SENSING MECHANISM IN SEMICONDUCTING HYBRID STRUCTURES FOR DMMP DETECTION

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In the last two decades, due to the intensified terroristic activity, the interest in chemical warfare agents, especially sarin, sensors has increased [1-3]. Because of the sarin high toxicity, in the laboratory work, sarin simulant, dimethyl methylophosphonate (DMMP) is used. Most of the papers regarding DMMP detection is focused on finding and modifying materials sensitive to DMMP. However, to properly design the highly sensitive and selective device with low production and operating costs, the deep insight into sensing mechanisms is necessary. In case of DMMP, those mechanisms were studied for semiconducting metal oxides (SMOs) commonly applied in gas sensors. The disadvantage of SMOs are lack of selectivity and high operating temperatures. Thus, also organic materials are tested as sensing materials with lower work temperatures and better selectivity. One group of organic semiconductors widely applied in electronics, including gas sensors, are phthalocyanines. Several papers reported phthalocyanines' sensitivity to DMMP. However, sensing mechanism has not been comperhensively described.

In this work sensing mechanisms in DMMP detection by phthalocyanines and hybrid structures based on phthalocyanines, palladium and palladium oxides were evaluated. The applied methodology consisted of theoretical and experimental parts. In the theoretical part, quantum chemistry methods were used to model DMMP adsorption on studied sensing structures. To verify theoretical results, experimental methods such as photoemission spectroscopies (XPS and UPS), thermal desorption spectroscopy (TDS) and sensor response measurement by resistance method were applied.

Two groups of sensing structures were studied: metal-free phthalocyanine (H_2Pc) with palladium (Pd) and palladium oxide (PdO) and metallo-phthalocyanines (MPcs). First, sensing mechanism has been described for H_2Pc/Pd/PdO structure that revealed sensitivity to DMMP in the room temperature. The results of the theoretical modeling indicated that DMMP adsorbes on H_2Pc through physical interaction that is enhanced by palladium either in the metallic form or as palladium oxide. The adsorption causes a significant change of adsorbant-adsorbate system dipolar momentum and only slight charge transfer. Theoretical results have been confirmed experimentally by H_2Pc/Pd/PdO structure Surface chemical composition analysis and sensor response measurements.

Next, in order to optimize the sensing structure, the mechanisms of DMMP interaction with MPcs have been investigated. DMMP forms a bond with a central atom of MPc thorough the oxygen. As a result of the preliminary theoretical calculations, ZnPc was chosen for the detailed sensing mechanism evaluation. The modeling of DMMP adsorption on ZnPc indicated that electrons are transferred from DMMP molecule to the phthalocyanine. Most of the charge accumulates on the topmost ZnPc monolayer and the strong surface dipole is formed. The theoretical results have been confirmed by a study of electronic and chemical changes in the thin ZnPc layer after DMMP adsorption. Additionally, for MPcs the theoretical study of sarin adsorption has been performed, confirming the validity of using DMMP as a sarin model.

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