CHEMIRESISTIVE DEVICES BASED ON GRAPHENE DECORATED WITH METAL OXIDE NANOPARTICLES FOR NO2 DETECTION

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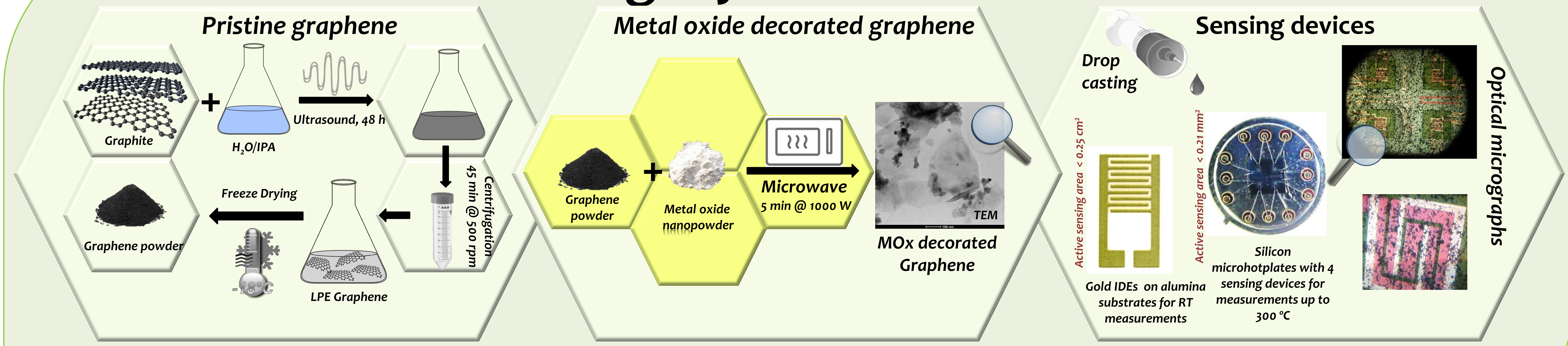
We present the sensing performances upon exposure to nitrogen dioxide of chemiresistors based on graphene, functionalized with several metal oxide NPs. Four types of sensors were analyzed: pristine graphene (Gr), ZnO doped graphene (GZnO), SnO2 doped graphene (GSnO2) and TiO2 doped graphene (GTiO2) sensors. The preparation of metal oxide NP doped graphene was performed by first freeze drying of graphene suspension previously prepared by liquid phase exfoliation method. The obtained graphene powders were mixed with metal oxide NP (3:1 mol/mol) and finally microwave irradiated for 5 minutes at 1000 W. The materials were characterized by SEM, TEM and Raman spectroscopy. Solutions of these powders in ethanol and isopropyl alcohol/water were deposited by drop casting onto two types of substrates: alumina substrates for room temperature measurements and silicon microhotplates for measurements up to 300 °C. The sensors were characterized in an automated gas line.

Sensing layers fabrication



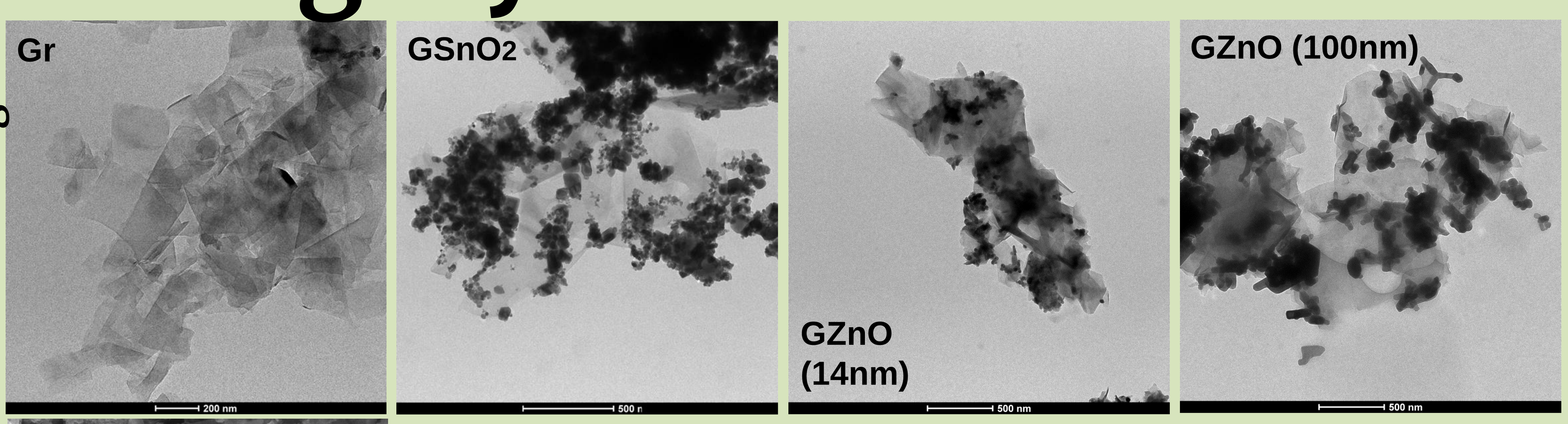
Graphite flakes were dispersed into a mixture of ultrapure water and i-propanol and sonicated. Unexfoliated graphite crystallites were removed by centrifuging. The ***concentration of the graphene*** *suspension was* ***0.1 ± 0.1 mg ml^{-1}***

Graphene powder was obtained by freeze drying of graphene suspension. 2.5 mg of graphene powder was mixed with 4 mg of metal oxide and microwave irradiated for 5 minutes at 1000 W

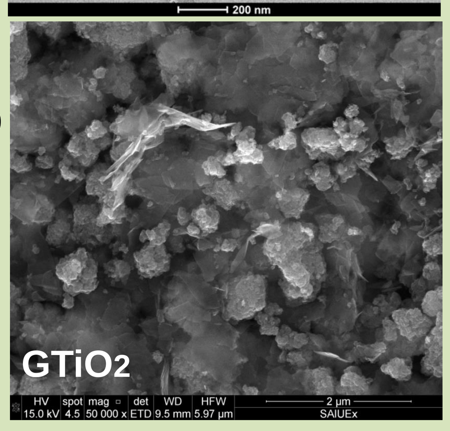
The resulting powder was dissolved in ethanol and isopropyl alcohol/water mixture and deposited by drop casting onto two types of transducers

Sensing layers characterization

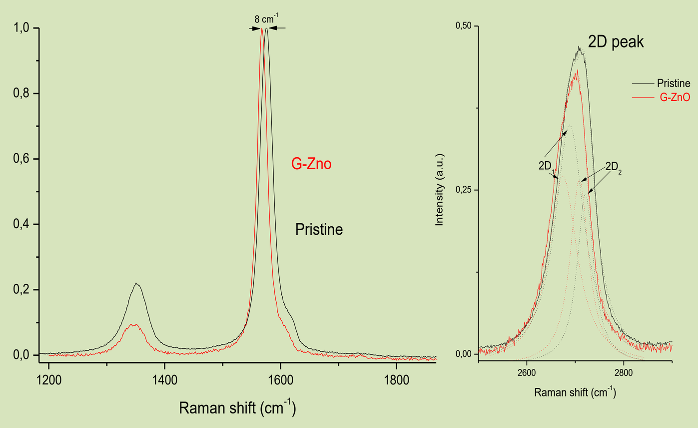
TEM images



SEM image



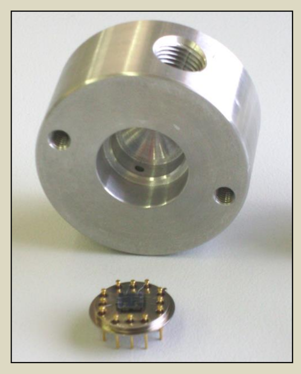
Raman spectra *of pristine graphene (black line) and GZnO (red line). Appreciable redshifts are observed for G and 2D peaks. Similar shifts were observed also for the other MOx decorated graphene materials presented herein.*



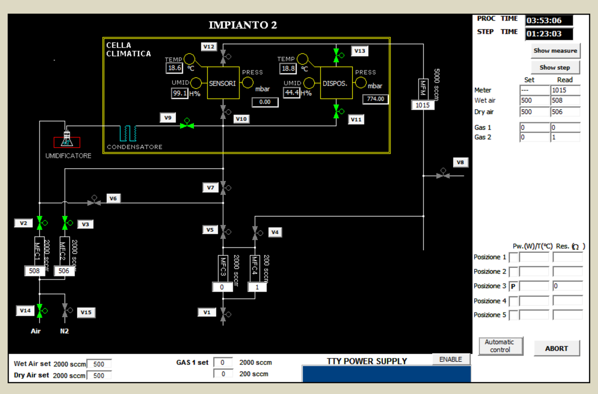
Device characterizations

Sensing chamber

Microsensor cell

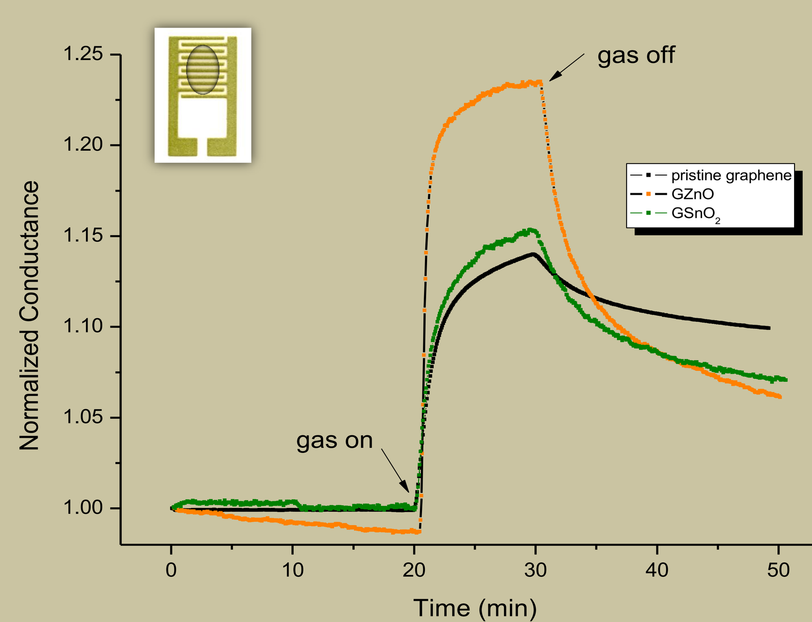


Equipment layout

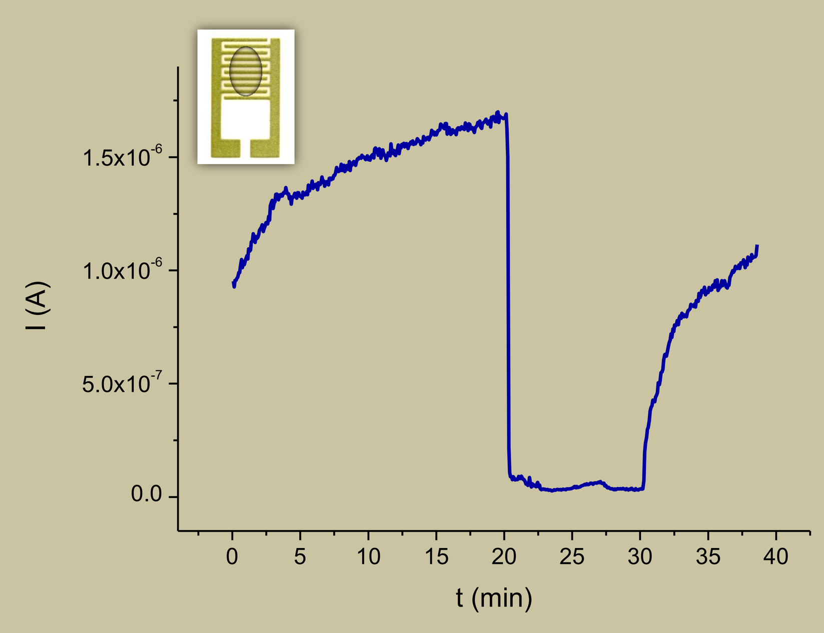


The chemiresistor conductance variations have been recorded in a ***Gas Sensor Characterization System (Kenosistec)*** *upon exposure to different concentrations of NO_2, keeping temperature and relative humidity constant in standard environmental conditions*

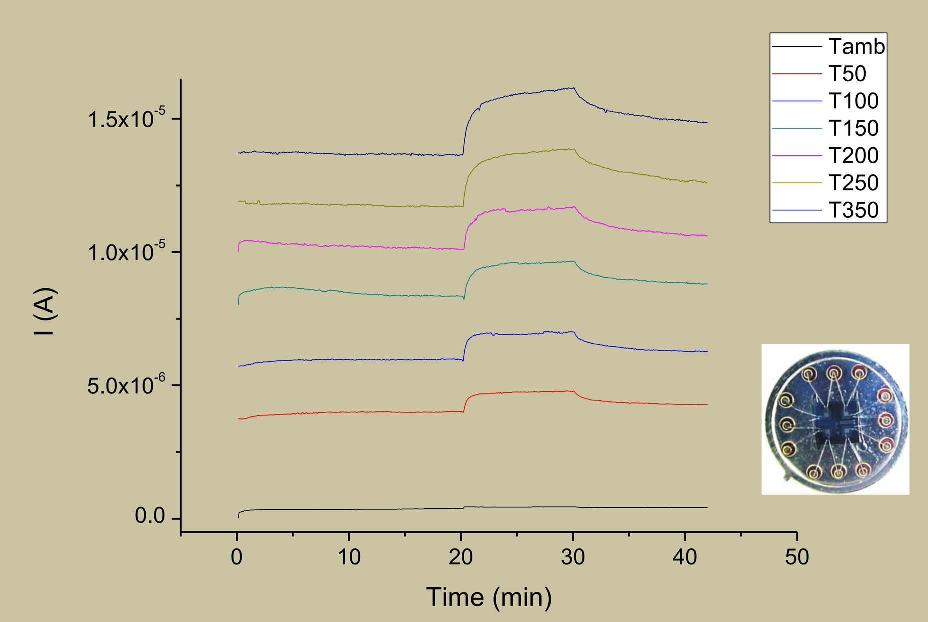
NO_2 sensing response



Dynamic response of ***pristine graphene***, *GZnO and* ***GSnO2*** *sensors to 1 ppm NO2 at room temperature*



Dynamic response of ***GTiO2*** *sensor to 1 ppm NO2 at room temperature*



Dynamic response of the ***GSnO2*** *device to 1 ppm NO2 in the whole temperature range*

Improvements of the responses were obtained for ZnO and TiO2 decorated materials at room temperature. In particular, device based on TiO2 decorated graphene shows a remarkable sensitivity gain towards NO2 gas.

For all the MOx decorated graphene, a sensing response increase with increasing the temperature is detected.

Finally, an overall enhancement of the sensor performance in terms of sensitivity and/or response time is demonstrated.

Conclusions

Results confirm that it is possible to tune graphene based sensor performance in terms of sensitivity and/or response time towards NO_2 gas and, in turn, that the functionalization with metal oxide nanoparticles can be an effective tool to modify the graphene sensing properties.

The NanoSen-AQM project has received funding from the Interreg-Sudoe Program of the European Union under gran agreement nº SOE2/P1/E0569)

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