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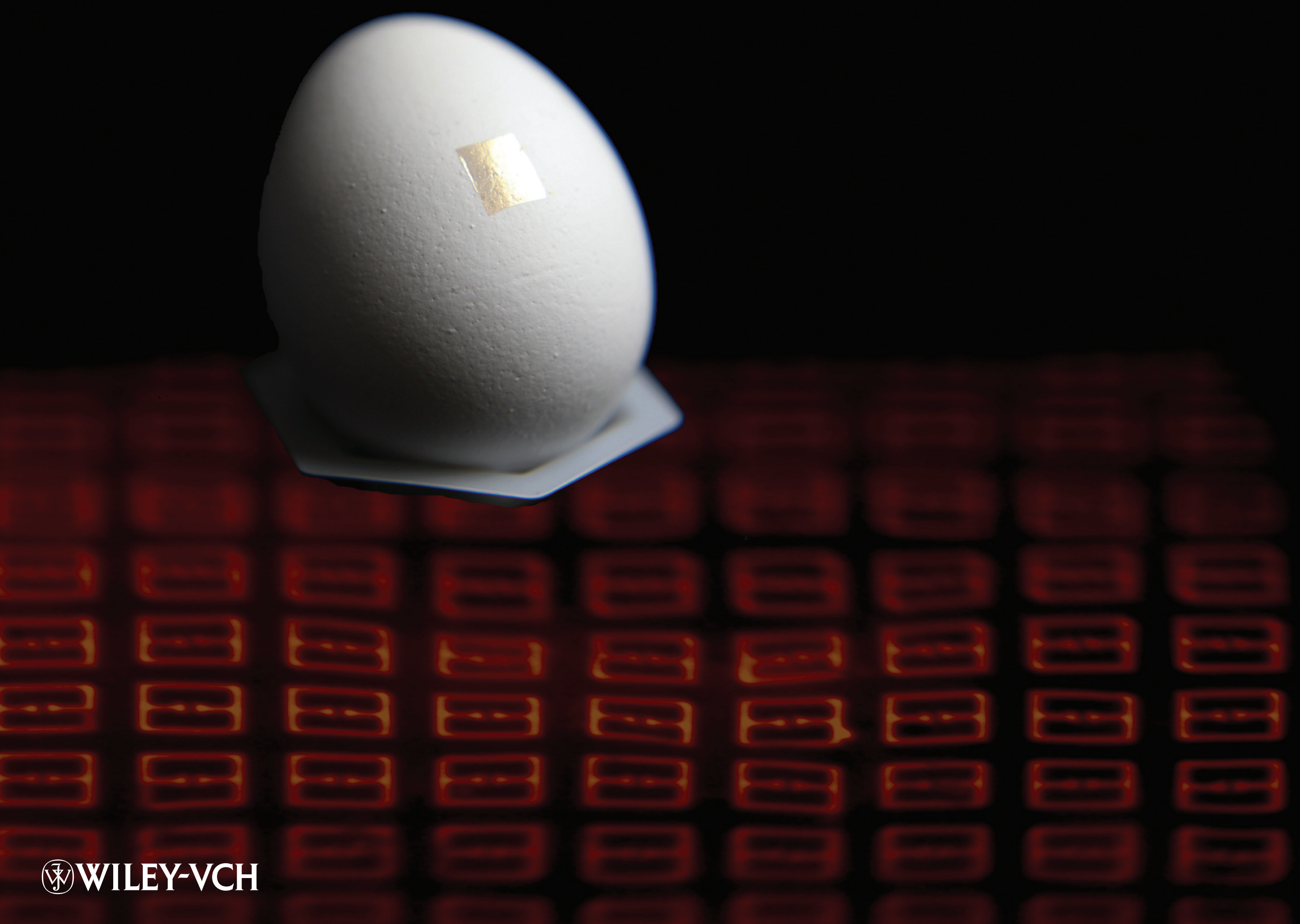

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Silk-Based Conformal, Adhesive, Edible Food Sensors

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Recent progress in making devices on unconventional substrates that conform to surfaces shows a promising future for consumer electronics for human health and food and environmental quality monitoring.[1] Significant progress has been made on curvilinear electronics such as flexible LEDs,[2] solar cells,[3] and transistors.[4] These flexible devices are formed by fabricating electrical components on thin, elastomeric films, most of which are rubber-like polymers such as poly(dimethylsiloxane) (PDMS), and can then be wrapped against non-planar objects.[5] Due to the contact-based nature of this process, the conformality depends on the curvature of the to-be-wrapped surfaces and local imperfections can occur on highly curved areas[6] and/or during vigorous movement, limiting applications. Further, these are non-biodegradable and non-edible substrates that also limit some applications.

Food safety is an increasingly important public health issue for both the consumer and food industry.[7] Characteristics such as color, firmness, odor, texture, etc., are routinely used in the quality control of agricultural and biological food products.[8] Early analytical techniques used in the food quality control required isolation of the food component of interest, which inevitably caused the damage to the tested samples.[9] Recent progress in the development of non-destructive approaches/instruments, for example gas chromatography, mass spectrometry, electronic noses and electronic tongues that could detect and recognize odors and tastes, has shown some success for food quality evaluation.[10] Though these techniques are of considerable interest to the food industry, oftentimes such analyses require sophisticated instrumentation and data processing software,[11] which could be time-consuming and are relatively expensive for daily use.

We present in this paper a concept for making wireless passive antennas on silk substrates across multiple regions (MHz, GHz, THz) of the electromagnetic spectrum. These antennas can be easily applied to curved objects (i.e., food in this work) and adhere conformally. The devices were tested for function by monitoring their resonant responses continuously during the spoilage process to assess the potential to monitor changes in food quality. Proof-of-principle demonstrations for this type of approach are demonstrated by monitoring fruit ripening with a conformally attached RFID-like silk sensor transferred onto the fruit skin, and spoilage of dairy products through surface contact (in the solid case) or immersion (for liquid goods). These types of passive, chip-less sensor, consists of an antenna or an array of antennas/resonators made of only a sub-micron thickness of gold, a level equivalent to common edible gold leaf/flakes used on cakes and chocolates. The resonators are fabricated on pure-protein silk film substrates, and can be used as sensing platforms that safely interface with consumable goods or can be in direct contact with food (and can potentially be consumed) for different applications.

An inexpensive sensor (or a sensor array) that can be non-invasively attached to the food for *in situ* detection of the localized change of the food-quality-related properties can be attractive.[12] Though various sensors (either physical or chemical ones) are available, the majority of these sensors exist in two-dimensional planar layouts on rigid and flat wafers that are usually not disposable. Strategies for overcoming the mismatch between the planar, rigid and brittle surfaces of semiconductor wafers and the inherently curved interfaces of most (if not all) natural objects, such as living organisms (e.g. tissues), environmental substrates (such as plants or stems), and foods (such as fruits and vegetables), are thus essential to implementation of such systems.[13] Robustness is also a desired feature for such devices due to the fact that, in theory, any material is bendable in sufficiently thin form, thereby improving conformal contact at the expense of increased difficulty in processing and handling.[14] This is especially important for food sensors, because they need to operate in a variety of different environments and under potentially harsh conditions during food storage and transportation (such as changing temperatures, transport shock and vibration, textured surfaces, etc.).[15]

As an ancient material that has been widely used in the textile industry over the past five millennia, silk has recently been

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recognized as an appealing biocompatible and eco-friendly material for various applications encompassing electronics, photonics, tissue engineering, and sensing.[16] Silk can be processed into various forms such as gels, sponges, foams and films. The latter are of particular interest because of their optical transparency, biocompatibility, bioresorbability, and mechanically robust and flexible nature. This makes them well suited to serve as a platform for conformal devices that can be potentially be resorbed or enzymatically digested inside the human body or in the environment.[17]

Efforts have been made to develop biocompatible hybrid silk devices such as implantable transistors and silk-based electrodes for in vivo neural activity measurements.[18] Compared with these active/powered devices, antenna-based passive devices (i.e., no power consumption) such as RFID tags are preferred in many wireless sensing applications where low cost, ease of production and disposability are prioritized. Though the primary application driving development of these antennas is identification for tracking purposes, passive antennas (not limited to traditional radiofrequency and microwave antennas, but also including optical and photonic options, such as metamaterial resonators[19] and surface plasmon resonators[20]) can be used to measure remotely the physical and chemical properties of their surroundings.

These passive antennas can be generally modeled as LC resonators and the resonant behavior is dependent on the geometry and dielectric properties of the constituent material. Any change in the electromagnetic properties (i.e., resistivity, capacitance, inductance) of the antenna structures will result in a change in their resonant responses, making them sensitive to the local environment.[21] This makes such devices useful for a variety of non-invasive/non-destructive sensing applications, specifically for food quality control, where spoilage and deterioration of food often involve a variation of its dielectric properties.[22] Thus, the construction of such devices from safe and edible components could add broad utility to such sensors allowing for direct integration with consumables.

The fabrication of silk-based conformal and adhesive sensors in this work starts with the aqueous silk solution as previously described.[23] Achieving precision fabrication on silk substrates is challenging and different fabrication strategies are needed. Most conventional chemical processes involved in micro-/nano fabrication such as photolithography and etching would cause contamination and thereby affect the biological compatibility of silk sensors by being exposed to chemicals used in the fabrication. We have developed a variety of techniques for chemical-free fabrication of silk sensors with various critical feature sizes that can operate in multiple electromagnetic regimes ranging from radio frequency (RF) and microwave to terahertz (THz), infrared and optical frequencies.

Figure 1 depicts the four most commonly used methods (see Supporting Information for details) for fabricating/transferring micro-/nanopatterns onto silk substrates, including: a) inkjet printing, b) shadow mask deposition process,[24] c) silk transfer applied micropatterning process (STAMP),[25] and d) contact transfer process, which directly transfers nano patterns from a donor substrate (i.e., silicon) onto the silk substrate by applying pressure and/or temperature[26] along with an image of Au-silk devices, namely (e) a GHz resonator, (f) a THz-metamaterial, and (g) a nanopatterned Au-nanoparticle plasmonic array on silk.

Figure 2 provides a schematic of the process for a passive silk sensor with an array of micro metamaterial antennas (i.e., split ring resonators) conformally wrapped on the curved surface and then adhered to the object. The silk substrate that acts as the carrier for the antennas (step 1) softens but retains its

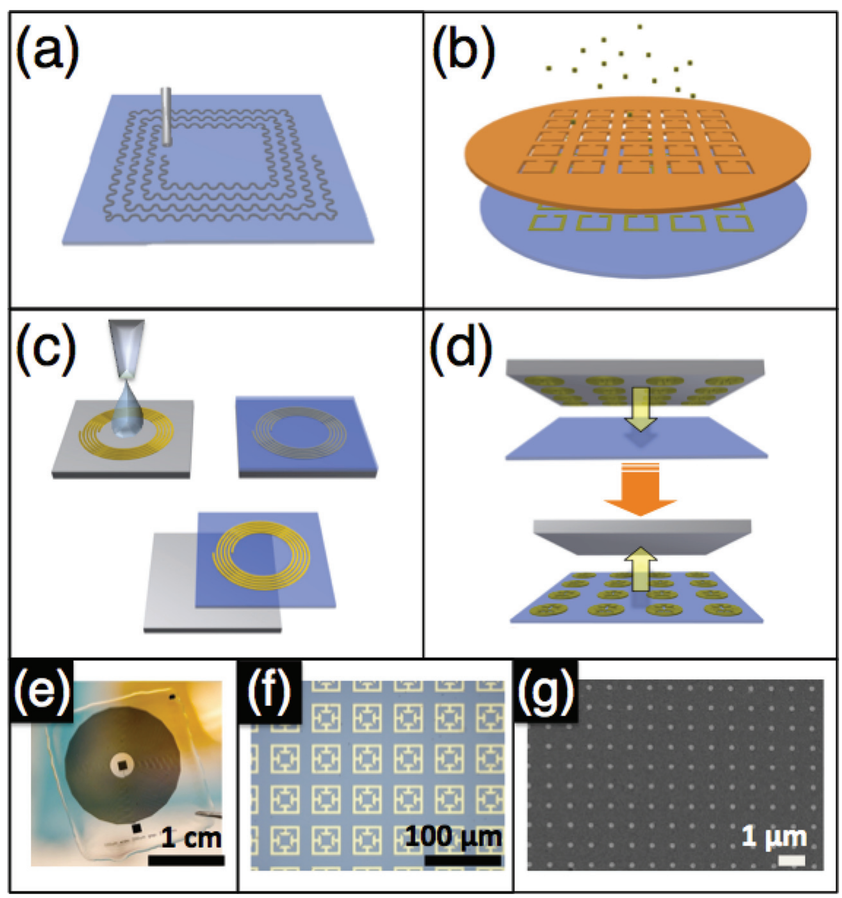

Figure 1. Schematics of fabrication processes for passive silk sensors. a) Inkjet printing of functional components directly onto the silk substrate. b) Shadow-mask transfer. c) Casting-liftoff process. Functional components are fabricated directly on silanized silicon wafers. Silk is cast directly onto the silicon substrate, and the functional components are transferred to the silk after drying under ambient conditions. d) Direct transfer. Functionalized surfaces are applied to the silk substrate, along with heat and pressure. Removal of the original substrate leaves the functional components on the surface of the silk substrate. e) Example of a GHz resonant coil on silk, fabricated using the STAMP process. f) A THz resonant silk metamaterial array fabricated via shadow mask deposition. g) An Au nanoparticle array on silk, fabricated using direct transfer.

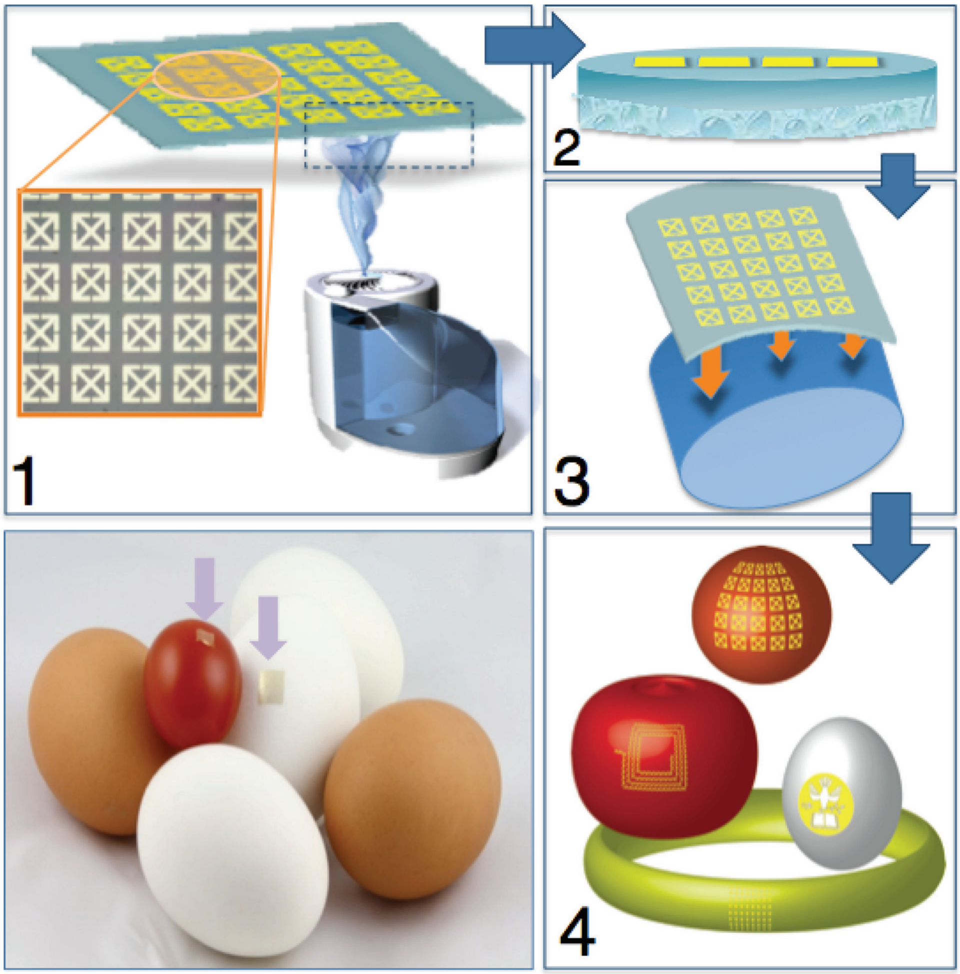

Figure 2. Schematic of steps for rapid transfer of silk antennas onto curved substrates. 1) Water vapor is applied to the back of non-crystalline functionalized silk films, yielding 2), a functionalized film in which the back surface of the film has been partially melted. 3) This melted surface is conformally applied to arbitrary surfaces, yielding 4), applied functional sensors on a variety of surfaces.

structural integrity after being exposed to water vapor generated by an ultrasonic humidifier or a steam vaporizer. This process lowers the glass transition temperature of the silk material and makes the film conform to the applied surface upon gentle pressure (steps 2, 3). The adhesive thin layer of silk forms on the back side of the silk substrate that is softened by the moisture during exposure to the vapor and acts as a "glue" to adhere the antenna onto the target surface. The procedure has been tested on several curved surfaces of different foods including eggs, tomatoes, meat, and apples (a subset of which is shown in Figure 2). Thus, brittle to soft substrates are amenable to the approach. No cracking or detachment of the applied silk sensors was observed suggesting that the transfer process is effective and the Au-silk sensor can maintain integrity during handling (See Supplemental information for details).

The resonant response of the silk antenna can be understood using a LC circuit model and the resonant frequency (f_0) is given by the expression of ($f_0 = \frac{1}{2\pi\sqrt{LC}}$), where the inductance (L) is mainly determined by the geometry of the antenna; however, the capacitance (C) highly relies on the supporting substrate and the surrounding environment. The antenna's resonant responses will be affected by the dielectric change of the object to be sensed (i.e., food in this work) and the shifts in the impedance and resonant frequency can be used to transduce (and monitor) the variation of dielectric properties associated with density/firmness and material composition. This includes parameters such as moisture, gas emission, and salt content that correlate to food quality. Good conformality intrinsically improves the sensitivity of the antenna based on the fact that the perturbing effect of the dielectric change on the resonant response of the antenna becomes more conspicuous with more intimate and distributed contact between the sensor and food. Strong adhesion is also important for relatively lengthy food quality monitoring that could last from days to several months.

In foods, the dielectric properties can be related to chemical composition, physical structure and frequency. The conformal sensors can be tuned to operate across a variety of electromagnetic regions by optimizing the antenna design for different applications. The depth of interaction between the sensors and the supported substrate - which depends on the electromagnetic wave frequency, the magnetic permeability and electric conductivity/dielectric loss of the food - can vary by several

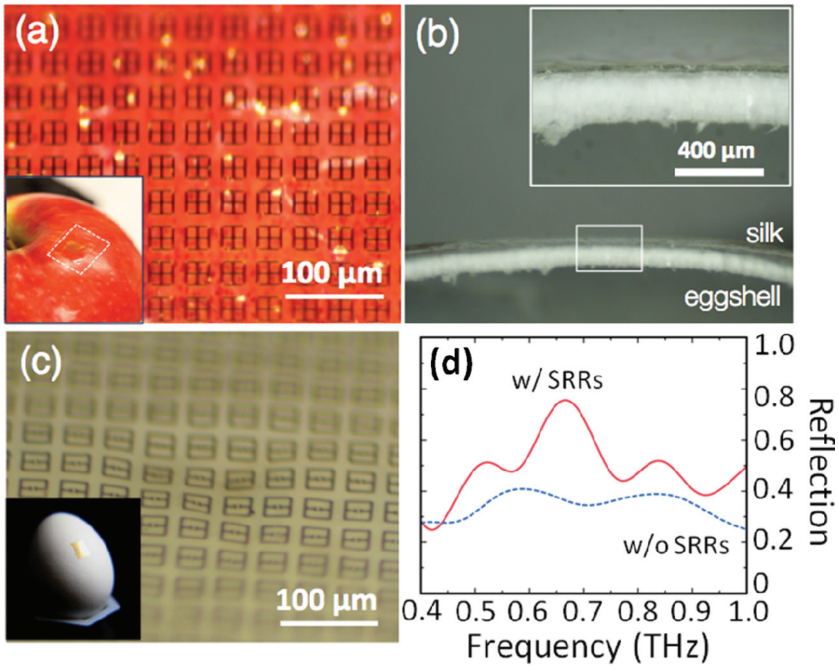

Figure 3. a) Photos of THz split ring resonators (SRRs) fabricated on the silk substrate wrapped on an apple. b) Cross-sectional view of the silk/egg shell interface. c) Photos of silk sensors conformally applied to an egg. d) Experimentally measured reflection spectra of the eggs with (red solid) and without (blue dash) the THz SRR sensor.

orders of magnitude ranging from a few millimeters to several meters in the RF and microwave regimes. Since the penetration depth ($d \approx \frac{1}{\sqrt{\pi f \mu \sigma}}$) is inversely proportional to the square root of the working frequency (f), magnetic permeability (μ) and electrical conductivity (σ) of the food, lower frequencies generally have a higher penetration rate, which is favored in most cases but usually requires a larger antenna for the longer operating wavelength.

Proof of principle demonstration of the conformal application of Au-silk sensors was carried out by applying a composite Au-silk antenna (that was fabricated with STAMP processing[25]) to a variety of relevant samples. These structures are transferred conformally to these surfaces as shown in **Figure 3** which illustrates the application of micron-scale metamaterials on the surface of an apple (Figure 3a) and on the surface of an egg, along with an inset illustrating the conformal adhesion of the device on the egg surface and its electromagnetic responses showing a notable resonant signature at THz frequencies (Figure 3b–d). THz waves have been found to be able to penetrate many everyday physical barriers such as clothing and packing materials and to be highly sensitive/absorptive to water, making this wavelength range appealing for chemical and biological sensing applications. We have previously demonstrated the use of THz metamaterial antennas to quantitatively monitor the water content of biopolymers[19] and glucose sensing with a sensitivity of 0.35 mmol/L.[24]

In this work, we focus on demonstrating the functionality of conformal silk antennas operating at RF and microwave frequencies, and monitoring the response of a variety of these resonant structures in contact with food. The results are illustrated in **Figure 4**. Figure 4a and 4b illustrate the application of an RFID-like antenna (with a resonant frequency of ~36 MHz) to a banana and monitoring the resonant response of the antenna during the ripening process of the fruit. There are many chemical and physical changes (notably ethylene emission) that occur throughout this process and that impact the properties of the banana such as color, flavor, texture, aroma and firmness. The experiment was conducted at room temperature (~20 °C) with a relative humidity of ~30% and the bananas initially appeared all green (day 0) and underwent their transition to the familiar yellow and dark brown appearance (with dark speckles over 70% of their surface) by day 9 which was arbitrarily defined as fully ripened for the purpose of this test. The frequency-dependent reflection spectra ($\mathbf{S}_{11}$) of the silk antennas (trace width: 100 µm; gap distance between traces: 200 µm: number of turns: 27) that were

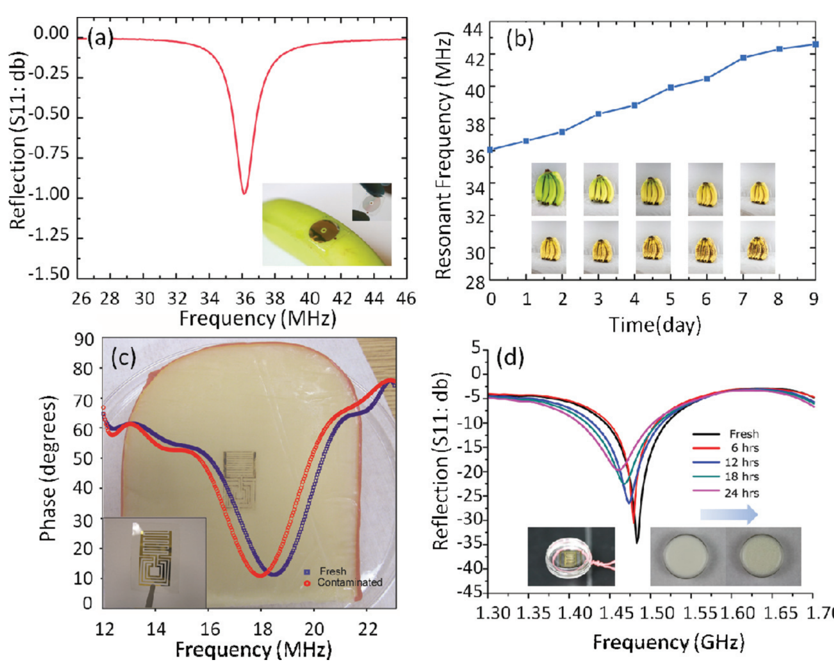

Figure 4. a) Experimentally measured reflection spectra of a silk RFID-like antenna attached to a banana. b) Experimentally measured time-dependent resonant frequencies of the silk antenna while the banana ripened over 9 days. c) Experimentally measured frequency-dependent impedance phase angle of a silk sensor applied to a slice of cheese to detect bacterial contamination. d) Experimentally measured frequency responses of a silk sensor attached to a plastic container filled with milk during spoilage.

transferred onto the bananas were measured every 24 hours using a network analyzer Hewlett Packard HP8754D with a primary sensing coil reader. An initial resonance of 36.1 MHz was observed at day 0 which then continuously shifted to higher frequency (up to 42.6 MHz at day 9) during ripening. It is worth mentioning that in certain cases the degradation likely involves a shape deformation that is tightly related with the water content within the food and can be detected also by means of dielectric properties measurements. The observed resonance shift to higher frequencies originates from a combination of both the geometric deformation of the antenna conformed to the banana and the change of the skin's dielectric properties during its ripening. These two correlated factors are typically reported as a decrease of the effective permittivity of the sample during ripening.[27]

In similar proof-of-principle experiments, an Au antenna on silk (shown in the inset of Figure 4c) was applied on a slice of cheese to detect bacterial contamination. The sample was exposed to pathogenic bacterial cells at room temperature and the impedance phase angle was monitored as a function of frequency. The monitored responses from the sample surface revealed a shift in resonant frequency associated to bacterial contamination.

To demonstrate function in contact with a fluid, an Au-silk antenna was transferred onto a plastic cap and then immersed in milk (Figure 4d) to detect its spoilage. The antenna was designed to be operate at ~1.5 GHz, within the reported minimum loss factor regime of the milk at the RF regime.[28] The sample was stored at room temperature for 24 hours to induce degeneration of the milk. RF responses were measured at 6 hour intervals. The resonance continuously shifted to lower frequency (from 1.482 GHz to 1.459 GHz) and became weaker, indicating an increase in relative permittivity (both real and imaginary parts) of the milk sample as it spoiled, in agreement with published data on the dielectric properties of milk.[29] While the silk sensors were relatively stable at ambient conditions and showed reasonable responses that effectively reflected the food spoilage process, their performance can be further improved by optimizing the antenna geometries, characterization system and analysis algorithm (e.g. employing principal component analysis methods[30]). Such approaches would lead towards better sensitivity and selectivity further decoupling the different effects (such as firmness, density and material composition) contributing to dielectric response modulation.

In conclusion, micro-/nanometallic patterns were successfully fabricated to serve as passive antenna sensors on an all protein-based silk substrates that were conformally transferred and adhered to curved surfaces. This process allows the opportunity for intimate contact of micro- and nanostructures that can probe their surrounding environment with surfaces of evolving properties, and accordingly monitor their changes. This was applied to provide in situ monitoring of food quality. It is to be noted that this type of sensor consists of all edible and biodegradable components – though it can also function as needed before consumption to monitor food quality, and then when the food is ready to be consumed, the portion of the food with the antenna on it can be readily sliced off and disposed of – holding utility and potential relevance for healthcare and food/consumer products and markets. Furthermore, the proof-of-principle silk sensors presented in this work can serve as a platform to be integrated with other organic electronic and optoelectronic components,[31,32] or adhered onto disparate (natural or artificial) surfaces, offering a promising path for a new set of biocompatible, conformal, and eco-friendly multifunctional devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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