Mechanochemical synthesis of porous SnO_2/TiO_2-based composite ceramics: Microstructure and humidity sensing characterization

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Abstract

Tin-oxide and titanium-oxide (SnO_2/TiO_2) based ceramics are modified by doping with Mo and Zn ions using a simple and economical mechanochemical procedure with low-cost starting precursors. Optimization of synthesis parameters is carried out to obtain high open porosity which provides better adsorption of water molecules when ceramics are used as sensing elements of the humidity sensors offering several advantages such as high chemical, mechanical and thermal stability. Correlations between the microstructure and electrical properties are investigated using several techniques: X-ray diffraction, scanning electron microscopy, and Raman and impedance spectroscopy. The most favorable synthesis conditions for achieving ceramics microstructure suitable for high-sensitivity and selectivity to chemisorptions, and relatively fast response and recovery time, as well as good stability and reliability, were determined.

Solid-state reaction synthesis

Starting powder precursors:
✓anatase TiO_2 and rutile SnO_2 in stoichiometry for $Sn_{0.2}Ti_{0.8}O_2$

↙ +1 mol % MoO_3

↘ +1 mol % MoO_3 + 1 mol % ZnO

↓

✓wet-milling in ethanol at 100 rpm for 210 min

Retsch GmbH PM100
- 5 mm diameter ZrO_2 grinding bals;
- 50 mL ZrO_2 grinding jar;

↓

Pre-calcination in furnace at 650 °C for 180 min

↓

Pressing under 1.176 GPa and sintering at 1100 °C for 240 min

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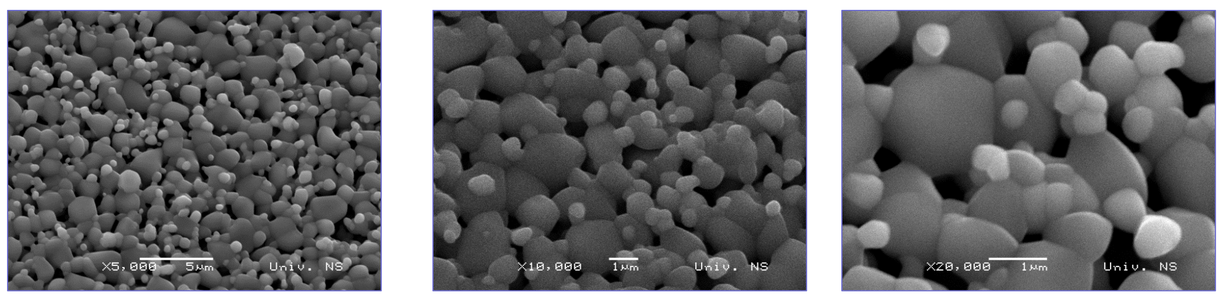
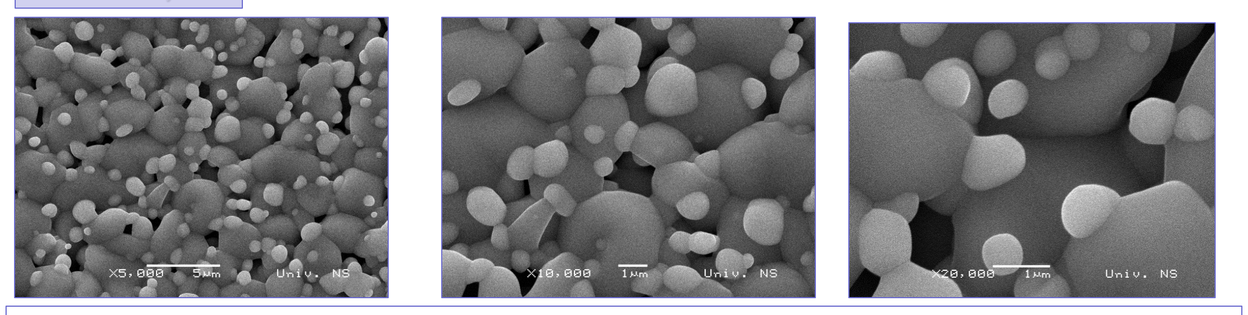
Sample 1: TTO:Mo — Sample 2: TTO:Mo,Zn

Microstructure – particle size and shape

TTO:Mo: — by SEM JEOL JSM -6460LV

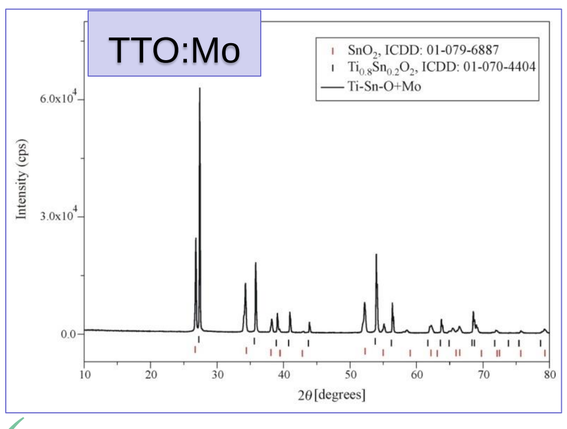


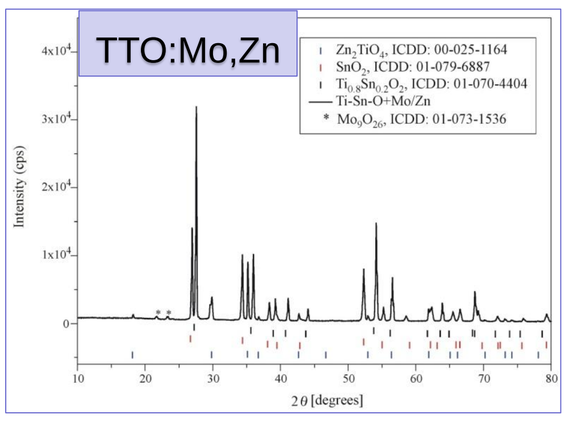
TTO:Mo,Zn:



✓Relatively high porosity ~20% achieved;
✓Double-doping decreases the porosity and increases the particle size;

Crystal structure



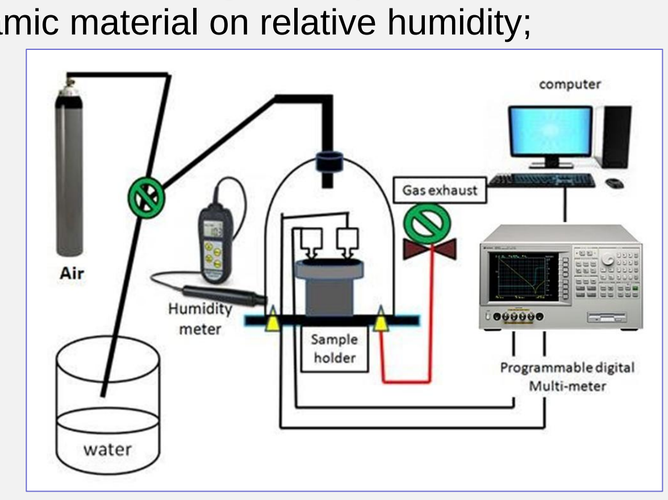


✓Crystal structure of SnO_2/TiO_2-based composite ceramics confirmed;
-major crystal phase indexed as $Sn_{0.2}Ti_{0.8}O_2$ (ICDD card no. 01-070-4404),
-impurity related XRD peaks indicate traces of SnO_2 (ICDD card no. 01-079-6889) in TTO-Mo and TTO-Mo,Zn; Zn_2TiO_4 (ICDD card no. 00-025-1164) in TTO-Mo,Zn; and Mo_9O_{26} (ICDD card no. 01-073-1536) in TTO-Mo,Zn).

Electrical measurements – Humidity sensing characterization

•Humidity sensors based on ceramic materials can detect humidity on the principle of changing the electrical properties of sensing materials by adsorption of water vapor and their penetration through open pores of ceramics;
•Sensors based on the dependence of sensing material impedance on relative humidity are most often used, but it is also possible to realize sensors on the principle of measuring the dependence of resistance or capacitance of the ceramic material on relative humidity;

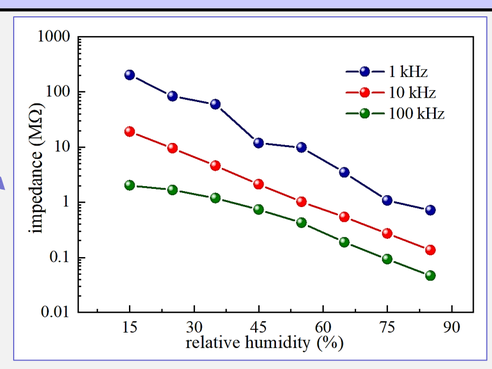
Measuring setup:



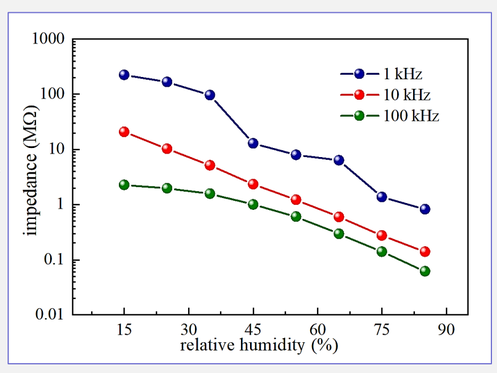
•For both samples, a linear response in the relative humidity range between 15% and 85% was observed at a relatively low frequency. But, TTO:Mo sample shows better sensing linearity at the optimal operating frequency of about 10 kHz;

•At higher frequencies, the impedance plot becomes flat because the direction of the applied electric field changes rapidly and the polarization of the adsorbed water molecules cannot catch up;

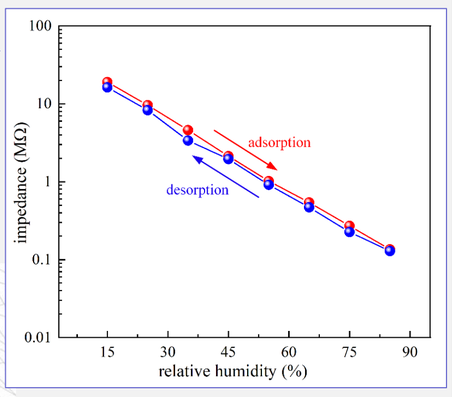
TTO:Mo



TTO:Mo,Zn



•Sensing curves for the adsorption and desorption processes almost overlap with each other showing very small hysteresis (TTO-Mo sample).
The hysteresis error was calculated to be about 2.8%, which indicates good reliability;
•Further research is needed in terms of stability as well as response and recovery time;



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