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Direct Capillary-Based Printing of Porous Coordination Networks on CMOS E-Nose Sensor for Plant Disease VOC Detection

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Summary:

Early detection of plant diseases can substantially reduce pesticide use, offering significant environmental and economic benefits. Agriculture consumes over 18,000 tons of pesticides annually in the EU alone, with 40–60% applied unnecessarily before disease symptoms manifest. Here, we present the surface functionalization of CMOS capacitive sensor arrays via SonoPlot direct writing of porous materials for low-power electronic nose (E-nose) applications. Utilizing advanced SonoPlot printing for precise material deposition, we functionalize sensor surfaces to optimize VOC adsorption, enabling real-time detection through capacitance changes. Our results show that a wide range of polymers and porous materials, including UV-curable inks, carbon nanoparticle-based polymers, metal-organic frameworks (MOFs) such as CAU-10 and CAU-23, and Prussian blue analogs (PBAs) such as CuPBA, exhibit high selectivity toward VOCs, including 1-nonanol, 2-nonanol, α-terpinene, tetradecane, 1-butanol, 2-butanol, 1-propanol, 2-propanol, ethanol, toluene, α-pinene, and water vapor. This research highlights the potential of SonoPlot printing technology to enable next-generation, high-performance, and cost-effective printable E-nose VOC sensors, offering significant promise for widespread environmental sensing applications.

Keywords: Metal organic frameworks (MOFs), Prussian blue analogues (PBAs), Volatile organic compounds (VOCs), Capacitive gas sensor, Electronic nose (E-nose)

Background, Motivation, and Objective

The intensification of global agriculture has led to a steep rise in pesticide use, with more than 18,000 tons applied annually in the EU, of which an estimated 40–60% is sprayed preventively before visible symptoms of plant disease appear [1]. This practice not only imposes high economic costs on farmers but also contributes to environmental pollution, biodiversity loss, and human health risks. Early, non-invasive detection of plant diseases is therefore essential to enable targeted treatment, reduce pesticide consumption, and support the UN Sustainable Development Goals on responsible production and climate action

Volatile organic compound (VOC) fingerprints emitted by plants and pathogens provide a powerful, label-free pathway for early disease diagnosis, often days to weeks before visual symptom onset. Electronic nose (E-nose) systems based on VOC sensing have shown promise in agriculture, environmental monitoring, industrial safety, and healthcare [2]. However, current E-nose platforms are often limited by high power consumption, poor selectivity, a lack of spatial-temporal resolution [3], and complex or costly

fabrication, hindering their deployment in large-scale, distributed sensor networks in the field.

A CMOS pixelated capacitive sensor (PCS) array offers an attractive route to low-power, highly integrated E-nose systems, but their performance critically depends on the functional materials and the changes in their dielectric constants upon VOC adsorption [4]. Each electrode (capacitor plate sensor) is 5 µm x 5 µm in size, separated from other sensors by 10 µm, in a 32 x 32 matrix format (Fig 1). Given their size, inkjet printing of diverse functional materials in pico-liter volumes with micrometer precision is a promising method for low-cost sensor functionalization [5].

The objective of this work is to demonstrate the feasibility of printing multiple inks with an ultrasonic-based inkjet printer (Sonoplot Inc., Germany) to detect multiple VOCs for plant disease detection. The CMOS-PCS array was printed with UV-curable polymer ink, carbon nanoparticle ink, and three types of porous coordination network (PCN) inks (within a binding UV-ink solution) – CAU-10, CAU-23, and CuPBA (Fig 1). Unprinted pixel sensors were used as reference sensors.

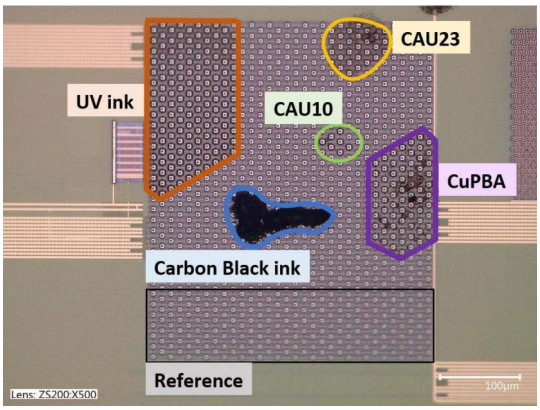


Fig. 1. Surface functionalized CMOS pixelated chip with multi-inks using an ultrasonic inkjet printer.

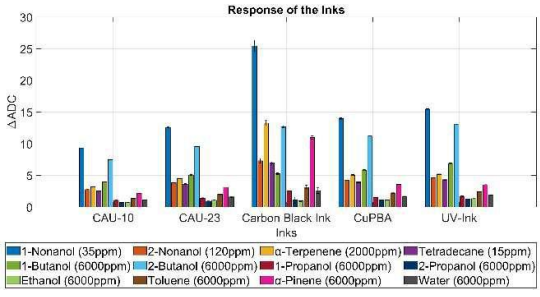


Fig. 2. E-Nose sensor's response to 11 different VOCs and humidity with 5 different inks functionalized on its surface. Tests were performed at parts-per-million (ppm) concentrations of VOCs.

The functionalized sensor array was tested for the detection of the following gases: 1-Nonanol, 2-Nonanol, α-Terpinene, Tetradecane, 1-Butanol, 2-Butanol, 1-Propanol, 2-Propanol, Ethanol, Toluene, α-Pinene, and water vapor (Fig. 2). Most of these VOCs are released by plants. The sensitivity in parts per million (ppm) and selectivity for VOCs of functionalized sensors are shown in Fig. 3. Our initial results indicate that the inks are selectively responsive to plant VOCs [4]. However, the inks of PCNs show a similar response to that of the pure UV ink. This indicates that the UV-ink in the ink solution plays a more dominant role than PCNs. Improving the ink formulation to address this point is ongoing work.

In conclusion, a low-power CMOS PCS array with 1024 sensors has been functionalized with 5 inks via inkjet printing and tested with 11 plant VOCs and humidity. The sensors respond to VOCs but lack selectivity, indicating that the response is dominated by the UV ink rather than the PBNs. As a next step, we optimize the ink formulation by increasing the PBN concentration.

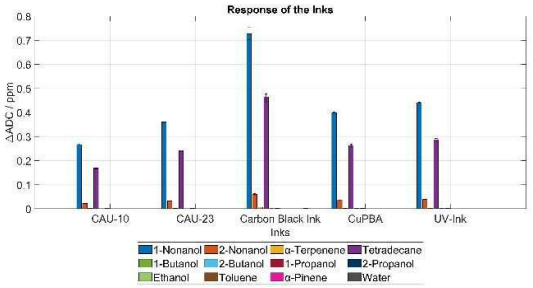


Fig. 3. E-Nose sensor's response to different concentrations of VOCs in ppm, indicating that inks can be very selective towards certain VOCs.

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