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Self-referenced sensing based on terahertz metamaterial for aqueous solutions

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We demonstrated a self-referenced sensing method in reflection geometry for characterizing aqueous solutions based on terahertz metamaterials. The sensing signal and the reference signal are taken in one measurement from different interfaces of the substrate. For ethanol-water mixture and aqueous solution of NaCl, the line-shape of the modulated response shows distinct polarity, while the peak-valley value near resonant region depends linearly on the solution concentration. These observations result from the variation of dielectric environment near the interface between the metamaterials and the aqueous solutions. This method holds promise for future application in monitoring real aqueous biosystems and ecological water systems. © 2013 AIP Publishing LLC [<http://dx.doi.org/10.1063/1.4802236>]

In spite of the fact that aqueous solutions play a vital role in many processes on our planet, particularly in our lives, the understanding of them is far from being sufficient.¹ For example, our body fluid is a balanced aqueous electrolyte which provides an appropriate micro-environment for the chemical and biochemical processes. Yet, we have only a very limited knowledge of the hydration processes in body fluid, which still remain a challenging research topic. The situation in simple aqueous solutions of inorganic salts is not optimistic either. It is always in high demand to develop highly sensitive, reliable, and noninvasive sensing techniques² to monitor aqueous solutions so as to further provide effective approaches for studying more complicated water systems.

Terahertz time-domain spectroscopy (THz-TDS) is a promising candidate tool due to its intrinsic high sensitivity to the dielectric relaxation of dipoles and hydrogen bonding.³ It has the capability to approach the wave number range below 100 cm^{-1} .⁴ For some substances in solid state, such as sugars,⁵ explosives,⁶ and some amino acids,⁷ there exist finger-printing signatures in THz range. Even though these features disappear when these substances are dissolved into liquid water, THz spectroscopy can, however, still be a powerful tool to access the hydration of proteins.⁸ Liquid water has an extremely huge absorption coefficient ($\alpha \approx 500\text{ cm}^{-1}$)⁹ for THz wave and subsequently reduces the effective dynamic range in THz-TDS measurements.¹⁰ Either one has to use an expensive free electron laser with high THz output power⁸ or the liquid cells for THz transmission measurement has to be limited to a thickness $\sim 100\text{ }\mu\text{m}$.¹⁰ In the latter case, the high frequency information may partially get lost. As an alternative, THz measurement in the reflection geometry was proposed by Jepsen *et al.*, applying it to the study of liquid water under different

temperature⁹ and alcohol-water mixture in different concentrations.¹¹ This method takes advantage of the dielectric information carried by reflection coefficient on the interface, which does not require the penetration of a water layer.

With regard to the enhancement of the sensitivity for aqueous solutions, THz metamaterials¹² promise a pleasant prospect. Metamaterial-based sensors have been available in the spectral ranges from microwave,¹³ through far-infrared,¹⁴ to the visible band.¹⁵ It was found that the resonant modes from the metamaterials are very sensitive to the micro-environment variation. Hence, metamaterial-based sensors, operated in THz range, has been employed in probing the specific interactions between biomolecules¹⁶ and self-assembled molecular monolayers on the metastructure.¹⁷ Remarkably, however, there are very few reports on water solutions sensing based on THz metamaterials, let alone the determination of molecular or ionic concentrations.³

In this work, we reported an aqueous solution sensing method by using THz metamaterials. Through comparative study on the ethanol-water mixture and aqueous solution of NaCl, each of different concentrations, it was demonstrated that the metamaterial sensor can be applied to identify solvent type and determine the corresponding concentrations. This method overcomes some disadvantages of the traditional THz transmission measurement and it may be applicable in monitoring ecological water systems and real biological systems.

The THz metamaterial sensors adopted in the current work are periodic arrays of split ring resonators (SRRs) of gold (80 nm thick) fabricated on the GaAs substrate. Fig. 1(a) shows the scanning electron micrograph of the SRRs. Dimension of the SRRs cell was the same as used in our previous work.¹⁶ The samples tested in the current work are ethanol (Beijing Chemicals Co. Ltd., China)-water mixture and aqueous solution of NaCl (Jiangsu Qinfen Pharmaceutical Co. Ltd., China). The concentration of the

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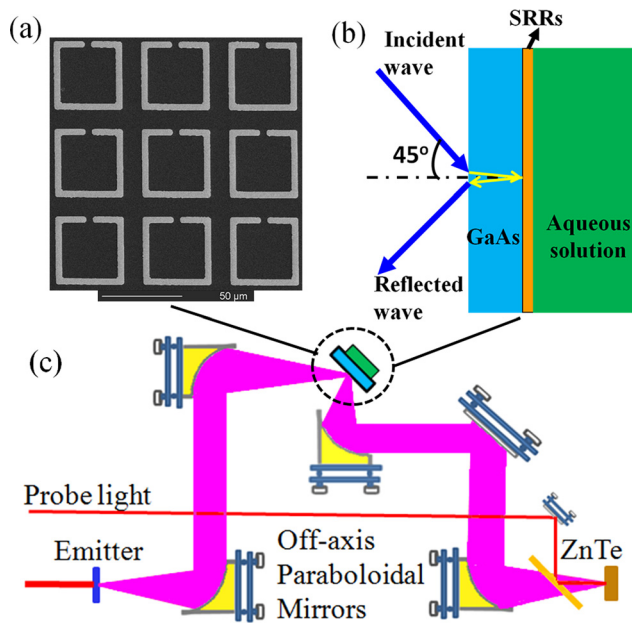


FIG. 1. (a) Scanning electron microscopy micrograph of the split ring resonators fabricated on GaAs; (b) schematic diagram of the experimental arrangement in reflective geometry for SRRs with aqueous solutions; and (c) experimental setup for THz-TDS measurement.

ethanol-water mixture was adjusted by changing the volume ratio of anhydrous ethanol to the doubly distilled water. Well sealed liquid cells particularly designed for the current work were used to hold the liquid. The thickness of the liquid layer measures 2 cm.

The measurement was carried out on a custom-designed THz-TDS spectrometer in reflection geometry as schematically shown in Fig. 1(c). THz pulses were generated by a low-temperature grown GaAs photoconductive antenna (Zomega Terahertz Corp., 50 μm gold gap, 80 V AC voltage) excited by a femtosecond Ti:sapphire laser beam (Maitai Spectra-Physics, central wavelength of 800 nm, repetition rate of 80 MHz, pulse width of 70 fs). The reflected THz pulses from sample surfaces were detected by a ZnTe detector through electro-optical sampling. All the results were obtained with an incident angle of 45°, as illustrated in Fig. 1(b). The optical path from THz source to the ZnTe detector was purged with dry nitrogen to eliminate the possible disturbance from water vapor in the ambient air.

Fig. 2 displays the THz temporal waveforms taken with pure ethanol and ethanol-water mixtures of different concentrations. The polarization of THz wave is along with the direction of the ring gaps.¹⁸ The signals at the shorter delay times (~ 4 ps) originate from the N_2/GaAs interface, which are quite the same for all samples and are used as references. The signals at the longer delay times (~ 20 ps) arise from the SRRs/solution interface, which are quite different for different samples and carry the dielectric information of the solution. To be noted, traditional THz-TDS measurement need to take two scans, one for reference without measurand and the other for sensing with measurand. However, our method can get both reference signal (reflection from N_2/GaAs interface) and sensing signal (reflection from SRRs/solution interface) in one scan. Clearly, the shape and intensity of the sensing signal (~ 20 ps) are sensitive to the change of the interfacial

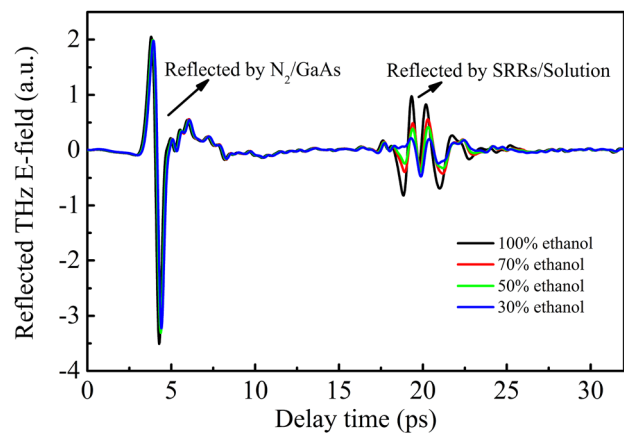


FIG. 2. Typical reflective THz time-domain waveforms from SRRs/GaAs. The signals observed at a shorter delay time (~ 4 ps) originate in reflection from the N_2/GaAs interface, while those of a longer delay time (~ 20 ps) come from the SRRs/solution interface.

dielectric properties. Remarkably, the intensity decreases monotonically with the decreasing ethanol content, which may allow a quantitative determination of the solution concentration.

The raw data for the time-domain waveforms as presented in Fig. 2 are processed in the following way. The time-domain signals are separated into two parts by temporal windows in the range of 0–15 ps and the range of 15–30 ps for each measurement. The first part is used as reference signal and the second part carrying solution information is used as sensing signal. After fast Fourier transform, the spectral amplitudes for the sensing signals are divided by that for the reference signals. Then the resulting spectral amplitudes is normalized to that for SRRs/water interface to compare the spectral change due to the different concentrations for further characterization of the solutions. Fig. 3(a) presents the results obtained for the pure ethanol and ethanol-water mixtures of three concentrations. The prominent feature of the curves is a resonant peak near ~ 0.4 THz, which increases in amplitude with the increasing ethanol content. This resonant mode is equivalent to a LC resonance due to the circular currents induced by the THz wave in the metamaterial.¹⁸ As done in our previous work,¹⁷ we define difference value between the maximum and minimum values as $\Delta\text{PV} = A_{\text{peak}} - A_{\text{valley}}$, where A_{peak} is the peak amplitude and A_{valley} is the valley amplitude (minimum value in case of valley absent as shown in Fig. 3(a)). Fig. 3(b) illustrates ΔPV as a function of the ethanol concentration. A linear relationship can be well established.

The self-referenced sensing method can be used for the aqueous solution of NaCl as shown in Figs. 3(c) and 3(d). It is evident that the shape of the amplitude, obtained with the data processing procedures specified above, changes compared with the ethanol-water mixtures. The spectrum show unsymmetrical polarity with a peak located at ~ 0.47 THz and a valley at ~ 0.4 THz. With the increasing of solution concentration, the valley at ~ 0.4 THz becomes sharper and deeper while the peak at ~ 0.47 THz increases moderately (Fig. 3(c)). The obvious difference in the amplitude line-shapes for ethanol-water mixture and aqueous solution of NaCl can find explanation in their dielectric constants.

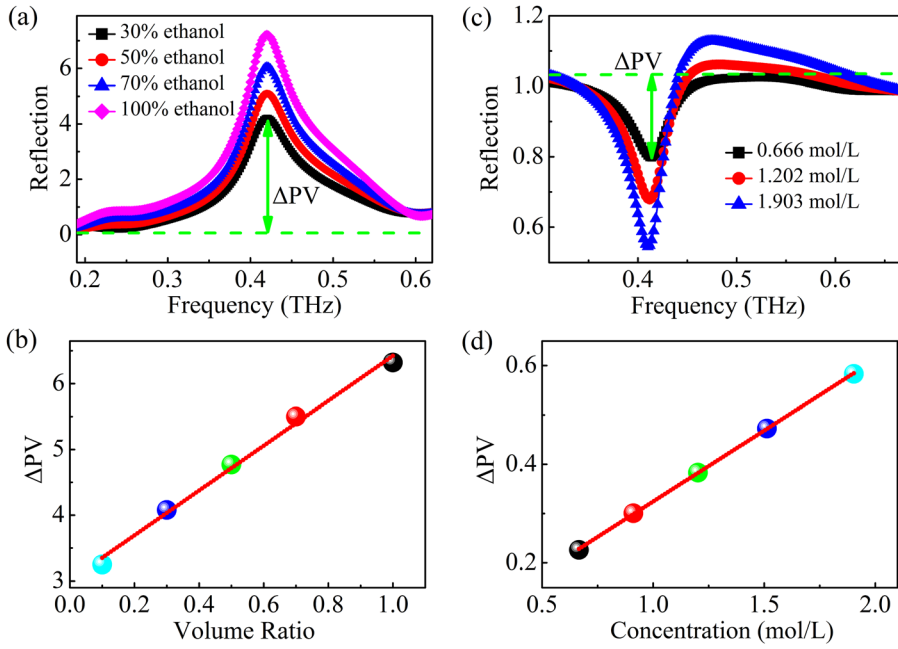


FIG. 3. Modulated reflective THz response of the LC resonances by (a) ethanol-water mixture, and (c) aqueous solution of NaCl of different concentrations. The signal is normalized to the response of SRRs with pure water; The ΔPV of the LC resonances as a function of (b) the ethanol-water mixture with the concentration specified as a volume ratio of ethanol to water, and (d) the aqueous solution of NaCl.

Taking the complex dielectric constant at 1 THz, for instance, it is $4.1 + 2.2i$ for pure water and it is $2.4 + 0.7i$ for pure ethanol. Both the real and imaginary parts will decrease with the increasing of ethanol content. However, for the aqueous solution of NaCl, both the real and imaginary parts of the dielectric constant increase with the increasing of NaCl concentration. Therefore, the polarity in resonant region reverses from a low dielectric constant to a high dielectric constant in the normalized spectrum. Furthermore, NaCl added both anions and cations into water and modifies not only the absorption coefficient but also the refractive index. The variation of the refractive index mainly induces the resonant frequency shift of the resonance, resulting in an asymmetric shape. However, for ethanol-water mixture, the frequency shift of the resonance is veiled by the broadening of the resonant peak due to the unlimited miscibility of the two liquids. The concentration dependence of ΔPV for the aqueous solution of NaCl is plotted in Fig. 3(d), which also demonstrates a striking linearity.

When a solute is added into water, the dielectric environment for the SRRs changes. In accordance with the simple effective medium model, the effective permittivity of an aqueous solution increases if the permittivity of added solute is larger than that of water. On the contrary, it will be reduced when the solute has a smaller permittivity. Moreover, water molecules may form several hydration layers around the solute molecules or ions. These microscopic features also provoke a variation of dielectric environment around SRRs. In the case of ethanol-water mixture, the complex dielectric constant derived from the Debye model¹⁹ is given by

$$\hat{\epsilon}(\omega) = \epsilon_{\infty} + \frac{S_1}{1 + i\omega\tau_1} + \frac{S_2}{1 + i\omega\tau_2} + \frac{S_3}{1 + i\omega\tau_3}, \quad (1)$$

where the first two frequency-dependent terms are attributed to pure water with one slow ($S_1 \approx 75$ ps, $\tau_1 \approx 8$ ps) and one fast ($S_2 \approx 1.8$ ps, $\tau_2 \approx 0.25$ ps) decay channels at room temperature. The third frequency-dependent term is introduced

by ethanol. However, for the aqueous solution of NaCl, the complex dielectric constant differs from Eq. (1)³

$$\hat{\epsilon}(\omega) = \epsilon_{\infty} + \frac{S_1}{1 + i\omega\tau_1} + \frac{S_2}{1 + i\omega\tau_2} + \frac{\sigma}{i\omega\epsilon_0}, \quad (2)$$

where σ is the ion conductivity (~ 2.0 – 33.0 mS/cm for aqueous solution of NaCl of different concentrations). The dielectric response of the solution is prone to variation with the coordination structure of the hydrated ions.

With Eqs. (1) and (2), we can simulate the modulated reflected THz responses by finite integral technique. In the simulation, the geometrical parameters of SRRs are taken from the structures used in the current work. The dielectric constant of GaAs is 12.9, and its dielectric loss is ignored. The dielectric constant of ethanol-water mixtures and the dielectric function of aqueous solutions of NaCl are taken from literature.^{11,19} The dielectric constant of pure water and ethanol are $4.1 + 2.2i$ and $2.4 + 0.7i$, respectively, which approximate the values at 1 THz. This can capture the main features of the experiment since the dielectric constant is relatively uniform when the frequency is higher than 0.5 THz. For the aqueous solutions of NaCl, of which the conductivity is highly correlated to its concentration, both the real and imaginary parts of its dielectric constant increase with the concentration. Figs. 4(a) and 4(b) shows the simulated amplitude spectra of both the aqueous solutions of ethanol and NaCl, respectively, where the results are also normalized to the signal for SRRs/water interface. The simulated profiles of the amplitude spectra agree well with the experimental observation. For the ethanol-water mixture, the symmetric line-shape was reproduced, while for aqueous solution of NaCl, the polarity of the amplitude spectra was revealed when the concentration is sufficiently high. The dielectric constant dependence of the quantity ΔPV is summarized in Figs. 4(c) and 4(d), respectively. It is obvious that ΔPV reduces in the ethanol-water mixture, while in aqueous solution of NaCl, it increases linearly with the increasing of dielectric constant. These suggest that in

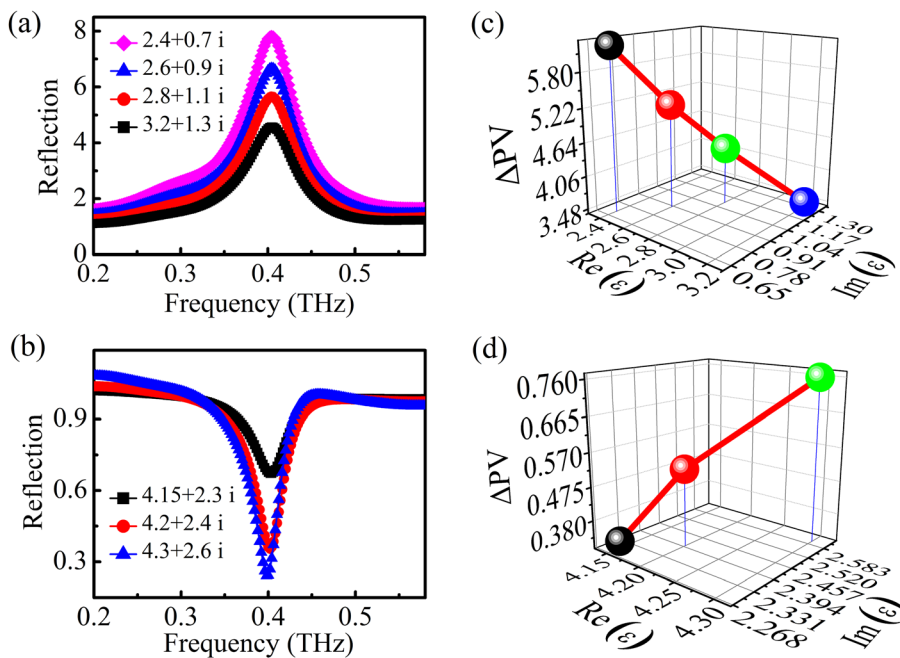


FIG. 4. Simulated THz reflective spectra of (a) ethanol-water mixture and (b) aqueous solution of NaCl in different concentrations. Simulated ΔPV as a function of the dielectric constant of (c) the ethanol-water mixture and (d) the aqueous solution of NaCl.

some sense ΔPV can capture the variation of both imaginary and real parts of the dielectric constants for the aqueous solutions.

Compared with traditional methods for aqueous solution monitoring, the self-referenced method based on THz metamaterials holds several advantages. The sensitivity of the sensing based on metamaterials can be optimized by the substrate thickness,²⁰ the substrate dielectric constant,¹⁶ aspect ratio,²¹ and the resonant enhancement.²² Although the mechanism of resonant enhancement is still under study, to our opinion, the resonant enhancement is mainly due to the localization of the electromagnetic field in the gap or corner regions in metamaterials. According to the near-field electric field mapping of the SRRs, the electromagnetic field for the resonance at ~ 0.4 THz is strongly localized and confined in the gap region of the SRRs (data not shown). Meanwhile, the quantitative estimation of the localization of the incident field suggests a very strong field enhancement in the resonant region of the SRRs.²² In fact, metamaterials can be used to realize the detection of extremely small amounts of analytes at simultaneously improved selectivity. The procedure presented in the current work can avoid the deviation introduced by liquid thickness measurement and minimize the influence from laser turbulence and dislocation of sample position. THz metamaterial sensors do not need strict coupling either, which is however highly desirable for surface plasmon resonant sensors. This work may inspire further researches toward label-free, highly sensitive, real-time, and high throughput biosensing that exploits the THz-based sensing techniques for aqueous solutions.

In summary, a self-referenced sensing technique for aqueous solutions based on THz metamaterial was demonstrated. It can not only identify the solution but also characterize the concentration through the modulated THz signals, thanks to the localization and resonant enhancement of electromagnetic field by the metamaterials. The linear dependence of the peak-valley value, which characterizes the modulated THz amplitude near the resonant region on the

concentration of the aqueous solution, provides a very good platform for aqueous solution sensing. In conjunction with numerical simulation, it is verified that it is the dielectric constant of aqueous solutions that induces the frequency shift and amplitude modification. This method may be applied to monitoring real aqueous biosystems and ecological water systems in the future.

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