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SONOCHEMICAL SYNTHESES OF METAL OXIDE NANOCOMPOSITES FOR GAS SENSING

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Abstract. *This paper proposes several sonochemical synthesis methods to obtain metal oxides nanopowders suitable for gas sensing. The synthesis process for metal oxide heterojunctions that combines n-type metal oxide semiconductors and p-type metal oxide semiconductors, such as ZnO-CuO, is presented. Examples of synthesis methods employing either chlorides only or acetates only as precursors are also inserted.*

Keywords: Sonochemistry, Gas Sensors, Metal Oxide Semiconductors

1. Introduction

Detection of flammable gases (methane, propane), volatile organic compounds (VOC) or other toxic gases (e.g. hydrogen sulfide) is of high importance for safety and process control in chemical, petrochemical and other manufacturing industries, as well as for safety of homes and buildings. The discovery of the property of the metal oxide (MOX) thin films to change their electrical conductivity as a function of the reducing and oxidizing gases from the ambient, more than fifty years ago, has triggered the realization and commercialization of the first solid state gas sensors based on these materials [1]. Even though these sensors can be used for both domestic and industrial portable applications, the power consumption needed for heating the substrate to the optimum sensing temperature and reading the detector response ranges between 660 mW and 850 mW. Such a high level of power consumption requires frequent battery replacement, which in applications such as portable personnel protection equipment for people working in hazardous environments (refineries, power plants, etc.), might lead to serious safety issues, besides an increased cost of operation. In addition, these sensors are detecting gases at relatively high concentrations. However, in safety applications, it is useful to detect lower gas concentrations. Therefore, there is a strong industrial motivation to decrease power consumption and increase both sensitivity and selectivity of sensors detecting gases such as CH_4, H_2, CO, benzene, H_2S etc.

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It is already largely accepted by the scientific community that the use of nanostructured sensing materials as gas sensing layers will allow the reduction of the power consumption and the increase of sensitivity, due to the large specific area and increased porosity, which increase the number of active sensing sites. The surface energy is high enough for the sensing reactions to take place without requiring too much thermal energy from outside.

In prior art, different technologies have been demonstrated on both thin and thick metal oxide sensing films. The most frequent technologies used for preparing these layers are: sol-gel, electrospinning, hydrothermal, sonochemistry, carbothermal, pulse laser deposition, solid state chemical reaction and sputtering electron beam evaporation. These methods aim to synthesize single component metal oxide, (e.g. WO_3, SnO_2, ZnO), doped metal oxides (e.g. Fe-doped MoO_3) or multiple-components metal oxide (such as MoO_3-CuO, SnO-CuO and ZnO-CuO). The methods based on synthesis from solution (sol-gel, hydrothermal, electro-spinning, sonochemistry) are very attractive since they manage to provide a larger and better controlled surface area. Among these solution-based methods, sonochemistry has the advantage that the layer (nano)structuring can be controlled by the value of the power and intensity of the acoustic radiation applied during cavitation, which activates the chemical reactions taking place between desired precursors and reagents.

Sonochemistry [2-5] is a preparation method, which does not need very high sintering temperatures to produce metal oxide nanopowders. Sonochemical synthesis is defined as one-pot, heterogeneous chemical reaction process which takes place in a chamber, where a solution containing the precursors (e.g. powders, aqueous or non-aqueous solvents, surfactants, etc.) is exposed to high intensity ultrasound radiation by means of a high power vibrating sonotrode, which is immersed in the solution. The sonochemical method for synthesizing MOX-based materials from the liquid phase is in the early stage of development. Only few results are reported in literature, all of them proving the potential of the method to enable a good control of the nanostructuring process for the realization of MOX nanopowders with large surface area and increased porosity level.

2. MOX for gas sensing

Semiconductor metal oxides have been used for the first time to detect VOC gases in 1962, when Taguchi patented the fabrication of a SnO_2 resistive gas sensor, produced by Figaro Engineering Inc. Ever since, several research groups have been working on testing different metal oxides that could potentially detect VOCs. Despite numerous research conducted in this area, there is still no firm conclusion on which is the most suitable MOX for sensing VOC. As stated in several papers [6-12] some of the materials that proved to have high sensitivity to VOCs are:

SnO_2, ZnO, WO_3, In_2O_3 and TiO_2. It was also concluded by Liu et al. [13] that the synthesis method highly influences the properties of the synthesized material.

In order to improve the gas selectivity and sensitivity, to increase stability, reliability and to eliminate drift, the following methods of changing the material microstructure can be employed: structure and architecture of the MOX can be changed to increase the porosity and surface area, dopant elements (such as Ag, Au, Pt, Pd) can be added [14], or grain size and morphology can be modified [12]. As stated in other reviews [7,13,15], the current research is based on developing new nanostructured materials such as: nanorods, hollow spheres, polycrystalline nanotubes, nanobelts and single crystalline nanowires.

Semiconductor metal oxides have also been used to monitor low concentrations of benzene. Materials such as ZnO nanorods [16], Ce-doped ZnO materials [17] or WO_3 thick films [18] have been investigated for their sensing properties. Despite numerous investigations on benzene sensing, the materials tested show a poor sensitivity.

2.1. MOX heterojunctions

The combination between *n*-type metal oxide semiconductors (SnO_2, ZnO, MoO_3, WO_3, etc.) and *p*-type metal oxide semiconductor (CuO, Cr_2O_3, CuO, NiO, etc.) has shown the highest sensitivity and selectivity for gas sensing (e.g. H_2S). The sensing properties of these materials could further be improved by nanosctructuring the nanocomposite containing the p-n heterostructures made of these semiconductor oxides. The nanostructuring can be easily controlled using sonochemistry.

A novel method employing sonochemistry, to synthesize a H_2S sensing material based on MOX heterojunctions, was proposed [19]. An example of the aqueous synthesis process is presented in **Fig. 1.**

In order to obtain ZnO-CuO nanocomposites, a mixture of nitrates (zinc nitrate hexahydrate and copper nitrate trihydrate dissolved in water) was added to a 4M NaOH solution. Final solution was exposed to power acoustic irradiation and the obtained powder was collected, washed and dried. The nanocomposite powder was mixed with a binder to form a slurry of controlled viscosity further on deposited on an interdigitated metal electrode structure, as a thick or thin sensing film. After the thermal consolidation of the sensing layer, the obtained chemo-resistor is suitable for H_2S sensing.

In the absence of H_2S, the electrical resistance of the chemiresistor is high due to the high barrier height at the interface between *n*-type and *p*-type metal oxides. In the presence of H_2S, the p-type metal oxide semiconductor reacts with H_2S, thus lowering the energy barrier and resistance of the chemo-resistor.

The reaction between the MOX and H_2S is reversible and the barrier height increases again with the oxide formed in the presence of clean air.

MOX heterostructures can also be synthesized and employed as VOC sensing material. A method was proposed [20] to synthesize Co_3O_4-CeO_2 nanocomposite powder from cobalt and cerium nitrates using sonochemistry. The flowchart of the aqueous synthesis is shown in **Fig. 2.** Nitrate precursors (cobalt nitrate and cerium (III) nitrate dissolved in ethanol) were mixed with cetyltrimethylammonium bromide (CTAB) solution and NaOH and exposed to power acoustic irradiation. Then, the obtained powder was collected, washed and dried and thin or thick films were obtained, using the same method described before.

2.2. Pd doped MOX

It is now accepted that the addition of noble materials (e.g. Pd, Ag, and Pt) improves both gas sensitivity and sensor response. SnO_2–based sensors are usually doped with noble metals that either alter (Ag and Pd) or not (Pt) its work function [21]. Based on this, one of two sensitization mechanisms is employed: either chemical (for Pt-doped SnO_2) or electronic (for Ag- and Pd- doped SnO_2).

The electronic sensitization consists in the fact that Pd atoms react with oxygen from ambient and they forms oxides (PdO), which are chemically stable in the absence of the reducing gases, like CH_4, CO, or H_2. In the presence of reducing gases in the ambient, the PdO phase formed as described above is reduced to Pd and thus the electrons resulted from these redox reactions between Pd and PdO phases will be directed to the metal oxide substrate which will thus increase its electrical conductivity.

The chemical sensitization consists in the fact that Pd loading of the metal oxide is catalyzing the dissociation of the reducing gases and those dissociated spilled-over components will react with negatively charged oxygen ions releasing electrons which will enter the conduction band of the metal oxide which will thus increase its electrical conductivity. Transmission electron microscopy measurements [21] showed that, in the case of Pd-SnO_2, Pd particles are uniformly distributed on the surface of SnO_2 and have diameters between 5 nm (at 3 wt.%) and 10 nm (at 5 wt.%). Nanostructured Pd doped metal oxides were successfully synthesized using sonochemistry [22]. To further improve the grain size and powder architecture of a SnO_2-Pd gas sensor prepared using sonochemistry, the addition of nanostructuring guiding agents (like dimethylformamide (DMF), Cetyl trimethylammonium bromide (CTAB) and Pluronic P-123 (P123)) was proposed [23]. Aqueous synthesis based only on chlorides or only on acetates as precursors has been used and examples of the synthesis process are presented in the flow diagrams shown in **Fig. 3** and **Fig. 4**.

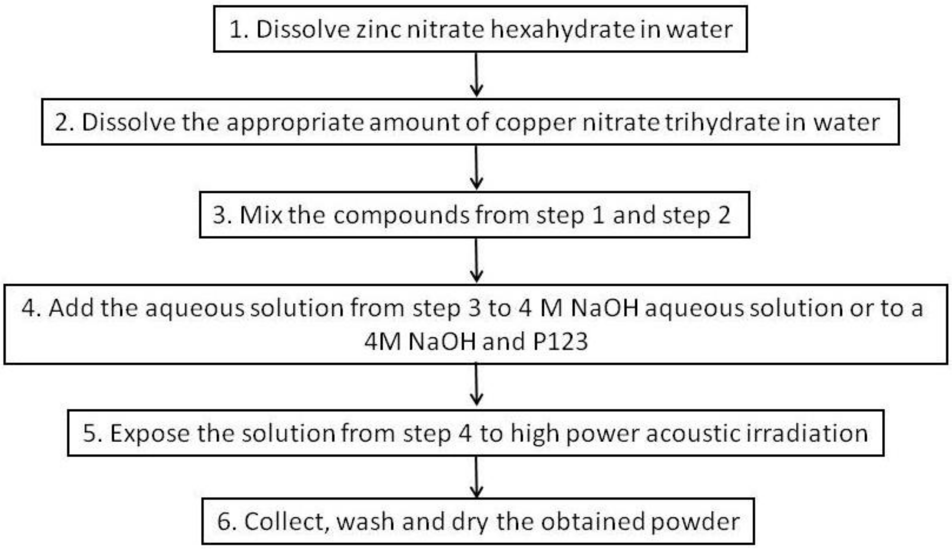

Fig. 1. Flowchart of synthesis method to obtain ZnO-CuO nanocomposite powder.

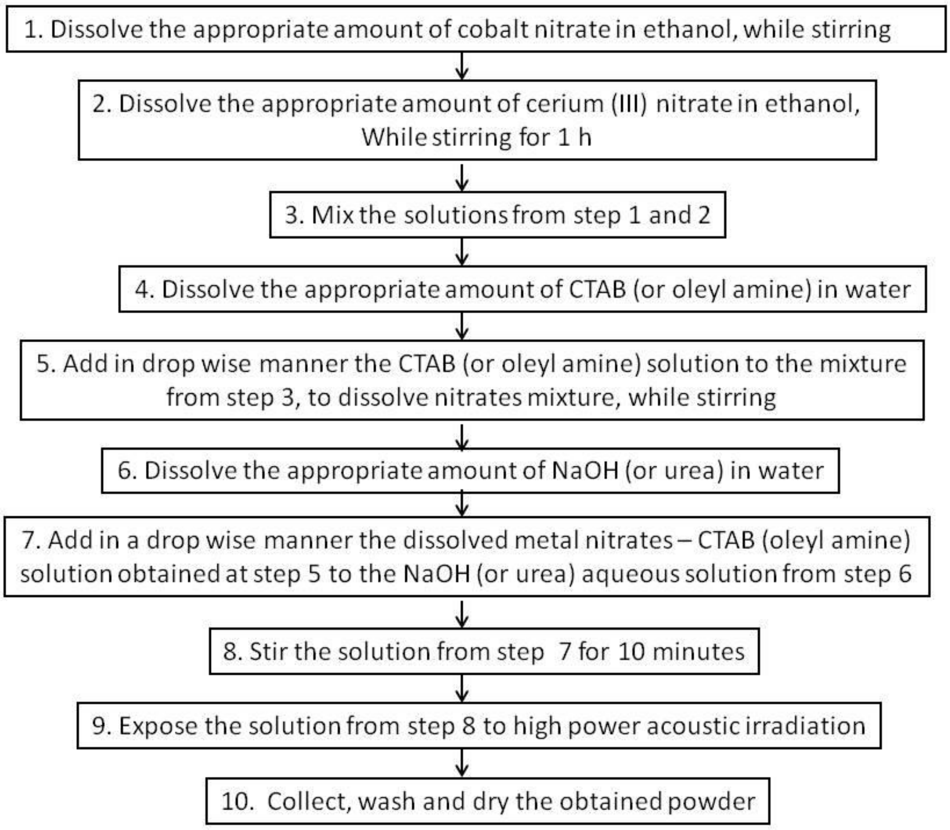

Fig. 2. Flowchart of synthesis method to obtain Co_3O4-CeO_2 nanocomposite powder.

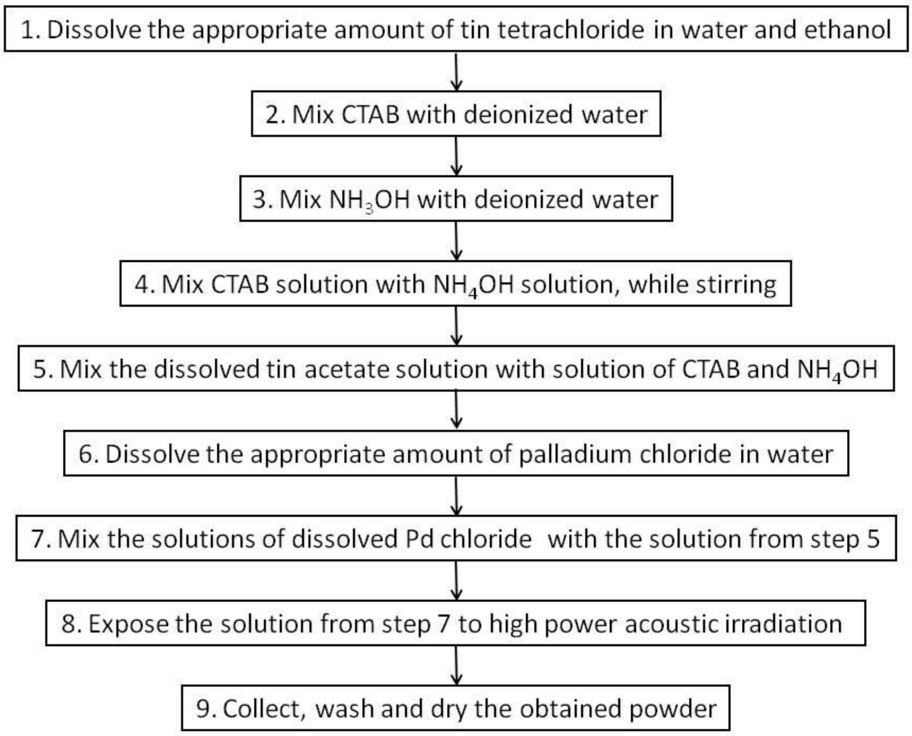

Fig. 3. Flowchart of synthesis employing only chlorides as precursors for obtaining Pd-SnO_2 nanocomposite powders.

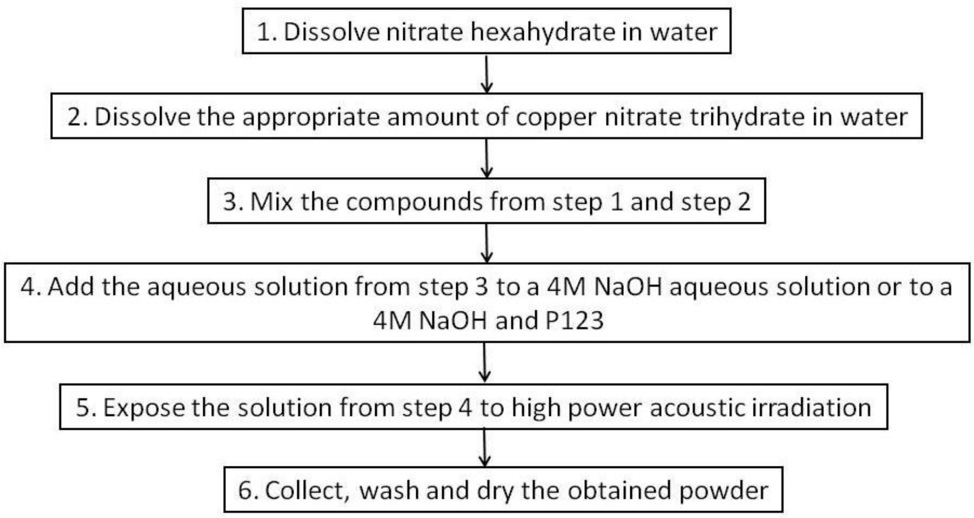

Fig. 4. Flowchart of synthesis employing only acetates as precursors for obtaining Pd-SnO_2 nanocomposite powders.

Flammable gas sensors based on Pd-SnO_2 thin films can be prepared by mixing the obtained powder with water-glycerol-bicine solution for getting a nanoink with controlled rheological properties compatible with the maskless direct printing tool. Then, the film is dried and fired at a temperature of 500 – 600°C. Chemo-resistive flammable gas based on Pd-SnO_2 thick films can be prepared by mixing the powders with terpineol, to obtain a paste which is screen printed on a metal interdigital electrode structure and annealed at a temperature of 500 – 600°C.

3. Conclusions and Future Prospects

It is now believed that MOX nanostructured materials have the potential to increase gas detectors sensitivity and to reduce their power consumption. Recent research has been dedicated to identify synthesis methods that could produce repeatable results and could be easily modified to manufacture nanopowders of desired architecture. The synthesis method should also allow for an optimization of the synthesis parameters in order to obtain the porosity, orientation and size of the desired nanopowders. Sonochemistry is a promising green synthesis method that has been shown to obtain nanostructured materials with good sensing performance [24].

As stated in this paper, it is believed that novel sonochemical synthesis methods of MOX heterojunctions and doped-MOX nanopowders are the future of gas sensing and could be used to improve the current available technology. A more thorough understanding of the sensing principles, chemical and physical phenomena that are taking place during the sonochemical process could lead to better designed nanopowders.

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