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Graphene oxide loading in hierarchical ZnO microflowers for room-temperature ethanol sensing and UVA photodetection

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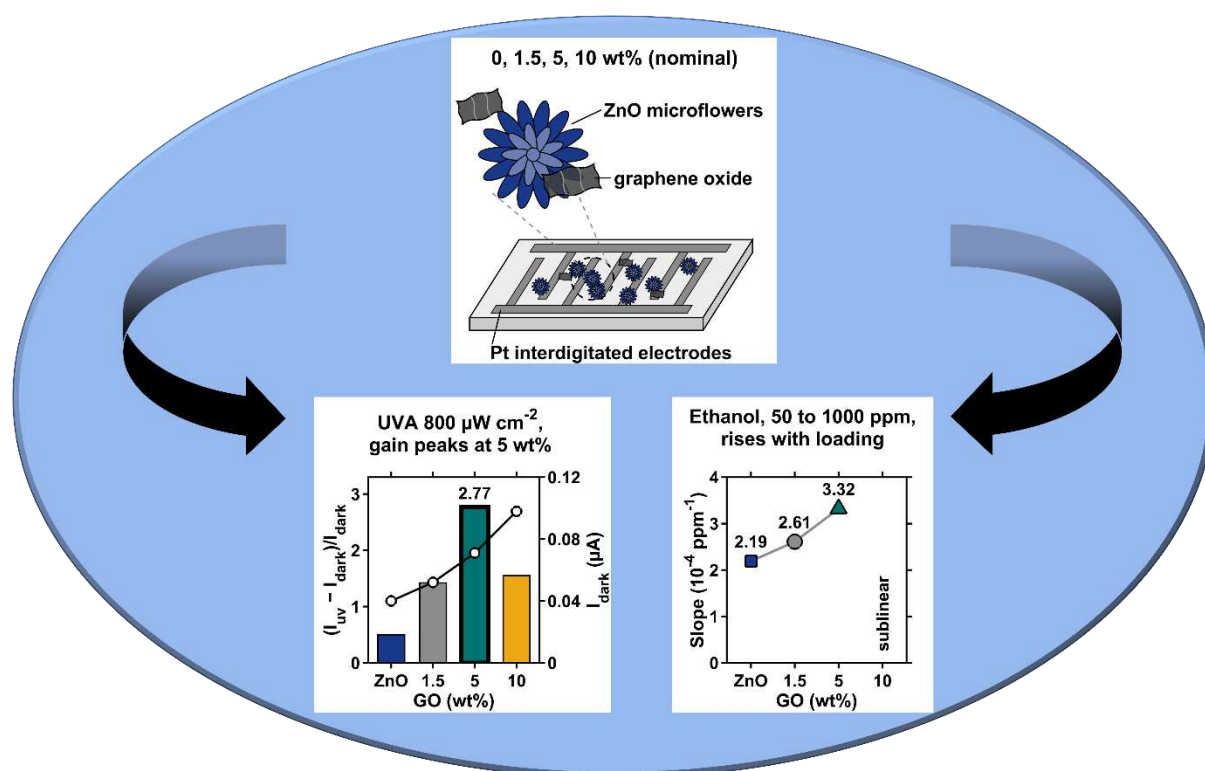
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Abstract

Hierarchical ZnO microflowers assembled from nanoplatelets were grown hydrothermally, combined with graphene oxide (GO) at nominal loadings of 1.5, 5 and 10 wt%, the composites annealed at 400 °C under argon, and all four powders drop cast onto interdigitated platinum electrodes. Films of the four powders were tested as room-temperature ethanol chemiresistors and as ultraviolet-A photodetectors on the same electrode geometry. Under 800 $\mu\text{W cm}^{-2}$ illumination the photocurrent gain $(I_{\text{uv}} - I_{\text{dark}})/I_{\text{dark}}$ rose from 0.5 for ZnO to 2.77 at 5 wt% GO and fell to 1.55 at 10 wt%, while the dark current increased from 0.040 to 0.098 μA and the t_{90} rise time shortened from 70 to 38 s. The ethanol response over 50 to 1000 ppm increased with loading. ZnO, ZnO/1.5 wt% GO and ZnO/5 wt% GO calibrated linearly at 2.19, 2.61 and $3.32 \times 10^{-4} \text{ ppm}^{-1}$, with calibration-based detection limits falling from about 89 ppm for ZnO to 47 ppm at 5 wt%, and the 10 wt% film gave the largest response, with a detection limit of about 30 ppm over 50 to 550 ppm. The photoresponse therefore turns over at 5 wt% GO while the ethanol response is still highest at 10 wt%. Wurtzite ZnO was retained at every loading. Photoluminescence near 385 nm was quenched progressively with loading and shifted to longer wavelength, while the Tauc band gap stayed at 3.25 to 3.31 eV (± 0.065 eV), so the red shift of the emission maximum does not follow a moving band edge.

Keywords

ZnO; Graphene oxide; Nanocomposites; Gas sensors; Ultraviolet photodetectors; Photoluminescence



1. Introduction

Ethanol is among the most targeted volatile organic compounds in chemiresistive gas sensing, and ultraviolet-A photodetection is a second low-power function for films of the same composition on the same electrode geometry. ZnO is the workhorse of both. Its wide direct band gap, large exciton binding energy and strong surface response to adsorbed oxygen place it inside the heterojunction taxonomy of ethanol sensors, which sorts oxide/oxide, oxide/sulfide, oxide/noble-metal and a fourth family of oxide with other materials, rare-earth metals, g-C₃N₄ and graphene among them, as separate design routes [1], and inside the photoconductive, Schottky-barrier and metal-semiconductor-metal architectures used for ZnO ultraviolet photodetectors [2]. The obstacle on the gas side is heat. Useful response and recovery on bare ZnO normally demand operation well above ambient, and much of the ZnO sensor literature aims at lowering that operating temperature [3]. Combining nanomaterials of different dimensionality is an established route to room-temperature operation [4].

Pairing ZnO with a carbon phase is one of the most used of those strategies. A review of carbon-based metal oxide composites for VOC sensing sets out four enhancement routes, added surface area and porosity, faster electron migration and spillover, more active sites with less agglomeration, and nano-heterojunction formation [5]. Graphene oxide has been credited with all four routes. The carbon network is also the limit. In ZnO nanoparticles loaded with reduced graphene oxide (rGO) the conductivity type inverts with loading, n-type below 0.6% rGO and p-type above 1.4%, and the response falls in that regime [6]. The response of Ni-doped ZnO nanoplates maximizes near 0.75 wt% rGO and drops at 1.5 wt%, where rGO interconnects the electrodes and shorts the heterojunction [7], percolation likewise costs performance at high GO content in three-dimensional GO-ZnO networks [8], and ZnO nanowires on GO sheets perform best at a nanowire-to-GO ratio of 1:5 [9].

The carbon phase in these loading series is split between the two forms. The ZnO nanoparticle and Ni-doped ZnO nanoplate series use reduced graphene oxide [6,7], the more conductive phase and the one that percolates soonest, whereas the three-dimensional networks and the nanowire hybrids start from graphene oxide [8,9]. Graphene oxide added as the oxide has a record of its own. Its oxygen functional groups carry the room-temperature response of CO₂ films [10], it has been blended with ZnO [11], and as an interlayer it passivates a TiO₂/perovskite photodetector [12]. The closest compositional analogue to the present series is graphene-like porous ZnO/GO nanosheets, in which the sheets act as template and sensitizer and give a response of 94 to 100 ppm acetone at an optimum operating temperature of 400 °C

[13], while the present films were read without heating. Two graphene-ZnO materials have been run in both functions. Three-dimensional GO-ZnO nano-heterojunctions work at room temperature as a chemiresistor for volatile biomarkers and as a visible-blind photodetector with a responsivity of 33 A W^{-1} [8]. The rGO@ZnO composite prepared by a one-step solid-state route at 1, 2.5, 5 and 10 wt% rGO gives its strongest photoresponse at 2.5 wt% and uses ultraviolet illumination to activate room-temperature triethylamine sensing [14]. Both functions on one graphene-ZnO material, and a series in carbon loading, are therefore already published in these two papers.

Hierarchical and flower-like ZnO grown hydrothermally is an established sensing morphology, reported for ethanol, ammonia at room temperature and n-butanol, built into nanosheet-assembled heterostructures, and examined in its own right for the surface chemistry of the flowers [15,16,17,18,19,20]. Two pieces of the present design are already published. Graphene oxide layers on hydrothermally grown ZnO nanorods quench and shift the near-band-edge emission by charge transfer [21], and a TiO₂/rGO series prepared from 1 to 10 wt% graphene oxide has been read as an ultraviolet photodetector at a fixed irradiance of 0.37 mW cm^{-2} and a 3 V bias [22]. What remains unreported is one set of films in which graphene oxide, added as the oxide and annealed at 400 °C under argon, is carried at several nominal weight fractions on hierarchical ZnO microflowers assembled from nanoplatelets, read both as a room-temperature ethanol chemiresistor from 50 to 1000 ppm and as a separately characterized ultraviolet-A photodetector on films of the same composition and electrode geometry. On such a series the two channels disagree, a photoresponse that turns over at 5 wt% against an ethanol response that does not.

Four samples were prepared, ZnO, ZnO/1.5 wt% GO, ZnO/5 wt% GO and ZnO/10 wt% GO, labeled by nominal loading, and characterized by FTIR, FE-SEM, XRD, ultraviolet-visible spectroscopy with Tauc band gaps, and photoluminescence. The results are reported in Section 3 and their limits in Section 4.

2. Materials and methods

2.1 Materials

Graphite powder (99.5 %, below 50 μm) was obtained from Aldrich, and zinc nitrate (98.5 %), hydrochloric acid (32 %), sodium nitrate (99 %), potassium permanganate (99 %) and ethanol (99 %) from Merck. Urea, sulfuric acid and hydrogen peroxide were used as received, with deionized (DI) water throughout.

2.2 Synthesis of graphene oxide

Graphene oxide was prepared by a modified Hummers method [23]. In a water and ice bath, 40 mL of 98 % sulfuric acid was stirred with graphite powder (1 g) and sodium nitrate (1 g), and potassium permanganate (6 g) was added slowly over 1 h, after which the mixture was cooled for 2 h. The temperature was raised to about 70 °C and 100 mL of DI water was added slowly. Outside the ice bath the suspension was stirred vigorously for 3 h at room temperature, turning green, then dark brown, then brick brown. Hydrogen peroxide was added until gas evolution stopped, then DI water until the total volume reached 400 mL. After 12 h of settling the upper phase was discarded, about 200 mL of DI water was stirred into the sediment, and the dispersion was filtered, acid washed and refiltered. Exfoliation used ultrasonication for 30 min with the bath below 50 °C. After centrifugation at 2000 rpm for 7 min the deep yellow supernatant was kept as the GO suspension, stock concentration 0.5 mg mL⁻¹.

2.3 Synthesis of ZnO microflowers and ZnO/GO composites

A solution of 2.7027 g of urea in 20 mL of DI water was added dropwise from a burette to a stirred solution of 1.3385 g of zinc nitrate in 25 mL of DI water, and stirring was continued for 15 min. The mixture was autoclaved in an oven at 120 °C for 6 h. The recovered material was washed three times with DI water and three times with ethanol, dried, and calcined at 400 °C for 1 h.

The composites were prepared by the same route, with GO suspension added slowly during the urea addition in the Table 1 volumes, and the dried powders were annealed at 400 °C for 1 h under argon, a step intended to reduce the GO and remove residual reagents. The degree of reduction reached was not measured.

Table 1. Volume of 0.5 mg mL⁻¹ GO suspension added during synthesis, the corresponding mass of GO, and the nominal loading.

GO suspension volume (mL)	GO added (mg)	Sample
1	0.5	ZnO/1.5 wt% GO
3	1.5	ZnO/5 wt% GO
6	3.0	ZnO/10 wt% GO

The composites are labeled by their nominal GO loading. The carbon fraction of the annealed powders was not measured. On the mass basis of Table 1 the 1, 3 and 6 mL additions correspond to 0.14, 0.41 and 0.82 wt% of the theoretical ZnO yield, calculated for zinc nitrate hexahydrate, the basis on which the stated 1.3385 g of zinc nitrate and 2.7027 g of urea

reproduce the recipe's 0.1 M and 1 M concentrations over the combined 45 mL. The labels are therefore identifiers rather than compositions, and only their ordering is used.

2.4 Characterization

Morphology was examined by field emission scanning electron microscopy (Hitachi SE-4160) at 20 kV, Raman spectra were recorded on a Bruker SENTERRA microscope with 785 nm laser diode excitation, X-ray diffraction patterns over 10 to 80° in 2θ on a Philips X'Pert PRO diffractometer with Cu Kα radiation, photoluminescence on a PerkinElmer LS 55 spectrometer at 290 nm excitation, and infrared spectra on KBr pellets in transmission mode over 400 to 4000 cm⁻¹. Each of those measurements was made on the powders. The graphene oxide Raman spectrum was fitted with four components, D, G, 2D and D+G, over 1000 to 3000 cm⁻¹. The graphene oxide was also imaged by atomic force microscopy after drying on silicon, and its absorbance recorded over 200 to 500 nm on a UV-Vis spectrophotometer.

Optical transmittance and absorbance were recorded over 200 to 600 nm on films of those powders rather than on the powders themselves. Band gaps were obtained by Tauc analysis for a direct allowed transition, with $(\alpha h\nu)^2$ plotted against $h\nu$ and the linear part of the absorption edge extrapolated to the energy axis, where α is the absorption coefficient, $h\nu$ the photon energy, A a constant and E_g the band gap.

$$(\alpha h\nu)^2 = A^2(h\nu - E_g) \quad (1)$$

Average crystallite sizes were obtained from the Scherrer relation with $k = 0.9$, interplanar spacings from the Bragg relation, and the lattice parameters of the hexagonal cell from the interplanar-spacing relation [24].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

$$n\lambda = 2d \sin \theta \quad (3)$$

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad (4)$$

2.5 Device fabrication

Devices were built on interdigitated platinum electrodes on a glass slide (Fig. S1 in Online Resource 1), the two pads connected to copper lead wires by conductive silver epoxy. Each powder was drop-cast onto the electrode area with a micropipette at one fixed concentration

for all four samples and dried in air. One device per composition was fabricated and measured for each of the two functions, and every ethanol and ultraviolet value reported is a single measurement on that device.

2.6 Ethanol sensing measurements

Ethanol sensing was carried out in the rig sketched in Fig. S2, with the device on a heating plate inside a cylindrical chamber, the air supplied by a pump. A Keysight E3640A 30 W DC supply biased the device through a series resistor R , and the signal was read with an APPA-505 multimeter logged over USB. The chamber heater was not energized, and all sensing measurements were made at ambient laboratory temperature. Ethanol vapor was introduced into the chamber at 50 to 1000 ppm in ten steps.

The response S was taken as the fractional resistance change,

$$S = \frac{R_a - R_g}{R_a} \quad (5)$$

where R_a and R_g are the resistances in air and in the ethanol-air mixture.

Each response was fitted against concentration in Origin with a straight line $S = aC + b$, where C is the ethanol concentration in ppm and a and b the slope and intercept. Slope uncertainties are 95 % confidence intervals from the residual standard deviation of each fit, sy/x , on $n-2$ degrees of freedom, where n is the number of fitted points. No baseline noise record was kept, so the limit of detection was estimated from the calibration as $LOD = 3 sy/x/a$, the 3σ criterion of the IUPAC definition [25] with sy/x in place of the standard deviation of the blank. For ZnO/10 wt% GO, which departs from linearity above about 600 ppm, the same estimate was made on the six points from 50 to 550 ppm. These statistics were computed on the responses read from Fig. 7, where one pixel corresponds to about 0.0006 in S , well below the fit residuals. Cross-sensitivity was probed with methanol and propanol at 500 ppm ethanol.

2.7 UV photoresponse measurements

Photoresponse was measured in a home-built dark box on an adjustable stand, with a Philips black-light UVA lamp at the top (Fig. S3). Incident ultraviolet and visible intensities were measured with a Lutron UV-340A ultraviolet meter and a TES-1339R visible light meter. Devices used the electrode geometry of Section 2.5, with the sensing layer in series with load resistors on a 2 V DC source. The dark-box current was logged with the same supply and multimeter chain as the gas rig. A fast shutter separated the ultraviolet response from interfering signals.

All four devices were illuminated at a fixed ultraviolet irradiance of $800 \mu\text{W cm}^{-2}$ through two on and off cycles, with the illumination held for 120 s and the dark interval for about 300 s. The current saturates within each illumination segment, so I_{uv} is the mean current over the last part of that segment and I_{dark} the current before the shutter opens. The photocurrent gain was taken as $(I_{\text{uv}} - I_{\text{dark}})/I_{\text{dark}}$. The response time t_{90} is the time after the shutter opens to reach 90 % of the plateau, and the recovery time t_{90} the time after it closes for the current to fall within 10 % of the plateau to dark difference above dark.

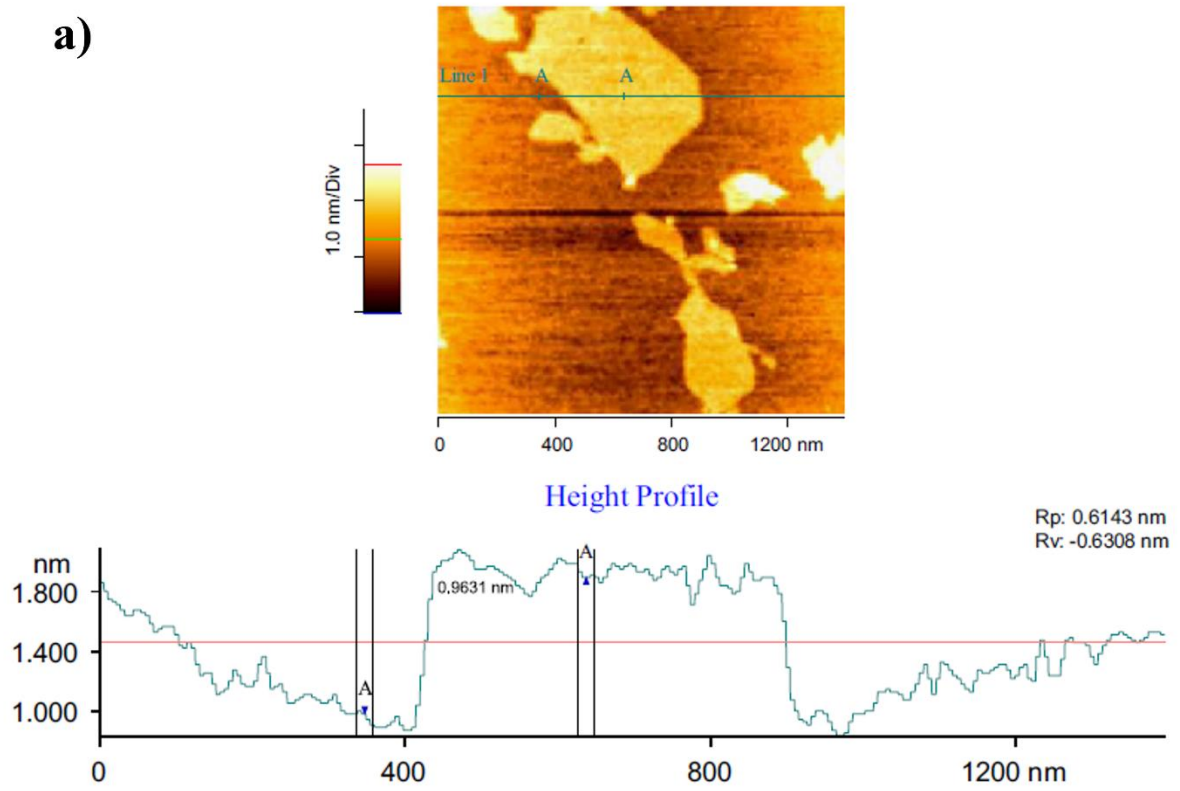
3. Results

3.1 Graphene oxide

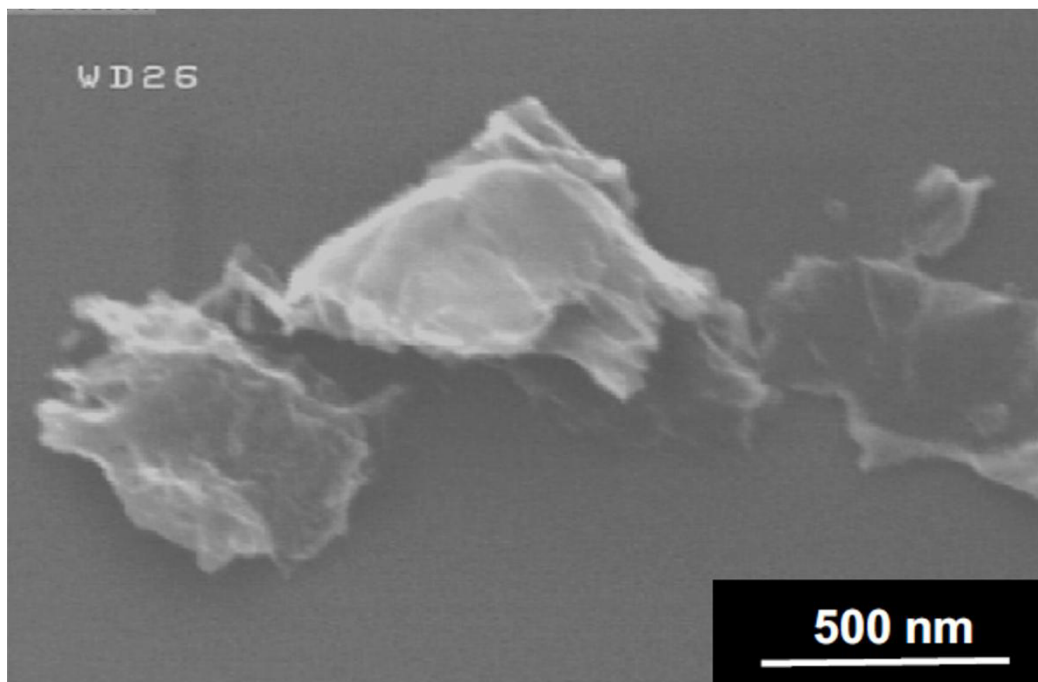
Atomic force microscopy of the graphene oxide dried on silicon shows flat sheets with straight edges (Fig. 1a). The height profile drawn along the marked line crosses one sheet edge and gives a step of about 0.96 nm. Electron microscopy (Fig. 1b) shows thin flakes with crumpled, folded edges several hundred nanometers across.

The infrared spectrum (Fig. 1c) carries labeled bands at 3420, 1729, 1627, 1216, 1052, 865 and 586 cm^{-1} . By the assignments established for Hummers-route graphene oxide [26,27,28], the broad 3420 cm^{-1} band, 1729 cm^{-1} , 1627 cm^{-1} and the 1216 and 1052 cm^{-1} pair correspond respectively to O-H stretching, carboxyl C=O, C=C of the unoxidized graphitic domains and C-O type vibrations. Optical absorbance (Fig. 1d) peaks at 230 nm, carries a shoulder near 300 nm and falls monotonically out to 500 nm. The Raman spectrum (Fig. 1e) was fitted with four components over 1000 to 3000 cm^{-1} , D at 1345 cm^{-1} , G at 1588 cm^{-1} , 2D at 2683 cm^{-1} and D+G at 2920 cm^{-1} , with D and G of comparable height against a measured maximum near 110 arbitrary units. The intensity ratio $I_{\text{D}}/I_{\text{G}}$ is 1.08, measured on the smoothed spectrum rather than on the fitted components.

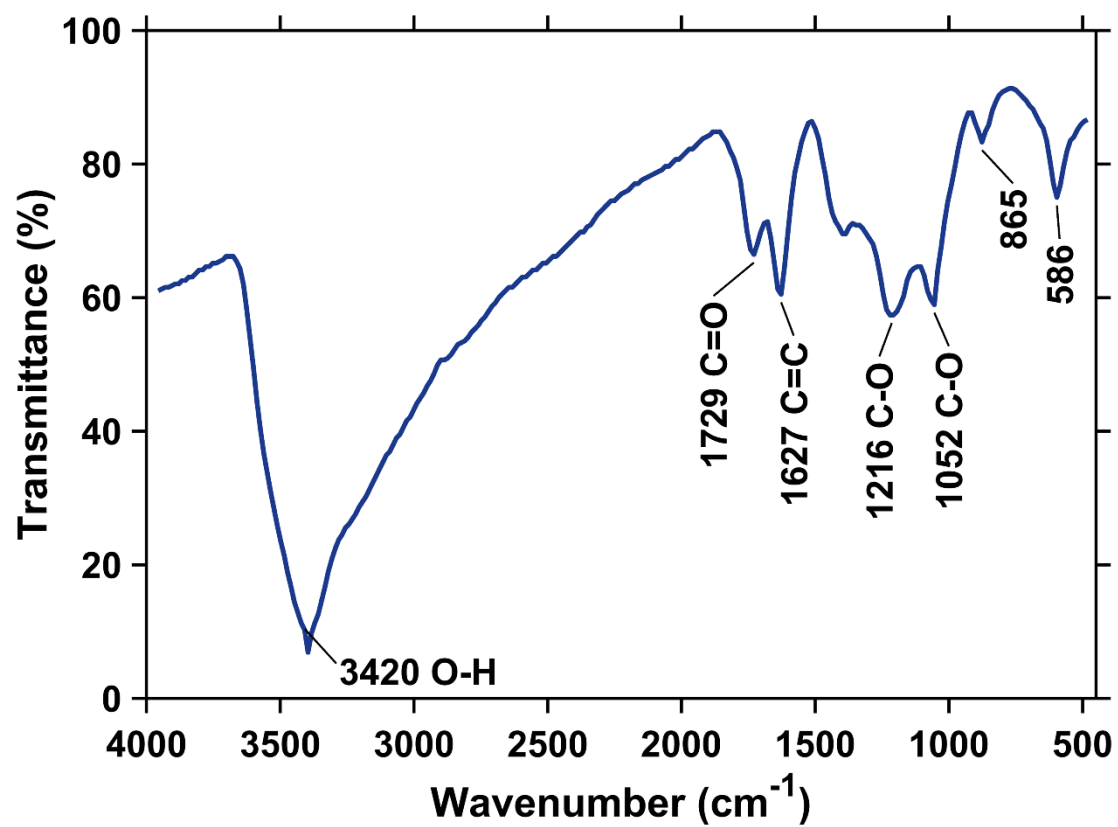
a)



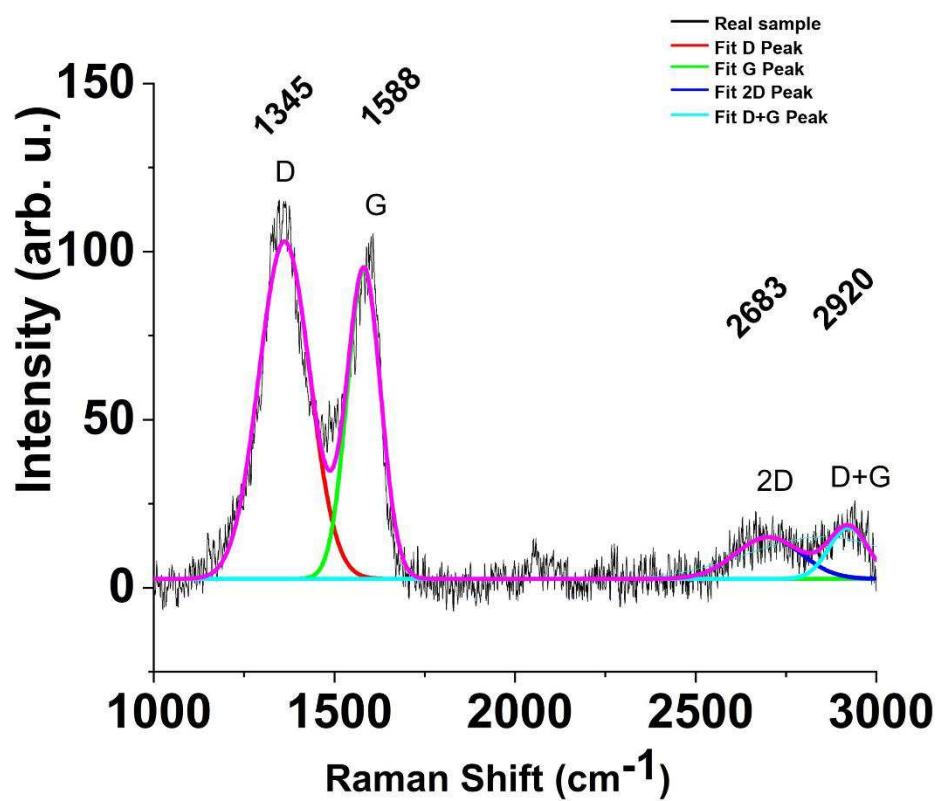
b)



c)



e)



d)

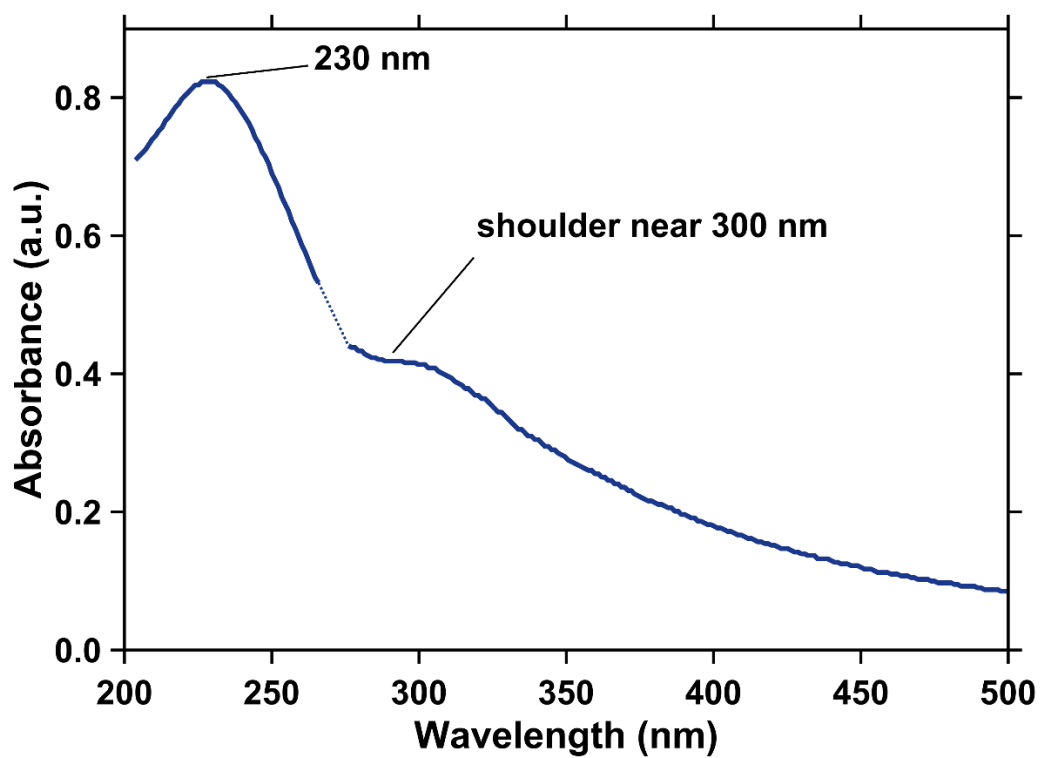


Fig. 1 Characterization of the synthesized graphene oxide. (a) Atomic force microscopy image with the height profile taken along the marked line, showing a step of about 0.96 nm between the points marked A. (b) Electron micrograph of graphene oxide flakes, scale bar 500 nm. (c) FTIR spectrum with the labeled band positions in cm^{-1} . The wavenumber axis was calibrated to the instrument's labeled band positions from 1052 to 3420 cm^{-1} , which it reproduces within 3 cm^{-1} , and the bands labeled 865 and 586 cm^{-1} , not used in the calibration, fall within 12 cm^{-1} of their calibrated positions. (d) Optical absorbance from 200 to 500 nm; the dotted segment between 266 and 276 nm marks where the original trace is not recoverable. (e) Raman spectrum over 1000 to 3000 cm^{-1} with the fitted D, G, 2D and D+G components and their sum

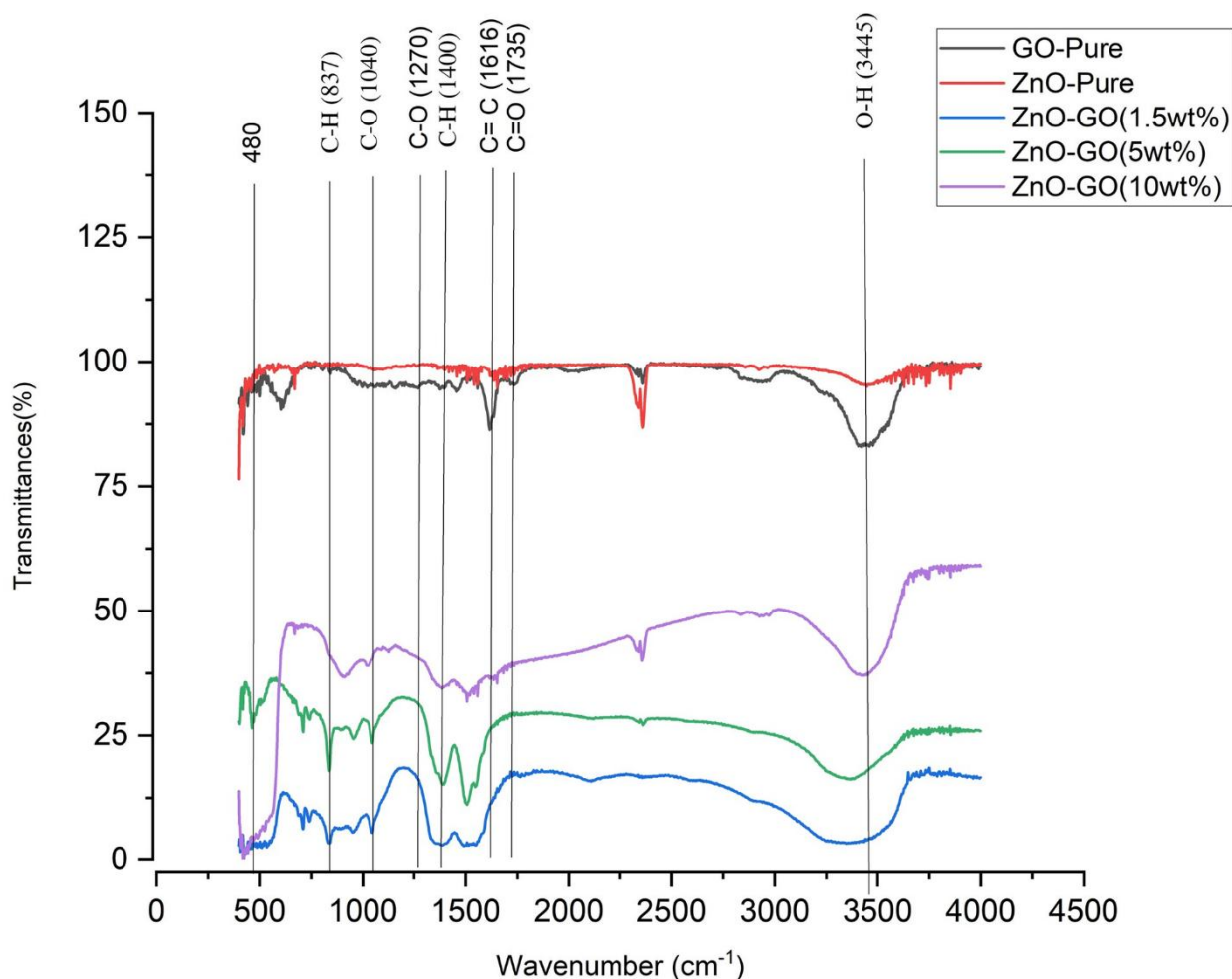


Fig. 2 FTIR spectra over 400 to 4000 cm^{-1} of graphene oxide, ZnO, ZnO/1.5 wt% GO, ZnO/5 wt% GO and ZnO/10 wt% GO, overlaid on one transmittance scale. Vertical lines mark 480, 837, 1040, 1270, 1400, 1616, 1735 and 3445 cm^{-1} . The five traces sit on different baselines, so band depths are not comparable between traces

3.2 FTIR of the composites

Fig. 2 overlays the infrared spectra of graphene oxide, ZnO and the three composites over 400 to 4000 cm^{-1} on one transmittance scale, with the band positions marked at 480, 837, 1040, 1270, 1400, 1616, 1735 and 3445 cm^{-1} . The graphene oxide trace carries its deepest feature at 3445 cm^{-1} , where the transmittance falls to about 83 %, with weaker features near 1616 and 1735 cm^{-1} and a broad shallow depression between 600 and 1300 cm^{-1} . The ZnO trace stays near 100 % over most of the range and drops below 500 cm^{-1} to about 76 % at the low end, where the 480 cm^{-1} Zn-O vibration is marked, and is otherwise nearly featureless. All three

composites reproduce the marked band positions of the graphene oxide trace and the 480 cm^{-1} feature together, and their bands are far deeper than those of the graphene oxide trace itself. The 3445 cm^{-1} minimum reaches about 3 % transmittance for ZnO/1.5 wt% GO, about 17 % for ZnO/5 wt% GO and about 37 % for ZnO/10 wt% GO, against baselines that lie near 17, 26 and 59 % respectively at 4000 cm^{-1} , so the depth of a band in Fig. 2 is not comparable between traces. The graphene oxide trace of Fig. 2 was recorded alongside the composites and is a separate measurement from the spectrum of Fig. 1c.

3.3 Morphology

ZnO (Fig. 3a to 3c) forms hierarchical microflowers assembled from stacked nanoplatelets, about $10\text{ }\mu\text{m}$ across against the $5\text{ }\mu\text{m}$ scale bar of Fig. 3a, separated by open porosity. At the 500 nm scale bar of Fig. 3c the platelets are elongated, stacked face to face in bundles, and on the order of tens of nanometers thick.

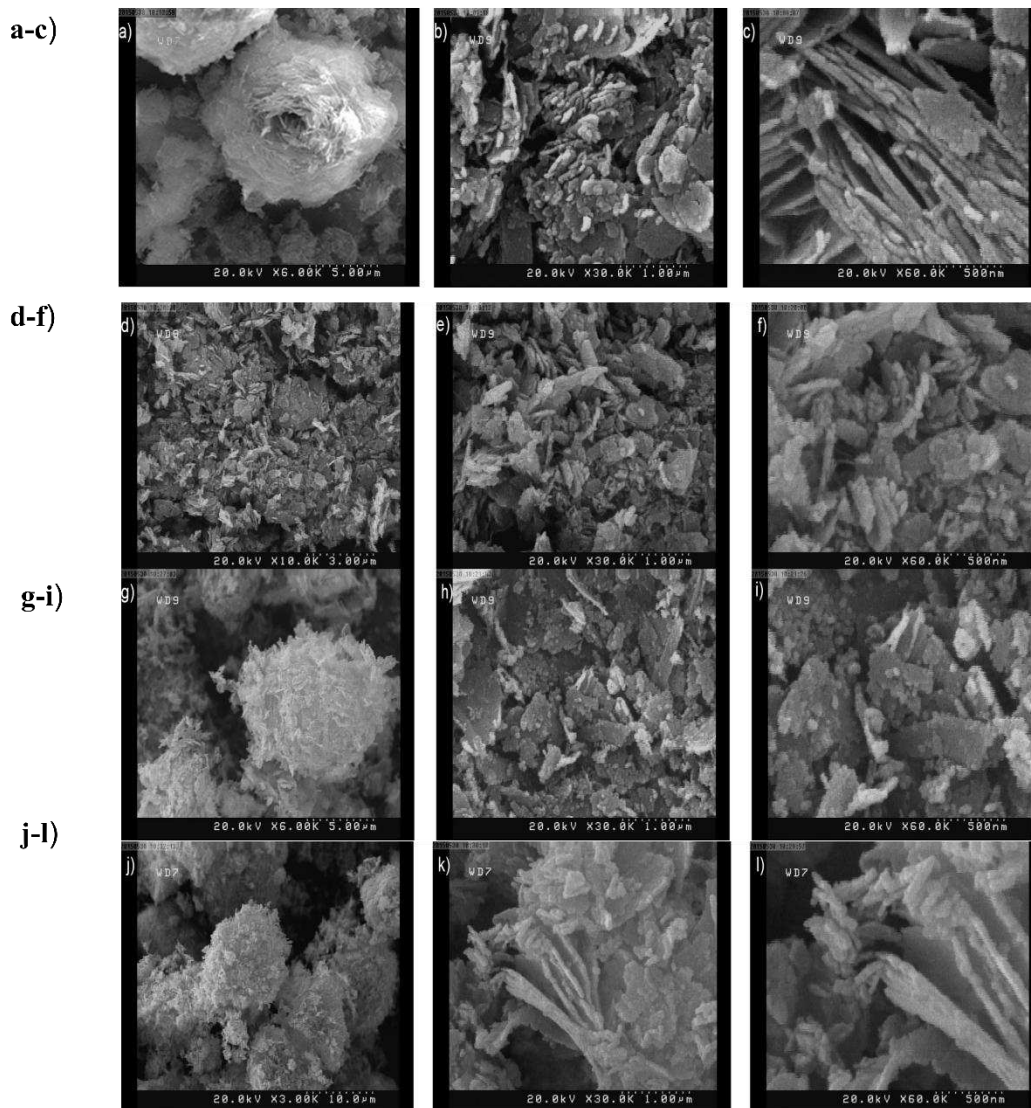


Fig. 3 FE-SEM micrographs recorded at 20 kV. (a to c) ZnO at 6k, 30k and 60k magnification, scale bars 5 μm , 1 μm and 500 nm. (d to f) ZnO/1.5 wt% GO at 10k, 30k and 60k, scale bars 3 μm , 1 μm and 500 nm. (g to i) ZnO/5 wt% GO at 6k, 30k and 60k, scale bars 5 μm , 1 μm and 500 nm. (j to l) ZnO/10 wt% GO at 3k, 30k and 60k, scale bars 10 μm , 1 μm and 500 nm

The 1.5 wt% composite (Fig. 3d to 3f) shows the same platelet microflowers, more densely packed, with thin flat features of higher contrast between the aggregates. In the 5 wt% composite (Fig. 3g to 3i) intact microflowers of about 10 μm coexist with a background of broken and finer platelets. The 10 wt% composite (Fig. 3j to 3l) again shows platelet microflowers, the platelets in Fig. 3k and 3l being longer and more splayed. Individual graphene oxide sheets cannot be distinguished from the ZnO platelets in the 5 and 10 wt% panels at magnifications of 3k to 60k.

3.4 Crystal structure

Fig. 4 overlays the diffractograms of the four samples on one absolute-intensity scale over 10 to 80° in 2 θ . The ZnO pattern is indexed throughout on hexagonal wurtzite ZnO, JCPDS 75-0576, with the seven reflections (100), (002), (101), (102), (110), (103) and (112), of which (101) is the most intense at about 3900 counts. The same seven reflections are resolved in the 1.5 and 5 wt% patterns, and in the 10 wt% pattern the wurtzite reflections are weak against the unassigned intensity. In each composite (101) remains the strongest wurtzite line, reaching about 100 counts at 1.5 wt%, about 550 counts at 5 wt% and about 500 counts at 10 wt%. The patterns are compared as recorded.

4)

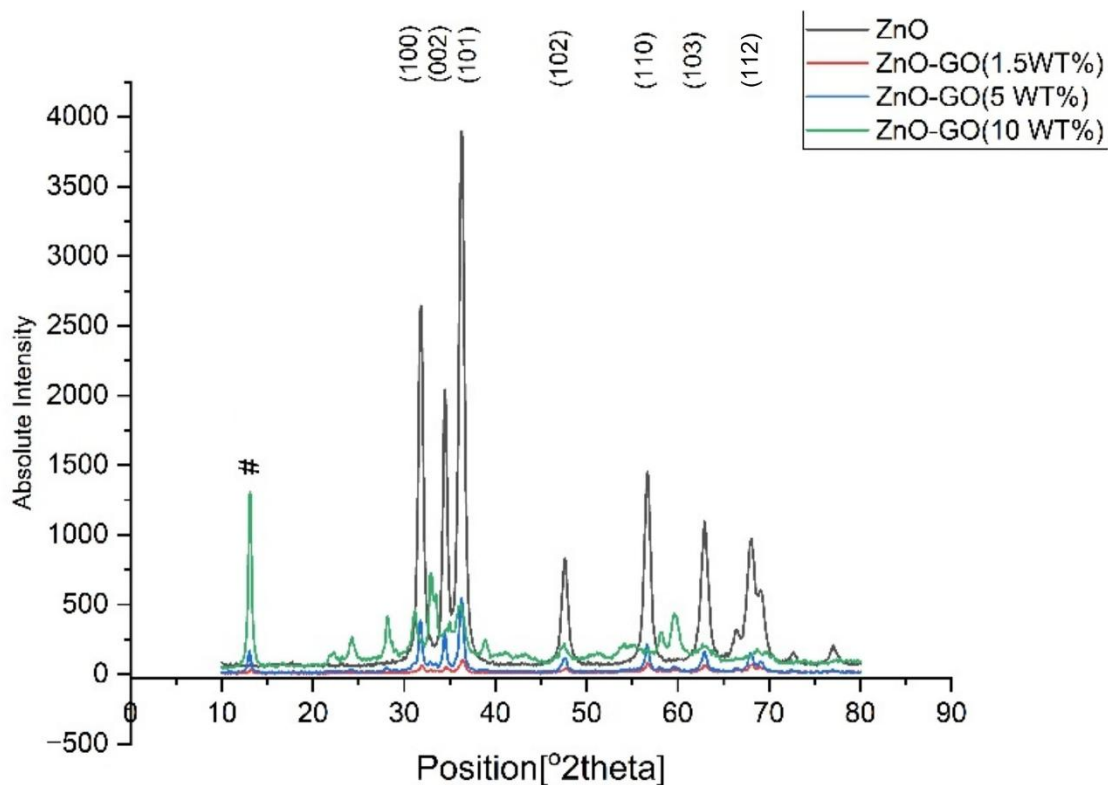


Fig. 4 X-ray diffraction patterns over 10 to 80° 2θ of ZnO, ZnO/1.5 wt% GO, ZnO/5 wt% GO and ZnO/10 wt% GO, overlaid on one absolute-intensity scale. The labeled wurtzite reflections are (100), (002), (101), (102), (110), (103) and (112), the last near 68°, indexed on JCPDS 75-0576. The reflection marked # near 13° is unassigned (Section 3.4)

Counting conditions and sample mass were not reported, so intensities are compared between samples only qualitatively. Lattice constants and average crystallite sizes are given in Table 2, and the (101) positions before and after fitting in Table 3, with the fits in Fig. S4. The (101) reflection lies between 36.22 and 36.42° across the four samples (Table 3), and the interplanar spacing from the Bragg relation is $d(101) = 2.47 \text{ \AA}$. Table 2 sizes are averages over the indexed reflections, 24.42 to 34.90 nm.

Table 2. Average shift, lattice constants and average crystallite size of the four samples. Average shift is the mean displacement of the indexed wurtzite reflections, reported to the

precision output by the fitting software, and crystallite sizes are averages over the same reflections.

Sample	Average shift ($^{\circ}$ 2 θ)	a = b (nm)	c (nm)	Average grain size (nm)
ZnO	-0.04146	0.32446	0.51975	24.42422
ZnO/1.5 wt% GO	0.03569	0.32305	0.5181	27.92903
ZnO/5 wt% GO	-0.06864	0.32472	0.52009	26.07166
ZnO/10 wt% GO	-0.04523	0.33115	0.51382	34.898

Table 3. Original and fitted positions of the (101) reflection.

Sample	Original (101) position, 2 θ ($^{\circ}$)	Fitted (101) position, 2 θ ($^{\circ}$)
ZnO	36.28	36.3
ZnO/1.5 wt% GO	36.42	36.39
ZnO/5 wt% GO	36.29	36.27
ZnO/10 wt% GO	36.22	36.13

A sharp reflection near 13° , marked # in Fig. 4, is weak in the 1.5 and 5 wt% patterns and dominates the 10 wt% pattern at about 1300 counts, against about 500 counts for the strongest wurtzite reflection of that sample. Its position is $2\theta = 13.11^{\circ}$, which by the Bragg relation is an interplanar spacing of 6.74 Å. That spacing is close to the (001) stacking reflection reported for graphene oxide in ZnO composites [29], but the line is not assigned here and is discussed in Section 4. Weak reflections near 24° and 28° appear in the 5 and 10 wt% patterns and are not indexed by wurtzite ZnO. The 10 wt% pattern carries further reflections near 22° , 33.5° , 38.5° and 59° that also remain unassigned. For that sample Table 2 gives $a = 0.33115$ nm and an average crystallite size of 34.898 nm.

3.5 Optical absorption and band gap

Film samples of the four powders were measured in transmission and in absorbance from 200 to 600 nm (Fig. 5a and 5b). Above 450 nm the ZnO film transmits about 100 % and the three composite films 88 to 93 %. The absorption edge lies near 370 nm for all four. Between 300 and 350 nm the ZnO, 1.5 wt% and 10 wt% films carry a transmittance shoulder of 25 to 33 %, while the 5 wt% film stays at zero transmittance up to about 360 nm. In absorbance the four films saturate at 6 to 7 arbitrary units below 300 nm, and the 5 wt% film saturates up to about 345 nm.

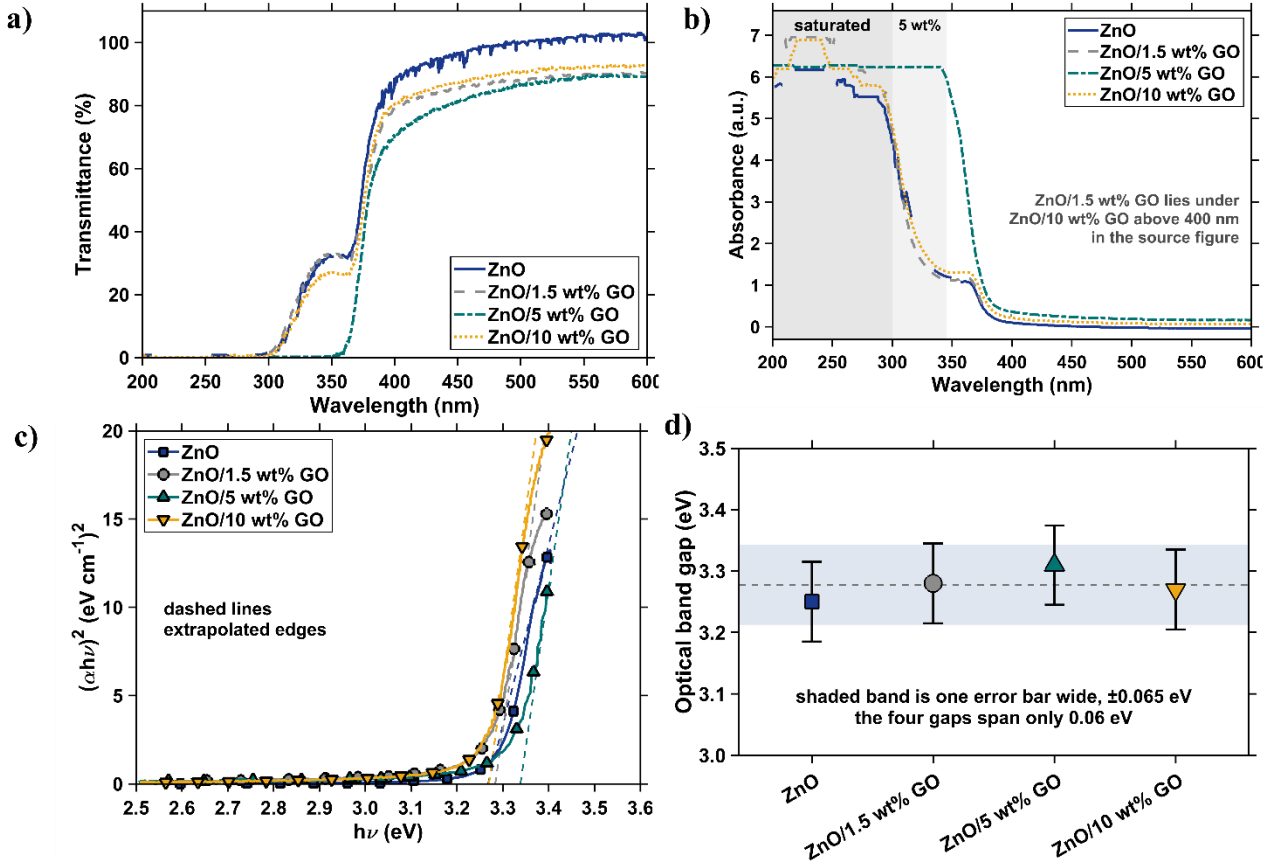


Fig. 5 Optical characterization of the four films. (a) Transmittance and (b) absorbance from 200 to 600 nm. (c) Tauc plot of $(\alpha h\nu)^2$ against $h\nu$ with the extrapolated linear parts. (d) Band gaps obtained from the extrapolations, with error bars

The Tauc plots of $(\alpha h\nu)^2$ against $h\nu$ are drawn in Fig. 5c and the band gaps extracted from the extrapolated linear parts in Fig. 5d. The values are 3.25 eV for ZnO, 3.28 eV for ZnO/1.5 wt% GO, 3.31 eV for ZnO/5 wt% GO and 3.27 eV for ZnO/10 wt% GO, each carrying an error bar of about ± 0.065 eV. The spread across the four samples is 0.06 eV, smaller than one error bar, and it is not monotonic in the graphene oxide loading.

3.6 Photoluminescence

All four samples emit a single envelope between about 300 and 550 nm with its maximum in the near-band-edge region, and no second band elsewhere in the 200 to 700 nm range (Fig. 6), recorded at an excitation wavelength of 290 nm.

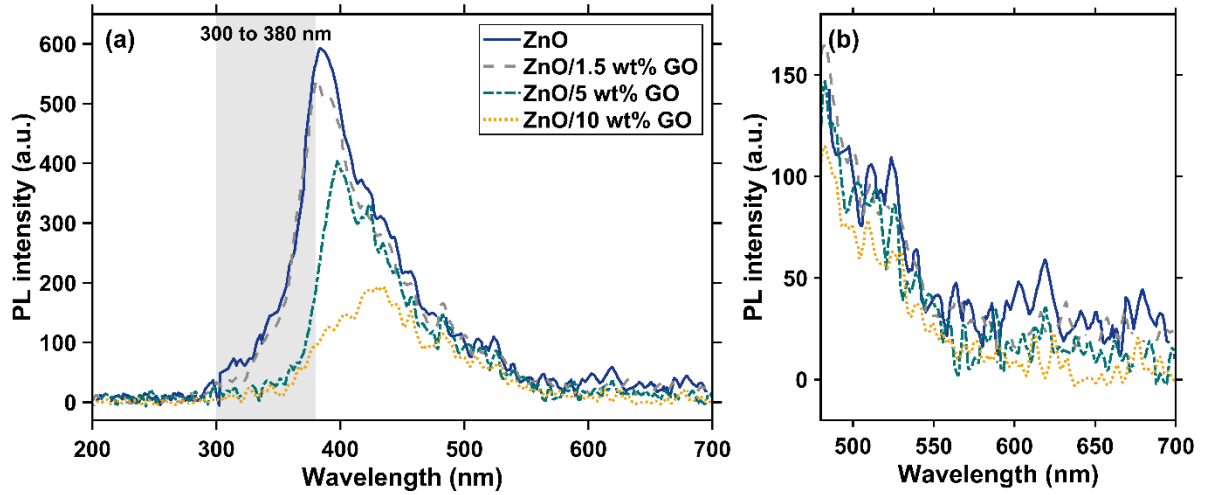


Fig. 6 Photoluminescence of ZnO, ZnO/1.5 wt% GO, ZnO/5 wt% GO and ZnO/10 wt% GO powders under 290 nm excitation. (a) Spectra from 200 to 700 nm, with the 300 to 380 nm flank shaded. (b) The 480 to 700 nm tail on an expanded intensity scale

Read from the figure, the maximum lies near 385 nm for ZnO at about 590 a.u., 383 nm for 1.5 wt% at about 545 a.u., 395 nm for 5 wt% at about 410 a.u. and 430 nm for 10 wt% at about 195 a.u. A weak shoulder appears near 480 nm in all four spectra. Emission intensity falls monotonically as the graphene oxide loading increases, and the envelope maximum moves to longer wavelength for the 5 and 10 wt% composites.

3.7 Ethanol response at room temperature

Fig. 7 gives the response S of the four devices to ethanol at ten concentrations from 50 to 1000 ppm. S rises with concentration for every sample and follows the ordering ZnO/10 wt% GO > ZnO/5 wt% GO > ZnO/1.5 wt% GO > ZnO up to 850 ppm, while at 1000 ppm the 5 and 10 wt% points differ by less than the plotting symbol. Read from the figure, S at 50 and 1000 ppm is about 0.02 and 0.23 for ZnO, 0.03 and 0.27 for 1.5 wt%, 0.04 and 0.36 for 5 wt%, and 0.05 and 0.37 for 10 wt%. The ZnO, 1.5 wt% and 5 wt% data follow a straight line over the whole range, while the 10 wt% data depart from linearity above about 600 ppm and rise more slowly over the last steps to about 0.37.

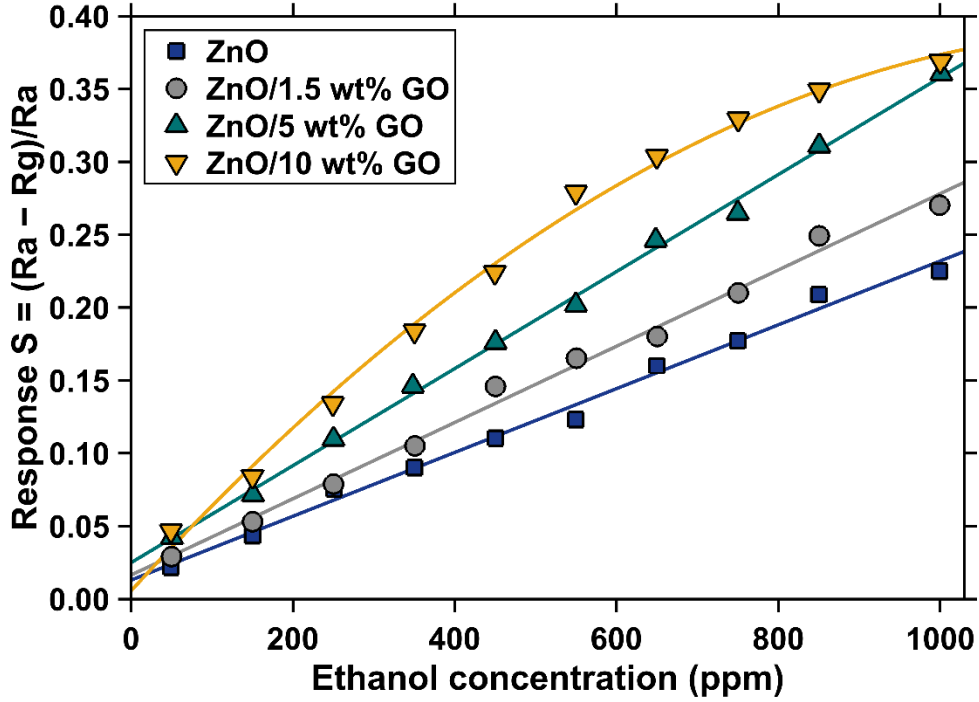


Fig. 7 Response $S = (R_a - R_g)/R_a$ of the four films to ethanol from 50 to 1000 ppm at room temperature. Lines are least-squares fits to the plotted points, linear for ZnO, ZnO/1.5 wt% GO and ZnO/5 wt% GO, reproducing the slopes in Table 4, and second order for ZnO/10 wt% GO

The fitted lines drawn in Fig. 7 are listed in Table 4. The fitted slope rises from $2.19 \times 10^{-4} \text{ ppm}^{-1}$ for ZnO to $2.61 \times 10^{-4} \text{ ppm}^{-1}$ for ZnO/1.5 wt% GO and $3.32 \times 10^{-4} \text{ ppm}^{-1}$ for ZnO/5 wt% GO, so the 5 wt% film has the steepest calibration of the three linear samples, and the 10 wt% data were fitted with a second-order polynomial curve. All four fits return R^2 of 0.98 or 0.99. The 95 % confidence intervals of the three linear slopes, 2.03 to 2.35, 2.44 to 2.79 and 3.20 to $3.46 \times 10^{-4} \text{ ppm}^{-1}$, do not overlap, so their ordering is resolved within the scatter of these single-device data. Fitted over its linear range from 50 to 550 ppm, the ZnO/10 wt% GO response has a slope of $4.66 \times 10^{-4} \text{ ppm}^{-1}$ (95 % confidence interval 4.36 to $4.96 \times 10^{-4} \text{ ppm}^{-1}$). The calibration-based limits of detection are about 89 ppm for ZnO, 81 ppm for ZnO/1.5 wt% GO, 47 ppm for ZnO/5 wt% GO and 30 ppm for ZnO/10 wt% GO on that linear range.

Table 4. Fitted response curves of the four devices against ethanol concentration. The coefficients of the second-order fit to ZnO/10 wt% GO were not retained.

Sample	Fitted equation, C in ppm	R^2
ZnO	$S = 2.19 \times 10^{-4} C + 0.0139$	0.99
ZnO/1.5 wt% GO	$S = 2.61 \times 10^{-4} C + 0.0179$	0.98
ZnO/5 wt% GO	$S = 3.32 \times 10^{-4} C + 0.0259$	0.99

Sample	Fitted equation, C in ppm	R ²
ZnO/10 wt% GO	second-order polynomial	0.98

3.8 UVA photoresponse

Photocurrent transients of all four devices were recorded at a fixed ultraviolet irradiance of 800 $\mu\text{W cm}^{-2}$ and a bias of 2 V, through two on and off cycles (Fig. 8). Every device responds at both cycles and saturates within the illumination segment. After the first off interval the current settles 3 to 6 % above the original dark level, and the second cycle reproduces the shape of the first with a correspondingly lower photocurrent gain. Read from the same traces, the second-cycle gain lies 5, 6, 2 and 6 % below the first-cycle value for ZnO, ZnO/1.5 wt% GO, ZnO/5 wt% GO and ZnO/10 wt% GO. Read from the figure, the dark and plateau currents are 0.040 and 0.062 μA for ZnO, 0.052 and 0.123 μA for ZnO/1.5 wt% GO, 0.071 and 0.263 μA for ZnO/5 wt% GO, and 0.098 and 0.247 μA for ZnO/10 wt% GO. The dark current rises with loading across the series, from 0.040 to 0.098 μA .

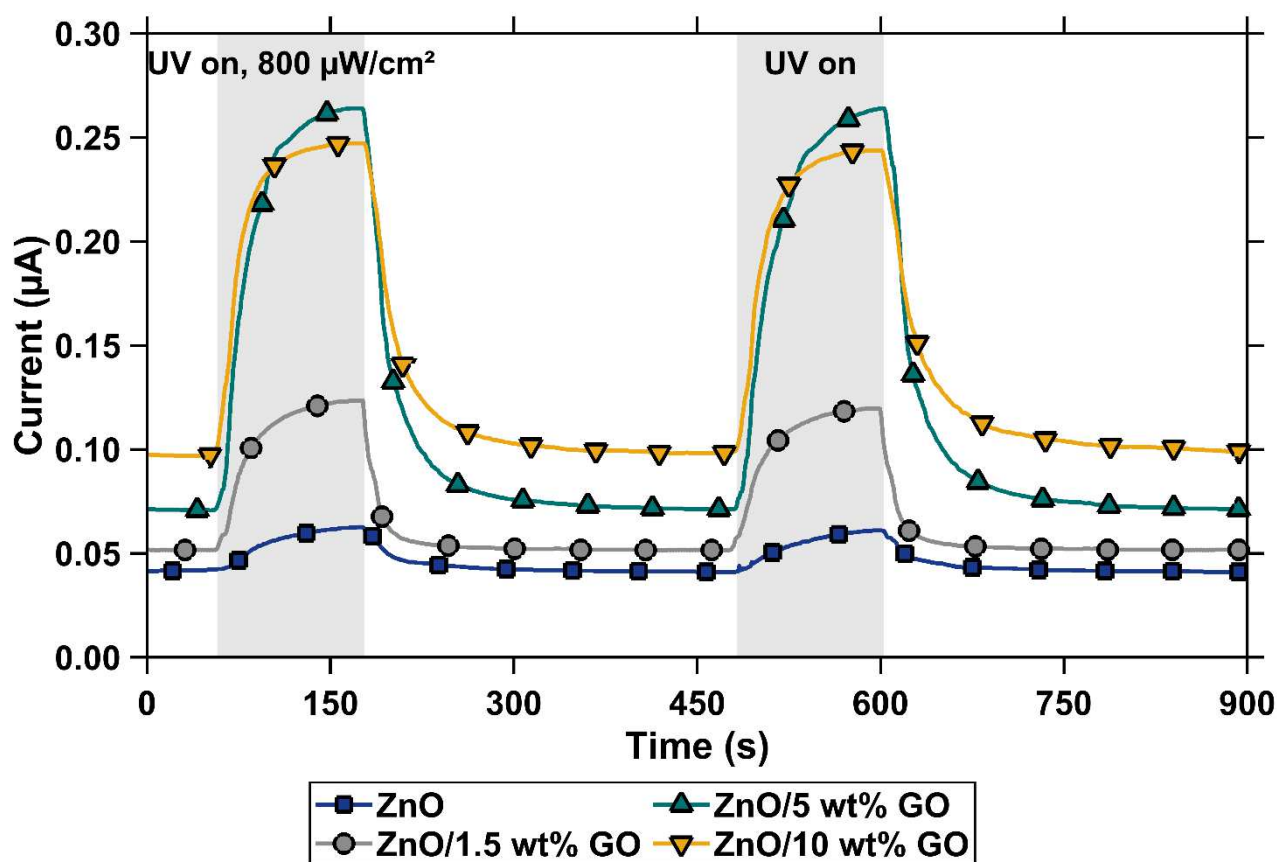


Fig. 8 Photocurrent of ZnO, ZnO/1.5 wt% GO, ZnO/5 wt% GO and ZnO/10 wt% GO under two on and off cycles of UVA illumination at $800 \mu\text{W cm}^{-2}$ and a bias of 2 V

Response and recovery times and the photocurrent gain are listed in Table 5. The values in Table 5 are taken from the first illumination cycle. The photocurrent gain follows the ordering ZnO/5 wt% GO > ZnO/10 wt% GO > ZnO/1.5 wt% GO > ZnO, with a maximum of 2.77 at 5 wt% and a fall to 1.55 at 10 wt%. The response time falls monotonically with loading, from 70 s for ZnO to 38 s for the 10 wt% composite. Recovery is fastest for ZnO/1.5 wt% GO at 21 s, against 77 s for ZnO, 54 s for 5 wt% and 58 s for 10 wt%.

Table 5. Response time, recovery time and photocurrent gain of the four devices under UVA illumination at $800 \mu\text{W cm}^{-2}$ and 2 V bias. Photocurrent gain is $(I_{\text{uv}} - I_{\text{dark}})/I_{\text{dark}}$, with I_{uv} the plateau current under illumination and I_{dark} the current before the shutter opens. Photocurrent gains are computed from the unrounded currents of Fig. 8 and differ slightly from ratios formed from the rounded currents quoted in the text.

Sample	t_{90} response (s)	t_{90} recovery (s)	Gain $(I_{\text{uv}} - I_{\text{dark}})/I_{\text{dark}}$
ZnO	70	77	0.5
ZnO/1.5 wt% GO	53	21	1.42
ZnO/5 wt% GO	47	54	2.77
ZnO/10 wt% GO	38	58	1.55

4. Discussion

The structural data place ZnO in every film and leave the carbon phase imperfectly identified. FTIR shows bands of oxygen-containing groups with the Zn-O band near 480 cm^{-1} in all three composites, consistent with an oxygen-functional carbon phase surviving the hydrothermal step and the anneal, although a carbonate residue from the urea route absorbs there too. No Raman or XPS spectrum of the composite powders was collected, so neither the presence of the carbon phase nor its reduction state rests on an independent measurement. XRD keeps the wurtzite reflections in all four samples. The difficulty is the reflection at 13.11° , an interplanar spacing of $6.74 \text{ \AA}$, which dominates the 10 wt% pattern alongside unindexed lines near 22° , 24° , 28° , 33.5° , 38.5° and 59° . It is left unassigned. [29] is retained only as the comparison for where the graphene oxide (001) reflection falls in ZnO composites, and a hydrothermal pot of zinc

salt, urea and a carbon source is known to yield layered hydrozincite carrying the carbon phase [30]. Assigning the line would require indexing it against reference patterns for hydrozincite, for $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ and for graphite oxide, testing whether those lines index on a single phase, and confirming the result through the carbonate infrared bands near 1380 and 830 cm^{-1} or through mass loss on heating. Until then the 10 wt% lattice constants and 34.9 nm crystallite size in Table 2 carry a caveat.

The optical measurement bounds how the emission can be read. Tauc analysis of the four films gives direct gaps of 3.25, 3.28, 3.31 and 3.27 eV with error bars of about ± 0.065 eV (Fig. 5d), above the 3.0 eV reported for hydrothermal ZnO nanoflowers of 21 nm average crystallite size [17]. The spread of 0.06 eV is smaller than the uncertainty on any single point and is not monotonic, since the 10 wt% value falls back below the 5 wt% one, so no change in the optical gap is resolved and no Burstein-Moss carrier-density argument can be built on these data. The movement of the emission maximum to longer wavelength therefore cannot be a shift of the band edge, which does not move within the uncertainty of the measurement that locates it. The gap was measured on films and the emission on powders (Section 2.4), so that comparison assumes the two specimen forms share a band edge. The closest published carbon-loading series on an oxide disagrees here. In TiO_2/rGO the optical gap falls from 3.60 to 3.04 eV as the graphene oxide feed rises from 1 to 10 wt% [22], while these films move from 3.25 to 3.31 eV inside ± 0.065 eV. Two readings remain. The host oxide and the film route differ, spray-pyrolysed TiO_2 there against drop-cast ZnO microflowers here, while both routes take the graphene oxide through a heating step, so the reduction state is not what separates them. The absorbance of the present films saturates below 300 nm, so an edge movement of a few tens of meV could sit inside the uncertainty of the Tauc fit. These data settle neither.

Photoluminescence is the only structural or optical characterization here that changes monotonically with loading, and three readings of that change stay open. The near band edge emission near 385 nm weakens monotonically with GO loading, falling to roughly a third of the pure-oxide intensity at 10 wt%. The reading Fig. 6 supports most directly is optical. The emission is attenuated across the whole band in order of loading, but unevenly. Read from Fig. 6, the 10 wt% trace keeps about 0.15 of the ZnO intensity between 300 and 380 nm, about 0.32 at the maximum and about 0.44 between 500 and 700 nm, while graphene oxide absorbs most strongly toward the ultraviolet, from 230 to 300 nm and through the blue (Fig. 1d). Attenuation that deepens toward short wavelength moves the maximum of the envelope without moving any emitting state, so reabsorption by the graphene oxide phase can account for part of the

quenching and for the apparent red shift. Two readings stay open beside it. Quenching of this kind is normally read as transfer of photoexcited electrons from ZnO into the carbon sheets, draining the radiative band-edge channel [31,32,33,34], and the closest system reported for photoluminescence is graphene oxide on hydrothermally grown ZnO nanorods, whose emission is quenched and shifted by exactly that route [21]. The same quench has also been assigned to interaction between oxygen-containing groups and ZnO surface states, where the sheets compensate surface oxygen vacancies while also carrying holes and suppressing recombination [35]. A single-excitation measurement on spectra not normalized to mass or absorbance separates none of the three, and a transmission-corrected or excitation-resolved measurement would.

The unassigned phase repays following through. If it were the basic zinc carbonate $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, which emits near 375 nm under 286 nm excitation with an intensity that grows with the amount of the phase present [36], it would be a candidate emitter at 290 nm excitation and a band near 385 nm. The 13.11° reflection grows with loading, so a growing 375 nm emitter would pull the envelope toward shorter wavelength and raise it. The measured envelope does the opposite on both counts, falling in intensity and moving to longer wavelength. Whatever the phase is, it accounts for neither trend, and if it emits at all the true quenching and red shift are larger than the traces show.

The ethanol data follow the trend the heterojunction picture predicts and cannot fix its magnitude. The response rises with nominal GO loading across 50 to 1000 ppm, in the direction implied by the four enhancement routes catalogued for carbon-based metal oxide VOC composites [5] and by the place of graphene composites in the ethanol heterojunction taxonomy [1]. Three of the four calibrations are linear, with slopes of 2.19, 2.61 and $3.32 \times 10^{-4} \text{ ppm}^{-1}$ for ZnO, ZnO/1.5 wt% GO and ZnO/5 wt% GO at R^2 of 0.99, 0.98 and 0.99 (Table 4), so the concentration sensitivity of the 5 wt% film is about 1.5 times that of the bare oxide. The 10 wt% film is the highest in absolute response and leaves linearity, flattening above approximately 600 ppm, a shape consistent with saturation of the adsorption sites and equally with a shunting carbon network or with surface chemistry from the unassigned phase. The first of those routes is surface area, and no BET measurement exists for these powders, so the open porosity of the hierarchical ZnO microflowers assembled from nanoplatelets stays qualitative. The labels are nominal, so the series cannot be placed on the absolute loading scale of the reported optima, which sit near 0.75 wt% rGO on Ni-doped ZnO nanoplates [7], above about 1.4 % rGO in rGO-loaded ZnO nanoparticles [6], and at high GO content in three-dimensional

GO-ZnO networks [8]. The carbon phase here was added as GO and annealed at 400 °C under argon, and its reduction state was not measured, so its conductivity relative to the rGO of those series is unknown. Graphene oxide added as the oxide has served with ZnO as a two-dimensional template and sensitizer at an optimum of 400 °C [13].

Magnitude is another matter, and the detection limit, reported in ppm by three of the sensors cited here, is the one figure of merit that crosses sources in a single unit. On the calibration estimate of Section 3.7 the present films reach about 47 ppm at 5 wt% and about 30 ppm at 10 wt% over 50 to 550 ppm, likely conservative values because the fit residuals include scatter beyond baseline noise. An SnO₂/rGO composite read at room temperature over 29 to 145 ppm reports a detection limit of 3 ppm, with response and recovery near two minutes [37], and ultraviolet-activated rGO@ZnO reaches 15.6 ppm for triethylamine [14]. Graphene sheets carrying hydrothermally grown ZnO nanowires reach 1 ppm with a response of 26, after the graphene lowered their optimum working temperature from 200 to 125 °C [38]. The estimates for ZnO and ZnO/1.5 wt% GO, about 89 and 81 ppm, lie above the lowest 50 ppm step, so the 50 ppm readings of those two films fall inside the scatter of their calibrations. Response magnitudes compare less directly, since each source reports a different quantity. At room temperature a ternary MoSe₂-ZnO heterojunction on rGO gives R_g/R_a of 50.2 at 500 ppm [39] and thermally reduced GO alone gives 15 % at 100 ppm [40]. Heating to 300 °C lets ZnO-rGO sensitized with g-C₃N₄ reach R_a/R_g of 178 at 100 ppm, about nine times the pure-oxide value [41], and on hydrogen a room-temperature ZnO/rGO bilayer with a catalytic contact reaches 484.1 % at 100 ppm [42]. The response S plotted here runs from about 0.02 to about 0.37 as a fractional resistance change, a different quantity from the ratios above (Table 6).

Table 6 places the present films beside the sensors cited above, each response quoted in the form its authors used, so it locates the series without ranking it.

Table 6. Room-temperature and heated graphene/metal-oxide chemiresistors compared with the present films. Values are quoted as reported in the cited works; response definitions differ between rows and are given in the fourth column. n.a., not available.

Sensing material	Analyte, temperature	operating Concentration	Response as defined by the source	Response /Ref. recovery
ZnO microflowers / GO, 1.5 wt% nominal (drop-cast)	Ethanol, room-temperature	50 to 1000 ppm	$S = (R_a - R_g)/R_a$ 1000 ppm; slope 2.19 to 3.32 × 10 ⁻⁴ ppm ⁻¹ ; detection limit about 89, 81, 47 and 30 ppm for ZnO, 1.5, 5 and	0.23 to 0.37 at not recorded calibration-based

Sensing material	Analyte, operating temperature	Concentration	Response as defined by the source	Response /Ref. recovery
			10 wt% (the last over 50 to 550 ppm)	
SnO ₂ / rGO composite	Ethanol, room temperature	29 to 145 ppm	sensitivity 12 ppm ⁻¹ , detection limit 3 ppm	123 ± 6 s / [37] 128 ± 42 s
MoSe ₂ -ZnO on rGO (ternary)	Ethanol, room temperature	1 to 500 ppm	R _g /R _a = 50.2 at 500 ppm	6.2 s / 12.9 s [39]
Thermally reduced GO (no oxide)	Ethanol, 28 °C	5 to 100 ppm	15 % at 100 ppm	3 s / 6 s [40]
ZnO / rGO / g-C ₃ N ₄	Ethanol, 300 °C	100 ppm	R _a /R _g = 178, about 9 times pure ZnO	n.a. [41]
Graphene / ZnO nanowires (hydrothermal)	Ethanol, 125 °C	1 ppm	response 26, about twice pure ZnO nanowires	n.a. [38]
Porous ZnO / GO nanosheets	Acetone, 400 °C	100 ppm	response 94	11 to 21 s / [13] 4 ± 1 s
Ni-doped ZnO nanoplates / rGO, 0 to 1.5 wt% (drop-cast)	H ₂ , 150 °C	100 ppm	about 63.8 % at 0.75 wt% rGO, falling at 1.5 wt%	n.a. [7]
ZnO nanoparticles / bilayer, Pd-Ag contact	rGOH ₂ , room temperature	100 to 10 000 ppm	484.1 % at 100 ppm	21.04 s / [42] 47.09 s
3D GO-ZnO network (GO content varied)	Volatile organic compounds, room temperature	down to 100 ppb	performance falls at high content	n.a. [8]
rGO@ZnO, (solid state), UV-activated	1 to 10 wt% Triethylamine, room temperature	detection limit 15.6 ppm	35 %	n.a. [14]

The solid-state rGO@ZnO series of [14] is the closest published design on the gas side. Its analyte is triethylamine at room temperature, its carbon phase is rGO at 1, 2.5, 5 and 10 wt% against a GO-derived phase of unmeasured reduction state here, and its ultraviolet light activates the gas measurement while the photoresponse here is a separate function on films of the same composition and electrode geometry. Their photo-response peaks at 2.5 wt% rGO and this one at nominal 5 wt% GO, on loading scales that are not interchangeable.

The ultraviolet channel is where this series turns over. Under 800 μW cm⁻² illumination all four films reach a plateau within each on segment (Fig. 8), and the photocurrent gain ($I_{uv}-I_{dark}$)/ I_{dark} rises from 0.5 for ZnO to 1.42 at 1.5 wt%, reaches 2.77 at 5 wt% and falls to 1.55 at 10 wt% (Table 5). The dark current instead rises monotonically, 0.040, 0.052, 0.071 and 0.098 μA, so the 10 wt% film, past the maximum in photocurrent gain, also carries the highest dark current. A percolating carbon network would produce that pairing, and so would a thicker or denser film, since neither the film thickness nor the electrode area was recorded. Such a network would

shunt the oxide grains whose depletion layers do the switching, lowering the fractional response while the absolute photocurrent stays high. How the carbon phase is arranged decides the sign of that effect. A continuous unreduced graphene oxide interlayer in a graphene-silicon Schottky diode suppressed the dark current while raising the photocurrent 2.73 times [43], which is the opposite of what these dispersed flakes do. The same argument covers the drop above 0.75 wt% rGO on Ni-doped ZnO nanoplates [7] and the loss of light and chemical response once a percolating GO network forms in three-dimensional GO-ZnO architectures [8]. Percolation of this kind has been measured directly in an oxide plus carbon detector film, as a weight fraction, at 0.20 to 0.25 wt% multiwalled carbon nanotube in TiO₂ [44], so thresholds of this kind are low and measurable. This series cannot be set against it, since the carbon fraction of these films was never measured. The t_{90} rise time falls monotonically, 70, 53, 47 and 38 s, consistent with the carbon phase adding a faster extraction path for photogenerated carriers, the role rGO plays as a recombination-suppressing hole transport layer on ZnO nanorod arrays [35]. The falling rise time here runs opposite to [45], where adding a reduced graphene oxide phase to ZnO nanowires enhanced the photoresponse but lengthened the rise time from 2.42 s to 28.46 s, on a system differing in carbon reduction state, morphology and bias, so the comparison bounds rather than explains. Recovery does not follow loading at all, at 77, 21, 54 and 58 s, so the return to the dark baseline is set by something the loading does not order, and recovery was not examined further.

The two channels disagree, and that is the result needing explanation. The ultraviolet response turns over inside the series, at nominal 5 wt%, the shape the rGO series report at their own optima, while the ethanol response is still highest at 10 wt%. Two candidates remain open, neither testable here. The nominal weight fractions may not order the carbon content the way the labels suggest, and the unassigned phase that dominates the 10 wt% diffractogram may contribute surface chemistry to the gas measurement that it does not contribute to the photoresponse. One comparison of magnitude survives. A continuous multilayer graphene membrane on ZnO nanoflowers, the nearest morphological analogue, reports millisecond response against tens of seconds for its pristine device [46], while the rise times here stay in the tens of seconds at every loading, plausibly because a continuous membrane spans the illuminated area as a transport path while dispersed GO-derived flakes complete only part of it.

Several limits bound how far these results can be taken. The composite labels are nominal and no dried composite mass was recorded, so the absolute loading scale is uncertain while its

ordering stands. Four loadings locate an optimum coarsely, and the ultraviolet maximum at 5 wt% rests on one point of the four. Only two on and off cycles were recorded under ultraviolet illumination and none for the gas measurement, so drift and reproducibility are untested, and neither a humidity series nor a temperature series was run, so how the room-temperature response depends on either is unknown. Methanol and propanol were admitted alongside 500 ppm ethanol and raised the response, with neither the interferent concentration nor the size of the deviation recorded, so these films cannot be ranked for selectivity. The detection limits of Section 3.7 rest on the calibration scatter of one device per loading, with no baseline noise record, and are estimates. The substrate, deposition route and thickness of the optical films, the concentration and dispensed volume of the drop-cast dispersions, and the gas-test bias, chamber volume, flow rate and vapor generation method were not recorded. Without a film thickness α is known only to within a constant factor, which does not move the Tauc energy intercept. The irradiance is known, $800 \mu\text{W cm}^{-2}$, while the electrode area is not, so responsivity cannot be computed. The unindexed reflections leave the 10 wt% phase content open.

Whether a GO-derived sheet of this reduction state behaves differently from rGO at equal carbon fraction is open while the reduction state and the secondary phase are unresolved. The measurements that would settle most of what remains are a weighed carbon fraction, Raman and XPS spectra of the four powders, the electrode area with a logged operating temperature, and re-indexing of the 10 wt% pattern. On the gas side they are a selectivity panel against other volatile compounds, repeated exposure cycles with a stability record, a humidity series and a detection limit from baseline noise.

5. Conclusion

Four films were characterized, hierarchical ZnO microflowers assembled from nanoplatelets and three nominal graphene oxide loadings, 1.5, 5 and 10 wt%. FTIR showed oxygen-containing groups alongside the Zn-O band in every composite without identifying the carbon phase, and XRD retained the wurtzite reflections at all loadings, while a sharp 13.11° reflection and a set of unindexed lines dominated the 10 wt% pattern and remain unassigned. Tauc gaps of 3.25, 3.28, 3.31 and 3.27 eV, each about ± 0.065 eV, resolved no change with loading, and the near-band-edge emission near 385 nm weakened and moved to longer wavelength. The room-temperature ethanol response increased with nominal loading from 50 to 1000 ppm, three films calibrated linearly at 2.19, 2.61 and $3.32 \times 10^{-4} \text{ ppm}^{-1}$, and the 10 wt% film gave the largest response, flattening above approximately 600 ppm. Calibration-based detection limits

fell from about 89 ppm for ZnO to 47 ppm at 5 wt% and, over 50 to 550 ppm, 30 ppm at 10 wt%. Under $800 \mu\text{W cm}^{-2}$ ultraviolet-A illumination the photocurrent gain passed through 2.77 at 5 wt% and fell to 1.55 at 10 wt%, the dark current rose from 0.040 to 0.098 μA , and the t_{90} rise time fell from 70 to 38 s while recovery did not order with loading. The ultraviolet channel showed an optimum inside the series and the ethanol channel none, methanol and propanol raised the response when co-admitted with ethanol, and a weighed carbon fraction, a logged operating temperature and the electrode area would place both functions in published ranges.

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Author Contributions

Mohammad Ghadimimehr: Formal analysis, Data curation, Visualization, Writing – original draft, Writing – review and editing. Mohammad H. Keshmiri: Investigation, Methodology, Resources. Mir Abdullah S. Sadjadi: Conceptualization, Supervision, Validation. Azimah Omar: Validation. Siti Rohani Sheikh Raihan: Validation. All authors read and approved the final manuscript.

Data Availability

The data supporting the findings of this study are not publicly available before the article is published. They are available from the corresponding author on reasonable request.

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