in dark conditions and under periodic UV illumination at 150 °C during the stepwise increase and subsequent stepwise decrease in the HCHO concentration (Figure 12). The results obtained allowed us to build the calibration curves (Figure 13a) and to determine the lower detection limit (LDL). As in the case of measurements at different temperatures, when using UV illumination, a decrease in the sensor response toward HCHO is observed, that may be due to the photodesorption of chemisorbed oxygen under UV light. The LDL values were calculated from the calibration curves as the gas concentration corresponding to the minimum measurable sensor signal R_{av}/(R_{av} − 3σ), where R_{av} is the average
sensor resistance in air at 150 °C, σ is the standard deviation of the resistance in air. A decrease in the sensitivity of nanocomposites is accompanied by an increase in LDL from 9–15 to 30–32 ppb (Table 4).

![Figure 11](image1.png)

**Figure 11.** (a) Estimated band alignment of the SnO2 (cassiterite) and TiO2 (anatase) phases (left) and SnO2/TiO2 n–n heterocontact (right); (b) TPR-H2 profiles of unmodified SnO2 (SnTi-0) and TiO2@SnO2 nanocomposites.

![Figure 12](image2.png)

**Figure 12.** Resistance of the TiO2@SnO2 nanocomposites at T = 150 °C under stepwise change of the HCHO concentration (a) in dark conditions; (b) under periodic UV (λmax = 365 nm) illumination. The numbers in the figure correspond to HCHO concentration (ppm).

The comparison of the sensor response toward 0.06–0.6 ppm HCHO for SnTi-2 nanocomposite with the literature data [7–11,20–23,28,86–117] is shown in Figure 13b and Table 5. There are very few papers that consider the detection of formaldehyde in a practically important sub-ppm concentration range. TiO2@SnO2 nanocomposites exhibit high sensitivity to HCHO in the sub-ppm range. Higher sensor response values were obtained only by the authors of [86], where metastable In4Sn3O12 was used as sensitive material at 350 °C and in Ref. [7], where Si modified SnO2 was used at 400 °C. It should be noted that TiO2@SnO2 nanocomposites have comparable sensitivity at much lower measurement temperature (150 °C vs. 350 °C or 400 °C), which can provide a significant reduction in the power consumption of semiconductor gas sensor.

In addition to reducing power consumption, a sufficiently low measurement temperature allows one to achieve an increase in the selectivity of sensors when detecting various VOCs. The cross sensitivity of SnO2 and TiO2@SnO2 nanocomposites was studied at a measurement temperature of 150 °C in the detection of formaldehyde, benzene, and acetone (Figure 14). It can be noted that the synthesized materials have low cross-sensitivity to benzene in the wide concentration range. As for
acetone, the interference of signals can occur if acetone concentration is in the range of $C > 1$ ppm and at least 20 times higher than formaldehyde concentration. SnTi-2 nanocomposite is characterized by the lowest response to acetone.

Figure 13. (a) Calibration curves for the HCHO detection using TiO$_2$@SnO$_2$ nanocomposites at $T = 150$ °C under stepwise change of the HCHO concentration in dark conditions (left) and under UV periodic illumination (right). (b) Comparison of the values of the sensor response of SnTi-2 nanocomposite (triangles) with the literature data [8–11,20–23,28,87–117] (squares), Ref. [7] (diamonds) and Ref. [86] (circles). The color of the symbol corresponds to the measurement temperature. For correct comparison all the data were recalculated as $S = (R_{\text{air}}/R_{\text{gas}} - 1)*100\%$.

Table 4. Sensor characteristics of unmodified SnO$_2$ and TiO$_2$@SnO$_2$ nanocomposites in HCHO detection at 150 °C.

| Sample  | S (to 0.06 ppm) | LDL, ppb | $R_{av}$, Ohm | $\tau_{90}$, s | $\tau_{90}^*$, s |
|---------|-----------------|----------|----------------|----------------|-----------------|
| SnTi-0  | 1.34            | 1.17     | 9              | 30             | 1.2\times10^5   | 1.1\times10^5   | 360             | 780             |
| SnTi-1  | 1.49            | 1.20     | 9              | 32             | 1.2\times10^6   | 7.4\times10^5   | 120             | 660             |
| SnTi-2  | 1.72            | 1.26     | 15             | 32             | 6.5\times10^7   | 2.2\times10^7   | 120             | 660             |
| SnTi-3  | 1.48            | 1.21     | 10             | 30             | 5.8\times10^6   | 3.5\times10^6   | 120             | 680             |

Table 5. Literature data on sensor response $S = (R_{\text{air}}/R_{\text{gas}} - 1)*100\%$ of metal oxide semiconductor gas sensor in formaldehyde detection.

| Material                                      | HCHO conc., ppm | Response S | $T$, °C | Ref. |
|-----------------------------------------------|------------------|------------|---------|------|
| Si-SnO$_2$ FSP * films                       | 0.003            | 6.5        | 400     | [7]  |
| In$_2$Sn$_3$O$_{12}$ thin films               | 0.02             | 110        | 350     | [86] |
| CuO nanocubes                                 | 0.05             | 4          | 300     | [87] |
| SnO$_2$-Au                                    | 0.05             | 2          | 300     | [8]  |
| In$_2$O$_3$ nanolamellas                      | 0.08             | 4          | 300     | [88] |
| TiO$_2$ UV activation                         | 0.1              | 67         | RT      | [22] |
| SnO$_2$-NiO                                   | 0.3              | 18         | 300     | [89] |
| Ag-LaFeO$_3$                                  | 0.5              | 2400       | 40      | [90] |
| Ag-LaFeO$_3$                                  | 1                | 2400       | 90      | [91] |
| TiO$_2$ hollow microspheres                   | 5                | 3900       | RT      | [23] |
| Au@ZrO$_2$ core-shell structure               | 5                | 957        | RT      | [92] |
| CdO-In$_2$O$_3$                               | 10               | 9900       | 95      | [93] |
| SnO$_2$ mesoporous                            | 10               | 9900       | 150     | [94] |
| TiO$_2$ macroporous                           | 10               | 6900       | RT      | [20] |
| Cd-In$_2$O$_3$ hollow fibers                  | 10               | 1500       | 280     | [95] |
Comparing the sensor characteristics of unmodified SnO$_2$ and TiO$_2$@SnO$_2$ nanocomposites in the detection of formaldehyde at 150 °C (Table 4) we can conclude that the SnO$_2$ is inferior in the magnitude of the sensor response and the dynamic characteristics (response and recovery time). For HCHO detection at concentrations of 60 ppb and above, the SnTi-2 nanocomposite, which exhibits the highest sensor response and the dynamic characteristics (response and recovery time). For

$$S = \frac{R_{\text{air}}}{R_{\text{gas}}} \times 100\%.$$  

**Table 5. Cont.**

| Material | HCHO conc., ppm | Response $S$ | $T$, °C | Ref. |
|----------|-----------------|--------------|----------|------|
| Ag-SnO$_2$ nanoparticles | 10 | 1340 | 125 | [96] |
| SnO$_2$/In$_2$O$_3$ nanofibers | 10 | 650 | 375 | [97] |
| SnO$_2$ nanowires | 10 | 145 | 270 | [98] |
| SnO$_2$/α-Fe$_2$O$_3$ hollow spheres | 10 | 100 | 250 | [99] |
| Pd-SnO$_2$ thin films | 10 | 55 | 250 | [100] |
| NiO thin films | 10 | 50 | 300 | [101] |
| TiO$_2$ nanotube arrays | 10 | 7 | RT | [21] |
| La$_2$O$_3$-SnO$_2$ thin films | 18.7 | 5400 | 250 | [102] |
| NiO thin films | 20 | 330 | 340 | [103] |
| ZnO UV activated | 50 | 10700 | RT | [104] |
| TiO$_2$-SnO$_2$ | 50 | 3000 | 360 | [28] |
| La$_{1-x}$Sr$_x$FeO$_3$ | 50 | 2500 | 200 | [105] |
| SnO$_2$-MWCNT | 50 | 300 | 250 | [106] |
| Au@SnO$_2$ core-shell structure | 50 | 190 | RT | [107] |
| SnO$_2$ microspheres | 100 | 3730 | 200 | [108] |
| Cd$_2$-TiO$_2$/SnO$_2$ | 100 | 1400 | 320 | [109] |
| ZnO/ZIF | 100 | 1100 | 300 | [110] |
| Au-ZnO octahedrons | 100 | 660 | RT | [111] |
| γ-Fe$_2$O$_3$ | 100 | 500 | 320 | [77] |
| α-Fe$_2$O$_3$ | 100 | 52 | 325 | [112] |
| CdO/Sn-ZnO | 200 | 200000 | 200 | [113] |
| ZnO-MnO$_2$ | 200 | 2600 | 320 | [114] |
| Ga-ZnO | 205 | 13 | 400 | [115] |
| LaFeO$_3$ hollow nanospheres | 500 | 1900 | 260 | [116] |
| ZnO | 1000 | 99600 | 210 | [117] |

* Flame spray pyrolysis; * Multiwall carbon nanotubes; ‡ Zeolitic Imidazolate Framework.

**Figure 14.** Cross sensitivity of SnO$_2$ (SnTi-0, black), SnTi-1 (red), SnTi-2 (blue) and SnTi-3 (green) nanocomposites toward HCHO (circles), benzene (squares) and acetone (triangles) at 150 °C.
As a summary, we have to conclude that compared to the sensor characteristics described in [7,86,118], the sensors based on TiO$_2$@SnO$_2$ nanocomposites are inferior in sensitivity and selectivity. However, their advantage is significantly reduced operating temperature. The increase in sensitivity while maintaining a low operating temperature should be possible due to the addition of modifiers of different chemical nature on the surface of TiO$_2$@SnO$_2$ nanocomposites. The increase in selectivity, in particular towards humidity, can be achieved using passive filters—selective membranes based on SiO$_2$ [6,118–120] or metal organic frameworks [110,121] as well as by the creation of multi-sensor systems operating using mathematical signal processing [6,122].

4. Conclusions

Nanocomposites TiO$_2$@SnO$_2$ obtained by ALD synthesis were investigated as sensitive materials for sub-ppm formaldehyde detection in dark conditions and under periodic UV (\(\lambda_{\text{max}} = 365\) nm) illumination. As observed by XRD and Raman spectroscopy, all nanocomposites contain nanocrystalline SnO$_2$ cassiterite and TiO$_2$ anatase as the main crystalline phases. Depending on Ti content in nanocomposites predeterminded by the number of ALD cycles, the minor TiO$_2$ phases brookite, rutile and anosovite have been found. A thorough study of nanocomposites using FTIR and TPR-H$_2$ methods made it possible to establish that nanocomposites have a higher concentration of chemisorbed oxygen and surface hydroxyl groups compared to unmodified SnO$_2$. When detecting formaldehyde in the sub-ppm range, TiO$_2$@SnO$_2$ nanocomposites exhibit a higher sensor signal than SnO$_2$ and a decrease in the optimal measurement temperature by 50 $^\circ$C. This result is explained based on the model considering the formation of n-\(n\) heterocontact at the SnO$_2$/TiO$_2$ interface. TiO$_2$@SnO$_2$ nanocomposites have high sensitivity toward HCHO at quite low measurement temperature 150 $^\circ$C that can provide a significant reduction in the power consumption and an increase in the selectivity of semiconductor gas sensors when detecting various VOCs.

Unexpectedly, UV illumination leads to a decrease in sensor response compared with the results obtained in dark conditions. So, we have to conclude that in the case of TiO$_2$@SnO$_2$ nanocomposites, the amplitude of the sensor response toward sub-ppm HCHO concentrations is determined mainly by the SnO$_2$/TiO$_2$ interface. The UV light stimulates the photodesorption of oxygen, while the processes of HCHO oxidation by photoactivated particles do not contribute to the sensor response.

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