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A humidity-resistant and room temperature carbon soot@ZIF-67 composite sensor for acetone vapour detection†

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Zeolitic imidazolate framework-67 (ZIF-67), carbon nanoparticles (CNPs), and the CNPs@ZIF-67 composite were prepared and used to fabricate sensors for the detection of acetone vapour. The prepared materials were characterized using transmission electron microscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy and Fourier-transform infrared spectroscopy. The sensors were tested using an LCR meter under the resistance parameter. It was found that the ZIF-67 sensor did not respond at room temperature, the CNP

selectivity, sensitivity and fast response recovery time; however, they operate at temperatures from 140 to 350 °C.¹⁵ ZIF-67 is made up of cobalt (Co²⁺) ions and 2-methylimidazole, possessing cubic crystal symmetry.¹⁶ ZIF-67 based sensor shows unresponsive behaviour towards VOCs at room temperature due to its high energy band gap and has been integrated with conducting materials to reduce the high working temperature.¹⁷ In this study, ZIF-67 and carbon soot are used as a composite to detect acetone vapour at room temperature. Carbon soot is commonly known as carbon nanoparticles (CNPs) and possesses good conductivity, a high surface-to-volume ratio, and surface oxygen species that enhance gas sensing properties.¹² The CNPs/ZIF-67 composite solid-state gas sensor works at room temperature and relatively high humidity, has a low limit of detection and is highly sensitive toward acetone.

2. Experimental

2.1. Chemicals and reagents

Cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O], 2-methylimidazole (99%), *N,N*-dimethylformamide (DMF, 99.5%), ethanol (EtOH, 98%), acetone (CH₃COCH₃, 99.5%), cyclohexane (C₆H₁₂, 99%), 4-methyl-1-hexene (C₇H₁₄, 99.5%), 3-pentanone (C₅H₁₀

where C is the vapour concentration (ppm), p is the density of the liquid analyte (g cm^{-3}), T is the temperature (K), V_s is the volume injected into the 20 L volumetric flask (μL), M_r is the molar mass of the liquid analyte and V is the volume of the volumetric flask (L).¹⁸

2.2.5 Sensor's response and recovery tests. The gas sensor's response time was defined as the time needed for the sensor to reach a 90% maximum response before it reaches the saturated (plateau) state, while recovery time was defined as the 90% time needed for the sensor to reach its baseline during the removal of the gas exposed from its plateau.

2.2.6 In situ FTIR-online LCR meter measurement. The *in situ* FTIR-LCR meter set-up was followed as reported.¹¹ IR spectra were recorded using an FTIR instrument (PerkinElmer Spectrum 100) with a resolution of 4 cm^{-1} and 16 scans. A gas cell is a cylindrical cell (approx. 110 mL volume) fitted with two KBr windows at both ends. The vessel with two inlets for the sample injection and sensor electrical connection was placed at the centre with a sensor positioned on the upper wall of the cell in such a way that the IR beam passes through the windows without

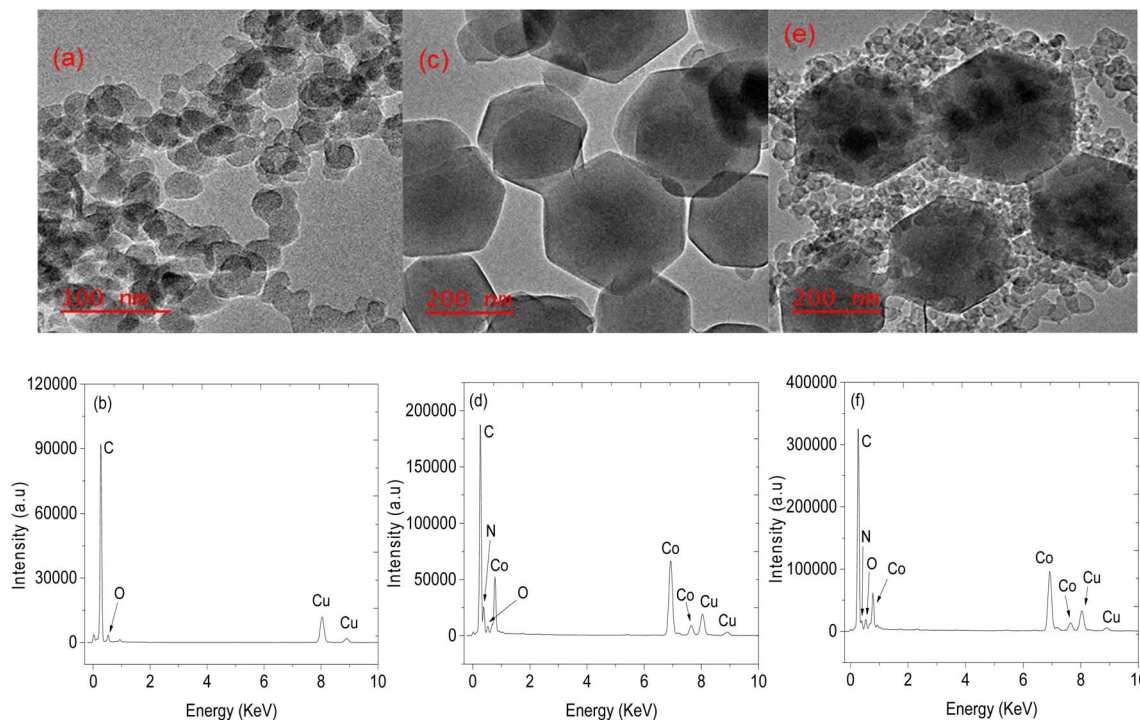


Fig. 3 TEM images of (a) CNPs, (c) ZIF-67 (e) CNPs/ZIF-67 and their respective EDS spectra, (b), (d) and (f).

possesses similar peaks to those found in the spectra of ZIF-67 and the CNPs as expected (Fig. 3f). The TEM image of the CNPs/ZIF-67 composite revealed that the CNP soot covers the surface

of ZIF-67 (Fig. 3e), which likely plays a crucial role in improving the electrical conductivity of the nanocomposite and facilitated the gas sensing process.



Fig. 5 XPS spectra and XPs survey of (a) CNTs, (b) ZIF-67 and (c) ZIF-67/CNPs and (d) O 1s of CNPs and (e) O 1s of ZIF-67.

Table 1 XPS O 1s oxygen species percentages

Materials	O _β	O _γ
CNPs	48.7%	51.7%
Z		

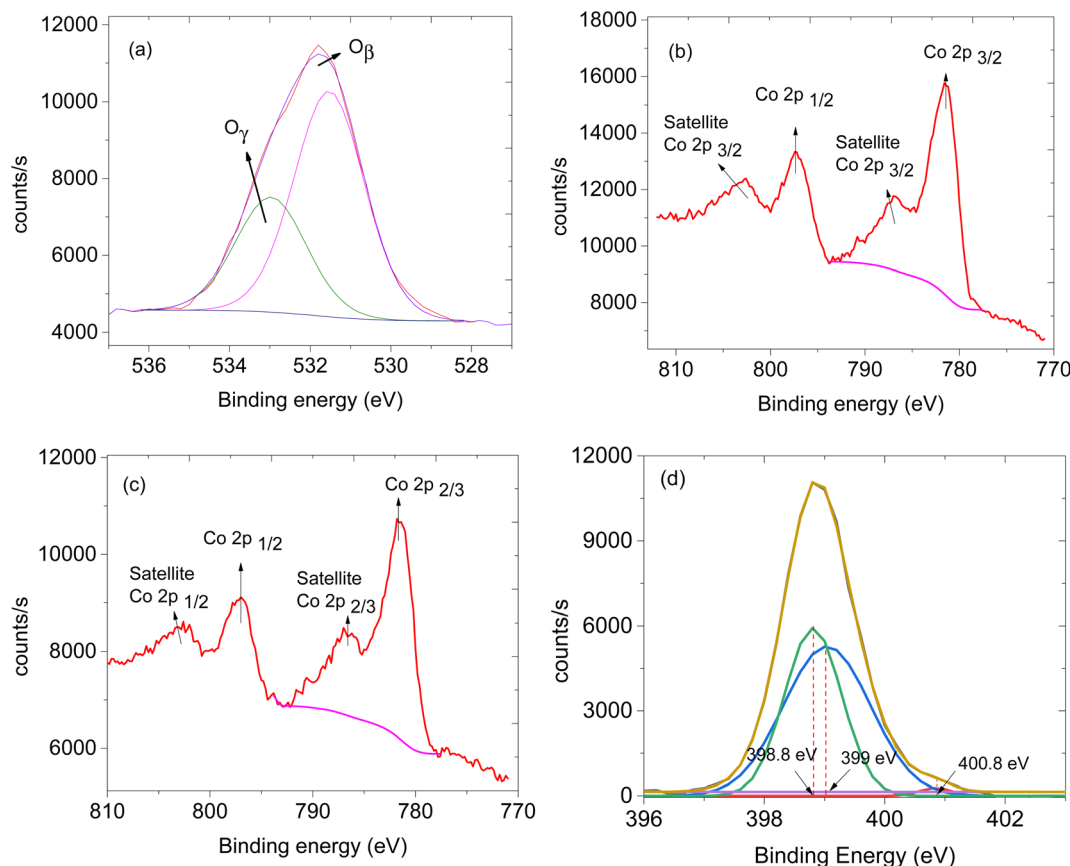


Fig. 6 XPS spectra, (a) O 1s of ZIF-67/CNPs, (b) Co 2p of ZIF-67, (c) Co 2p of ZIF-67/CNPs and (d) N 1s of ZIF-67.

198, 524 and 616 cm^{-1} are all assigned to F_{2g} and the signal at 477 cm^{-1} and the strongest signal at 684 cm^{-1} are assigned to A_1 and E_g mode respectively.^{22,23} FTIR spectra presented in Fig. 4d–f show that the CNPs (Fig. 4d) had a broad peak at 3555 $\text{$

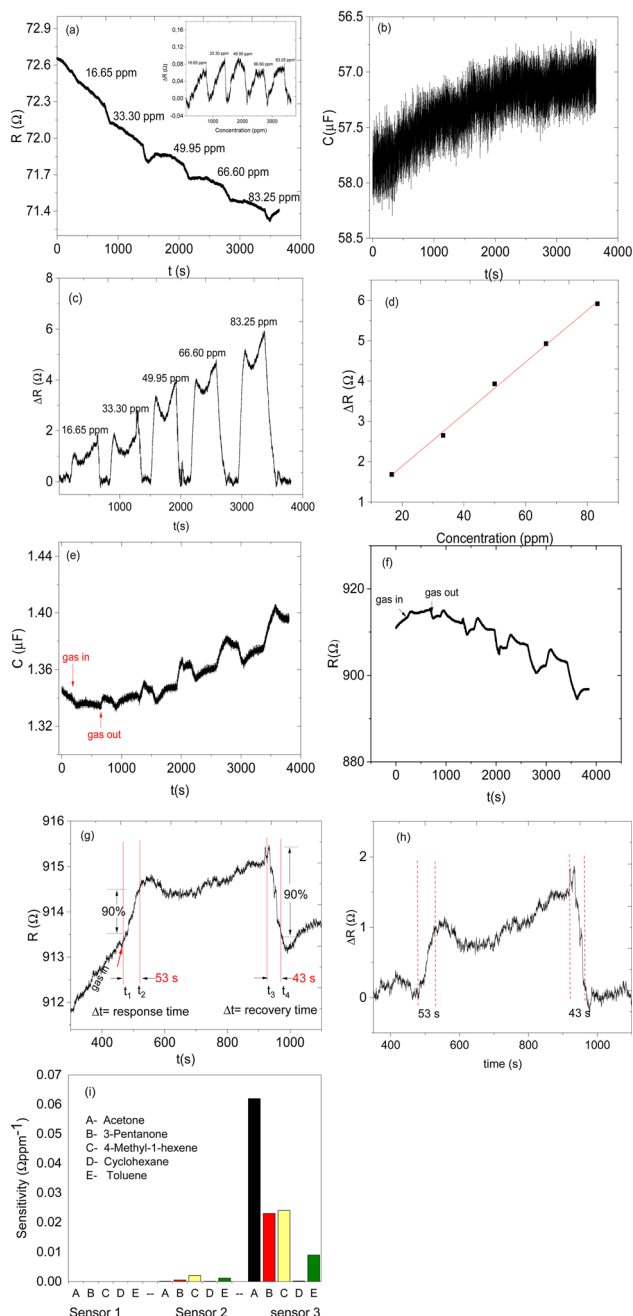


Fig. 7 (a

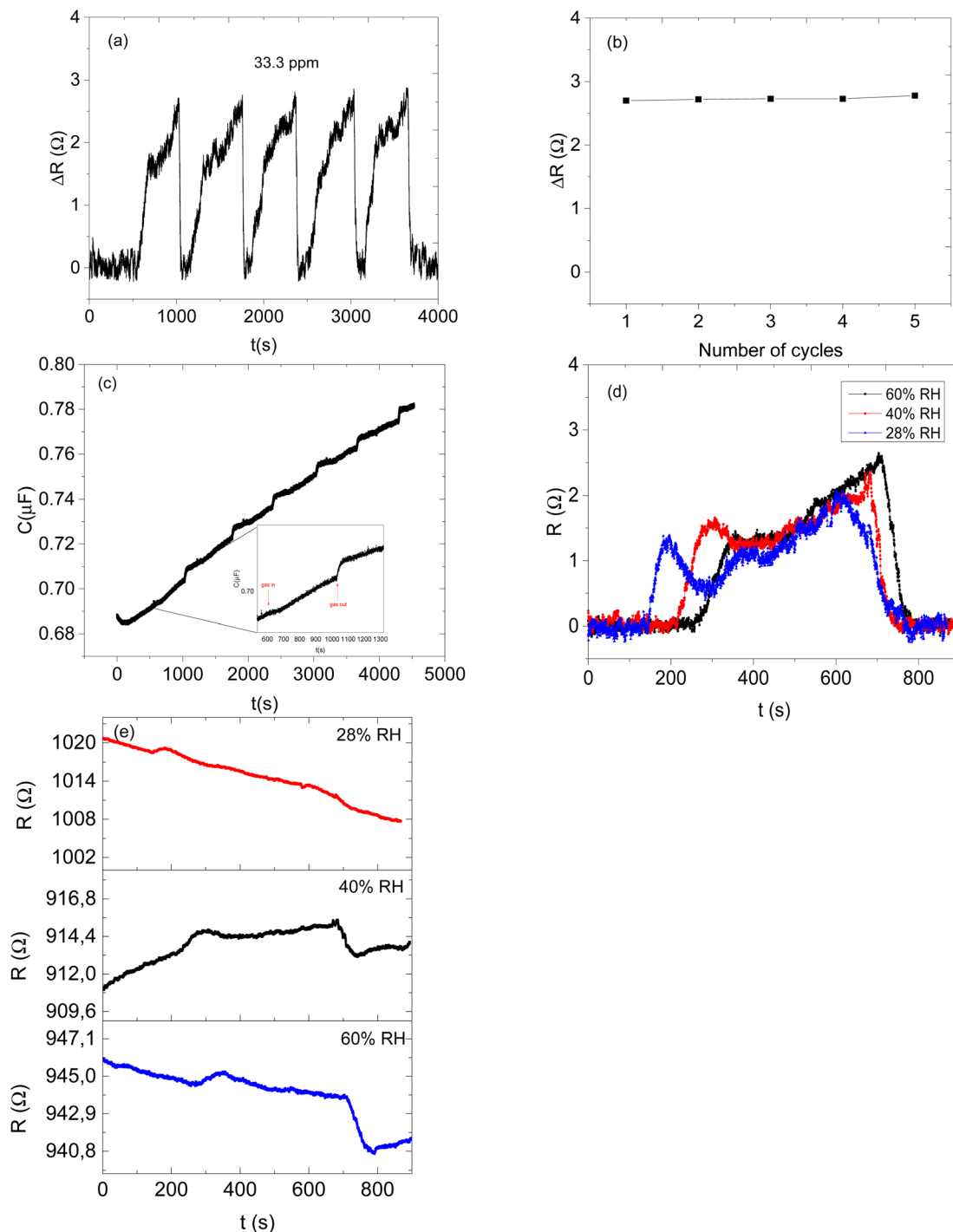


Fig. 8 (a) Repeatability of the CNPs/ZIF-67 sensor on acetone vapour, (b) its maximum amplitude of the response peaks and (c) a capacitance transient response repeatability test of the sensors, (d) acetone vapour relative response at different relative humidities and (e) transient acetone vapour response at different relative humidities.

molecules are slower to diffuse through the sensing material. The reason why the recovery time is faster than the response time is that the concentration of the analyte was dropped to a lower level due to the air being flashed through the chamber.



Fig. 9 The response and recovery times versus relative humidity.

Fig. 8c shows that the sensor responded apart from the response drifting away from the baseline.

It has been widely reported that





Fig. 11 Static response–recovery curve of sensor 3.

species on CNPs were confirmed using XPS characterisation (Fig. 5d and Table 1). These reactive oxygen species on the sensor catalyse the decomposition of acetone into carbon dioxide and water. The synergistic effect of the CNPs and ZIF-67 in

and the CNPs/ZIF-67 composite was prepared from physical mixing. All the prepared materials were characterized using TEM, FTIR, XPS, Raman spectroscopy and XRD. All sensors were tested at room temperature. The CNPs/ZIF-67 sensor improved the sensitivity of the CNP sensor by 155 times during the detection of acetone vapour while the ZIF-67 sensor did not respond to any analyte. And the CNPs/ZIF-67 sensor was found to be highly sensitive to acetone vapour and less sensitive to cyclohexane, 3-pentanone, 4-methyl-1-hexene, and toluene vapours. In addition, the sensor was found to be humidity insensitive and had fast response–recovery times and the LOD was found to be 484 ppb on the detection of acetone vapour. Thus the CNPs/ZIF-67 sensor is a promising candidate for a fast, portable, non-invasive, and inexpensive diabetes diagnosis method and to maintain good health in high acetone vapour environments.

Author contributions

L. Malepe performed all the experiments and investigations and wrote the manuscript. M. A. Mamo conceived the idea and guided and reviewed the manuscript. P. Ndungu and D. T. Ndinteh are responsible for providing resources, editing, and reviewing the manuscript.

Conflicts of interest

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