Non-invasive plant disease diagnostics enabled by smartphone-based fingerprinting of leaf volatiles

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Plant pathogen detection conventionally relies on molecular technology that is complicated, time-consuming and constrained to centralized laboratories. We developed a cost-effective smartphone-based volatile organic compound (VOC) fingerprinting platform that allows non-invasive diagnosis of late blight caused by *Phytophthora infestans* by monitoring characteristic leaf volatile emissions in the field. This handheld device integrates a disposable colourimetric sensor array consisting of plasmonic nanocolorants and chemo-responsive organic dyes to detect key plant volatiles at the ppm level within 1 min of reaction. We demonstrate the multiplexed detection and classification of ten individual plant volatiles with this field-portable VOC-sensing platform, which allows for early detection of tomato late blight 2 d after inoculation, and differentiation from other pathogens of tomato that lead to similar symptoms on tomato foliage. Furthermore, we demonstrate a detection accuracy of \geq 95% in diagnosis of *P. infestans* in both laboratory-inoculated and field-collected tomato leaves in blind pilot tests. Finally, the sensor platform has been beta-tested for detection of *P. infestans* in symptomless tomato plants in the greenhouse setting.

lant diseases cause severe threats to global food security by devastating crop production in every region of the world. Statistically, around 20-40% of all crops losses globally are due to pre- or post-harvest plant diseases¹; in the United States, estimated annual crop losses due to non-indigenous arthropod species and plant pathogen introductions are US\$14.1 billion and US\$21.5 billion, respectively². Late blight caused by oomycete P. infestans (Mont.) de Bary^{3,4} is one of the most 'armed and dangerous' plant diseases⁵ with serious implications for the production of economically important crops such as potato and tomato. Late blight alone accounts for global financial losses of nearly US\$5 billion dollars6. Late blight is identified by blackish brown lesions on the surface of plant tissues that result in sporulation of P. infestans, spread of sporangia to other plants and death of infected plants in a few days if the plants are left untreated. Furthermore, the pathogen spreads rapidly under favourable weather conditions. In the 2009 late blight pandemic in the eastern United States, it only took about 2 weeks for the pathogen to spread from infected transplants to over 50% of the counties in New York⁷. Therefore, developing a rapid and effective method for early diagnosis of P. infestans and many other plant pathogens is critical to the prevention of spread of pathogens and subsequent crop diseases and reduction of economic losses in agriculture.

Currently, plant pathogen detection is heavily focused on a wide variety of molecular assays, including nucleic acid-based technologies such as PCR^{8,9}, loop-mediated isothermal amplification^{10,11} or DNA microarrays¹²; and immunological approaches such as antibody-based lateral flow assays (LFA)¹³ and enzyme-linked immunosorbent assays (ELISA)^{14,15}. Nucleic acid-based methods are sensitive and specific but dependent on cumbersome assay protocols. Immunoassay technology offers simplicity and portability for on-site detection but is limited by detection sensitivity and specificity for certain applications. Alternatively, field-portable sensors have seen rapid development in the past few years and hold great promise. For example, a few lab-on-a-chip PCR devices for detection of plant pathogens have recently been demonstrated¹⁶⁻¹⁸. However, few miniature systems are capable of high analytical performance while at the same time maintaining simplicity and cost-effectiveness.

We report a smartphone-integrated plant VOC profiling platform using a paper-based colourimetric sensor array that incorporates functionalized gold nanomaterials and chemo-responsive organic dyes for accurate and early detection of late blight in tomato leaves. In our sensor array, cysteine (Cys)-functionalized gold nanoparticles (Au NPs) or nanorods (Au NRs) were used as plasmonic aggregative colourants for specific recognition of gaseous (E)-2-hexenal, one of the main VOC markers emitted during P. infestans infection¹⁹. Using this handheld device, we demonstrated the identification of ten common plant volatiles including green leaf volatiles and phytohormones (for example, methyl jasmonate and methyl salicylate) within 1 min of reaction. The multiplexed sensor array was scanned in real time by a three-dimensional (3D)-printed smartphone reader and calibrated with known concentrations of plant volatiles to provide quantitative information on volatile mixtures released by healthy and diseased plants. Using an unsupervised pattern-recognition method, this smartphonebased VOC-sensing platform allows for the sub-ppm detection of (E)-2-hexenal and low-ppm discrimination of a range of diseaserelated plant VOCs. Finally, the performance of the smartphone device was blind-tested using both laboratory-inoculated tomato leaves and field-collected infected leaves for detection of P. infestans and validated against PCR results.

Results

Development of a smartphone-based VOC-sensing platform. We developed a handheld optical scanning platform that integrates a disposable VOC-sensor array with the smartphone camera module for digital quantification of relevant plant volatiles (Fig. 1,

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Fig. 1 | Design of the smartphone imaging platform for plant volatile sensing. a, Schematic representation of the smartphone device for sensor array scanning, consisting of a smartphone to provide light source and to capture images, a phone attachment with an external lens and a diffuser and a sensor cartridge containing the chemical sensor array. **b**, A photograph of the actual sensor cartridge with a loaded sensor array. **c**, COMSOL simulation of the gas flow in the array chamber. **d**,**e**, Photographs of the back (**d**) and front (**e**) of the smartphone-based VOC-sensing device.

Supplementary Fig. 1 and Methods). The disposable VOC-sensor strips were prepared by deposition of an array of chemical sensors onto nitrocellulose paper substrates. The paper device was placed in the centre of the 3D-printed cartridge and sealed with a microscope cover glass and a rubber O-ring by compression of a sealing cover onto the cartridge to create a leak-free space for gas exposure (Fig. 1b and Supplementary Fig. 1d,e). The COMSOL simulation of the gas flow in the sensor cartridge showed the superiority of the streamlined gas channel design (Fig. 1c and Supplementary Fig. 2a) over other geometries, such as a square-shaped flow chamber design that produced much less uniformity of the flow rate along the gas flow path (Supplementary Fig. 2b). The sensor cartridge was inserted into the smartphone attachment and imaged by the camera of the smartphone (Fig. 1a).

Nanoplasmonic materials as plant volatile sensors. The ligandfunctionalized plasmonic NPs could be used as alternative colourants to organic dyes to detect gaseous analytes of interest. Metallic nanomaterials have been widely used in biological sensing and imaging^{20–22}. One common sensing mechanism is dependent on changes in localized surface plasmon resonance (LSPR) through the introduction of nanoparticle agglomeration by the binding of target molecules to bio-specific receptors on the nanomaterials. While various aggregation-based colourimetric assays have been developed in solution, few attempts have been made to trace small gaseous molecules associated with plant pathogens using plasmonic nanomaterials in a dehydrated state. To detect gaseous (E)-2-hexenal, one of the main C6 green leaf volatiles and a reported VOC marker for late blight¹⁹, we synthesized a series of cysteine (Cys)-capped Au NPs or NRs as LSPR gas sensors (Supplementary Fig. 3). Surface functionalization of nanomaterials was done by the ligand exchange of cetyltrimethylammonium bromide (CTAB) with Cys (Fig. 2a). UV-visible spectra of Au NRs exhibited no notable shifts in plasmon resonance peaks after Cys conjugation (Supplementary Fig. 4a). Fourier-transform infrared spectroscopy (FTIR) results clearly indicated the ligation of Cys to the surface of Au NRs by the detection of characteristic carboxyl (O-C=O) stretching absorption at 1,735 cm⁻¹ in Cys-capped Au NR inks (Supplementary Fig. 4b). The specific chemical reaction between Cys and (E)-2-hexenal was inspired by previous work using α , β -unsaturated carbonyl moiety-conjugated probes for sensitive detection of Cys or homocysteine^{23,24}. These functionalized nanomaterials are highly responsive to aliphatic α , β -unsaturated aldehydes through the 1,4-Michael addition reaction, which cleaves the protective Cys ligands off the surface of Au NRs and leads to their aggregation through the formation of a seven-membered ring imine adduct, (3R, S)-7-propyl-2,3,6,7-tetrahydro-1,4-thiazepine-3-carboxylic acid (Fig. 2b). The reaction mechanism and byproducts (cleaved molecules) of this reaction were validated by both nuclear magnetic resonance (NMR) and mass spectrometry (MS) analyses (Supplementary Figs. 5 and 6). UV-visible spectra and transmission electron microscopy (TEM) results clearly indicate



Fig. 2 | Vapour detection of the characteristic C6 plant aldehyde using functionalized Au NRs. a, Formation of Cys-capped Au NR via ligand exchange at room temperature (RT). b, Mechanism of the aggregation of Au NRs occurring at the gas-solid interface induced by exposure to (*E*)-2-hexenal.
c, Before- and after-exposure smartphone images of various Cys-Au NR sensors following exposure of different vapour concentrations of (*E*)-2-hexenal (0.1–100 ppm) for 1 min; three measurements were repeated with similar results; inset shows a photograph of various Au NR inks in solution.
d, Corresponding RGB differential images of each gas exposure; three replicates were averaged. For display purposes, the RGB colour range was rescaled from 3–10 to 0–255. e, Response curves of all Cys-Au NR sensors as a function of the vapour concentration of (*E*)-2-hexenal. f, LOD calculation of the most responsive sensor, Cys-Au NR with the absorption of 535 nm; the curve was fitted by an exponential function with *R*² = 0.96. A LOD of ~0.4 ppm was obtained on the basis of the Euclidean distance of a blank control (N₂ gas) plus three times the standard deviation (3*σ*) of the control (red dotted line). For e and f, data were presented as means ± s.d., *n*=3 independent experiments. a.u., arbitrary unit.

the considerable particle aggregation of Au NRs upon exposure to (*E*)-2-hexenal at 10 ppm level (Supplementary Fig. 7).

We then evaluated the performance of various paper-based Cys–Au NR sensors for effective (E)-2-hexenal detection. Ten Cys– Au NR suspensions with their longitudinal resonant peaks in the range of 530-650 nm were drop-casted on a nitrocellulose paper and dried out as a linear array for gas exposure (Fig. 2c). The nanoplasmonic sensor array was exposed to different concentrations of (E)-2-hexenal vapours generated from a gas dilution platform (Supplementary Fig. 8). The Cys-Au NR sensors showed quick reactivity to ppm levels of (E)-2-hexenal vapours, and the reaction equilibrium can be reached in around 1 min for analytes at 1 ppm or higher (Supplementary Fig. 9). Figure 2c shows colourimetric responses of various Cys-Au NR sensors to different concentrations of (E)-2-hexenal after exposure for 1 min. Solid-state Au NRs generally turn purple or grey in response to analytes due to particle aggregation but the extent of colourimetric responses was highly dependent on the aspect ratio of nanorods. Hypsochromic Au NRs (shorter absorption wavelength range 530-570 nm) tended to be more responsive with more distinguishable colour changes than bathochromic Au NRs (longer absorption wavelength range 580-650 nm; Fig. 2c). Figure 2d represents a differential colour map

 $(\Delta R, \Delta G, \Delta B)$ of the sensor responses which was developed by subtracting the control (pre-exposure) image from each post-exposure images to better visualize the colourimetric response. The results suggest that our low-cost LSPR-based gas sensors can trace hexenal down to the ~1 ppm even with the naked eye.

Quantitatively, we determined the limit of detection (LOD) of each Cys–Au NR sensor for detection of (*E*)-2-hexenal using the Euclidean distance (ED), which is the straight-line distance between two points in the Red, Green, Blue (RGB) colour space (defined as $ED = \sqrt{\Delta R^2 + \Delta G^2 + \Delta B^2}$; Fig. 2e). The LOD was determined by finding the minimum concentration whose corresponding ED value is above the mean of the blank control (that is, pure N₂ at 50% relative humidity) plus three times its standard deviation (3 σ). It turns out that Cys–Au NR with the UV-visible absorption at 535 nm gives the best LOD of ~0.4 ppm (Fig. 2f and Supplementary Table 1), which is two orders of magnitude lower than the vapour concentration of (*E*)-2-hexenal produced by infected potato tubers as determined by gas chromatography–mass spectrometry (GC–MS) (>10 ppm; Table 1)²⁵.

To investigate the effect of particle size and shape in the detection of gaseous aldehyde, eight spherical Au NP suspensions with absorption range 520–580 nm (particle size 10–100 nm; Supplementary

Table 1 | LODs of six representative plant volatiles detected by the chemical sensor array on the smartphone, as compared to the vapour levels detected in *P. infestans*-infected potato tissues by GC-MS

Plant VOCs	LODs (ppm)	Vapour level (ppm) ^a
(E)-2-Hexenal	0.4	12-18
(Z)-3-hexenal	1.1	6-12
1-hexanal	1.7	3-6
4-ethylphenol	1.8	3-6
Benzaldehyde	0.9	0.3-1.5
2-phenylethanol	5.2	1.5-3

^aData recalculated from ref. ²⁵.

Fig. 10) and six elongated Au NR inks with longitudinal resonance in the range 750–930 nm (aspect ratio 3–6; Supplementary Fig. 11) were prepared and functionalized with Cys as previously described. Sensor responses to gaseous C6 leafy aldehyde were found to be highly dependent on the optical properties of these nanomaterials: for spherical Au NPs, the reactivity gradually decreases with increases of particle size and the most sensitive response was achieved by 530-nm Au NPs (Supplementary Fig. 12). On the contrary, the response of near-infrared Au NRs is slightly enhanced with the increase of aspect ratio (Supplementary Fig. 13). Overall, the LODs of spherical Au NPs and near-infrared Au NRs were not as good as those of short-wavelength Au NRs (Supplementary Fig. 14 and Supplementary Table 1).

Multiplexed sensor array for pattern identification of plant volatiles. We then developed a multiplexed sensor array combining Cys-functionalized Au nanomaterials and conventional organic colourants for the detection and differentiation of a variety of leaf volatiles. This ten-element colourimetric sensor array contains five representative Au nanomaterials (535-nm and 530-nm Au NPs; 535-nm, 830-nm and 930-nm Au NRs), along with the other five conventional organic dyes including two pH indicators, two solvatochromic probes and a generic aldehyde/ketone-sensitive dye (Fig. 3a and Supplementary Table 2). A typical colourimetric sensor array requires the use of multiple cross-reactive dyes to probe a wide range of chemical properties of a single analyte or an analyte 'bouquet'26,27. For this particular application, the chemical interactions used in our sensor array include Lewis and Brønsted acidity/ basicity, molecular polarity, redox property and solvatochromism associated with plant vapour emissions. Previous research has proved the long shelf-life and good resistance to environmental changes of a similar colourimetric sensor array²⁸. In this study, we also observed little variation in sensor response in detection of positive samples (10 ppm (E)-2-hexenal) against a variety of factors, including humidity, gas flow velocity, temperature and common interfering agents such as CO₂ and H₂S (Supplementary Fig. 15), which demonstrates the robustness of our sensor array to environmental variation.

The sensor array was then tested with ten plant volatiles, including three green leaf volatiles ((Z)-3-hexenal, 1-hexenal and (E)-2-hexenol), two phytohormones (methyl jasmonate and methyl salicylate), two characteristic late blight markers ((E)-2-hexenal and 2-phenylethanol) and three aromatic VOCs (benzaldehyde, 4-ethylguaiacol and 4-ethylphenol) to demonstrate the capability for multiplexing. The sensor array was exposed to 10 ppm of each plant volatile and repeated in triplicate. Figure 3a depicts representative smartphone images of the sensor array before and after exposure to (E)-2-hexenal for 1 min. All Cys-functionalized Au nanomaterials showed distinct and visible colour changes after (E)-2-hexenal exposure. A dose-dependent measurement of (E)-2-hexenal is shown in Fig. 3b. More importantly, readily distinguishable patterns were observed for all ten plant volatiles tested (Fig. 3c). We collected response profiles of six representative analytes (Fig. 3b, Supplementary Figs. 16 and 17) and calculated their detection limits, which are all well below the diagnostically notable vapour levels as determined by GC–MS on infected plant tissues (Table 1).

Although the LOD is a widely used figure to describe the detection sensitivity of a sensor device, it does not indicate the ability of a sensor to identity a specific analyte in a mixture. The point at which one can discriminate a particular analyte from others is defined as the limit of recognition (LOR), which varies depending on the library of analytes among which a specific target can be differentiated. To determine the LOR of our sensor array, we examined all ten plant volatiles at 10, 5 and 2.5 ppm. A multivariate technique, principal component analysis (PCA)^{29,30} was performed to give a measurement of the dimensionality of the data library. PCA results showed that for the dataset collected at each concentration, it generally requires five to six dimensions to account for >95% of total variance for accurate classification (Fig. 3e). For the simplicity of plotting and visualization, we only use the first three principal components that account for >80% of total variance to show the overall classification. As shown in Fig. 3d, nine out of ten plant volatiles are perfectly clustered and well-separated from the control (N₂ gas) at 10 ppm. In contrast, the volatiles are moderately discriminable at 5 ppm but indistinguishable at 2.5 ppm (Supplementary Fig. 18). We therefore estimate that the LOR of the sensor array for differentiating main plant volatiles is between 5 and 2.5 ppm, about five to ten times higher than their LODs.

Non-invasive detection of P. infestans. For actual applications, we improved the smartphone reader device by incorporating a diaphragm micropump for active sampling of unknown gaseous analytes in the field (Fig. 4a and Supplementary Fig. 19). To assess its efficacy for detection of P. infestans-infected plants, fresh tomato leaves were inoculated by spraying 1 ml P. infestans sporangia suspensions (1,000–10,000 sporangia ml⁻¹; Fig. 4b) onto the leaf; their VOC profiles were monitored by the smartphone sensor device daily for up to 6d after inoculation. A general workflow of the smartphone device for profiling VOC emissions from plant leaves is shown in Fig. 4a. Conditions used for pathogen detection were carefully optimized, including accumulation time for headspace gases (60 min; Fig. 4c) and gas sampling time (1 min; Supplementary Fig. 9). The batch-to-batch reproducibility of disposable volatile test strips was also tested and consistent readout was confirmed (Fig. 4d). The smartphone-based sensor response patterns of P. infestansinfected tomato leaves are shown in Fig. 4e, where control samples (healthy leaves) showed a relatively weak VOC background. Unique patterns related to potential pathogen infection emerged 2d after inoculation and the patterns became more visually distinguishable on subsequent days (Fig. 4e). Due to the highly mixed nature of the plant leafy volatile emissions, more sensor elements were turned on by the leaf headspace gas (Fig. 4e) compared to previous single VOC species tests (Fig. 3c).

VOC profiles sampled over different times after infection show a steady increase of *ED* values as a function of days after inoculation (Fig. 4f). By applying PCA, infected tomato leaves at varying stages of infection and healthy leaf controls can be readily discriminated by using the first three principal components (Fig. 4g). Leaf samples profiled 2–4d after inoculation are clearly clustered and separated from those profiled 1 d after inoculation or healthy leaf controls; they become indistinguishable at the later stages of infection (5 or 6 d after inoculation) because of the saturation of the sensor signals. Therefore, we conclude that our smartphone-based VOC-sensor device is viable for early detection of *P. infestans* and responds to



Fig. 3 | Sensor response of the multiplex array to ten major plant volatiles at the vapour level of 10 ppm for 1 min exposure and their chemometric analysis. a, Before- and after-exposure images of the ten-element sensor array in response to 10 ppm (*E*)-2-hexenal; three measurements were repeated with similar results. **b**, RGB differential profiles of the sensor array exposed to different concentrations of (*E*)-2-hexenal (0.5-25 ppm). **c**, RGB differential profiles of ten representative plant volatiles at 10 ppm. Each measurement is averaged over three replicates. For display purposes, the RGB colour range is rescaled from 3-10 to 0-255. **d**, PCA score plot using the first three principal components; all plant VOCs can be differentiated except for two weakly responding esters, jasmonate and salicylate; *n* = 3 independent experiments. **e**, PCA scree plot that recombines the RGB vectors of all ten sensor elements. After recombination, only six dimensions are needed to account for >95% of total variance.

the infection within 2 d after inoculation before visible symptom development.

To demonstrate the specificity for P. infestans detection, we compared the VOC pattern of P. infestans with those of two other pathogens of tomato (fungi Alternaria solani for early blight and Septoria lycopersici for Septoria leaf spot). The volatile composition of leaves inoculated with the three pathogens and the healthy control was first characterized by GC-MS analysis, which revealed distinguishable VOC signatures for the pathogens (Fig. 5a). The sensor response profiles of the three pathogens (3 d after inoculation) plus a healthy control are shown in Fig. 5b, which shows quantifiable differences in the overall sensor responses. A higher level of (E)-2hexenal was observed in the cases of P. infestans and A. solani infection as indicated by sensor spots numbered 1-5 and 10, whereas S. lycopersici tended to emit a larger content of 4-ethylphenol and 4-ethylguaiacol that result in higher responses of spots 6 and 7 (Fig. 5b). The sensor responses are generally in a good agreement with the GC-MS measurements. Moreover, a healthy leaf sample spiked with 5 ppm(E)-2-hexenal produced a VOC response pattern similar to that of a pathogen-infected sample, while other aldehydes (for example, 1-hexenal) did not respond (Fig. 5b). These results

further confirm that (*E*)-2-hexenal is a major diagnostic VOC marker for *P. infestans*. Using PCA, we were able to differentiate each of three typical tomato pathogens plus a healthy control with an overall classification accuracy of 95.4% (that is, only 3 errors out of 65 measurements in total; Fig. 5c).

Finally, the performance of the smartphone-based VOC-sensor was evaluated by two blind tests for detection of P. infestans in both laboratory-inoculated and field-collected leaves, as well as a greenhouse pilot test for continuously monitoring of VOCs from the same tomato plant before and after inoculation over a period of 1 month. For the double-blinded laboratory test, 40 anonymous tomato leaf samples were measured on the smartphone VOC-sensing platform by personnel who were not involved in sample preparation and PCR validation. The sample pool contained both infected and healthy leaves to challenge the device. PCR tests were run for each sample and used as a standard for validation (Supplementary Table 3). From the previous tests, we observed that the VOC level of healthy tomato leaves averaged around 10.4 ± 1.2 (Fig. 6a, red points). Therefore, a diagnostic threshold of 14.0, which is the mean of controls plus three times the standard deviation, was chosen for the determination of diseased leaf samples (grey dashed line, Fig. 6a).

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Fig. 4 | **Detection of** *P. infestans* **in tomato leaves by the smartphone VOC-sensor. a**, A general workflow showing the procedure for the analysis of plant volatiles using the portable smartphone VOC-sensing device. **b**, Sensor response of infected leaves on days 2, 4 and 6 when inoculated with four different spore concentrations (1,000-10,000 sporangia ml⁻¹). c, Sensor response as a function of gas accumulation time (15, 30, 45, 60 min, 2 h and 4 h) for 2,500 or 10,000 sporangia ml⁻¹ of inoculates collected on days 0, 2 and 4. **d**, Reproducibility tests of four separately prepared batches of sensor arrays. **e**, Differential RGB profiles of volatiles released from infected tomato leaves up to 6 d after inoculation with *P. infestans*. **f**, Response plot showing the Euclidean distance of all ten sensor elements as a function of the duration of pathogen infection. **g**, PCA score plot of infected tomato leaves for different periods of infection. Point colours represent the different days after inoculation. For reproducibility testing, data were presented as means ± s.d., n = 3 biologically independent samples for experiments shown in **b-d**; and n = 7 biologically independent samples for experiments shown in **b-d**;

Using this threshold value, our smartphone VOC-sensor was able to rapidly generate binary diagnostic results—positive (+) or negative (-)—on the 40 blind samples tested (Supplementary Table 3). Only two samples were misdiagnosed by the smartphone VOC-sensor (Fig. 6a, red circle in the middle panel), with a detection sensitivity (true positive rate) of 100%, specificity (true negative rate) of 90% and overall detection accuracy of 95%, when compared to the PCR results (Table 2 and Supplementary Table 3).

For the blind field sample test, 40 tomato leaves were collected, including 20 PCR-positive (+) leaves with suspicious symptoms and 20 symptomless samples representing PCR-negative (-). All infected leaves were collected from tomatoes grown at the Mountain Research Station in Haywood County, North Carolina on 20 August 2018 (ref. ³¹). In this pilot study, VOC emissions from all 40 pieces of leaves collected from the field were analysed using the smartphone VOC detector. Results were then compared

side-by-side to results of quantitative PCR (qPCR) following conventional CTAB-based DNA extraction. Out of 20 samples that were identified as positive (+) by qPCR analysis (Supplementary Table 4), 19 samples were correctly diagnosed by our smartphone VOC-sensor, while all negative samples were correctly diagnosed, representing an overall detection sensitivity, specificity and accuracy of 95%, 100% and 97.5%, respectively (Table 2 and Fig. 6a, blue points). Combining all data together, healthy and infected tomato leaf samples (either laboratory-inoculated or field-collected) exhibited a clear classification in the PCA plot, on the basis of the first two principal components (Fig. 6b). The subtle difference between laboratory-prepared and field-collected infected samples was also captured by the smartphone VOC-sensor: laboratoryinoculated samples showed a narrower distribution of leafy VOC levels (Fig. 6a, green points) due to better control of the inoculum dose and time, whereas field samples exhibited a wider spread of

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Fig. 5 | Validation of the specificity of the smartphone-based VOC-sensor. a, GC-MS spectra obtained from headspace of three infected tomato leaves and the healthy control; three measurements were repeated with similar results. **b**, Differential RGB profiles of uninfected tomato leaves, infected leaves with three pathogens (3 d after inoculation) and spiked healthy leaves. **c**, PCA plot of infected tomato leaves versus the healthy control. Each infected species was measured in 15 trials; n = 15 biologically independent samples for three infected leaves and n = 20 biologically independent samples for the healthy control.

ED values as a result of the heterogeneous nature of field samples (Fig. 6a, blue points).

For the greenhouse measurements, VOC profiles of healthy leaf controls (three tomato plants) were collected once every other day by the smartphone sensor device for 24d. The plants were then inoculated with *P. infestans* on the 25th day and after that the VOCs of infected leaves were monitored daily for another 8d until the plants completely died. The response curve obtained from this 1-month monitoring experiment showed a stable baseline VOC response from healthy tomato plants in the first 24d and a rapid increase of VOC emissions 1–2d after inoculation (Fig. 6d). These results confirm the ability of the smartphone volatile sensor to capture pathogen-induced leaf volatile changes immediately as infection occurred.

Last but not least, the VOC levels obtained on the smartphone gas sensor from infected samples demonstrated an inversely proportional linear correlation (R^2 =0.81) to the cycle numbers (Cq) of the *P. infestans*-specific qPCR assay (Fig. 6d and Supplementary Table 4), indicating that higher VOC emission level was associated with higher pathogen DNA content in tomato leaf samples and therefore lower *Cq* values.

Discussion

VOC emission by plants has recently emerged as a non-invasive diagnostic marker of infectious plant diseases^{32–34} due to the rich chemical information of VOC^{35–37} and their unique functionality in plant self-defence and interplant communications^{38–42}. Although several portable detection platforms such as electronic noses (e-noses)^{43–45} have been previously demonstrated for plant volatile analysis, most e-nose technologies only use weak chemical interactions and therefore suffer from several limitations, including: (1) low sensitivity for sub-ppm detection of compounds, (2) limited chemical specificity to discriminate volatiles with similar chemical structures and (3) severe interference from environmental variation including humidity and temperature.

Alternatively, our smartphone-based VOC-sensing method uses chemically specific sensing elements consisting of cross-reactive plasmonic nanomaterials and dyes with notably stronger chemical interactions, and therefore results in unprecedented detection sensitivity (Fig. 2f and Table 1), multiplexity (Fig. 3c,d) and chemical selectivity (Fig. 5). We also demonstrated that our chemical sensor array is robust and reproducible (Fig. 4d) in signal readout when working under various conditions (Supplementary Fig. 15). Certain toxic gaseous molecules, such as H₂S, may cause sensor drift (for example, ~5% increase in sensor response at 5 ppm H₂S), which suggests that the use of VOC strips may be limited in certain special scenarios, such as near rotting vegetables or fruits. However, the environment-induced signal drift of VOC strips ($\leq 5\%$) is in general much smaller than e-nose sensors (up to 30%)⁴⁵. In addition, the cost of the chemical sensor array is estimated to be about 15 cents per test and the smartphone attachment is about US\$20 (excluding the phone), which is orders of magnitude less expensive than commercial e-nose sensors.

The main innovation of this work lies in two areas: first, we use plasmonic nanostructures as a new class of sensing elements to greatly expand the library of targets that can be analysed on a conventional chemical sensor array^{28,46-48}; and second, we have integrated a portable smartphone reader to facilitate field deployment and implementation. Although the concept of using LSPR for gas sensing has been explored by several other groups⁴⁹⁻⁵², most previous studies rely on bulky and expensive spectrometers for monitoring wavelength shifts or absorption changes, limiting their potential for field applications. Instead, the plasmonic materials in this study are used as chromogenic aggregative colourants embedded in a paper matrix, whose signals-colour changes-can be easily detected and quantified by low-cost reader devices such as smartphones. A mobile application is in development to conduct image analysis also on the same platform. The detection specificity of plasmonic gas sensors is achieved by the capturing ligands immobilized on the surface of nanostructures, therefore allowing versatile ligand design to extend the applications to a broad range of gaseous targets. On the other hand, despite the great progress in smartphone-based imaging and sensing technology recently⁵³⁻⁵⁹, only a few applications for gas detection have been demonstrated⁶⁰⁻⁶⁴ and



Fig. 6 | Evaluation of the smartphone-based VOC-sensor for blind detection of *P. infestans* in tomato leaves. **a**, Box plots of VOC emission levels measured from different groups of samples. From left to right: healthy control (red points, n = 20 biologically independent samples), blind laboratory-prepared healthy and disease leaves (cyan and green points, n = 40 biologically independent samples) and blind field-collected healthy and disease samples (violet and blue points, n = 40 biologically independent samples). A diagnostic threshold of 14.0 (grey dashed line) was established by using the mean of the healthy controls (red points) plus three times its standard deviation to generate binary diagnostic results on the phone. For box plots, the bottom and top of boxes represent the first and third quartile, respectively; the middle line is the median and the whiskers represent the maximum and minimum values. Red circles indicate the misdiagnosed samples by the smartphone in each blind pilot trial. **b**, PCA results showing the separated clusters of infected and healthy leaves using the first two principal components; n = 100 biologically independent samples. **c**, VOC response curves of the same tomato plants monitored in the greenhouse over 1 month; error bars were on the basis of three parallel measurements on three individual plants; data were presented as means \pm s.d., n = 3 biologically independent samples. **d**, Bar plot shows the correlation between pathogen DNA contents in the 20 field and 20 greenhouse infected samples as determined by qPCR (Cq values) and overall VOC levels (ED values) as detected by the smartphone VOC-sensor. The least-squares fitting method was used to determine the correlation; n = 40 biologically independent samples.

 Table 2 | Quantification of the detection sensitivity, specificity and accuracy of the smartphone VOC-sensor in the blind tests, on the basis of PCR results used as the gold standard

	Blind laboratoryBlind fieldsamples $(n = 40)$ $(n = 40)$		l samples	
	PCR	voc	qPCR	voc
True positive (TP)	20	20	20	19
False positive (FP)	-	2	-	0
True negative (TN)	20	18	20	20
False negative (FN)	-	0	-	1
Sensitivity (TP/P)	-	100%	-	95%
Specificity (TN/N)	-	90%	-	100%
Accuracy ((TP+TN)/ n))	-	95%	-	97.5%

no smartphone-based systems have been reported yet for specific, rapid and non-invasive plant pathogen detection in the field.

The gas sample processing steps in our approach are relatively simple. The use of glass vials for collecting leafy headspace gas from detached samples provides a stable and reproducible testing environment. Moreover, although a 1-h gas accumulation step has been implemented in this initial study, a gas collection time as short as 15 min is sufficient to differentiate uninfected samples from infected leaves 3-4d after inoculation (Fig. 4c). Therefore, the quickest sample-to-result time could be less than 20 min for field testing. Alternative sampling methods are possible to completely remove the leafy headspace collection step and shorten the total assay time. For example, the sensor patches could be attached directly to the plant leaves for in planta monitoring, where the signals could be continuously received by remote monitoring devices. The wearable design may be more advantageous than smartphonebased scanning in terms of long-term monitoring of symptomless plants and deployment of larger numbers of sensors over a large scale to more efficiently detect early infections in fields. Although we observed that undetached leaves produce 10-15% less volatile emissions than those from detached leaves (Supplementary Fig. 20), such difference may be compensated by a better sensor and gas sampling design in future. The current smartphone-based VOC pathogen sensors could be integrated into a disease forecasting system for late blight. They could be used by field extension workers or farmers to trigger a spray event, whereas current late blight forecast systems are mostly weather-based⁶⁵.

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In conclusion, we developed a cost-effective, field-deployable and integrated VOC-sensing platform installed on a smartphone for non-invasive profiling of infectious plant diseases such as late blight with a high degree of detection sensitivity and specificity. The multiplexed chemical sensor assay used in this system is built on plasmonic nanomaterials to target green leafy aldehyde, (E)-2hexenal, a major late blight VOC marker down to sub-ppm level of LOD. The smartphone reader device itself integrates bright-field imaging modality, a micropump for active gas sampling and wireless connectivity to be used in the field or resource-limited settings. We demonstrated the performance of this portable VOC-sensing system for simultaneous detection and classification of ten individual plant volatiles. By combining this with a pattern classification algorithm such as PCA, diagnosis of tomato late blight as early as 2 d after inoculation was achieved on the smartphone, which is much earlier than the manifestation of visible symptoms. Moreover, this smartphone-based VOC-sensing platform can accurately identify late blight from infected tomato leaf samples either inoculated in the laboratory or collected from the field with a detection accuracy of above 95%. The device has been beta-tested in the greenhouse setting for monitoring of infection progression for a period of 1 month. Considering the design flexibility, multiplexity and cost-effectiveness, this integrated optical gas sensor platform can be potentially applied to detect other common plant pathogens at very early stages, as well as to monitor various abiotic stresses of plants in the field.

Methods

Reagents and materials. All reagents and materials were analytical reagent grade and used without further purification. Reagents for Au nanomaterial synthesis including HAuCl₄, CTAB, AgNO₃, cysteine, NaBH₄ and common solvents were purchased from Sigma–Aldrich; nitrocellulose membrane (0.45 µm, catalogue no. MCE4547100G) was purchased from Sterlitech Corporation; Sensor cartridges were made by 3D-printing using a thermoplastic, ABS*plus*-P430 (Eden Prairie).

Preparation of the smartphone VOC reader device. The smartphone attachment and sensor cartridge were designed with Autodesk Inventor and prototyped using a 3D-printer (uPrint SE Plus, Stratasys). The sensor array is illuminated by the default LED flash of the phone (LG V10) and the illumination was uniformed by an optical diffuser ($6 \times 9.5 \times 2.3$ mm³, parts no. 02054, Edmund Optics) placed in front of the LED flash. An external lens (12 mm in diameter) with focal distance of 48 mm (parts no. 65-576, Edmund Optics) was placed in between the smartphone camera and sensor array to collect the colourimetric signals of the array. The lens provided a demagnification factor of about six times (30-mm object distance) so that the entire sensor array could be captured in the field of view of the smartphone reader. The current attachment is designed for an Android smartphone (LG V10), and likewise a similar platform can be easily manufactured for other brands of smartphones such as an iPhone or tablet, after minor modifications to the footprint of the base attachment.

A diaphragm micropump (T5-1IC-03-1EEP, Parker Hannifin) was installed at the back of the reader device for pulling VOC analytes from real plant tissues onto the sensor array. The micropump was powered by three AA batteries and connected to the sensor cartridge via microtubings (parts no. 21564304, Versilon). This battery-powered micropump generates a gas flow rate of 480 standard cubic centimetre per minute (sccm) to the sensor array.

Synthesis of plasmonic nanomaterials. Short Au NRs. The highly concentrated Au NRs were prepared according to the scale-up, two-step seed-growth method⁶⁶. First, the seeds were made by adding 0.364 g of CTAB to 10 ml of 0.25 mM HAuCl₄. Then 0.6 ml of 0.01 M NaBH₄ solution was added dropwise to the above solution while it was stirring at 800 r.p.m. The colour of the solution instantly became light brown and the seeds were aged for 5 min and used for all experiments. Second, a two-step seed-growth synthesis was performed: the first growth solution was prepared by mixing HAuCl₄ (0.5 ml, 5 mM), AgNO₃ (8 µl, 0.1 M), ascorbic acid (53 $\mu l,$ 0.1 M), CTAB (0.364 g) and Milli-Q water (8.5 ml) at room temperature. Then 1 ml of the seed solution was added into the growth solution, with a waiting period of 5 min before further addition of reagents. During the second growth, 100× concentration of each precursor was added to the solution obtained from the first step, which contained HAuCl₄ (5 ml, 50 mM), AgNO₃ (80 µl, 1 M), ascorbic acid (530 µl, 1 M), CTAB (0.364 g) and Milli-Q water (4.5 ml). The mixture was allowed to react for 10 min before centrifugation and collection of the final product. The particle concentration was estimated to be ~0.02 mM on the basis of the measured optical density and the previously determined extinction coefficients, which was about 50 times as high as that obtained by the conventional seedmediated method.

Near-infrared Au NRs. The synthesis of NIR Au NRs follows the same protocol of short Au NRs except that a co-surfactant, benzyldimethylammonium chloride (BDAC), was used along with CTAB in both the first and second steps of seed-mediated Au NR synthesis⁶⁶⁶⁷. Six concentrations of BDAC (0.025, 0.05, 0.075, 0.1, 0.125 and 0.15 mM) were applied that yielded six NIR Au NRs with absorption wavelengths ranging from 750 to 930 nm.

Spherical Au NPs. Spherical Au NPs with different diameters were synthesized by varying the molar ratio of citrate to Au(III) precursor⁶⁸. Briefly, HAuCl₄ (10 ml, 0.5 mM) was placed in a 50 ml single-neck round flask. The flask was then immersed in an oil bath without reflux and heated to 100 °C under vigorous stirring at 800 r.p.m. for 10 min. While the Au(III) solution was boiling, different volumes (0.25, 0.5, 0.5, 1.25, 2, 4, 7 and 12 ml) of citrate solutions (5 mM) preheated at the reaction temperature were quickly added in. The product was allowed to cool down to room temperature after the reaction proceeded for another 10 min, then centrifuged and washed three times and then dissolved in 0.2 ml nanopure water to make it about 50 times as concentrated as the initially obtained Au NP solution.

Oxidation and ligand exchange of nanoplasmonic materials. For particle oxidation, different amounts $(10-100\,\mu$ l) of a mild oxidant, HAuCl₄ (5 mM), were added to the Au NR solution⁶⁹. The oxidation process occurred 5 min after the addition of Au(III), which was monitored by a UV-visible spectrometer to record the extinction spectra over time. Once each of the ten desired longitudinal plasmon resonance wavelengths (530–650 nm) were achieved, the oxidation process was stopped by precipitating Au NRs with centrifugation and redispersing them in 0.1 M CTAB solution. The aspect ratio (AR) of Au NRs were tuned in between 1 to 2.5, which produces nanorods with an average width of 20 nm and varied length from 20 nm to 50 nm, as evidenced by TEM images (Supplementary Fig. 3). For ligand exchange, 1 ml of 0.1 M cysteine was added to 1 ml CTAB-capped Au NR solution and the mixture was stirred at room temperature for 24h. The final products were collected with centrifugation and redispersed in 0.1 M cysteine before the preparation of sensor arrays.

Characterization of Au nanomaterials. For the studies of surface chemistry and nanoparticle morphologies, FTIR spectra were acquired on a Perkin Elmer Frontier spectrometer from 4,000 cm⁻¹ to 1,000 cm⁻¹. UV-visible absorption data was collected on a Thermo Evolution 201 UV-visible spectrophotometer. TEM was performed on a JEOL 2000FX with an acceleration voltage of 200 kV.

For the validation of chemical reaction mechanism during nanoparticle aggregation, 1:1 molar mixture of cysteine (3.02 g, 25 mmol) and (E)-2-hexenal (2.45 g, 25 mmol) were dissolved in D₂O (20 ml) and stirred at room temperature for 2h to simulate the gas-phase sensing reaction. The solids were filtered, washed with D₂O and dried under vacuum to give the white product (4.22 g; yield 84%). NMR solution was prepared by redissolving the purified product (20 mg) in D₂O (0.75 ml) and DCl (0.05 ml). ¹H and ¹³C NMR spectra of the as-synthesized product were recorded on a Varian 600 MHz spectrometer. ¹H NMR (600 MHz, D2O) chemical shifts (8): 7.5 (doublet of doublets (dd), 1 H), 4.63 (singlet, 1 H, solvent), 4.02 (dd, 1 H), 3.47 (dd, 1 H), 3.24 (dd, 2 H), 2.48 (doublet of doublets of doublets, 2 H), 1.52 (dd, 2 H), 1.40 (dd, 2 H), 1.06 (triplet, 3 H); 13C NMR (125 MHz, D₂O) 8: 173.9, 67.4, 65.7, 47.6, 47.1, 35.8, 32.4, 19.6, 17.2. Mass spectra were collected on a Waters Q-TOF Premier Mass Spectrometer. Electrospray ionization mass spectrometry (ESI-MS) mass-to-charge (m/z) ratio: calculated $C_9H_{15}O_2NS [M+H]^+ = 202.0$; detected = 201.9. Both NMR and MS results support the formation of seven-membered ring imine product, (3R, S)-7-propyl-2,3,6,7tetrahydro-1,4-thiazepine-3-carboxylic acid, as the major product during the nanoparticle aggregation.

Sensor array preparation. Each of the Au nanomaterial inks was used as is, while the other five organic dyes were prepared in the sol–gel formulations (in porous silica made from the hydrolysis of tetraethoxysilane and ethyltriethoxysilane, as reported previously⁴⁶). About 150 nl of each Au nanomaterial ink or dye formulation was transferred by slotted stainless steel pins (parts no. FP4CB, V&P Scientific) and drop-casted onto the nitrocellulose substrate to form a round coloured spot with ~1 mm in diameter, using a LEGATO 180 pl syringe pump (KD Scientific). Detailed composition and concentration of each sensor element can be found in Supplementary Table 2. Before the measurements, colourimetric sensor arrays were stored in a nitrogen-filled desiccator for 24 h. The sensor arrays are stable for 1 month under storage in N₂.

Gas exposure and image capturing experiment. Gas mixtures were prepared according to previous methods⁴⁵. Briefly, MKS mass flow controllers were used to achieve gas streams with the desired concentration (for example, 0.1–100 ppm of (*E*)-2-hexenal), flow rate (500 sccm) and 50% relative humidity by mixing the proper portion of saturated vapour of the liquid analyte with dry (0% relative humidity) and wet (100% relative humidity) nitrogen gas. Arrays were exposed to a control stream (50% relative humidity N₂) for 1 min followed by 1 min exposure of an analyte stream. A photo was taken by the camera of a smartphone, LG V10, at the end of 1 min exposure to either the control or the analyte, as the before- or after-exposure image.

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Inoculation of tomato leaves and detection of headspace gas. Tomato seedlings were purchased from local supermarket and cultivated in a greenhouse at 25 ± 3 °C under 16h of light per day. A typical *P. infestans* strain (NC 14-1, US-23) was cultured on rye medium in the dark at 20 °C. Leaves collected from tomato plants at the five-to-six leaf stage were inoculated with suspensions of *P. infestans* sporangia (~10,000 sporangia ml⁻¹) in a sterile acid-washed Petri dish (100×15 mm²). Healthy tomato leaves treated with sterile water were used as controls and kept under the same condition. The infected leaves and the control leaves were quickly transferred into borosilicate scintillation vial (20 ml) with screw lids and incubated at room temperature with 95% relative humidity. The capped vials were further sealed with Parafilm (Bemis) to allow the headspace gases to accumulate for 1 h before the measurement. The headspaces above each of the infected leaf samples and the controls were sampled by the micropump-equipped smartphone VOC-sensing device every 24 h after inoculation over the next several days.

Solid-phase microextraction GC-MS test of plant volatiles. Solid-phase microextraction sampling was performed using non-polar divinylbenzene/ carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibres. The screw thread solid-phase microextraction vials were fitted with Teflon septa and loaded with a healthy leaf or each of the three inoculated leaves to accumulate the vapour for 1 h. The fibre then penetrated into the septa to extract the volatiles for 2 min. GC-MS experiments were carried out using an Agilent Technologies 7890A GC-MS equipped with a flame ionization detector and mass selective detector. The injector temperature was kept at 80 °C and analytes were desorbed for 2 min. The carrier gas was helium (1 ml min⁻¹). For analysis, the initial oven temperature was maintained at 80 °C for 2 min, increased at a ramp rate of 5 °C min⁻¹ to 305 °C for 45 min. The GC-MS built-in NIST libraries were used to interpret the mass spectra.

qPCR analysis of field leaf samples. For CTAB-based DNA extraction, approximately 10 mg homogenized leaf sample was taken in a microcentrifuge tube and mixed with 150 µl extraction buffer (0.35 M sorbitol, 0.1 M Tris, 0.005 M EDTA, 0.02 M sodium bisulfite, pH7.5), 150 µl nuclei lysis buffer (0.2 M Tris, 0.05 M EDTA, 2.0 M NaCl and 2% CTAB, pH 7.5) and 60 µl 5% N-lauryl sarcosine. Then, the tube was incubated at 65 °C for 30 min. After incubation, 300 µl chloroform was added to the tube and centrifuged at 12,000 r.p.m. The aqueous phase containing DNA was transferred to a new tube and mixed with 300 µl cold isopropanol (100 %) and 30 µl of 3 M sodium acetate (pH 8). The sample was stored overnight at -20 °C and then centrifuged at 13,000 r.p.m. for 5 min to pellet the precipitated DNA. After discarding the supernatant, 1 ml cold ethanol (70%) was added to wash the pellet. The sample was centrifuged again at 13,000 r.p.m. for 5 min and the ethanol solution was disposed. Finally, the DNA pellet was air-dried in a fume hood and resuspended in 100µl TE buffer (10 mM Tris-HCl, 0.1 mM EDTA, pH 8.0). For qPCR amplification, 1 µl template DNA was used with two P. infestans-specific primers PINF (CTCGCTACAATAGGAGGGTC) and HERB1 (CGGACCGCCTGCGAGTCC), which generate an amplicon length of ~100 base pairs (bp) using a previously published thermocyling procedure70.

Greenhouse measurements. Three robust tomato plants grown in the pots were placed in a clear plastic bin and cultivated in the greenhouse under room temperature, with 12 h illumination per day. A damp paper towel at the bottom of the bin was used to keep high relative humidity. The VOC level of each plant during the healthy growth phase was monitored and recorded daily over 24 d. At the 25th day, 1 ml of sporangia solution $(5 \times 10^3 \text{ sporangia ml}^{-1})$ was evenly misted onto the leaves of plants and the lid of the bin was completely closed to allow for 100% relative humidity and to avoid spreading of the pathogen. Symptoms of late blight became apparent 3 d after inoculation. The VOC level was continuously monitored by the smartphone detector until the 8th day after inoculation, when the complete death of the plants occurred.

Reporting Summary. Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability

The data supporting the findings of this study are available in the paper and its Supplementary Information. All data generated or analysed are available from the corresponding authors on reasonable request.

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Author contributions

Z.L., Q.W. and J.B.R. designed the experiments. Z.L. prepared the Au nanoplasmonic inks and the multiplexed chemical sensor array, carried out sensing experiments and analysed data. R.P. conducted the COMSOL simulation of gas flows. J.C.H. collected the fresh field samples for qPCR and VOC tests. R.P., T.Y., Z.L., A.C.S. and J.C.H. performed the leaf inoculation experiments and conducted PCR or qPCR analyses of the pathogens. Z.L. and T.B.T. designed and fabricated the smartphone imaging attachment. Z.L., Q.W. and J.B.R. wrote the manuscript. All authors contributed to the editing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Reporting Summary

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Statistics

For	all st	atistical analyses, confirm that the following items are present in the figure legend, table legend, main text, or Methods section.
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	\square	The exact sample size (n) for each experimental group/condition, given as a discrete number and unit of measurement
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\boxtimes		The statistical test(s) used AND whether they are one- or two-sided Only common tests should be described solely by name; describe more complex techniques in the Methods section.
\boxtimes		A description of all covariates tested
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	\boxtimes	A full description of the statistical parameters including central tendency (e.g. means) or other basic estimates (e.g. regression coefficient) AND variation (e.g. standard deviation) or associated estimates of uncertainty (e.g. confidence intervals)
\boxtimes		For null hypothesis testing, the test statistic (e.g. <i>F</i> , <i>t</i> , <i>r</i>) with confidence intervals, effect sizes, degrees of freedom and <i>P</i> value noted Give <i>P</i> values as exact values whenever suitable.
\boxtimes		For Bayesian analysis, information on the choice of priors and Markov chain Monte Carlo settings
\boxtimes		For hierarchical and complex designs, identification of the appropriate level for tests and full reporting of outcomes
\boxtimes		Estimates of effect sizes (e.g. Cohen's d, Pearson's r), indicating how they were calculated
		Our web collection on <u>statistics for biologists</u> contains articles on many of the points above.

Software and code

Policy information al	pout <u>availability of computer code</u>
Data collection	All mobile phone images of the sensor array were collected by the basic camera functioning module of an Android smartphone, LG V10 (LG Corp.).
Data analysis	Adobe Photoshop CS5 (Adobe Photoshop version 12.0, by Adobe Inc.) was used for the measurement of RGB color changes of each sensor element, and fungal DNA analysis using qPCR was conducted by GENEX program version 1.0 (Bio-Rad, by Bio-Rad Laboratories). All RGB color difference profiles were created by Microsoft Excel 2010 (Microsoft Corp.).

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All manuscripts must include a data availability statement. This statement should provide the following information, where applicable:

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Field-specific reporting

K Life sciences

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Life sciences study design

All studies must disclose on these points even when the disclosure is negative.

Sample size	For two blind tests (Fig 6), n=40 laboratory-inoculated samples and n=40 field-collected leaves were used for measurement of VOC emissions and PCR analysis. For green house test (Fig 6c), n=3 independent tomato plants were measured. For classification of late blight from other infections (Fig 5), n=35 biologically independent leaf samples were tested. For monitoring of VOC emission as a function of infection dates (Fig 4), n=7 biologically independent leaf samples were tested. For basic characterization of VOC sensor responses, each measurement was repeated in 3 independent experiments. Statistics have been derived to calculate error bars and generate box plots. All error bars are defined as the standard deviation of replicates.
Data exclusions	No data were excluded from the final analyses.
Replication	All analyses throughout the entire study were repeated multiple times (from 3 to 15, depending on the particular purpose of each experiment) to check consistency of the results. All attempts at replication were highly statistically accurate and reproducible.
Randomization	For both the laboratory-inoculated and field measurements, all candidate leaf samples were randomly selected from a group of healthy or infected plants.
Blinding	We have conducted two blind tests for pathogen detection in both laboratory-inoculated and field-collected leaves. For the double-blinded lab test, leaf inoculation and PCR tests were performed independently by some of the authors from the Department of Entomology and Plant Pathology of NC State University who were not involved in the development and testing of the sensor device.

Reporting for specific materials, systems and methods

We require information from authors about some types of materials, experimental systems and methods used in many studies. Here, indicate whether each material, system or method listed is relevant to your study. If you are not sure if a list item applies to your research, read the appropriate section before selecting a response.

Materials & experimental systems	Methods
n/a Involved in the study	n/a Involved in the study
Antibodies	ChIP-seq
Eukaryotic cell lines	Flow cytometry
Palaeontology	MRI-based neuroimaging
Animals and other organisms	
Human research participants	
Clinical data	

Animals and other organisms

Policy information about stu	dies involving animals; ARRIVE guidelines recommended for reporting animal research
Laboratory animals	The study did not involve laboratory animals.
Wild animals	The study did not involve wild animals.
Field-collected samples	Field-infected leaves were collected from the Mountain Research Station in Haywood County, NC on Aug 20, 2018. A normal condition of housing (greenhouse), temperature (22-30 oC), humidity (~90% relative humidity), and photoperiod (12 h illumination/day, from 7 am-7 pm) was provided before and after the infection were reported.
Ethics oversight	The Phytotron laboratory from NC State University has approved and provided guidance on the study protocol of the greenhouse experiments.

Note that full information on the approval of the study protocol must also be provided in the manuscript.