Graphene Oxide-Based Hybrids for Chemiresistive VOCs Sensors

Eleonora Pargoletti[1,2*], Antonio Tricoli[3], Silvia Orsini[1], Valentina Pifferi[1,2], Mariangela Longhi[1,2], Vittoria Guglielmi[1,2], Luigi Falciola[1,2], Giuseppe Cappelletti[1,2]

[1]Dipartimento di Chimica, Università degli Studi di Milano, Italy, eleonora.pargoletti@unimi.it
[2]Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Firenze, Italy
[3] Nanotechnology Research Laboratory, Research School of Engineering, Australian National University, Canberra, Australia

INTRODUCTION

The sensing of gas molecules is of primary importance for environmental monitoring, control of chemical processes, medical applications, and so on[1]. In recent years, graphene-based gas sensors have attracted much attention due to enhanced graphene thermo-electric conductivity, surface area and mechanical strength. Thus, different structures have been developed and high sensing performances and room temperature working conditions were achieved[1]. However, they still suffer from several problems, which could be overcome by covering the graphene surface with metal oxide nanoparticles[2]. Furthermore, studies regarding the detection of Volatile Organic Compounds (VOCs) are still at the beginning[1]. Hence, the present work will be aimed at: *i*) optimizing the synthetic routes of *ad hoc* composite VOCs sensing materials (based on graphene oxide/SnO_2 or ZnO hybrids) and their deep physico-chemical characterizations; *ii)* engineering the gas sensor device; and *iii*) evaluating the sensing performances at both high and mild temperatures (also exploiting the UV light) towards gaseous ethanol, acetone and ethylbenzene.

EXPERIMENTAL/THEORETICAL STUDY

Starting from pure graphite, graphene oxide (GO) powder was synthesized by adopting the Hummer's modified method[2]. The synthetic route was deeply investigated by modulating both the starting carbon material (powder or flakes graphite) and the concentration of the H_2O_2 (*i.e.* the quenching/oxidizing agent), thus tailoring the final GO surface/structural properties. Once optimized this step, SnO_2 or ZnO were grown on its surface by a hydrothermal method, varying the starting salt precursor/GO weight ratio (Zn_xGO or Sn_xGO, x = 4, 8, 16, 32). For comparison, pure SnO_2 and ZnO (both commercial and home-made) were also tested. Several physico-chemical techniques have been used to characterize all the as-prepared nanopowders, such as XRPD, BET, Raman, FTIR, XPS, TEM and electrochemical analyses (CV and EIS). Subsequently, a homogeneous layer was deposited by spraying technique onto Pt-Interdigitated Electrodes (IDEs) starting from an ethanol suspension of each sample (2.5 mg mL^{-1}). Then, gaseous ethanol, acetone and ethylbenzene (the more interesting one, being nowadays the less studied VOC) were sensed by using a Linkam Scientific stage, equipped with an electrochemical workstation for the chronoamperometric measurements.

RESULTS AND DISCUSSION

The effective synthesis of graphene oxide sheets and, subsequently, the growth of metal oxide nanoparticles on its surface were confirmed by exploiting different physico-chemical techniques. As concerns the VOCs sensing analyses, we obtained very promising results (in terms of both response/recovery time and sensibility down to ppb levels) for either pure and hybrid materials at 350°C, and at lower temperatures (150°C to RT, by exploiting UV light) for the graphene-based samples (Figure 1), thanks to the presence of the carbon material.

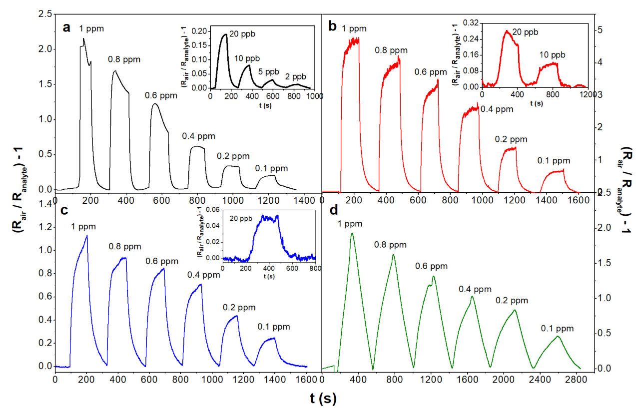

Fig. 1 Ethanol testing response obtained by **a)** pure home-made SnO_2 at 350°C (no UV), and $Sn_{32}GO$ at **b)** 350°C (no UV), **c)** 150°C (with UV), and **d)** RT (with UV).

Furthermore, a similar behavior has been noticed towards acetone and ethylbenzene pollutants.

CONCLUSION

Very promising results have been obtained with graphene oxide-based materials, which reveal to be more performing than the corresponding pure samples. Hence, these powders may represent very potential candidates for the gas sensing of highly toxic VOCs traces, both for environmental and medical diagnosis[1] purposes.

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