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Synergistic Effect of Nanocrystalline SnO_2 Sensitization by Bimetallic Au and Pd Modification via Ingle Step Flame Spray Pyrolysis Technique †

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Abstract: Convenient and scalable single step flame spray pyrolysis (FSP) synthesis of bimetal AuPd sensitized nanocrystalline SnO_2 for gas sensor application is reported. The materials chemical composition, structure and morphology has been studied by XRD, XPS, HAADFSTEM, BET, ICP-MS techniques as well as thermo-programmed reduction with hydrogen (TPR-H_2). Superior gas sensor response of bimetal modified SnO_2 towards wide concentration range of reducing (CO, CH_4, C_3H_8, H_2S, NH_3) and oxidizing (NO_2) gases compared to pure and monometallic modified SnO_2 is reported. The observed enhanced gas sensor performance is concluded to arise from combination of facilitated oxygen molecule spillover on gold particles and electronic effect of Fermi level control by reoxidizing Pd-PdO clusters, homogeneously distributed over SnO_2 particles surface.

Keywords: metal oxide; semiconductor; gas sensor; sensitization; bimetal; flame spray pyrolysis

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1. Introduction

The use of bimetallic nanoparticles (NPs) in order to sensitize semiconductor metal oxide gas sensors attracts more and more attention lately [1]. Particularly gold-containing NPs with Pt-group metals have been reported to provide profound improvements in certain gases detection [2–6]. Currently bimetallic NPs functionalized semiconductor metal oxides are obtained in a two step process: either separately prepared bimetallic nanoparticles or noble metal precursors with further reduction are being deposited on the previously synthesized metal oxide matrix. Such procedure is time and labor consuming and bears risks if introduction of impurities in the final nanocomposite or deviations of NPs content. In this work we report superior gas sensing properties towards a wide spectrum of gases of bimetal—Au and Pd—modified nanocrystalline SnO_2, obtained in single step via flame spray pyrolysis (FSP) technique.

2. Experimental

The design of custom made apparatus for materials synthesis, as well as synthesis protocol were based on the earlier reports of pioneering researchers [7]. Materials were characterized by XRD, ICP MS, XPS, STEM with EDX mapping, BET, TPR-H_2 techniques. Gas sensor performance was tested towards reducing and oxidizing gases in flow through sensor cell in DC mode.

3. Results

Parameters of synthesized samples are summarized in Table 1. XPS indicate presence of both Au and Pd on the surface of SnO_2 in a metallic state, however most part of Pd exists in the oxidized Pd^{2+} form. EDX mapping shows uniform homogeneous distribution of modifiers over the surface of bimetal modified sample. This nanocomposite demonstrates significantly higher response values towards both reducing and oxidizing gases compared to monometallic modified nanocomposites (Figure 1a–h).

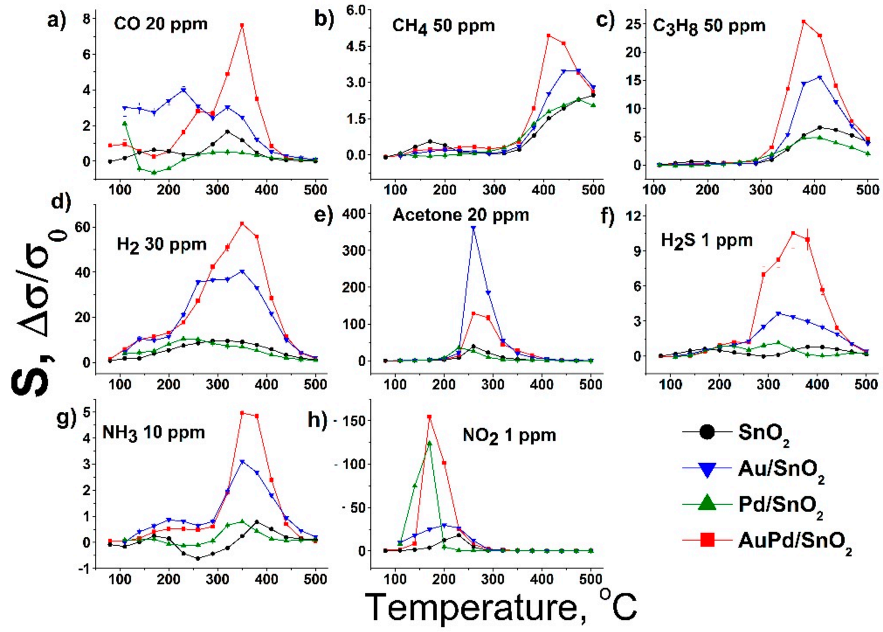

Figure 1. Dependence of gas sensor response of synthesized materials on sensor working temperature towards (**a**) CO 20 ppm, (**b**) CH_4 50 ppm, (**c**) C_3H_8 50 ppm, (**d**) H_2 30 ppm, (**e**) acetone ppm, (**f**) H_2S 1 ppm, (**g**) NH_3 10 ppm, (**h**) NH_3 10 ppm in dry air.

Table 1. Parameters of synthesized nanocomposites.

Sample		Au load		Pd Load %, mol	ICP MS, %mol		d, nm	S_{BET}, m²/g
№	Name	%, mass	% mol		Au	Pd		
1	SnO_2	--	--				14	52
2	Au/SnO_2	0.4	0.31		0.29 ± 0.02		10	70
3	Pd/SnO_2	--	--	0.31		0.29 ± 0.02	11	69
4	AuPd/SnO_2	0.2	0.15	0.15	0.16 ± 0.01	0.15 ± 0.01	11	58

4. Conclusions

The homogeneous distribution of Au and Pd component over the structure of nanocrystalline SnO_2 based nanocomposites, achieved by flame spray pyrolysis synthesis technique, gives rise to a superior gas sensor performance of thus obtained material. The excellent gas sensor properties arise from synergistic combination of chemical catalytic effect of gold and electronic effect of Fermi level control by surface Pd clusters, prone to switch to PdO state in oxidizing conditions and back to Pd^0 in the presence of reducing component. Besides being a highly effective in achieving of such synergistic effect, FSP is proven to be a convenient technique, which allows to obtain a bimetallic modification of SnO_2 with Au and Pd components in a single synthetic step with high level of content control.

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