Innovative ozone sensors for environmental monitoring working at low temperature

Summary

Ozone (O_3), a gas that is well known for its oxidant properties, has drastically incremented its amount in the troposphere in the last decenniums. Considering that high O_3 concentration is well-known to be hazardous for the human health (especially for the respiratory system), the development of valid strategies to detect it appears an urgent need.

The analytical techniques available in the market for measuring O_3 are expensive and they require expert technicians (e.g. spectroscopic UV adsorption). For this reason, cheap alternatives have been investigated for online measurement of O_3. Among them, chemical gas sensors exhibit a great potential because they are cost-effective, easy to use, stable in time, reliable and integrable in portable electronics.

The features of a gas sensor could save human health and the environment respectively from diseases and disasters, controlling continuously the air pollution. For this reason, human generation is intimately related to the potential of gas sensors.

The aim of this PhD thesis is the investigation of innovative materials to produce gas sensors able to detect O_3 and the main interfering gases: humidity, ammonia and nitrogen dioxide. To reach this goal, chemical sensors were realized by techniques like screen printing and dip coating. The sensitive materials were successfully obtained by different synthesis methods (i.e. hydrothermal synthesis and auto-combustion sol-gel route) and fully characterized. In this way, an understanding of the relations between the structural characteristics of the materials and the gas sensing phenomena was accomplished. The proposed sensitive materials can find application in an array of sensors able to distinguish the presence of O_3 in a real environment.

This PhD thesis is composed by 7 parts that here are explained more in details

In the **Chapter 1** the issues related to O_3 in troposphere are described in detail, including the effect on the human health and the recommended threshold limit values.

Chapter 2 discusses the gas sensors principles that are depicted with a special focus on Semiconducting Metal Oxide (SMOx) and carbon-based sensors. Advantages and disadvantages of both types of gas sensing systems are elucidated, and a preminary presentation of the material selected in this work is given.

Chapter 3 reports the technologies for chemical sensor preparation and the principles of the instruments used for materials characterization.

In **Chapter 4** results of O_3 tests achieved firstly with $BaFe_{12}O_{19}$ thick films, synthetized by auto-combustion sol gel method and innovative spray-coated detectors based on functionalized single-walled CNTs by covalent modification with octadecylamine (ODA).

In **Chapter 5**, the best results among O_3 sensors were presented by using n-type indium oxide (In_2O_3): a commercial In_2O_3 powder was doped with different contents of tungsten trioxide (WO_3) by impregnation method to enhance its sensing capability. With the aim to diminish the size of crystallitea and agglomerates and to enhance the specific surface area of the nano-powder, In_2O_3 and WO_3 doped-In_2O_3 were synthetized by hydrothermal synthesis and used as O_3 sensitive materials

working close to room temperature. Moreover, DRIFT (Diffuse Reflectance Infrared Fourier Transform spectroscopy) analysis were performed on In_2O_3 and WO_3 doped-In_2O_3 for understanding which species are generated during the interaction of the metal oxide in oxidant atmospheres like NO_2 and O_3.

The main drawback of SMOx sensors is the modest selectivity. For this reason, in **Chapter 6** novel solutions for the monitoring of humidityare described. For humidity mesurements, three different biochars were used for the first time: SWP-Softwood pellets, OSR-Oil Seed Rape and WCG-waste coffee ground.

Finally, the final **Chapter 7** displays the results of sensors realized for N-based interferences: ammonia and nitrogen dioxide. For ammonia detection, a spinel type Co_3O_4 realized by auto-combustion sol-gel route was utilized, whereas different ZnO-based screen-printed sensors were applied for the dection of NO_2 at relatively low temperatures.

This PhD work has been developed through relationships with different research groups: Carbon group directed by prof. Tagliaferro with the surpervision of dr. Jagadale, the groups of prof. Specchia and prof. Cauda in Politecnico di Torino. Moreover, international collaborations were fulfilled: the Weimar group in the University of Tübingen with the surpervision of Dr. Barsan, E. Bekyarova from Carbon Solutions company and K. Naishadam from Georgia Tech University.