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Synthesis and sensory sensitivity of copper(I) iodide thin films to various groups of volatile analytes

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This article examines nanocomposite organometallic thin films based on copper iodide for their potential use as gas sensor materials. The synthesis of the materials, the thin film production method, and the results of IR spectroscopy and thermogravimetric studies of the compound are described. Using this coordination polymer, resistive thin-film samples were prepared, the resistance dependence on ammonia vapor concentration was measured, and the selectivity for other analytes was assessed.

Keywords: thin-film structures, gas sensors, ammonia sensor, organometallic compounds.

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Monitoring of the concentration level of pollutants in the atmosphere and its strict regulation are crucial for environmental protection. Resistive sensors are a key tool for air quality control and monitoring; their simplicity and compatibility with standard electronic systems allow for a wide range of applications. It is the simplicity and low cost of electronic sensors that make it possible to collect chemical and physical data on gas components and generate signals that are easy to record, process, store, and analyze [1,2]. One of the significant sources of pollution are volatile organic compounds, which are produced as a result of human activities ranging from paint production to the pharmaceutical industry and from the combustion of hydrocarbon fuels to refrigerants [3]. Of particular note is ammonia (NH_3), which is common in everyday life and is often used in agricultural fertilizers, chemical systems, food industry, and livestock farming [4,5]. In addition, NH_3 acts as a harmful pollutant: when its concentration exceeds 300 ppm, NH_3 may pose a significant threat to human health [6]. Therefore, the availability of high-performance NH_3 sensors is of great practical importance for monitoring the living environment and human health [7].

A variety of gas sensors based on semiconductor polymers designed for detection of all kinds of volatile organic compounds have already been produced [8]. Their active materials are copper (II) oxide (CuO), copper (I) oxide (Cu_2O) [9], titanium dioxide (TiO_2) [10], and tin (IV) oxide (SnO_2) [11]. In addition to these materials, two-dimensional (2D) materials have become promising candidates for sensor applications in recent years: graphene [12,13], molybdenum disulfide (MoS_2) [14], tungsten diselenide (WSe_2) [15], germanium selenide (GeSe) [16], etc.

Owing to its high sensitivity, ease of synthesis, and high thermal stability, zinc oxide (ZnO) is considered to be a fine candidate metal oxide semiconductor for gas sensors. The results of gas probing revealed that ammonia elicits the greatest response from ZnO structures among all the gases tested. The response magnitude to 400 ppm ammonia vapor was ~ 38.5 [17]. Organometallic compounds known as coordination polymers are organic hybrid materials consisting of inorganic units linked by organic ligands [18]. Cu(I) complexes based on the 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide compound are a cheaper alternative to traditional platinum-group metal complexes [19]. The rich coordination chemistry of Cu(I) ions allows one to fine-tune its properties by altering organic and inorganic ligands. Moreover, the characteristics of Cu(I) complexes may be adjusted not only by changing the molecular structure, but also under the influence of external factors [20]. However, literature data on the use of organometallic Cu(I) compounds in sensorics (including the design of gas sensors) are extremely scarce. Therefore, an attempt was made to use thin Cu(I) films as a sensitive layer of an electrical gas sensor. The present study is aimed at finding new composite materials for sensors that are characterized by high response speed, low energy consumption, minimal hysteresis, and cost-effectiveness.

The organometallic 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide compound (inset in Fig. 1) was synthesized using a method similar to the one detailed in [19]. Methanol (20 ml) and chloroform (20 ml) were poured into a 100 ml flat-bottomed conical flask. With stirring and without heating, 0.262 g (0.001 mol) of triphenylphosphine and 0.232 g (0.001 mol) of oxadiazole were then dissolved in the mixture. After that, 0.190 g (0.001 mol) of copper (I) iodide were added, and the reaction mixture was heated to 60 °C and stirred for 15 min. The heating was then turned off, and the mixture was stirred for another 40 min and finally filtered through a folded paper filter. The resulting filtrate was left for slow evaporation

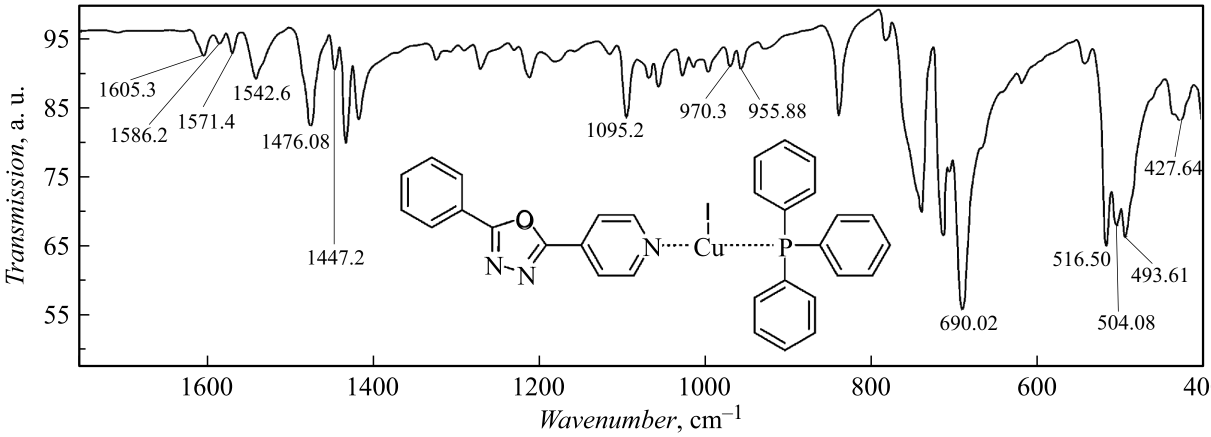

Figure 1. IR transmission spectra of 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide. The inset shows the molecular structure of the obtained compound.

in order to precipitate the target product. Owing to a high evaporation rate of the solvent, the evaporation vessel was fitted with a thin permeable film to slow down the process and improve the quality of the target product. A mixture of the target product and unreacted reagents accumulated on the vessel walls over the next two days. The target product precipitated in the form of yellow rhombic crystals that emitted yellow-orange light under ultraviolet irradiation. The structural formula of the obtained organometallic Cu(I) compound is shown in the inset in Fig. 1.

Thin films were formed from the initial powdered materials by centrifugation in a PE 6900 centrifuge. Non-aromatic chloroform CH_3 was used as a solvent. The mass of powdered materials was controlled using a Sartogosm SE124-S high-precision analytical balance. The concentration of the initial materials in the solution was 1 ± 0.1 mg/ml. Following thorough mixing and holding for at least 48 h at room temperature, the resulting solution with a volume of 1 ml was applied with a pipettor to optically transparent dielectric and conductive substrates. The centrifuge rotation speed was increased gradually to 1500−3000 rpm in 500 rpm steps.

An experimental setup for testing the samples in the process of measurement of electrical characteristics was designed. It consisted of two main units: an evaporator chamber and a measurement section, which were connected by a gas supply system to ensure precise control over temperature, concentration, and environmental parameters and obtain reproducible results. The following volatile organic compounds, alcohols, and acids were used: ethanol (C_2H_5OH), hexane (C_6H_{14}), hydrochloric acid (HCl), methanol (CH_3OH), and ammonia (NH_3).

The homogeneity and roughness of the surface of the obtained films was examined by optical spectroscopy using a LOMO MII-4M microinterferometer with additional semiconductor laser illumination and an extended optical path to a camera with a 1/2FF 10MP sensor [21,22]. It was found in initial analysis that the film surfaces were relatively homogeneous. The approximate thickness of the Cu(I) film was $2 \pm 0.5\,\mu$m. The formation of individual agglomerates with a diameter of $\sim 40\,\mu$m on the film surface was also noted (Fig. 2, *a*).

PerkinElmer STA6000 analyzers were used for thermogravimetric analysis (TGA). The TGA data (Fig. 2, *b*) revealed a mass loss of up to 55 %, which is accompanied by an endothermic effect, within the temperature range of 180−200 °C. This corresponds to removal of a coordinated water molecule. The compound is thermally stable up to a temperature of 350 °C. Slow decomposition of the sample is initiated when it is heated above 350 °C. Thus, the obtained results suggest that the 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide compound is thermally stable at temperatures up to 180 °C, which is an unquestionable advantage in the context of application in gas sensors.

Infrared (IR) spectra of the studied organometallic Cu(I) compound were recorded using a PerkinElmer Spectrum Two Fourier transform IR spectrometer within the 8300−350 cm^{-1} range with a resolution of 0.5 cm^{-1}. The obtained IR spectrum features bands at 1605.3−1447.2 cm^{-1}, which are characteristic of vibration of the aromatic ring found in 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole and triphenylphosphine. It is important to note that the 1542.6 cm^{-1} band has a higher intensity than the bands lying before it, which is typical exactly of vibrations of the aromatic ring. A slight shift of the peak at 1095.2 cm^{-1}, which is characteristic of the Cu(I)−P bond and arises due to the formation of a coordination bond of a copper molecule with a donor phosphorus atom of triphenylphosphine, may also be noted in the spectrum. The used instrument had no technical capability to record signals at a spatial frequency below 400 cm^{-1}. However, this region should theoretically contain oscillations characteristic of Cu(I)–I and Cu(I)–N bonds (Fig. 1).

Electrophysical parameters in the DC mode were examined using a Keysight B1500A (Keysight Tech., United

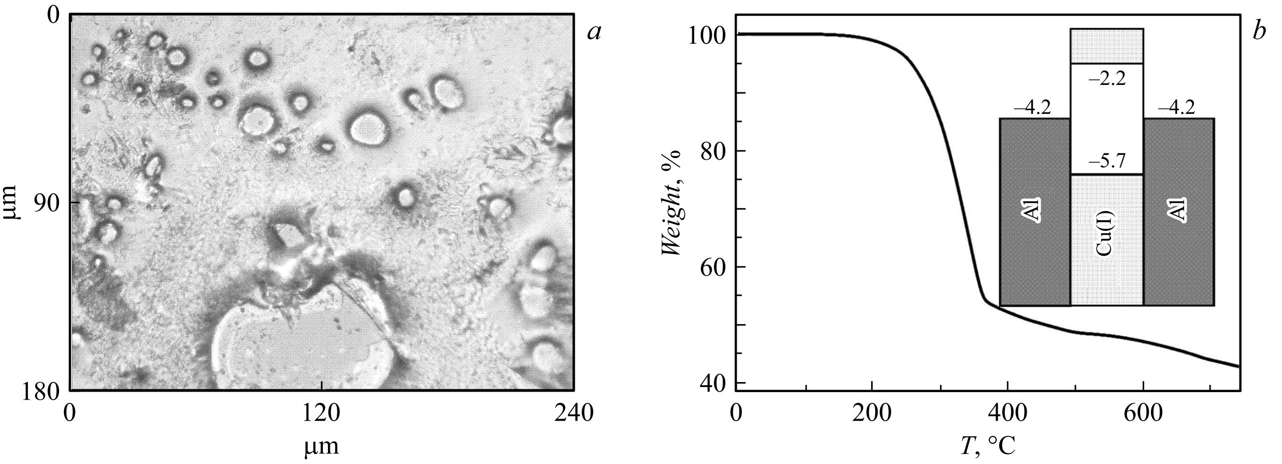

Figure 2. Results of optical spectroscopy of thin Cu(I) films (*a*) and thermogravimetric study of the obtained Cu(I) compound (*b*).

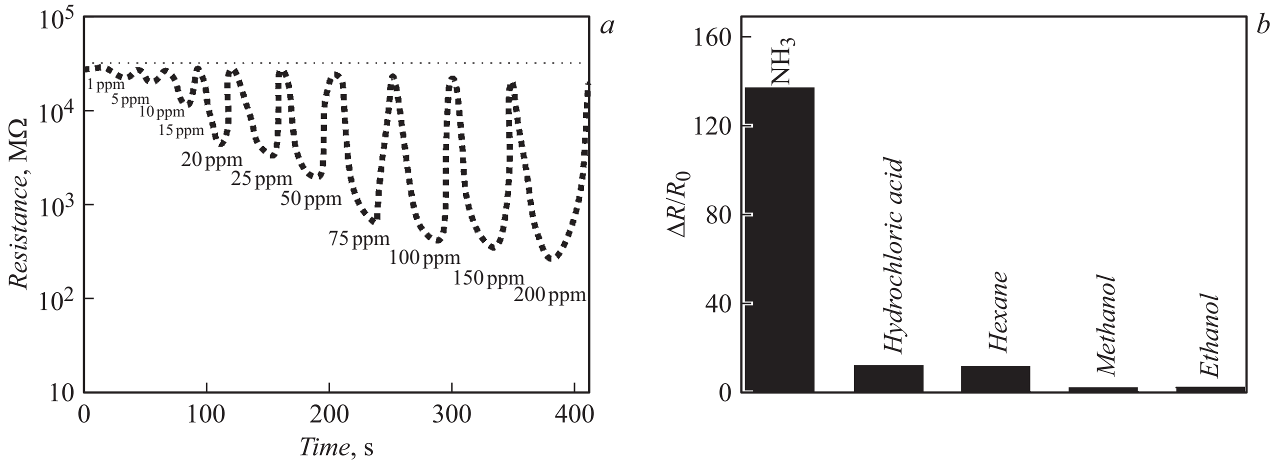

Figure 3. *a* — Variation of resistance of Cu(I) thin films at different ammonia concentrations at room temperature (25 °C); *b* — ratio of resistance change ΔR of thin Cu(I) films exposed to different analytes to resistance R_0 of these films under normal conditions at room temperature.

States) semiconductor analyzer. In order to examine the conductive characteristics of organometallic Cu(I) compounds, the solution was applied to thin (120 nm) aluminum films obtained by vacuum deposition onto sitall with a resistance of $20\,\Omega/\square$ [23], which was followed by the formation of an Al−Cu(I)−Al structure. This measurement system had an energy diagram shown in the inset in Fig. 2, *b*. Sandwiched between the aluminum electrodes with a work function of −4.2 eV, the Cu(I) film had HOMO and LUMO levels that were calculated from the oxidation and reduction potentials to be located at −5.7 and −2.2 eV, respectively [19].

Measurements were performed within the voltage range from −5 to 5 V. The geometric dimensions of conducting substrates were 10×10 mm. Figure 3, *a* shows the typical transient response curves of the gas sensor exposed to various ammonia concentrations ranging from 1 to 200 ppm at 50 % RH (relative humidity) and room temperature. The response magnitude increased with ammonia concentration (Fig. 3, *a*). The responses were ~ 1, 4.5, 8.3, 40.2, and 63.4 s for 5, 25, 50, 100, and 200 ppm of ammonia, respectively. These results indicate that the Cu(I)-based sensor may operate repeatedly with high response speed that is comparable to the parameters of well-proven film structures based on, e. g., ZnO [17].

Selectivity is another key issue for sensor application in practice. This characteristic of the polymer gas sensor based on copper iodide was examined at a concentration of 50 ppm of such analytes as ammonia, ethanol, hexane, hydrochloric acid, and methanol. Compared to other analytes, ammonia elicits a pronounced response (see Fig. 3, *b*). The ratio of resistance change ΔR of thin films based on Al−Cu(I)−Al exposed to various analytes to resistance R_0 of these films under normal conditions at room temperature is as follows (Fig. 3, *b*): 136.4 for NH_3; 10.9 for HCl; 10.5 for C_6H_{14}; 1.1 for CH_3OH; and 1.06 for C_2H_5OH. These results demonstrate that sensors based on the 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide compound are highly selective.

Thus, the increased selectivity toward NH_3 may be attributed to the fact that electron-rich ammonia molecules tend to donate their electrons to the copper iodide-based organometallic thin film. This donor-acceptor interaction leads to efficient adsorption of donor ammonia molecules at the electron-acceptor layer of Cu(I). In addition, the selectivity for ammonia dominates over that for other tested analytes due to the small molecular diameter of ammonia molecules (0.326 nm), which allows them to diffuse into the Cu(I) sensitive material, facilitating interaction and adsorption.

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Conflict of interest

The authors declare that they have no conflict of interest.

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