Efficient Structural, Compositional and Morphological Modifications of TiO₂-based Hierarchical Multicomponent Materials for Chemical Sensing

V. Galstyan¹, A. Ponzoni², I. Kholmanov³, M.M Natile⁴, I. A. Glisenti⁴, G. Sberveglieri¹, E. Comini¹ Sensor Lab, Department of Information Engineering, University of Brescia, Via Valotti 9, 25133 Brescia, Italy,

² National Research Council (CNR), National Institute of Optics (INO) – Unit of Brescia, Brescia, Italy, ³ Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, USA, ⁴ National Research Council (CNR), Institute of Condensed Matter Chemistry and Technologies for Energy (ICMATE), Department of Chemical Sciences, University of Padova, Via F. Marzolo 1, 35131 Padova, Italy

Corresponding author's e-mail address vardan.galstyan@unibs.it

Abstract:

We have synthesized pure, mixed and multicomponent structures by coupling different cost-effective techniques. Prepared TiO₂-based hierarchically assembled nanostructures have been thoroughly characterized by scanning electron microscope, X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. The sensing properties of materials have been studied towards explosive and toxic gaseous compounds. Investigations have shown the material crystalline structure, the variation of mixture concentration in the material and the modification of carbon-based layers have crucial effect on the response and the selectivity of materials. The obtained results demonstrate that the prepared multicomponent structures can be applied in the area of chemical sensors for the environmental monitoring and medical diagnoses.

Key words: TiO₂, hierarchically assembled, nanotubes, multicomponent structures, chemical sensor.

Introduction

Among the transition metal oxides TiO2 with its unique physical and chemical properties is a very attractive material for the manufacturing of functional devices. TiO2 is one of the most studied materials of last years for the fabrication of gas sensors to provide security and environmental monitoring [1]. Moreover, recently TiO2 have been studied for the application in breath analysis and clinical diagnostics [2]. Especially, one-dimensional TiO₂ nanotube arrays with their large surface to volume ratio and superior electron transport properties have been used for the fabrication of chemical sensors. The studies have shown that the TiO₂ nanostructures with the porous shape have good response towards volatile organic compounds and explosive gases. Then, the researchers carried out intensive studies to develop efficient strategies to improve the sensing performance of porous TiO₂ nanostructures.

Carbon has attracted and great interest for the application in functional devices due to the discovery of its allotropes (fullerenes, graphene nanotubes). Carbon-based carbon nanomaterials with their high strength, excellent resistance to corrosion, exceptional electrical and thermal conduction, and stability are used in a wide range of fields, including sensors, energy harvesting, energy storage and medicine. However, despite numerous researchers faced advances challenges regarding the synthesis, stability reproducibility of carbon-based materials at the relatively high operating temperatures. Thus, to be able to develop new applications of these materials further improvements of properties are in need.

Herein, we report efficient strategies for the preparation and the enhancement of sensing properties of well aligned TiO₂ nanotube arrays.

Experimental

We have fabricated pure, mixed and multicomponent structures based on TiO₂

nanotubes and modified graphene-based materials.

The structures were prepared by combination of sputtering, chemical and electrochemical oxidation approaches. We studied the obtained materials by means of scanning electron microscope (SEM) equipped with field emission gun, X-Ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy. The gas sensing performance of the samples was studied towards different gases, such as acetone ethanol, hydrogen, carbon monoxide, ammonia and nitrogen dioxide.

Results

Fig. 1 reports the morphologies of the obtained TiO_2 nanotubes and multicomponent structures. XRD measurement of the TiO_2 tubular arrays is reported in Fig. 2. Fig. 3 reports the isothermal dynamic response of the obtained pure (S1), mixed (S2) and multicomponent (S3) samples towards different concentrations of carbon monoxide (30, 60 and 120 ppm) and hydrogen (120, 240 and 480 ppm) at 300 °C.

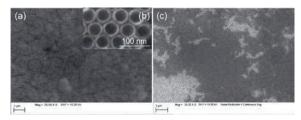


Fig. 1. (a) and (b) SEM images of the TiO₂ nanotubes with the different magnifications. (c) SEM micrographs of the prepared multicomponent structures.

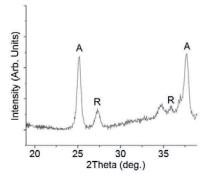


Fig. 2. XRD pattern of the TiO₂ nanotubular structures.

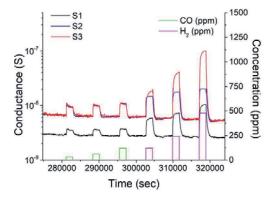


Fig. 3. Dynamic response of the prepared samples towards different concentrations of carbon monoxide and hydrogen.

Conclusion

Pure, mixed and multicomponent structures based on TiO₂ nanotubes and modified graphene-based layers were prepared trough the sputtering, chemical and electrochemical oxidation techniques. We studied the effect of each material on the sensing properties of the samples. In the presence of reducing gases, the obtained materials showed highly sensitive, reversible and reproducible responses. The response and the selectivity of structures are improving depending on the modification of their composition and operating temperature. Meanwhile, we developed a cost-effective and easy synthesis method for the fabrication of high performance and small size chemical gas sensors.

Acknowledgements

This work has been supported by the FP7 project N. 313110 "Sniffer for concealed people discovery (SNOOPY)" and the project N. 611887 "MSP: Multi Sensor Platform for Smart Building Management" by the European Community's 7th Framework Programme.

References

- [1] V. Galstyan, E. Comini, G. Faglia, G. Sberveglieri, *Sensors* 13, 14813-14838 (2013); doi: 10.3390/s131114813-
- [2] M. Righettoni, A. Amann, S. E. Pratsinis, Breath analysis by nanostructured metal oxides as chemo-resistive gas sensors, *Materials Today* 18, 163-171 (2015); doi: 10.1016/j.mattod.2014.08.017
- [3] I. Kholmanov, S. Domingues, H. Chou, X. Wang, C. Tan, J-Y. Kim, H. Li, R. Piner, A. Zarbin, R. Ruoff, Reduced Graphene Oxide/Copper Nanowire Hybrid Films as High-Performance Transparent Electrodes. Acs Nano 7 (2), 1811-1816 (2013); doi: 10.1021/nn3060175