Photoacoustic spectroscopy of surface adsorbed molecules using a nanostructured coupled resonator array

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Abstract

A rapid method of obtaining photoacoustic spectroscopic signals for trace amounts of surface adsorbed molecules using a nanostructured coupled resonator array is described. Explosive molecules adsorbed on a nanoporous anodic aluminum oxide cantilever, which has hexagonally ordered nanowells with diameters and well-to-well distances of 35 nm and 100 nm, respectively, are excited using pulsed infrared (IR) light with a frequency matching the common mode resonance frequency of the coupled resonator. The common mode resonance amplitudes of the coupled resonator as a function of illuminating IR wavelength present a photoacoustic IR absorption spectrum representing the chemical signatures of the adsorbed explosive molecules. In addition, the mass of the adsorbed molecules as an orthogonal signal for quantitative analysis is determined by measuring the variation of the localized, individual mode resonance frequency of a cantilever on the array. The limit of detection of the ternary mixture of explosive molecules (1:1:1 of trinitrotoluene (TNT), cyclotrimethylene trinitramine (RDX) and pentaerythritol tetranitrate (PETN)) is estimated to be $\sim$100 ng cm^{-2}. These multi-modal signals enable us to perform quantitative and rapid chemical sensing and analysis in ambient conditions.

S Online supplementary data available from stacks.iop.org/Nano/25/035501/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Quantitative and rapid chemical analyses generally require multiple instruments and techniques [1, 2]. However, these are usually quite bulky and expensive. Therefore, a method employing a simple platform with high performance has been highly sought-after. Over the last couple of decades, micro/nanosensors and sensing systems have been utilized as ultra-sensitive transducers in chemical analysis [3–5]. However, the ultra-sensitivity achieved by miniaturizing transducer platforms is impractical for rapid chemical analysis which requires real-time detection of target analytes at ultra-low concentrations when the convection, reaction and diffusion of molecules are considered [6–8]. The extremely small surface area of micro/nanosensors limits the number of effective adsorption sites available for
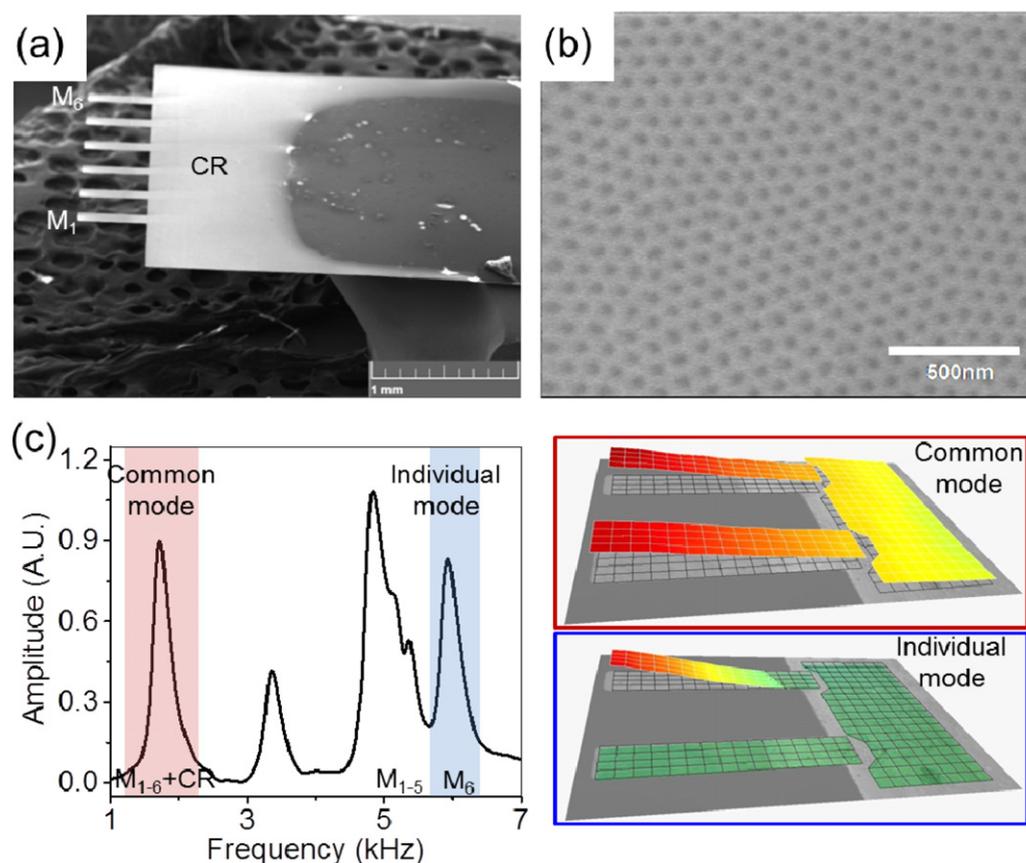
Figure 1. (a) Scanning electron microscope (SEM) image of the nanostructured coupled resonator array which consists of six microcantilevers, M_1–M_6, and a common resonator, CR. (b) Enlarged SEM image of nanopores on the resonator. (c) Frequency response of the nanostructured coupled resonator array characterized by a scanning laser Doppler vibrometer with an acoustic excitation. All microcantilevers vibrate with the common resonator at the common mode resonance frequency, 1790 Hz (red box), and each cantilever vibrates at its own localized, individual mode resonance frequency (blue box for M_6).

impingement by target analytes, leading to increased detection time and reduced practical sensitivity. Recently, many researchers have started fabricating nanostructured sensors which provide a large interfacial surface area for molecular interaction and thereby they have demonstrated dramatic sensitivity enhancement [9–14]. Moreover, nanostructured microresonator platforms have been demonstrated as sensitive tools for quantitative measurements. Combining these nanostructured microresonators and a spectroscopic technique into a single platform enables us to perform both quantitative and rapid chemical analysis.

Conventional photoacoustic (PA) spectroscopy, such as gas-microphone PA spectroscopy, usually employs an acoustic chamber which resonantly amplifies PA spectroscopic signals. In general, target molecules are introduced into an acoustic chamber in the vapour phase and illuminated with pulsed light at different wavelengths. As the target molecules absorb photons at specific wavelengths which resonantly excite the molecular vibrations, they undergo a rapid heating and cooling cycle with each light pulse. This rapid heating and cooling generates an acoustic wave which is amplified in the acoustic chamber and detected by the transducer [15, 16]. A plot of sound intensity as a function of wavelength shows the characteristic PA absorption spectrum of the target molecules in vapour phase [17–21]. In addition,

this technique has been widely applied to condensed phase samples which show homogeneously broadened spectral peaks [15, 22, 23]. However, this technique requires tedious sample loading and calibration processes for quantitative analysis. In order to address the problems inherent in conventional PA spectroscopy, we utilized a piezoelectric quartz crystal tuning fork as a sensitive PA detector as well as a resonator in order to sense surface adsorbed explosive molecules with very low vapour pressures [24]. However, the plain surface of a quartz crystal tuning fork only captures very sticky molecules and does not have any capability to retain molecules on it. Thus, we have fabricated a nanostructured coupled resonator array with anodic aluminum oxide (AAO) in order to capture and retain molecules and exploit the coupled resonator array as a very sensitive detector. By employing a high power quantum cascade laser (QCL) and the coupled resonator array, the PA spectrum as well as the mass of surface adsorbed molecules can be simultaneously measured in an open environment, unlike the conventional PA spectroscopic method which requires an acoustic chamber with an enclosed detector. To the best of our knowledge, this paper reports the first demonstration of the quantitative PA spectroscopic detection of surface adsorbed molecules using a nanostructured coupled resonator array.
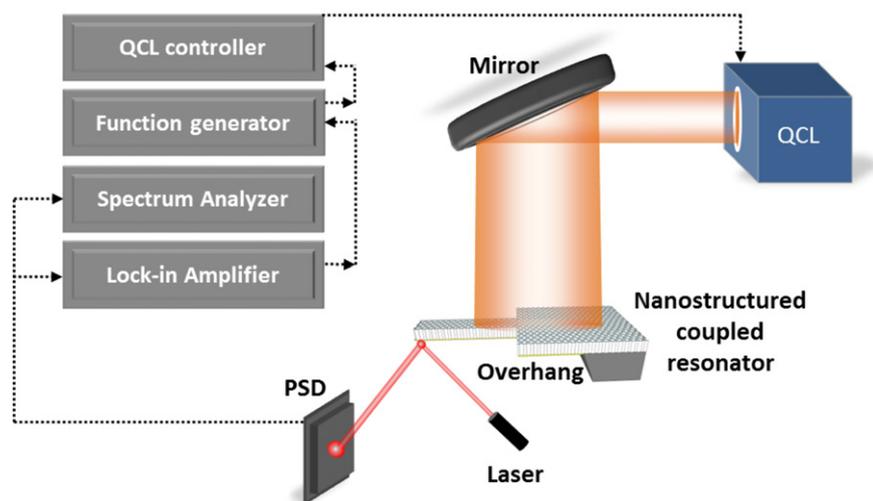
Figure 2. Schematic drawing of the experimental setup. The 200 kHz pulsed IR light with 10% duty cycle from the QCL is electrically burst at 1790 Hz, directed to the nanostructured coupled resonator, and scanned from 7.1 to 8.73 μm (1408–1145 cm^{-1} in wavenumber) with a step size of 5 nm. The PA spectroscopic signals are measured by an optical beam deflection method using a red laser and a position sensitive detector (PSD).

2. Materials and methods

First, we designed and fabricated a nanoporous coupled resonator array with hexagonally ordered nanowells from AAO, as shown in figure 1(a). This device is composed of six slightly different microcantilevers, M_1 to M_6, connected to a common resonator, CR. Each microcantilever in the array is approximately 500 μm long, 100 μm wide and 2 μm thick, and the common resonator is approximately 1.2 mm long, 3.0 mm wide and 2 μm thick. This coupled resonator array contains hexagonally ordered nanowells with diameters and well-to-well distances of 35 nm and 100 nm, respectively (figure 1(b)). The effective Young's modulus of the AAO cantilevers was determined to be ∼30 GPa, which is ∼6 times smaller than that of a plain silicon cantilever (170 GPa) and the surface area of the nanostructured cantilever is ∼23 times larger than that of a plain cantilever with the same dimensions. The fabrication and characterization process of the AAO cantilevers has been described in detail elsewhere [11, 25]. Back side overetching was performed during the final step in order to create a large overhang as a common resonator. A 100 nm thick gold layer was deposited with a 5 nm thick chromium adhesion layer on the bottom side of the resonator by electron beam evaporation to enhance the reflectivity of the probing laser beam and the PA spectroscopic signal. The frequency response of the coupled resonator array was initially characterized using an MSA-500 scanning laser Doppler vibrometer (Polytec Inc., Irvine, CA) with acoustic excitation to choose the right cantilever for our application. In accordance with previous reports by another group [26, 27], multiple resonance peaks were obtained with our coupled resonator array (figure 1(c)). A microcantilever showing a well separated resonance peak, M_6, was chosen to probe the localized, individual mode frequency response for the determination of adsorbed mass (blue box) as well as common mode coupled resonance amplitudes for acquisition of the PA spectrum (red box) simultaneously.

Three standard explosive samples (trinitrotoluene (TNT), cyclotrimethylene trinitramine (RDX), pentaerythritol tetranitrate (PETN)) were purchased from AccuStandard, Inc. (New Haven, CT) and used without further purification. As indicated by the manufacturer, the standard concentration of each explosive is 1 mg ml^{-1}.

For our PA spectroscopy experiments, the nanostructured coupled resonator array was mounted on a stainless steel cantilever holder attached to the head unit of a MultiMode atomic force microscope (Bruker, Santa Barbara, CA). A schematic illustration of our current experimental setup is shown in figure 2. 200 kHz pulsed infrared (IR) radiation with a 10% duty cycle from a ÜT-8 QCL (Daylight Solutions, San Diego, CA) is electrically burst at the common mode resonance frequency of the coupled resonator array (1790 Hz) using a DS345 function generator (Stanford Research Systems, Sunnyvale, CA) and directed to the cantilever. The common mode resonance frequency of the coupled resonator was chosen as the pulse frequency of our light source due to its low susceptibility to added mass. Figure 3 shows the common mode resonance frequencies of the coupled resonator before (black) and after (red) deposition of TNT molecules (1.1 μg cm^{-2}). The background PA spectrum was directly used to acquire the PA spectrum of the surface adsorbed molecules without changing the IR pulse frequency. The IR wavelength was scanned from 7.1 to 8.73 μm (1408–1145 cm^{-1} in wavenumber) with a step size of 5 nm. The PA IR spectra were recorded using an SR850 lock-in amplifier (Stanford Research Systems, Sunnyvale, CA) and the localized, individual mode resonance frequencies of the microcantilever were measured using an SR760 spectrum analyzer (Stanford Research Systems, Sunnyvale, CA). Fourier transform infrared (FTIR) spectra of TNT, RDX, PETN and a 1:1:1 mixture of each explosive (∼1 μg cm^{-2} for each explosive molecule) on the nanostructured coupled resonator array chip were obtained using an FTIR microscope
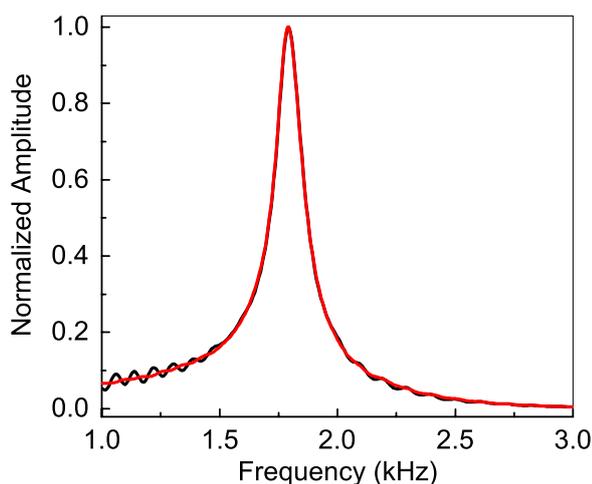
Figure 3. Common mode resonance frequencies of the coupled resonator before (black) and after (red) deposition of TNT molecules (1.1 μg cm^{-2}).

(Nicolet Continuμm FTIR microscope) in reflection mode as references. The number of registered scans was 200 with a spectral resolution of 4 cm^{-1}.

Assuming that the explosive molecules are evenly adsorbed on the coupled resonator array surface and do not affect the stiffness of the M_6 cantilever, the adsorbed mass of explosive molecules in air, δm, can be calculated from the simple approximate equation [28]

$$\delta m = \frac{k}{(2\pi)^2 n}\left(\frac{1}{f_1^2} - \frac{1}{f_0^2}\right) \qquad (1)$$

where k is the spring constant, n is a geometric factor (0.24 for a rectangular cantilever), f_1 is the measured resonance frequency with adsorbed molecules and f_0 is the initial resonance frequency of the cantilever. After recording the background PA IR spectrum of the coupled resonator array and the initial resonance frequency of the M_6 cantilever, explosive molecules were deposited either using a home-made vapour generator or with a micropipette. All the experiments were repeated with the same chip. The coupled resonator array was thoroughly cleaned using acetone and ethanol followed by UV–ozone exposure. Real-time surface concentrations of adsorbed explosive molecules were determined using equation (1) by monitoring the localized, individual mode resonance frequencies of the M_6 cantilever.

3. Results and discussion

3.1. Detection of vapour phase analytes

To deposit vapour phase TNT molecules on the coupled resonator, dry air at a fixed flow rate of 50 ml min^{-1} was used as a carrier gas and passed through a home-made vapour generator (a tube with quartz wool loaded with TNT sample solution heated to 45 °C in order to generate a higher concentration of TNT vapour). TNT molecules were deposited on the resonator for 3 min. Figure 4(a) shows the real-time adsorbed mass of TNT molecules on the M_6
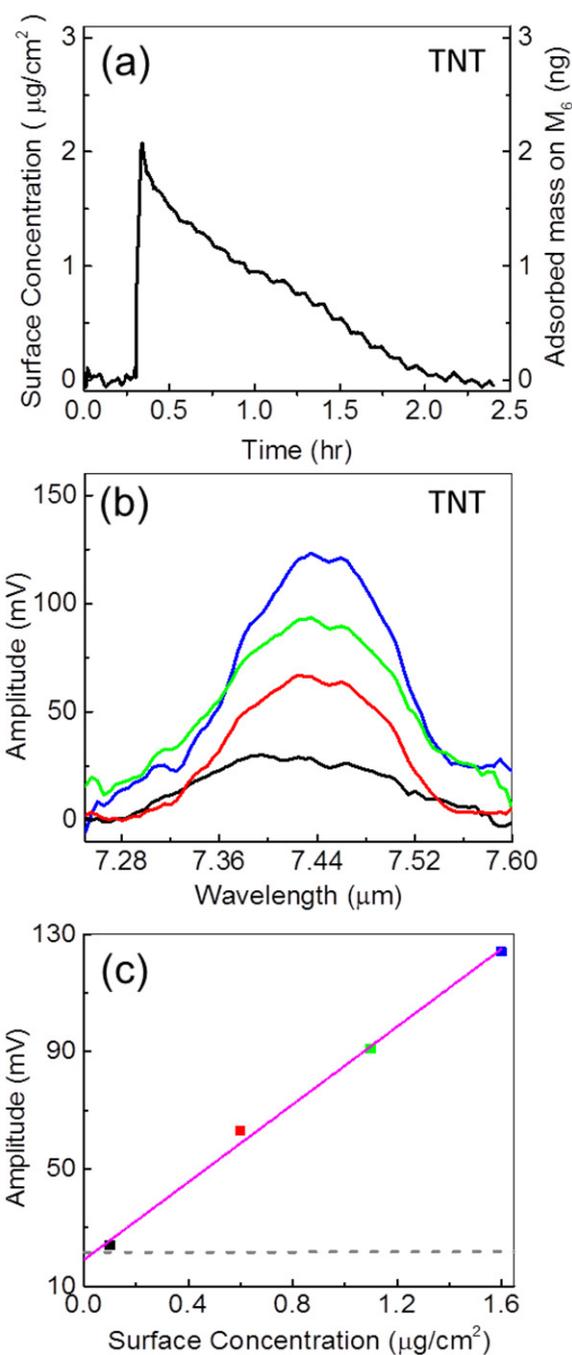

Figure 4. (a) Determined surface concentration of TNT on the nanostructured coupled resonator array during vapour deposition and natural desorption. The measured mass of TNT on the microcantilever M_6 is used to determine the surface concentration. (b) Measured PA spectra of TNT molecules as a function of TNT surface concentration: 1.6 μg cm^{-2} (blue), 1.1 μg cm^{-2} (green), 0.6 μg cm^{-2} (red) and 0.1 μg cm^{-2} (black). (c) The PA spectra peak amplitude at 7.46 μm as a function of TNT surface concentration. The straight line is a linear fit of the peak amplitudes and the LOD is determined as the intersection of the straight line and the dashed line which represents minimum PA spectrum peak amplitude of TNT with a signal-to-noise ratio of 3.

cantilever and the estimated surface concentrations on the coupled resonator array chip during adsorption and desorption of the vapour phase analyte under ambient conditions. From
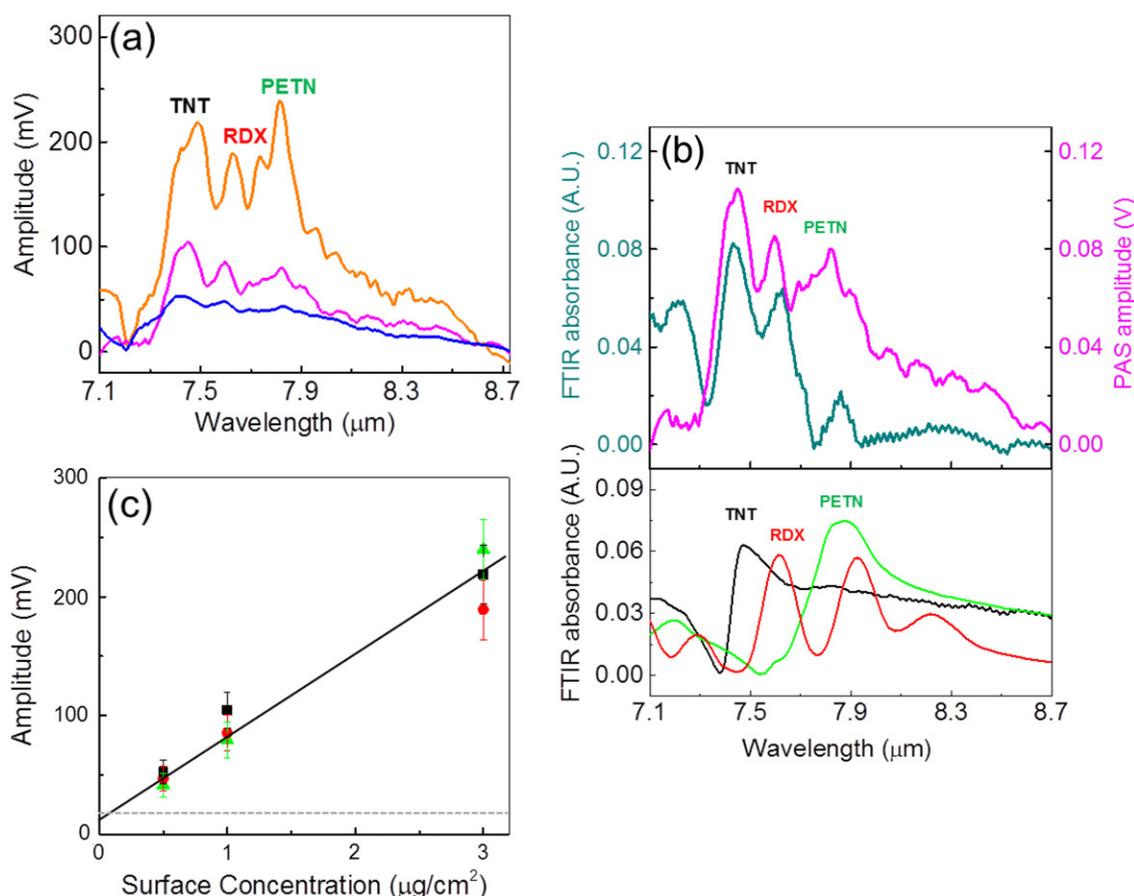
Figure 5. (a) PA spectra of ternary mixtures (TNT:RDX:PETN) of explosives deposited on the nanostructured coupled resonator array by drop casting as a function of each sample solution concentration with the same mass ratio: 333 ng μl^{-1} (orange), 111 ng μl^{-1} (magenta) and 55 ng μl^{-1} (blue). The PA spectra peaks at 7.46, 7.60 and 7.82 μm come from TNT, RDX and PETN, respectively. (b) FTIR spectra of TNT (black), RDX (red), PETN (green) and a 1:1:1 mixture of each explosive (dark cyan) as well as a PAS spectrum of a 1:1:1 mixture of each explosive (magenta). The surface concentration of each explosive molecule was estimated to be ∼1.1 μg cm^{-2}. (c) Measured PA spectra peak amplitude as a function of the surface concentration for each explosive molecule: TNT (black), RDX (red) and PETN (green), with the error bars corresponding to the standard deviation. The straight line is a linear fit of the averaged peak amplitudes and the LOD is determined as the intersection of the straight line and the dashed line which represents the minimum PA spectrum peak amplitude with a signal-to-noise ratio of 3.

the first-order linear regression, the adsorption and desorption rates of TNT molecules on the AAO cantilever surface at room temperature were found to be ∼12 pg s^{-1} and ∼0.27 pg s^{-1}, respectively. The PA spectra in figure 4(b) represent the IR absorbance of the NO_2 (nitro) group bonds with carbon ($C–NO_2$) in TNT at four different surface concentrations. The major peak at 7.46 μm corresponds to the symmetric stretching vibration of the nitro group bonds with carbon in TNT and decreases over time due to the desorption of TNT molecules at ambient conditions [29, 30]. Figure 4(c) shows the PA spectra peak amplitudes at 7.46 μm as a function of the TNT surface concentration. The peak amplitude obtained with the nanostructured AAO cantilever is ∼11 times larger than that obtained with a plain silicon microcantilever that has comparable thermomechanical sensitivity (see the supplementary information available at stacks.iop.org/Nano/25/035501/mmedia). The straight line is a linear fit of the peak amplitudes. The limit of detection (LOD) for surface adsorbed TNT molecules at this wavelength is estimated to be approximately 70 ng cm^{-2}. The LOD is determined as the intersection of the straight line and the dashed line

which represents the minimum PA spectra peak amplitude of TNT with a signal-to-noise ratio of 3 at this wavelength. Within a certain dynamic range, the slope of this linear fit can serve as the normalized peak amplitude which can be utilized to estimate the relative surface concentration ratio of surface adsorbed mixture molecules since the IR spectrum of a mixture is a linear superposition of individual spectra [31].

3.2. Detection and quantification of analytes dissolved in solution

In order to show the capability of quantitative detection and analysis, we deposited 1 μl of diluted ternary mixtures (TNT:RDX:PETN) of explosive solutions (55, 111 and 333 ng μl^{-1}) on the coupled resonator array chip using a micropipette. After quick evaporation of the solvent, the surface concentrations of each explosive molecule were estimated to be approximately 0.5, 1.1 and 3 μg cm^{-2}. These values corresponded well with the surface concentrations of each ternary mixture of explosives which was calculated by using the measured frequency in equation (1). Figure 5(a)

shows the PA spectra of the ternary explosive mixtures (TNT:RDX:PETN) as a function of each sample solution concentration with the same mass ratio (1:1:1). The IR absorption peaks between 7.1 and 8.73 μm are from the symmetric stretching vibration of the NO_2 (nitro) group bonds with carbon (C–NO_2) in TNT (7.46 μm), nitrogen (N–NO_2) in RDX (7.60 μm) and oxygen (O–NO_2) in PETN (7.82 μm), respectively [32]. The peak positions of the PA spectrum of a ternary mixture ($\sim$1.1 μg cm^{-2} for each of the explosive molecules) agree quite well with those obtained using a standard FTIR microscope, as shown in figure 5(b). It is very difficult to quantify the surface concentration of each explosive molecule from the FTIR spectra of TNT, RDX and PETN. The FTIR spectra measured at different spots have different intensities due to the inhomogeneity in the surface concentration of explosive molecules, known as the coffee ring effect [33]. However, our PA spectroscopic technique can provide quantitative measurements resulting from its inherent capability to measure added mass. Figure 5(c) shows PA spectra peak amplitudes at the characteristic positions of each component as a function of the surface concentration of each explosive molecule, with the error bars corresponding to the standard deviation. The experiments were performed in triplicate and found to be reproducible. The LOD of the ternary mixture of explosive molecules was estimated to be $\sim$100 ng cm^{-2}. The main advantages of this technique are the short response time of the coupled resonator, making our measurements fast, as well as the demonstrated capability of quantitative chemical analysis. Surface adsorbed chemical samples in the field can be collected and dissolved in solvent, then deposited on the coupled resonator for rapid chemical analysis.

4. Conclusion

We have successfully fabricated a nanostructured coupled resonator array with AAO and demonstrated the quantitative PA spectroscopy capability of the resonator as a multi-modal device for chemical and mass sensing and analysis. By measuring the localized, individual mode resonance frequency of a cantilever, we can determine the mass of surface adsorbed molecules and estimate the surface concentration. In addition, the measured common mode coupled resonance amplitude as a function of IR wavelength yield the PA spectrum of the surface adsorbed molecules. These multi-modal signals enable us to perform quantitative and rapid chemical sensing and analysis in ambient conditions.

Acknowledgments

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