

Hybrid Nanomaterial Networks for Dynamic VOC Sensing

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Summary:

We present recent advances in the formation of molecularly cross-linked nanomaterial networks for the selective detection and recognition of volatile organic compounds (VOCs). Using cost-effective ink-based fabrication procedures, we combine inorganic nanomaterials, including gold nanoparticles and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes, with molecular cross-linkers, such as dithiols or diamines. The resulting hybrid materials exhibit chemiresistivity and composition-tunable selectivity. Our work focuses on tuning analyte/sensor interaction kinetics and exploiting dynamic response patterns for VOC recognition.

Keywords: hybrid nanomaterials, VOC sensing, analyte discrimination, nanoparticles, MXenes

Volatile organic compounds (VOCs) comprise multiple hundreds to thousands low-vapor-pressure molecular species, and are found, to name just a few examples, in emissions from industrial processes, in the headspace above food during ripening, in breath, and as environmental pollutants. The chemical diversity of VOCs is associated with distinct properties: While some VOCs pose severe health hazards,[1] others may indicate the degree of ripening or degradation of fruit or vegetables.[2] Specific VOCs or VOC patterns can further act as markers in breath or headspace above body fluids for diagnostic purposes.[3]

Therefore, the mere detection of VOCs is insufficient for several emerging applications. Rather, the identification of individual VOCs or VOC patterns in complex gas mixtures is required for industrial safety monitoring, non-invasive medical diagnostics, food quality control, and environmental monitoring. While methods such as gas chromatography - mass spectrometry (GC-MS) offer excellent selectivity, these techniques are expensive and have limited portability and point-of-care applicability. Hence, there is a strong demand for inexpensive, portable sensing devices that enable analyte classification.

Hybrid Nanomaterial Networks

Molecularly cross-linked nanomaterial networks are promising and highly configurable candidates for chemiresistive VOC sensors with tunable selectivity. VOC sorption within these materials, particularly at the organic interfaces

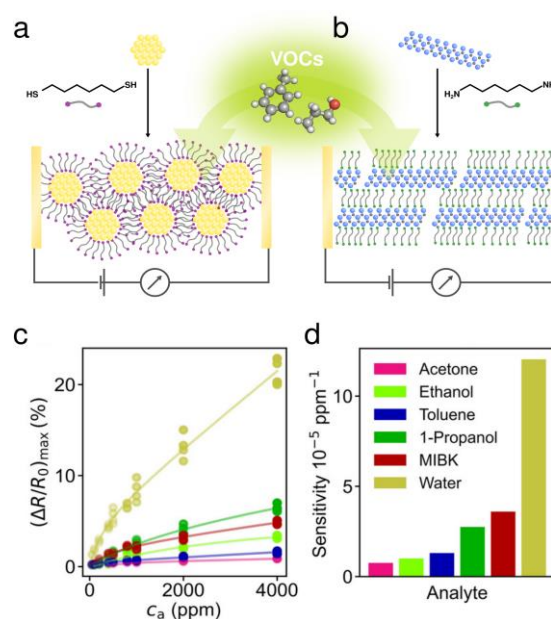


Fig. 1. a,b) Schematics depicting the fabrication of nanomaterial networks from a) dithiol cross-linked gold nanoparticles and b) diamine cross-linked $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. c) Sorption isotherms and d) vapor sensitivities of 1,6-hexanediamine cross-linked $\text{Ti}_3\text{C}_2\text{T}_x$ chemiresistors. c) Solid lines depict fits of a Langmuir-Henry sorption model.[4]

between the inorganic nanomaterials, sensitively affects charge transport across the composite, resulting in resistance changes that serve as sensing signals. While networks of molecularly stabilized noble metal nanoparticles (Figure 1a) have attracted significant interest in recent years, we here report an entirely ink-based,

efficient process for the deposition of a new class of thin films, namely, diamine cross-linked $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes (Figure 1b), and demonstrate their suitability for chemiresistive sensing (Figure 1c,d).

Dynamic Sensing

Apart from quasi-static response amplitudes, observable after saturation of sorption-based VOC sensors, such devices also exhibit distinct saturation kinetics. While saturation response amplitudes depend on thermodynamic sorption equilibria, dynamic response features are governed by kinetic physicochemical processes. Both contain valuable information, and their combination can significantly enhance analyte recognition.

We tailor nanomaterial networks to deliberately slow down and achieve analyte-selective sorption kinetics (Figure 2a,b). For example, selecting short alkanedithiol molecules as cross-linkers for gold nanoparticle (GNP) networks causes their chemiresistive response kinetics to strongly depend on the size of the analyte molecules.[5] Thus, analyte sorption kinetics complement saturation responses, which are strongly governed by the analyte polarity. By combining suitable nanomaterial networks and evaluation of their dynamic response data using machine-learning algorithms, we achieve robust analyte recognition. Figure 2c exemplarily depicts the result of a linear discriminant analysis of response data acquired using a sensor array of eight sensing elements consisting of different cross-linked gold nanoparticle networks. We demonstrate utilization of these data to classify a set of VOCs at varying concentrations, enabling discrimination even between isomers.[5]

Still, the analysis of real world samples requires the recognition and classification of analytes, as well as the determination of their concentrations in complex mixtures. To understand how analyte mixtures interact with sorption-based nanomaterial network chemiresistors, we present a recent investigation of their response to binary VOC mixtures. As schematically depicted in Figure 2d, we discuss how responses to VOC mixtures can be deconvoluted to assess their composition.

Finally, we discuss recent developments in multi-layered chemiresistor stacks, which possess an enhanced capability to kinetically separate analyte mixtures upon entry and provide spatiotemporal sensor responses for further improved analyte recognition.

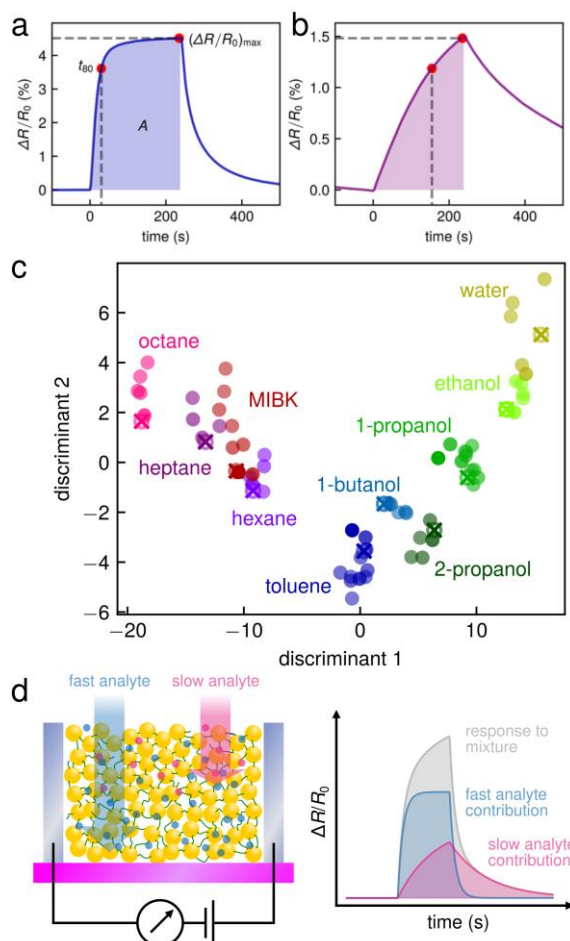


Fig. 2. a,b) Responses of a GNP chemiresistor to a) toluene and b) heptane. c) Linear discriminant analysis of dynamic responses from a VOC sensor array based on GNP sensing elements to different VOCs at varying concentrations. a-c) Adapted with permission from [5]. Copyright 2021 American Chemical Society. d) Schematic depicting the response behavior of a sorption-based chemiresistor to a mixture of analytes having different sorption kinetics. For certain analytes and concentration ranges, the sensor response is a superposition of the individual responses to the pure components.

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