

Enhanced hydrogen gas sensing using a tin/activated carbon modified titanium dioxide nanocomposite

Elham Hani Naser¹, Baha'a A. M. Al Hilli², Ashwaq A. Jabor¹,
 Alaa H. Alminshid³ , Hayder A. Alalwan^{4*} 

¹ Scientific Research Commission, Ministry of Higher Education and Scientific Research, Baghdad- Iraq

² Physics Dept, College of Education, Mustansiriyah University, Baghdad, Iraq

³ Chemistry Department, College of Science – Mustansiriyah University, Baghdad, Iraq

⁴ Department of Mechatronics Engineering Technology, College of Technical Engineering-Baghdad, Middle Technical University, Baghdad, Iraq

* Corresponding author's e-mail: hayder.alalwan@mtu.edu.iq

ABSTRACT

This work presents a cost-effective TiO₂ nanocomposite doped with Sn⁺² (1.8wt%) and activated carbon (1 wt%) used as an active layer in hydrogen gas sensing applications. The prepared nanocomposite has a particle size of 46 ± 2 nm, roughness 4.31 nm, high surface area (202 ± 11 m²/g), and a bandgap of 2.7 eV. It was synthesized via a simple sol-gel method followed by calcination at 500 °C, to enhance room-temperature H₂ gas sensing. A thin film (470 ± 10 nm thick) was deposited on silicon via chemical bath deposition, exhibiting an anatase-rutile structure, 150 ± 10 nm grains, 3.2 eV bandgap, and roughness (45 nm RMS) as confirmed by XRD, FTIR, AFM, SEM, and UV-Vis analyses. The sensor demonstrated superior performance to H₂ (100–5000 ppm), achieving 45.7% sensitivity at 1000 ppm, response/recovery times of 18/42 s, showing competitive performance compared to selected Sn-doped TiO₂ and carbon-based sensors due to synergistic oxygen vacancies, porosity, and p-n junction effects – enabling reliable detection for safety-critical applications.

Keywords: tin-doped TiO₂, thin film chemi resistor, sol-gel method, chemical precipitation, room-temperature gas sensing.

INTRODUCTION

Globally, hydrogen gas continues to grow rapidly, by roughly 6% per year, reaching \$155 billion by 2022 [1]. Hydrogen is used as an industrial gas because it plays a major role in the decarbonization of the world's energy supply. While hydrogen performs well as a fuel, it is considered an explosion hazard among many other gas fuels. Thus, hydrogen leaks are common, and even very small leaks can be easily ignited, potentially affecting ecosystems, biodiversity, and human lifestyles. Therefore, increasing the uptake of hydrogen technologies requires continuous monitoring of the safety of reliable hydrogen gas systems. Such a gas, odorless, tasteless, and colorless, once leaked,

needs to be detected by developing various sensors, including electrochemical gas sensors, solid electrolyte gas sensors, graphene-based gas sensors, and metal oxide gas sensors [2].

Metal oxide materials have been tested as promising and effective conductive gas sensors, which detect gases due to the shift occurring in their resistance or conductance of the metal oxide materials [3]. This sensitivity is tied to the adsorption processes happening at the gas-thin film surface interface [4]. Researchers pointed out that the chemical sensors perform better if the gas-sensing materials show a high response to the adsorption/desorption parameters defined for oxygen or targeted gases [5]. Moreover, metal oxide semiconductor (MOS) devices get a lot of use in gas

detection due to their reliability, simplicity, cost-effectiveness, and ease of mass production [6]. Tungsten oxide (WO_3) [7], tin oxide (SnO_2) [8], and zinc oxide (ZnO) NPs are among the most effective metal oxide nanoparticles [9], which are used for sensor applications. ZnO is found to be adequate for chemical gas detectors due to several advantages, such as low cost, sensitivity to gases, high chemical stability, and non-toxicity [10]. Because of its high surface-to-volume ratio [11], broad direct band-gap ($\sim 3.37\text{ eV}$) at room temperature [10], and high excitonic binding energy (60 meV) [12], ZnO NPs have been used in different techniques to make high-sensitivity gas sensors, such as the radio frequency RF technique [13].

Other highly privileged materials increasingly utilized in gas sensors are the nanocomposites [14], which have shown great promise due to their unique physicochemical properties in different applications [15–17]. Activated carbon has been reported to be an excellent adsorbent material due to its high surface area and large porous sites [18]. Once it is doped with metal oxide nanoparticles, it can modify the surface chemistry and morphology of these materials and enhance adsorption capacity by boosting the interaction between gas molecules and the NPs' surface. Incorporating tin(IV) chloride (SnCl_4), used as a precursor in a nanocomposite with activated carbon, has demonstrated high efficiency in adsorption for environmental and chemical applications [19].

Recent developments in MOS for H_2 gas sensing have been centered on the doping of TiO_2 with metals, such as Sn [20] and carbon-based materials [21] to improve the sensitivity, response time, and selectivity at room temperature. For instance, Sn-doped TiO_2 nanoparticles were found to exhibit 85% sensitivity to 100 ppm H_2 , with a 2.8 eV bandgap and a 25 nm grain size, but suffered from slow recovery ($>120\text{ s}$) due to limited surface area [22]. Similarly, TiO_2 -activated carbon composites achieved detection limits of 10 ppm via increased porosity (BET surface $\sim 800\text{ m}^2/\text{g}$), but showed poor stability under humid conditions [23]. Triple-doped systems like TiO_2 -Sn-graphene showed superior performance (response time $<30\text{ s}$, sensitivity 150%) but required complex hydrothermal synthesis at high pressures [24]. Thus, several gaps are present in this field, such as (i) a lack of simple low-temperature synthesis for Sn/AC- TiO_2 , (ii) limited room-temperature response/recovery, and (iii) insufficient comparison with thin films. Nonetheless, one problem still exists in terms of

engineering, that is, the need for simplicity, low temperatures (room temperature), hydrogen sensitivity, quick response and recovery time, and fabrication scalability, since the current titanium dioxide hydrogen sensors have either complex preparation procedures, low surface area, poor recovery, or a lack of comparison between nanocomposite powders and thin films.

This work addresses these gaps by combining Sn^{+2} and activated carbon via a simple sol-gel route, yielding a 2.7 eV bandgap, $46 \pm 2\text{ nm}$ grains, and $202 \pm 11\text{ m}^2/\text{g}$ surface area—enabling faster adsorption/desorption and cost-effective scalability without specialized equipment. Specifically, this work focused on the synthesis of a remarkable nanocomposite TiO_2 NPs doped with Tin (Sn^{+2}) at 1.8 wt% and activated carbon (AC) at 1.0 wt% concentrations using a straightforward Sol-Gel method. Then, a thin film was prepared by depositing a silicon substrate in a $\text{TiO}_2/\text{Sn}/\text{AC}$ solution using chemical bath deposition at room temperature. The Sol-Gel method is used for the synthesis of high-purity materials shaped as powders, thin film coatings, monoliths, fibers, and self-supported bulk structures [25], whether only TiO_2 NPs or doped TiO_2 NPs with other constituents. The advantage of this method expedites the synthesis of nanometer-sized crystallized TiO_2 powder with high purity at relatively low temperature, homogeneity, ease of preparation, and ease of introducing dopants [26]. Therefore, this study highlights the proper synthesis of new nanocomposites and thin films, which are successively applied for gas sensor applications.

MATERIALS AND METHODS

Materials

Titanium (IV) tetraisobutoxide (TTIB) 99.9% used as a titanium precursor. Tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and activated carbon (AC) were used for doping, while ethanol and acetylacetone were used as solvents and stabilizing agents; all were supplied by Sigma-Aldrich.

Sol-gel preparation

Pure TiO_2 NPs were prepared by dissolving 10 mL of titanium (IV) tetraisobutoxide (TTIB, 97%, Sigma-Aldrich) in 20 mL of absolute ethanol (99.8%) under vigorous magnetic stirring (500 rpm) at $25\text{ }^\circ\text{C}$. Separately, four milliliters of

distilled water and two milliliters of nitric acid (0.1 M) were mixed. This hydrolysis solution was added dropwise to the TTIB solution over 30 min, maintaining a pH between 2 and 3. The sol was stirred for two hours, then aged 24 hours at room temperature to form a yellow gel. The gel was dried at 100 °C for four hours and calcinated at 500 °C for two hours (ramp rate: 5 °C/min) in air to yield white TiO₂ powder.

TiO₂/Sn/AC nanocomposite (1.8 wt% Sn, 1 wt% AC) was prepared by mixing 9.5 milliliters TTIB (0.032 mol) with 20 milliliters ethanol and one milliliter acetylacetone (stabilizer, 1:20 molar ratio to TTIB) under stirring (500 rpm, 25 °C). In a separate beaker, 0.21 g SnCl₂·2H₂O (0.00064 mol Sn, 1.8 wt% Sn/Ti) and 0.12 g activated carbon (AC, surface area >1000 m²/g) were dissolved/dispersed in four milliliters of distilled water plus 20 milliliters of ethanol and two milliliters of nitric acid (0.1 M). This dopant solution was added dropwise over 30 min to the TTIB mixture. The sol was stirred for four hours (500 rpm), aged for 24 hours to gel, dried at 100 °C (four hours), and calcined at 500 °C (two hours, 5 °C/min). The resulting gray powder was ultrasonically cleaned (Elmasonic S-300H, 37 kHz, 90 milliliters of ethanol, 90 min), centrifuged (5000 rpm, 10 minutes repeated three times), and dried at 100 °C.

Thin film preparation

Chemical bath deposition (CBD) is one of the wet chemical methods available to grow

semiconductor materials on solid surfaces (as substrates). The desired material to be deposited can be in the form of a thin film with a dense structure or a porous-type structure. The films can be crystalline, amorphous, single-phase, or multi-phase. This technique has long been employed for depositing semiconductors, especially in the past decade or so, due to its strong performance in thin-film sensors and photovoltaic cells [27]. The CBD apparatus is shown in Figure 1.

The silicon substrates were cleaned using acetone by ultrasonication for 15 min and then washed with distilled water. The film was prepared by immersing the silicon substrate in the solution phase of nano TiO₂ doped with Sn⁺² and activated carbon for 12 hours at room temperature.

Morphology characterization

To characterize the prepared nanocomposite and the thin film morphologies, various analytical techniques were used. X-ray diffraction (XRD, Shimadzu 7000, Rigaku, Japan) was used to identify the structural properties of the measured samples. The XRD patterns were obtained by an X-ray diffractometer using Cu-K α X-ray radiation ($\lambda = 0.15406$ nm) at a scan rate of 0.2 degrees.s⁻¹. A FTIR-8400S Fourier transform infrared spectrophotometer (Shimadzu, Japan) equipped with an attenuated total reflectance (ATR) accessory was used to determine the FT-IR spectrum in the range of 600–4000 cm⁻¹ at room temperature and scan time of 60s and 4 cm⁻¹ resolution. Atomic

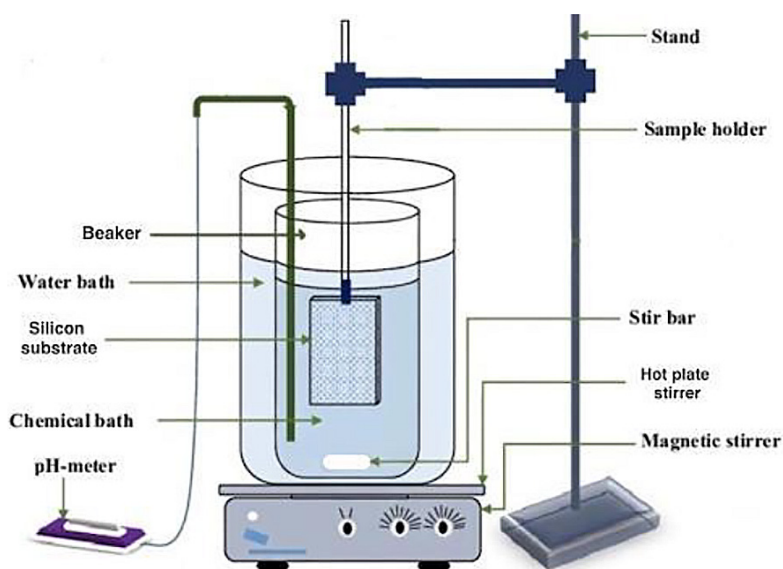


Figure 1. The CBD apparatus

Force Microscopy (AFM, Angstrom Advanced AA 3000, 220 v, USA) was used to determine the surface characteristics. The BET surface area of the prepared nanocomposite was measured using the Brunauer-Emmett-Teller (BET) technique, where N_2 was used as the adsorbate gas after a three-hour degassing process at 105 °C to remove any moisture that might impact the BET measurement. The BET measurement was triplicated, and the average value was adopted here. Elemental composition analysis was performed using a Hitachi S-3400N scanning electron microscope, which was also used to image the nanocomposites to determine their average particle size.

Band gap energy measurement

UV-visible spectroscopy (CARY 100 Conc.) was used to calculate the band gap energy values. The band gap energy was calculated using Equation 1.

$$E = h \times C/\lambda \quad (1)$$

where: E , h , C , and λ are the band gap energy (eV), Planck's constant (6.626×10^{-34} J/s), light speed (3.0×10^8 m/s), and the cut-off wavelength (nm), respectively.

Furthermore, the band energy calculation was performed using diffuse reflectance spectroscopy. The band gap energy was further confirmed by using the Tauc equation (Equation 2).

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

where: α , h , A , ν , and E_g are the absorption coefficient, Planck's constant representing the frequency, and the band gap, respectively, while the n value is 1/2 for the direct allowed transition.

The Kubelka-Munk equation (Equation 3) was used for the calculation of the absorption coefficient (α) by using the diffuse reflectance.

$$F(R) = (1 - R)^2/2R = k/s \quad (3)$$

where: R , s , and k are the absolute reflectance, the scattering coefficient, and the molar absorption coefficient, respectively.

The Kubelka-Munk function $F(R)$ was calculated by using the assimilated diffuse reflectance spectrum that was equivalent to the absorption coefficient (α).

The quantity $(\alpha h\nu)^2$ was plotted against photon energy ($h\nu$) to obtain the band gap energy for $TiO_2/Sn^{+2}/AC$ and the thin film. The thickness of the $TiO_2/Sn^{+2}/AC$ thin film on Si was determined from its UV-Vis transmission spectrum using an interference-based optical method. In the weakly absorbing region, the positions of successive transmission maxima and minima were identified and used to construct upper and lower envelopes of the spectrum. From these envelopes, the effective refractive index of the film was estimated, and the physical thickness d was calculated using the standard interference relation $2nd = m\lambda$, where n is the refractive index of the film, λ is the wavelength, and m is the interference order. The reported thickness value ($\approx 4.7 \times 10^{-7}$ m) corresponds to the average obtained from several adjacent fringe pairs, which minimizes uncertainty associated with fringe indexing and experimental noise.

Gas sensing measurements

The $TiO_2/Sn/AC$ thin film (470 ± 10 nm thick on Si) was tested as an n-type chemiresist or at room temperature in a sealed chamber (one liter volume, dry air carrier gas, 50% RH). H_2 concentrations of 100, 500, 1000, and 5000 ppm were introduced via mass flow controllers (total flow: 200 sccm). Resistance was measured in dark conditions (bias: 1 V, current via Keithley 2400) across three replicate sensors per condition. Chemical sensitivity was evaluated by measuring the shift in resistivity as current output in response to the film surface being exposed to H_2 gas. The gas sensitivity can be evaluated according to Equation 4 [28].

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100\% \quad (4)$$

where: R_g – is the gas resistance and R_a – is the air resistivity.

The gas sensor consisted of the $TiO_2/Sn/AC$ sensitive layer deposited on a p-type Si substrate (10×10 mm²), with two parallel gold interdigitated electrodes (finger width and gap ≈ 200 μ m, active area ≈ 0.25 cm²) patterned on top of the film by thermal evaporation through a shadow mask. The same electrode geometry was used for the undoped TiO_2 thin film to ensure a fair comparison. The chemiresistive response was monitored in a two-probe configuration by applying a constant DC bias of 1 V across the electrodes

and recording the resulting current as a function of time. The baseline resistance in dry air, R_a , was defined as the steady-state resistance obtained after exposing the sensor to pure air for at least 30 min until the signal drift was below 1%/10 min. The gas resistance (R_g) is the resistance defined at the end of the response transient after H_2 was introduced at a certain concentration, usually when the signal reached 90% of its total change. Before each new concentration step, the chamber was purged with dry air at 200 sccm until the resistance was within $\pm 2\%$ of the initial baseline value. This is to ensure baseline stability and reproducibility for subsequent measurements.

RESULTS AND DISCUSSION

Structural characterization and morphological studies of nanocomposites

Figure 2 shows the XRD diffraction of $TiO_2/Sn^{+2}/AC$ nanocomposite, which shows multiple peaks and high intensity of anatase TiO_2 phase at ($2\theta = 25.25^\circ, 37.76^\circ, 48.1^\circ, 54.08^\circ, 55.079^\circ, 68.5^\circ, \text{ and } 75.1^\circ$), which correspond to (101, 004, 200, 110, 211, 204, 116, and 215), respectively, in agreement with JCPDS card 21-1272. The presence of Sn is also evidenced in the XRD pattern. More specifically, the presence of Sn in the peaks from its 101, 211, and 301 planes of Sn(rutile/cassiterite structure) at $2\theta = 34^\circ, 52.4^\circ, \text{ and } 66.1^\circ$, which are common in Sn-based nanocomposites, including those designed for H_2

sensors. This shows that Sn domains are successfully incorporated within the TiO_2 matrix. The activated carbon (AC) displays a broad weak (002) peak at $2\theta = 24^\circ$. The absence of a sharp peak in the AC indicates that it is amorphous, owing to its turbostratic structure and high surface area. Table 1 summarizes the main diffraction peaks of the $TiO_2/Sn^{+2}/AC$ nanocomposite, including their positions, intensities, full widths at half maximum (FWHM), and assigned planes.

Figure 3, which shows the semi-quantitative EDS analysis of the prepared nanocomposite, confirms the presence of O, Ti, Sn, and a trace of N, C, and I. Since EDS is mainly used for elemental identification and their approximate weight percentages rather than exact stoichiometry, the best description is that the nanocomposite contains a TiO_2/Sn^{+2} phase supported on activated carbon, with surface-bound or residual carbon/nitrogen/iodine species also detected.

Figure 4 shows the FTIR spectrum of $Ti/Sn^{+2}/AC$ nanocomposite in the range of (600 to 4000) cm^{-1} . The peak at 615.29 cm^{-1} is attributed to Sn-O, while the peaks at 422.41, 457.13, 493.78, 545.85, and 567.07 cm^{-1} are generally assigned to Ti-O-Ti/Ti-O lattice vibrations of TiO_2 . The activated carbon appeared as a band at 1541.12 cm^{-1} [98]. The absorption bands at 999.13 and 1111.0 cm^{-1} are attributed to C-O stretching bands in primary alcohol. The bands appearing at 2852.72 to 2922.16 cm^{-1} are associated with symmetrical and asymmetrical stretching vibration of CH_2 , respectively[2]. Finally, the peaks appearing at 1625, 3423.65,

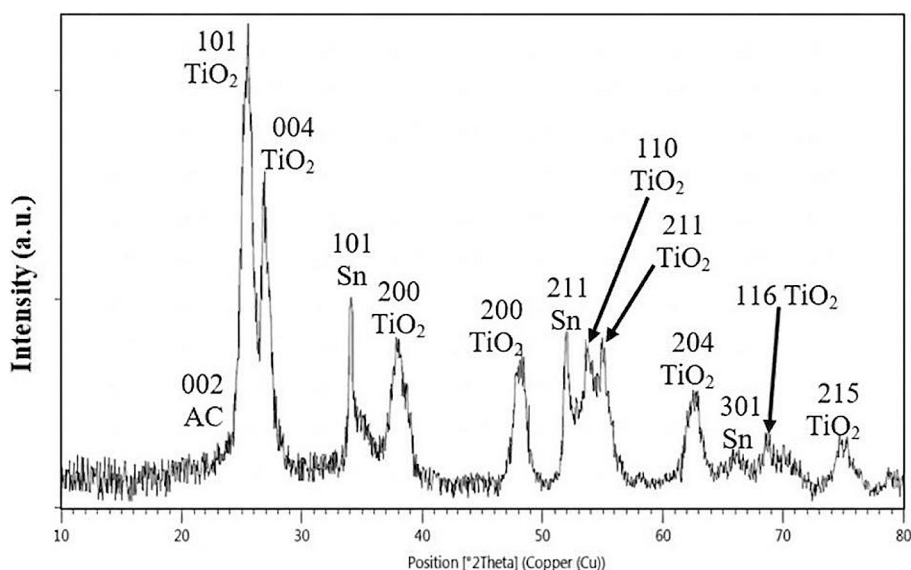
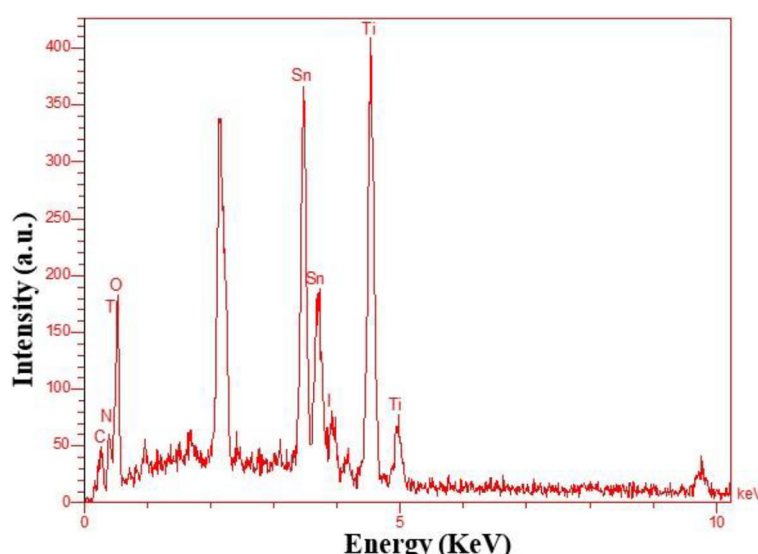


Figure 2. The XRD pattern of $Ti/Sn^{+2}/AC$ nanocomposite

Table 1. XRD peak parameters of TiO₂/Sn²⁺/AC nanocomposite

Pos. [°2θ]	Height [cts]	FWHM [°2θ]	d-spacing [Å]	Rel. Int. [%]	Assigned plane	Phase
25.62	181.85	0.89	3.478	100.0	(101)	TiO ₂ (anatase)
26.82	132.64	0.49	3.325	72.9	(004)	TiO ₂ (anatase)
34.08	78.96	0.25	2.631	43.4	(101)	Sn-TiO ₂ (rutile)
37.91	56.29	0.98	2.374	31.0	(200)	TiO ₂ (anatase)
48.10	56.20	0.96	2.369	30.6	(200)	TiO ₂ (anatase)
51.98	74.85	0.34	1.759	41.2	(211)	Sn-TiO ₂ (rutile)
54.08	55.20	0.99	2.479	40.6	(110)	TiO ₂ (anatase)
55.079	58.42	0.7872	1.66740	32.13	(211)	TiO ₂ (anatase)
62.82	35.04	1.08	1.478	19.3	(204)	TiO ₂ (anatase)
66.10	13.23	0.31	1.22	11.2	(301)	Sn-TiO ₂ (rutile)
68.50	18.76	0.98	1.34	15.7	(116)	TiO ₂ (anatase)
75.10	18.99	0.96	1.31	15.9	(215)	TiO ₂ (anatase)


Figure 3. EDS analysis of the prepared TiO₂/Sn²⁺/AC nanocomposite

3446.79, and 3523.95 cm⁻¹ suggest the existence of absorbed hydroxyl (OH) groups resulted from surface water [29]. It should be noted that some of the C–O related bands, particularly those in the 1000–1500 cm⁻¹ region, may also include contributions from residual organics originating from the sol–gel precursors and solvents (ethanol and acetylacetone) that were not completely removed during calcination, in addition to the functional groups of the activated carbon itself. More specifically, C–O stretching in alcohol/alkoxy-like surface species or some other carbonate-related modes appears in the region between 1000–1100 cm⁻¹, while the range between 1300–1500 cm⁻¹ can include carbonate, bicarbonate, or carboxylate-related asymmetric/

symmetric vibrations that can overlap strongly with other surface species. The peak at 1743 cm⁻¹ is assigned to a carbonyl C=O stretching vibration of adsorbed organic residue on the TiO₂ surface.

The surface topography of the TiO₂/Sn²⁺/AC nanocomposite and the prepared thin film were examined by atomic force microscopy (AFM), as shown in Figures 5 and 6, respectively, which present their two- and three-dimensional (2D and 3D) images. In Figure 5a, the 3D image shows that the composite has a bumpy shape with many valleys. This structure creates a rough surface, which enhances the sample's adsorption ability. The 2D images show quasi-uniform stacked particles. The average grain size was determined by

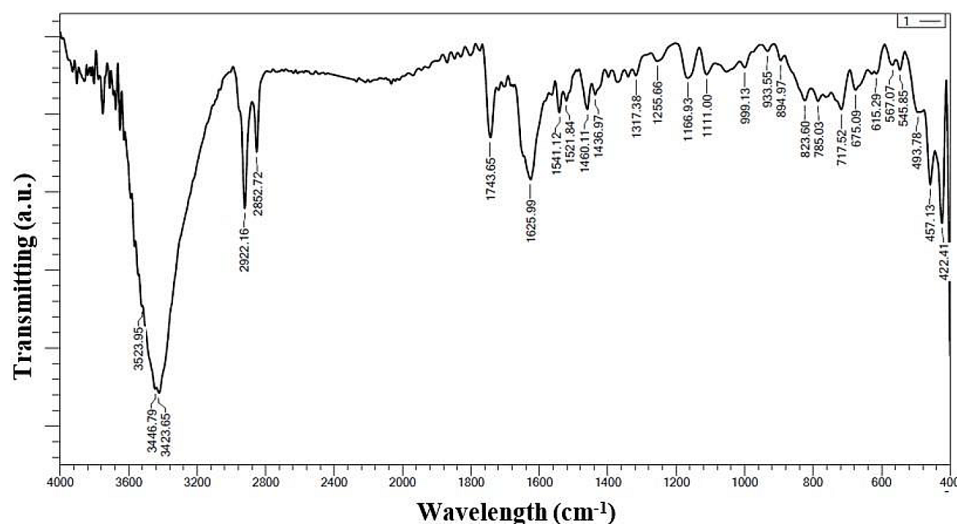


Figure 4. The FTIR spectrum of the prepared $\text{TiO}_2/\text{Sn}^{+2}/\text{AC}$ nanocomposite

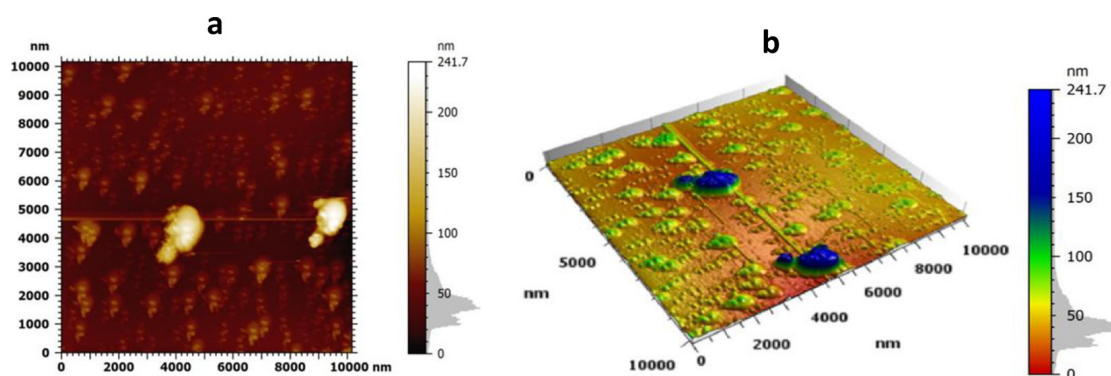


Figure 5. a) Pseudo-color view of the surface, b) 3D AFM topography images of $\text{TiO}_2/\text{Sn}^{+2}/\text{AC}$ Nanocomposite

image analysis of more than 200 individual grains taken from several AFM scans, providing statistically reliable values for the reported diameter. The average diameter is 46 ± 2 nm, and the average roughness is 4.31 nm with a very high surface area of 202 ± 11 m^2/g measured from the BET test. These statistical data indicate that the nanocomposite has good porosity and a high surface area, which leads to a highly efficient adsorption

when activated carbon is embedded. This is a crucial factor that greatly boosts its hydrogen detection performance by enabling faster gas adsorption and stronger sensor responses. The AFM image of the TiO_2 NPs thin film shown in Figure 6b reveals that the grain size and the average diameter increased to 150 ± 10 nm and the roughness to 45 nm due to high deposition rate at room temperature. The average particle size of the

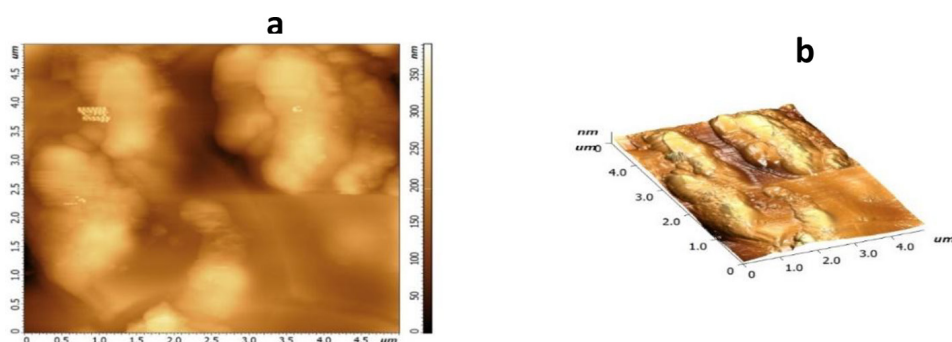


Figure 6. a) 2D, b) 3D AFM topography images of $\text{TiO}_2/\text{Sn}^{+2}/\text{AC}$ thin film

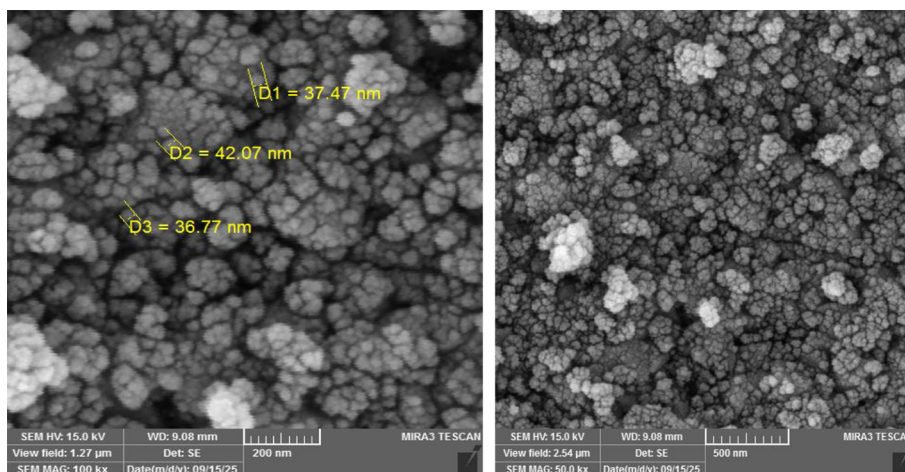


Figure 7. SEM image of $\text{TiO}_2/\text{Sn}^{2+}/\text{AC}$ nanocomposite

prepared nanocomposite measured by SEM was found to be 39 ± 3 nm. The calculation was done by averaging the particle size of more than 100 particles from several images. Figure 7 shows a sample of the SEM images with random samples of the measurements.

Band gap study

Band gap energy and gas-sensing efficiency were studied, as shown in Figure 8. The thickness of the thin film, determined from the interference fringes in the UV–Vis spectrum, was 470 ± 10 nm. The film thickness was extracted from the interference fringes in the UV–Vis transmission spectrum using a Swanepoel-type envelope method. In this approach, the positions of consecutive transmission maxima and minima in the weak absorption region were used to construct upper and lower envelopes, from which the effective refractive index of the $\text{TiO}_2/\text{Sn}/\text{AC}$ layer and its physical thickness were calculated. Assuming a non-absorbing, homogeneous film on a non-absorbing Si substrate in the considered spectral range, the thickness d was obtained from the standard interference relation $2nd = m\lambda$, where n is the refractive index, λ is the wavelength, and m is the interference order. The reported value ($\approx 4.7 \times 10^{-7}$ m) is the average thickness obtained from multiple adjacent maxima–minima pairs, which decreases the uncertainty related to fringe indexing.

The direct energy gap E_g is calculated from the plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) using the Tauc formula (mentioned earlier in the experiment section), as shown in Figure 8. A direct allowed transition ($n = 1/2$) was assumed

in the Tauc formalism because nanocrystalline anatase TiO_2 and related TiO_2 -based composites frequently exhibit optical behavior dominated by direct-like transitions, particularly when the crystallite size is in the tens of nanometers. To verify the robustness of this assumption, we also constructed Tauc plots using the indirect model ($n = 2$) and obtained bandgap values that were slightly shifted in absolute magnitude but showed the same relative trend ($\text{TiO}_2/\text{Sn}^{2+}/\text{AC} > \text{thin film}$), confirming that our conclusions on bandgap modulation are not sensitive to the chosen transition type. The lower bandgap value (2.7 eV) of the nanocomposite ($\text{TiO}_2/\text{Sn}^{2+}/\text{AC}$) is attributed to

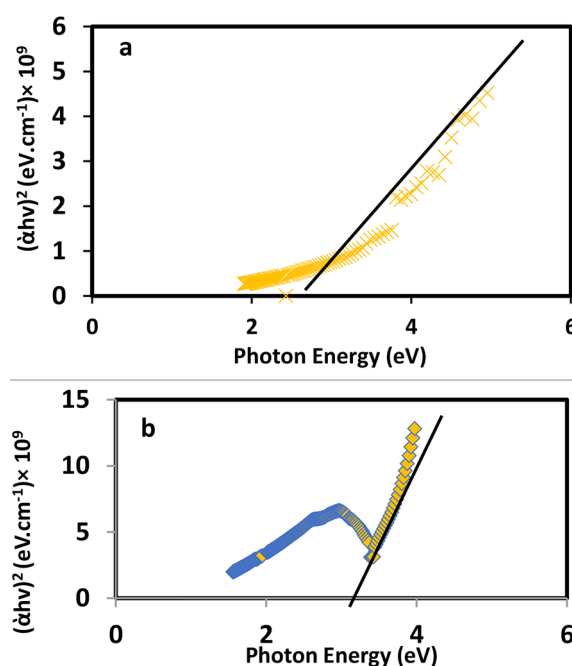


Figure 8. The plots of the energy gap of: (a) $\text{TiO}_2/\text{Sn}^{2+}/\text{AC}$, (b) TiO_2 thin film

the existence of activated carbon, which increases the charge transfer due to its high surface area. The high bandgap value (3.2 eV) of the TiO₂ thin film is attributed to reduced charge transfer, because the film deposited on the silicon substrate attracts charges into small regions.

Thus, the lower band gap observed for the doped nanocomposite should be attributed to the doping with metal (Sn); the dopant metal can act as an electron or hole capture site.[30]. When TiO₂ is doped with this metal, the action of the conduction band of TiO₂ as a sink for electrons can decrease the charge transfer[31]. In addition, the lower bandgap value (2.7 eV) of the nanocomposite (TiO₂/Sn⁺²/AC) is attributed to the presence of activated carbon, which increases charge transfer due to its high surface area. The large bandgap value (3.2 eV) of the thin film is attributed to the decrease in the charge transfer, because of the difference in space charges of the p-type Si-substrate and the n-type thin film.

Gas sensing performance

The gas-sensing behavior of the TiO₂/Sn⁺²/AC nanocomposite was systematically compared with that of the TiO₂ thin film toward H₂ in the concentration range 100–5000 ppm at room temperature. Both structures respond to hydrogen, but their performance differs markedly due to their distinct morphology, microstructure, and electronic properties.

The nanocomposite sensor, composed of TiO₂ particles doped with 1.8wt% Sn⁺² and 1 wt% activated carbon, exhibits a small particle size (46 ± 2 nm), low surface roughness (4.31 nm), and an exceptionally high specific surface area of 202 ± 11 m²/g, with an optical bandgap of 2.7 eV. Compared to the other methods, the chemically deposited thin film (thickness $\approx 470 \pm 10$ nm) possesses larger

grains (~ 150 nm) and a much rougher surface (45 nm RMS). Additionally, it exhibits a wider bandgap (3.2 eV). These structural and optical disparities are reflected in the sensing characteristics.

It is observed that, under similar testing conditions, the response of the TiO₂/Sn⁺²/AC nanocomposite to H₂ is considerably higher compared to that of the thin film. At 1000 ppm H₂, the sensitivity of the nanocomposite is 45.7%, whereas the response of the thin film is considerably lower, confirming the higher response of the nanostructure system at room temperature. Moreover, the response and recovery times of the nanocomposite are 18 s and 42 s, respectively, whereas the response and recovery times of the thin film are considerably longer, indicating that the highly porous structure and high surface area of the nanocomposite help in the rapid adsorption and desorption of hydrogen and oxygen species.

The improved performance of the TiO₂/Sn⁺²/AC sensor can be explained by a number of factors. First, the addition of Sn⁺² ions and activated carbon increases the number of oxygen vacancies. This increases the number of active sites on the material. Second, the intimate contact between the semiconductor material, tin-containing sites, and activated carbon increases the number of junctions. This increases the modulation of the depletion region when the material reacts with hydrogen gas. This results in a greater change in resistance. Third, the reduced bandgap (2.7 eV) of the nanocomposite material increases the number of charge carriers even at room temperature. This increases baseline conductivity. As a result, the material shows a greater percentage change in conductance. These are the main reasons why the nanocomposite material shows improved performance over both the undoped thin film prepared in this work and other tin-containing titanium dioxide or carbon-based composites for hydrogen gas sensing.

Table 2. H₂ sensing metrics (25 °C, mean $\pm$ SD, n=3)

H ₂ (ppm)	Sensor type	Sensitivity S (%)	t _{res} (s)	t _{rec} (s)	R _g (MΩ)
100	Thin film	10.5 $\pm$ 1.1	30 $\pm$ 3	50 $\pm$ 5	1.6 $\pm$ 0.1
100	Nanocomposite	12.5 $\pm$ 1.2	25 $\pm$ 4	55 $\pm$ 6	2.04 $\pm$ 0.18
500	Thin film	20.2 $\pm$ 3.1	25 $\pm$ 2	40 $\pm$ 4	1.00 $\pm$ 0.25
500	Nanocomposite	28.4 $\pm$ 2.1	20 $\pm$ 3	48 $\pm$ 5	1.65 $\pm$ 0.15
1000	Thin film	40.3 $\pm$ 4.0	21 $\pm$ 2	39 $\pm$ 5	1.01 $\pm$ 0.11
1000	Nanocomposite	45.7 $\pm$ 3.0	18 $\pm$ 3	42 $\pm$ 5	1.25 $\pm$ 0.12
5000	Thin film	73.3 $\pm$ 3.5	19 $\pm$ 2	30 $\pm$ 3	0.35 $\pm$ 0.05
5000	Nanocomposite	78.3 $\pm$ 4.5	15 $\pm$ 2	35 $\pm$ 4	0.50 $\pm$ 0.08

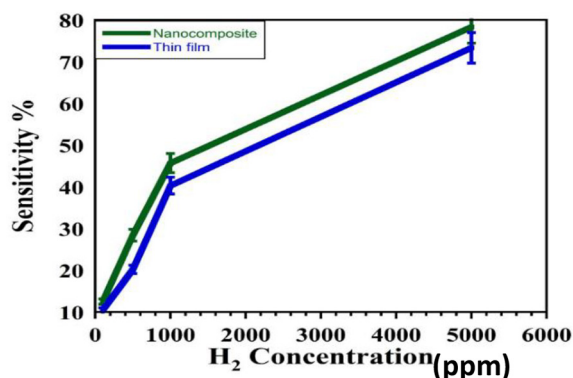


Figure 9. Sensitivity of H₂ gas sensor for nanocomposite and thin film

On the other hand, the thin film, despite the presence of the continuous network of anatase and rutile with reasonable roughness, possesses a reduced effective surface area as well as the number of defect sites. Gas diffusion is limited, and the number of active grain boundaries is reduced. Consequently, the thin film possesses a reduced signal with a reduced response/recovery time compared to the TiO₂/Sn²⁺/AC nanocomposite.

Overall, the results demonstrate that engineering TiO₂ into a Sn²⁺/AC-doped nanocomposite is far more effective for room-temperature H₂ detection than using a compact thin film. The combination of high surface area, tailored band-gap, abundant oxygen vacancies, and interfacial junctions in the nanocomposite enables reliable, fast, and sensitive hydrogen sensing suitable for safety-critical applications (Table 2).

Figure 9 shows the dynamic response curves to an explosion of different H₂ concentrations (100–5000 ppm) for the nanocomposite. It shows an approximately proportional increase in *S* from 100 to 1000 ppm; further experiments are needed to establish the true detection limit and linear range. The 45.7% response at 1000 ppm surpasses undoped TiO₂ (15–25%) due to Sn²⁺ oxygen vacancies and AC-enhanced adsorption. Fast kinetics (*t*_{res} = 18 ± 3 s and *t*_{rec} = 42 ± 5 s) vs.

doped-TiO₂ (23–70 s at >100 °C) reflect porous morphology [32–35].

Table 3 benchmarks the H₂-sensing performance of the TiO₂/Sn/AC nanocomposite against selected TiO₂-based materials reported in the literature at 1000 ppm. At room temperature (25 °C), the present sensor exhibits a higher sensitivity (45.7%) than a previously reported TiO₂–graphene system (32%), while maintaining comparable response and recovery times. In comparison to Sn–TiO₂ nanoparticles and TiO₂/AC composites that require elevated operating temperatures (150–200 °C) to reach sensitivities of 22–38%, the TiO₂/Sn/AC sensor achieves similar or better *S* at significantly lower temperatures, which is advantageous for low-power and safety-oriented applications. These comparisons highlight that, under equal H₂ concentration, the main benefit of the proposed material lies in combining relatively high room-temperature sensitivity with moderate response/recovery dynamics, rather than in universally outperforming all systems across every metric

The starting precursors used in this work (TTIB, SnCl₂·2H₂O) and commercial activated carbon) are widely available commodity chemicals, whereas many graphene- and graphene oxide-based sensor materials rely on specialty carbon precursors or CVD films whose research-grade prices are typically one to two orders of magnitude higher on a per-mass basis than bulk TiO₂ precursors.

In addition to the measurements at 50% relative humidity (RH) used as the standard baseline condition, a limited set of tests was carried out to assess the influence of humidity on sensor response. At moderate humidity (~15% RH), the hydrogen sensitivity changed by less than 5% relative to the 50% RH baseline, whereas at higher humidity levels (RH > 70%), a reduction of approximately 20% in *S* was observed, consistent with competitive adsorption of water and hydrogen species on the active sites. Humidity data is based on preliminary measurements without full statistical replication and is therefore

Table 3. Comparison of H₂-sensing performance of TiO₂-based materials at 1000 ppm

Material	T (°C)	S@1000 ppm H ₂ (%)	<i>t</i> _{res} / <i>t</i> _{rec} (s)	Ref.
TiO ₂ /Sn/AC	25	45.7	18/42	This work
Sn-TiO ₂ NPs	200	38	25/6	[36]
TiO ₂ /AC composite	150	22	45/90	[37]
TiO ₂ -graphene	25	32	28/55	[36]

only reported here as an indication. A systematic investigation of humidity-dependent sensing properties will be the focus of future research.

Although the room-temperature response to H_2 is promising, the present work is limited with respect to the lack of systematic cross-sensitivity tests with respect to typical interfering gases like CO, CH_4 , and VOCs, as well as the preliminary humidity measurements discussed above. As a consequence, the applicability of the $TiO_2/Sn/AC$ gas sensor under realistic conditions with respect to varying gas mixtures and humidity is not fully clarified. Future studies will concentrate on systematic cross-sensitivity measurements under varying humidity conditions, as well as long-term stability and cycling tests, to more clearly define the working window of the $TiO_2/Sn/AC$ gas sensor. Interpretation of the obtained results can be done only considering the investigated experimental conditions due to the lack of systematic studies of selectivity, long-term stability, and complete humidity effects. The obtained results can be applied to the detection of hydrogen in the atmosphere at room temperature by means of $TiO_2/Sn^{+2}/AC$ sensor only.

CONCLUSIONS

The current work achieved successful synthesis of a TiO_2 nanocomposite co-doped by Sn^{+2} (1.8 wt%) and activated carbon (1 wt%) using a simple sol-gel technique, having a novel crystal structure of anatase and rutile phases, refined crystallites of 46 ± 2 nm, a reduced bandgap of 2.7 eV, ultrahigh surface area of 202 ± 11 m²/g, and optimal thin film morphological features of 150 ± 10 nm grains and 45 nm RMS roughness by CBD on silicon. The H_2 sensor showed excellent room temperature response, 45.7% sensitivity at 1000 ppm, and rapid response/recovery times of 18/42 s, along with improved metrics over the reported values of Sn-doped TiO_2 and carbon-based nanocomposites. These properties of the $TiO_2/Sn/AC$ system offer a promising, cost-effective, and scalable system for reliable H_2 leak detection, resolving the limitations of sensitivity, kinetics, and room temperature response of the current H_2 sensors. Further studies could be conducted to improve the selectivity of the H_2 sensor to other gases, such as CO and CH_4 , and its response at increased temperatures for the detection of very low concentrations of H_2 , using

flexible substrates, and employing machine learning to compensate for the drift of the response.

It should also be emphasized that, at this stage, the selectivity and humidity dependence of the sensor have only been explored preliminarily, so more extensive interference and environmental testing will be necessary before implementation in complex real-gas mixtures.

Acknowledgment

The authors would like to thank Scientific Research Commission, Mustansiriyah University (www.uomustansiriyah.edu.iq), and Middle Technical University for their support in the present work.

REFERENCES

1. Rajagopal D., Meegada V.S., Karthikeyan C.P., Dharmalingam B., Hydrogen as fuel: Global and national status, low and zero carbon clean fuels, CRC Press, 2026; 171–183.
2. Alminshid A.H., Alalwan H.A., Mohammed M.M., Abbas M.N., Spectroscopic study of methane reaction mechanism on MgO nanoparticles, Ionics, 2025; 1–6. <https://doi.org/10.1007/s11581-025-06170-y>
3. Thejas R., Naveen C., Khan M.I., Prasanna G., Reddy S., Oreijah M., Guedri K., Bafakeeh O.T., Jameel M., A review on electrical and gas-sensing properties of reduced graphene oxide-metal oxide nanocomposites, Biomass Conversion and Biorefinery, 14, 2024; 12625–12635. <https://doi.org/10.1007/s13399-022-03258-7>
4. Shi Z., Hsiao Y., Chang S., High-sensitivity NO_2 gas sensor based on Zn-doped indium oxide, IEEE Sensors Journal, 2025; <https://doi.org/10.1109/JSEN.2025.3567290>
5. Ciftiyurek E., Schierbaum Z., Adsorbed oxygen ions and oxygen vacancies: their concentration and distribution in metal oxide chemical sensors and influencing role in sensitivity and sensing mechanisms, Sensors, 2022; 23: 29. <https://doi.org/10.3390/s23010029>
6. Zhang Z., Qiu P., Deng Y., Luo Y., Recent advances in functionalizing metal oxide semiconductors for highly sensitive gas sensors, Small Methods, 2025; 9: 2500228. <https://doi.org/10.1002/smt.202500228>
7. Yadav A., Singh P., Gupta G., Dimension dependency of tungsten oxide for efficient gas sensing, Environmental Science: Nano, 2022; 9, 40–60. <https://doi.org/10.1039/d1en00872b>
8. Aguir K., Bernardini S., Lawson B., Fiorido T., Trends in metal oxide thin films:

- Synthesis and applications of tin oxide, Tin oxide materials. 2020; 219–246. <https://doi.org/10.1016/B978-0-12-815924-8.00008-6>
9. Yadav M., Kumar M., Chaudhary S., Yadav K., Sharma A., A review on chemiresistive hybrid zinc oxide and nanocomposites for gas sensing, *Industrial & Engineering Chemistry Research*. 2023; 62: 11259–11278. <https://doi.org/10.1021/acs.iecr.3c00242>
10. Waqas A., Sharma A., Kumar S., Mohammad J., Awad M., VOC detection with zinc oxide gas sensors: a review of fabrication, performance, and emerging applications, *Electroanalysis*. 2025; 37: e202400246. <https://doi.org/10.1002/elan.202400246>
11. Liu Y., Young S., Ji L., Chu Y., Chang S., High-sensitive ethanol gas sensor using Ag modified ZnO nanosheets, *Talanta Open*. 2024; 10: 100386. <https://doi.org/10.1016/j.talo.2024.100386>
12. Chu Y., Young S., Huang Y., Arya S., Chu T., Highly sensitive ethanol gas sensors of Au nanoparticle-adsorbed ZnO nanorod arrays via a photochemical deposition treatment, *ACS Applied Electronic Materials*. 2025; 7: 2327–2338. <https://doi.org/10.1021/acsaelm.4c02091>
13. Aleksanyan M., Sayunts A., Shahkhatuni G., Simonyan Z., Kananov D., Michalcová A., Koláčný L., Kopecký D., Flexible gas sensor based on the RF-grown Fe₂O₃/ZnO/CNTs material for propylene glycol vapor detection, *ACS Applied Electronic Materials*. 2024; 6: 6893–6904. <https://doi.org/10.1021/acsaelm.4c01269>
14. Zhu J., Chen L., Ni W., Cheng W., Yang Z., Xu S., Wang T., Zhang B., Xuan F., NiO/ZnO nanocomposites for multimodal intelligent MEMS gas sensors, *ACS sensors*. 2025; 10: 2531–2541. <https://doi.org/10.1021/acssensors.4c02789>
15. Shadhar M.H., Salih B.M.M., Khaleel O.R., Kadhim Y.M., Mohammed M.M., Alalwan H.A., The influence of eggshell nanoparticles as a partial replacement of cement in concrete, *Innovative Infrastructure Solutions*. 2024; 9: 465. <https://doi.org/10.1007/s41062-024-01765-2>
16. Youssif S., Shabeeb O., Mahan H., Konovalov S., Ismael A., Experimental study of vapor compression refrigeration system using mixing refrigerant (R290/R600a) compare with nano refrigerant (R600a/Al₂O₃), *Advances in Science and Technology Research Journal*. 2025; 19: <https://doi.org/10.12913/22998624/205278>
17. Hassan Q.H., Alalwan H.A., Alminshid A.H., Mohammed M.M., Comparing adding Co₃O₄ and Fe₃O₄ nanoparticles to improve the performance and emission of biodiesel fuel prepared from waste oils in diesel engines, *Advances in Science and Technology Research Journal*. 2025; 19: 150–161. <https://doi.org/10.12913/22998624/208317>
18. Bhadra B.N., Shrestha L.K., Ariga K., Porous carbon nanoarchitectonics for the environment: detection and adsorption, *CrystEngComm*. 2022; 24: 6804–6824. <https://doi.org/10.1039/d2ce00872f>
19. Francis S., Babu S., Thiruvengadam V., Preparation and characterization of mesoporous activated carbon-supported tin oxide nanocomposites from agro-waste (Cyperus Corymbosus Grass Stem) and its use as a highly efficient catalyst in a three-component reaction, *Materials Science*. 2025; 31: 218–228. <https://doi.org/10.5755/j02.ms.37968>
20. Bashal A.H., Divergent effects of Sn and Mn dopants on TiO₂: From extreme band gap widening to dielectric enhancement, *Ceramics International*. 2026; <https://doi.org/10.1016/j.ceramint.2026.01.094>
21. Ismail N.S., Rithwan A., Thongmee S., Yusoff S., Adnan R., Kaus N., Assessing the photocatalytic performance of carbon-based semiconductors in the degradation of pharmaceutical wastes, building a low-carbon society through applied environmental materials science, *IGI Global Scientific Publishing*. 2025; 455–486. <https://doi.org/10.4018/979-8-3693-0003-9.ch017>
22. Maziarz W., Kusior A., Trenczek-Zajac A., Nanostructured TiO₂-based gas sensors with enhanced sensitivity to reducing gases, *Beilstein journal of nanotechnology*. 2016; 7: 1718–1726. <https://doi.org/10.3762/bjnano.7.164>
23. Alsaiairi M., Biomass-derived active carbon (AC) modified TiO₂ photocatalyst for efficient photocatalytic reduction of chromium (VI) under visible light, *Arabian Journal of Chemistry*. 2021; 14: 103258. <https://doi.org/10.1016/j.arabjc.2021.103258>
24. Peng Y., Zheng L., Zou K., Li C., Enhancing performances of a resistivity-type hydrogen sensor based on Pd/SnO₂/RGO nanocomposites, *Nanotechnology*. 2017; 28: 215501. <https://doi.org/10.1088/1361-6528/aa6a96>
25. Yang H., Zhu M., Li Y., Sol–gel research in China: a brief history and recent research trends in synthesis of sol–gel derived materials and their applications, *Journal of Sol-Gel Science and Technology*. 2023; 106: 406–421. <https://doi.org/10.1007/s10971-022-05750-y>
26. Barcelos D.A., Gonçalves M.C., Daylight photoactive TiO₂ sol-gel nanoparticles: sustainable environmental contribution, *Materials*. 2023; 16: 2731. <https://doi.org/10.3390/ma16072731>
27. Sengupta S., Aggarwal R., Raula M., A review on chemical bath deposition of metal chalcogenide thin films for heterojunction solar cells, *Journal of Materials Research*. 2023; 38: 142–153. <https://doi.org/10.1557/s43578-022-00539-9>
28. Kanwate A., Kathwate L., Chandak V., Panse V., Effect of annealing temperature on chemiresistive ammonia gas sensing properties of nickel oxide thin

- films deposited by SILAR, *Int J Sci Res Sci Technol*. 2025; 12: 501–509. <https://doi.org/10.32628/IJSRST>
29. Alalwan H.A., Alminshid A., Mohammed M.M., Mohammed M.F., Spectroscopic investigation of carbon dioxide interactions with transition metal-oxide nanoparticles, *Chemical Engineering & Technology*. 2023; 46: 587–594. <https://doi.org/10.1002/ceat.202200250>
30. Bhagya T.C., Rajan A., Shibli S., In situ tuning of band gap of Sn doped composite for sustained photocatalytic hydrogen generation under visible light irradiation, *International Journal of Hydrogen Energy*. 2021; 46: 16360–16372. <https://doi.org/10.1016/j.ijhydene.2020.08.110>
31. Irfan F., Tanveer M.U., Moiz M.A., Husain S.W., Ramzan M., TiO_2 as an effective photocatalyst mechanisms, applications, and dopants: a review, *The European Physical Journal B*. 2022; 95: 184. <https://doi.org/10.1140/epjb/s10051-022-00440-8>
32. Joo S., Muto I., Hara N., Hydrogen gas sensor using Pt-and Pd-added anodic TiO_2 nanotube films, *Journal of the Electrochemical Society*. 2010; 157: J221–J226. <https://doi.org/10.1149/1.3374643>
33. Lyson-Sypien B., Kusior A., Rekas M., Zukrowski J., Gajewska M., Michalow-Mauke K., Graule T., Radecka M., Zakrzewska K., Nanocrystalline $\text{TiO}_2/\text{SnO}_2$ heterostructures for gas sensing, *Beilstein journal of nanotechnology*. 2017; 8: 108–122. <https://doi.org/10.3762/bjnano.8.12>
34. Li Z., Ding D., Liu Q., Ning C., Hydrogen sensing with Ni-doped TiO_2 nanotubes, *Sensors*. 2013; 13: 8393–8402. <https://doi.org/10.3390/s130708393>
35. Li M., Yang H., Ma C., Zhang Y., Ge S., Yu J., Yan M., A sensitive signal-off aptasensor for adenosine triphosphate based on the quenching of Ru (bpy) $32+$ -doped silica nanoparticles electrochemiluminescence by ferrocene, *Sensors and Actuators B: Chemical*. 2014; 191: 377–383. <https://doi.org/10.1016/j.snb.2013.10.020>
36. Khera N., J. Pethaiyan, Fabrication of $\text{TiO}_2 @ \text{SnS}$ 2 core–shell nanocomposites via a thermal decomposition approach for sunlight-driven photodegradation of crystal violet, *Nanoscale Advances*. 2025; 7: 6032–6048. <https://doi.org/10.1039/d5na00533g>
37. Prutsch D., Wilkening M., Hanzu I., Electrochemical preparation of tin–titania nanocomposite arrays, *RSC advances*. 2016; 6: 98243–98247. <https://doi.org/10.1039/c6ra19209b>