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Transition metals (Co, Cu) as additives on hydrothermally treated Tio_2 for gas sensing

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Abstract

Titania-supported Cu or Co nanoparticles have been prepared with loading of 0.5 wt.% and have been tested for the detection of CO. Characterization with XRD showed that Cu and Co did not change appreciably the titania grain size. However, the anatase-to-rutile phase transformation was promoted. XPS results manifested a conspicuous coating of the additives on the TiO_2 surface, and suggested chemical states of values 0 and +2 for Cu at 600 and 800 °C respectively, and +2 for Co at both calcination temperatures. The evaluation of the gas sensing properties highlighted an adequate n-type response to CO for the Cu–TiO_2 and Co–TiO_2 materials calcined at 600 °C, while the response of the same materials calcined at 800 °C was diminished and exhibited a p-type characteristic, which could be related to the formation of a inversion layer localized in the surface.

Keywords: TiO_2; Cobalt; Copper; Hydrothermal; Gas sensor

1. Introduction

Semiconducting metal oxide materials, such as TiO_2, SnO_2, In_2O_3, etc., play an important, steadily increasing role in almost all fields of electronics. Especially their application to gas sensors demand nanosize control strongly. The principle of operation of semiconductor gas sensors is based on the interaction of a gas molecule with the surface, which produces an interchange or trapping of free carriers. This sensing mechanism implies that the surface of the material is extremely important. From a basic point of view, three key factors have been recognised to control the sensor response, that is, the receptor function, the transducer function and the utility factor [1,2]. The receptor function is supplied either by the surface of the grains or by a foreign material dispersed on them. Therefore, in order to have more sensitive surfaces, catalytic additives are incorporated to the basis metal oxide [3–6]. The transducer function is related to the grain boundaries and intensified extraordinarily when the grain size becomes smaller than twice the thickness of the space charge layer [7]. The utility factor is the ratio of the grains accessible for the target gas. Thus, getting small particles would improve the sensing efficiency. In the case of TiO_2, these parameters can be effectively controlled by hydrothermal treatments. Nanoscale pure titanium dioxide with pertinent solid-state properties can be obtained by adopting hydrothermal treatments for the nanoprocessing of materials [8].

In this work, hydrothermally treated TiO_2 has been modified with different transition metals (Co, Cu). Such metals have been proved as attractive to be added to titania for enhancing the catalytic power or the gas sensing features [9–11]. The nanoparticles were calcined at several temperatures and characterized. The hydrothermal treatment stabilized the TiO_2 suppressing the thermal induced grain growth and shifting up the temperature of the anatase-to-rutile phase transformation. Besides the control of size and phase, the hydrothermal process highlighted how to obtain highly stable

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colloidal suspensions of titanium dioxide. Electrical measurement showed a particular behaviour (n- or p-type) depending on the calcination or the operating temperature. The main purpose has been to analyze the effects of two transition metals (cobalt and copper) as additives on TiO_2 nanomaterials. Firstly, we have studied the structural modifications induced by the transition metals to titania and, secondly, we have evaluated the sensing properties, focusing on the type of conduction and the sensor response.

2. Experimental set-up

The materials were prepared starting by a wet chemical process. A sol–gel route was followed for the synthesis of TiO_2, in which titanium isopropoxide was used as precursor. A 0.5 M solution of the alkoxide diluted in isopropanol was added dropwise to acidic aqueous solutions. The hydrous titania gel resulting from the hydrolysis-condensation process was suspended in acidic water and subjected to an hydrothermal treatment in an autoclave. Further details of the preparation procedure can be found in [8]. After the hydrothermal treatment, we obtained stable TiO_2 suspensions which were impregnated with catalytic additives. The impregnation process was carried out starting from copper and cobalt nitrates as precursors. By this procedure we obtained pure hydrothermally treated TiO_2 and TiO_2 modified with 0.5 wt.% of Co or Cu. The powders were then calcined at 600 or 800 °C, characterized by XRD, XPS and TEM, and printed as thick films to test their electrical response in air and under CO exposure. The sensor response was evaluated as the ratio R_{air}/R_{gas} for the n-type materials and as R_{gas}/R_{air} for the p-type.

3. Results and discussion

3.1. Structural and chemical characterization

regard to the pure TiO_2, we have previously reported the properties of hydrothermally treated TiO_2 [8]. Briefly, the main findings of the comparison between untreated and hydrothermally treated titania were as follows: XRD revealed that the hydrothermal treatment suppressed the anatase-to-rutile transformation and was effective for inhibiting the grain growth, which was supported by TEM micrographs (see Fig. 1). We observed that after calcination at 800 °C the hydrothermally treated titania was predominantly anatase with average size of about 34 nm. According to the structural characterization, we could mention that the hydrothermal treatment allowed the preparation of pure nanophase TiO_2 with controlled microstructure. Moreover, the hydrothermal treatment was suitable for obtaining gas sensing films robust for high temperature applications. In view of these essential features, we could assume that we have obtained an optimized starting material for gas sensors. The next step is the sensitization of the surface. For that purpose, we

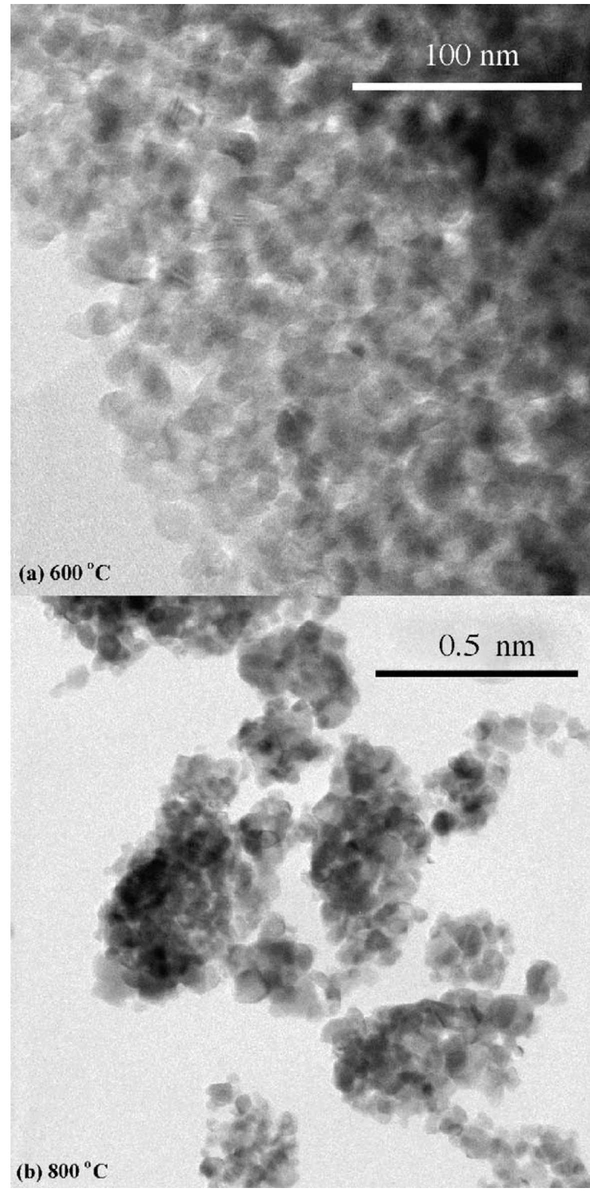

Fig. 1. TEM micrographs of the hydrothermally treated TiO_2 calcined at 600 °C (a) and 800 °C (b).

prepared hydrothermally treated TiO_2 impregnated with Co or Cu acting as catalysts.

Concerning the effects of the two transition metals on TiO_2, in the X-ray diffraction patterns presented in Fig. 2 it is observed qualitatively that the two metals promoted the anatase-to-rutile transformation. Diffractions ascribable to the metals were not detected, suggesting that they are fairly well dispersed on titania. From these diffractograms we can determine the crystallite size and the rutile content [11]. When loaded with the metal additives, the anatase crystallite size values tended to diminish slightly but the rutile content increased to be near 100% at calcination temperature of 800 °C. Table 1 summarizes the numerical results together with the surface Co or Cu contents as found by XPS measurements. XPS highlighted a strong surface segregation