CHEMICAL SENSING

The feel of catalysis

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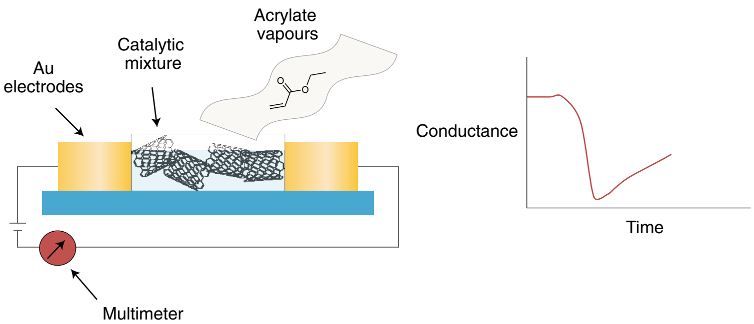

Unlike enzymatic reactions, which have a long tradition in chemical sensing, organometallic catalysis has rarely been employed to design sensors. Now, Timothy Swager and co-workers at the Massachusetts Institute of Technology report the development of a single-walled carbon nanotube (SWCNT) chemiresistive sensor for the detection of acrylates based on a palladium-catalysed aerobic oxidative Heck-coupling as the chemical selection system. Acrylates are toxic substances employed for the preparation of polymers and resins, and are often encountered in different industrial workplaces. At present, they can only be detected indirectly by gas chromatographic analysis of air samples. In their work, however, the researchers showed the possibility of monitoring the level of acrylates in the environment in real time by using the conductivity properties of SWCNTs exposed to a typical catalytic mixture and connected to two gold electrodes under a constant applied voltage (pictured).

In a proof-of-principle experiment, the device containing an ionic-liquid-based catalytic mixture — palladium acetate, halobenzene and sodium acetate — experienced a large conductance change when exposed to ethyl acrylate vapours. Control experiments in the absence of palladium, together with the NMR analysis of the ethyl cinnamate product in the reaction mixture, confirmed that the response is solely induced by the coupling of the halobenzene with the acrylate partner. To increase the linear range of the system, the authors successively focused on a homogenous catalytic mixture, in which palladium(II) tetrafluoroborate tetraacetonitrile is used as the metal source, and 4,5-diazafluorenone and phenylboronic acid are used as the ligand and the coupling partner, respectively.

After solvent optimization, the device showed high selectivity towards ethyl acrylate vapours in air, compared with other volatile organic compounds, with good stability and sensitivity down to the ppm range. Under aerobic conditions, SWCNTs are in a p-doped state due to the presence of oxygen. Therefore, the ability of Pd(0) — generated reversibly during the catalytic cycle — to consume such physisorbed oxygen relates to the change in conductance and is the core of the device's operating principle.

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