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Short communication
Nanostructured semiconducting metal oxides for ethanol gas sensing. A possible HSAB interpretation

B. C. SERBAN[1,*], O. BUIU[1], M. BREZEZEANU[2], O. IONESCU[1], and C. COBIANU[1]

[1]National Institute for Research and Development in Microtechnologies, IMT-Bucharest, Romania
[2]University Politehnica of Bucharest, Romania
[*]E-mail: bogdan.serban@imt.ro

Sensing and detection of ethanol are important processes in various areas of domestic and industrial activity such as wine industry (control of fermentation process), food industry (quality control of beverages), chemical industry (chemical reaction monitoring), medical field (breath monitoring) [1 – 3]. Besides detection methods such as gas chromatography, calorimetry, FTIR spectroscopy [4], chemiresistive and FET – based sensors with semiconducting metal oxides (MOX) as sensing layers are widely used in the last decades with good result in the terms of sensitivity, selectivity and recovery time [5].

On the other side, the Hard Soft Acid Base (HSAB) theory is a qualitative concept, developed by Ralph Pearson in the early 1960s, which explains, among others, preferences of some chemical species to interact with other species [6, 7]. It is possible to quantify this concept by using interactions between HOMO and LUMO. HSAB concept has proven to be a useful investigation tool in many areas of chemistry such as: medicinal chemistry, toxicology [8], quantum dot functionalization and design of quantum dot solar cell [9 – 10], adsorbtion phenomena [11], corrosion [12], surface and adhesion phenomena [13].

Very recently, the HSAB principle was used in selecting and designing gas sensing layers for diverse types of sensing structures, based on technologies such as chemiresistive [14], surface acoustic waves [15 – 19] or colorimetric [20].

In this short communication we propose and use, for the first time to our knowledge, Pearson's Hard-Soft Acid-Base concept, as a new tool to coherently explain the sensitivity of the large number of semiconducting metal oxides used as sensing layer for ethanol detection in different types of sensing structures (chemiresistive and FET-based sensors).

HSAB theory operates with Lewis bases and acids, a well – known classification; according to this, a molecule which is capable to donate a pair of electrons is a base, while a molecule capable to accept it is an acid. Pearson classified Lewis acids and Lewis bases as soft, hard and borderline. Soft acids exhibit large ionic radii (>90pm), low or partial positive charge, while soft bases have large atoms (>170 pm) with intermediate electronegativity and high polarizability. By contrast, hard bases tend to have low radii, high energy HOMO, while hard acids have empty

Table 1. List of hard, borderline and soft acids and bases, according to HSAB principle

	Soft	**Bordeline**	**Hard**
Bases	H_2S, C_2H_4, RSH, R_2S, CO, CN^-, RCN, H^-, R_3P, C_6H_6, RS^-, I^-	Ar-NH_2, C_5H_5N (pyridine) N_2, Br^-, N_3^-	MeOH, MeO^-, C_2H_5OH, $C_2H_5O^-$, HO^-,$(C_2H_2)_2O$, N_2H_4, $MeNH_2$, H_2O, CO_3^{2-}, F^-,Cl^-
Acids	Cd^{2+}, Cu^+, Ag^+, I_2, Hg^{2+}	SO_2, Bi^{3+},Ni^{2+}, Zn^{2+}, $C_6H_5^+$, Pb^{2+}, Cu^{2+}	Sm^{3+}, Ga^{3+},In^{3+}, Gd^{3+}, Li^+,Mg^{2+}, Al^{3+}, Fe^{3+}, Co^{3+}, Ti^{4+}, La^{3+},Cr^{3+}, Zr^{4+}, Sn^{4+}

orbitals in their valence shells, high positive charge and high energy LUMO [21, 22]. Borderline species have an intermediate character between hard and soft species.

Examples of hard, soft and borderline acids and bases are given in Table 1. According to this theory, the species classified as described above react preferentially with species of similar hardness or softness. In other words, a hard base prefers to interact to hard acid, soft base prefers to interact to soft acid, while a borderline acid tend to bond to borderline base. The interaction between hard acids and hard bases is mostly ionic while the interaction between soft acids and soft bases is predominantly covalent.

From the HSAB concept point of view, ethanol is classified as *hard base* (marked in red in the table depicted above). Therefore, in accordance with the HSAB rule, hard acid species (marked in red, also) are potential candidates for ethanol detection. Indeed, reviewing the vast majority of literature data confirms that the most of semiconducting metal oxides, which are used as sensitive layer in resistive or FET-based sensors for ethanol detection, are in agreement with this principle. Using the HSAB rules for analyzing the chemiresistive ethanol sensor based on semiconducting metal oxides, three different cases have been identified:

1) The sensing layer is monocomponent and the cations of the semiconducting metal oxide are classified as hard acid. Synthesized by different methods such as sol-gel, solvothermal, carbothermal reduction and used as nanorods, nanobelts, nanowhiskers, nanoflowers , metal oxides such as: SnO_2 [23 – 25], TiO_2 [26 – 28], In_2O_3 [29, 30], Fe_2O_3[31, 32], Ga_2O_3 [33] were used as sensing layer in chemiresistive sensors for ethanol detection. All these sensing layers exhibit high sensitivity.

2) The sensing layer contains two types of semiconducting metal oxides, one of them acts as promoter. Both metal oxides contain cations which are classified as hard acid according to HSAB theory. SnO_2 nanowires functionalized with La_2O_3 [34], Gd_2O_3 – doped SnO_2 [35], nano-sized α-Fe_2O_3 with SnO_2 solid solution [36], were all used as sensing layer for ethanol detection. It is important to mention that promoter enhance the sensitivity of the sensing layer and, last but not least, ensure the selectivity of the sensing layer.

3) The sensing layer contains two types of semiconducting metal oxides, one of them acts as promoter. Only the promoter's cations are classified as hard acid. Sm_2O_3 - loaded flower-like ZnO nanostructure [37], In_2O_3 - decorated NiO hollow nanostructures [38] are just two examples for this category. In both cases the promoter enhances the sensitivity of the sensing layer toward ethanol molecules.

In all the presented cases we suppose that, at least in first stage, the interaction between the analyte (ethanol) and the sensing layer it is described by the HSAB principle. Without claiming that this approach will exhaustively discriminate between sensitive and non-sensitive layers, we believe that HSAB theory can be considered a valuable tool for anticipate and understand the sensing properties of semiconducting metal oxides for ethanol gas molecules. This conclusion is supported by a plethora of results reported in literature. More sophisticated calculus in terms of electronegativity, HOMO and LUMO orbitals and local hardness are needed probably for better evaluation of key sensing properties of MOX toward ethanol molecules.

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