High Water Content Prediction of Oil–Water Emulsions Based on Terahertz Electromagnetically Induced Transparency-like Metamaterial

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ABSTRACT: This work aims to investigate the electromagnetically induced transparency-like (EIT-like) metamaterial for high water cut emulsions’ detection in the terahertz band. The electromagnetic responses of the selected metamaterial covering emulsions exhibit red-shifted resonant frequency with increasing water volume from 60 to 98%. Three numerical models coinciding with theory analysis were built based on the extracted resonant frequencies at the transmission peak and dips to predict water concentration. The results show that the built models accurately predicted the water content with absolute errors less than 0.26, 0.41, and 0.24%, respectively. The EIT-like resonance is introduced by coupled bright and dark modes, making it similar to a weakened plasma resonance. Consequently, the permittivity-dependent frequency would help develop both economically feasible and socially beneficial sensors for high water content prediction.

1. INTRODUCTION

Determining the water content is significant in evaluating crude oil dehydration, logging, refining, and exportation. So far, many conventional approaches have been employed to determine the water content of oil–water emulsions in different situations according to specific needs, such as the microwave technique, the ray, the capacitance, the Karl Fischer titration method, and near-infrared spectroscopy. In recent years, requirements for accurate high water content measurement in oil have been more and more exigent and attracted widespread attention in theoretical and experimental work. An open measurement method was proposed to accurately measure water content using a suitable electromagnetic wave with the right wavelength based on Rayleigh scattering, which was further proved to be applicable to oil-wells whose water content is more than 80%. An all-optical detection method based on a noncontact laser source and receiver was introduced to measure water content from 0 to 100% in crude oil. The theoretical values of the effective medium model agreed with the experimental results. In addition, terahertz (THz) spectroscopy, as a new noncontact technique, has been proposed for predicting subtle changes of water in emulsions owing to the sensitivity of the THz wave to the fluctuations of water dipole moments occurring on the picosecond (ps) timescale. THz time-domain spectroscopy has been used to measure the water content ranging from 50.05 to 100% in crude oil and to characterize the distribution of oil, air, and water simultaneously. Subsequently, combined with 3D printing technology, oil–water mixtures with water content from 1.8 to 90.6% were measured and analyzed with the THz parameters. However, THz waves are strongly attenuated by a water layer, which is a practical limitation in detecting water content for high water cut emulsions. As a result, to accurately detect high water cut emulsions in the THz range, a sensing system without suffering large attenuation effects in the polar liquids is required.

Metamaterials are a new type of artificially fabricated material with exotic properties such as super lensing, negative refraction, cloaking, and sensitive sensing. These properties are mostly derived from their ability to support resonance, which is mainly determined by geometrical parameters. Recently, metamaterials have been employed as sensitive sensors for chemical and biological detection because their spectral resonance frequency substantially depends on the dielectric condition of surrounding media, which provides a new solution for us to overcome the limitation mentioned...
above in oil—water emulsion measurement by THz spectroscopy. Despite these advances, they still suffer from low quality factors (Q-factors) because of the existing radiative losses, which is less than 10 typically.21−23 Thus, their wider utilization in many aspects is limited by the sensing capabilities and filter performance.

In the past few years, the phenomenon of electromagnetically induced transparency (EIT), as a concept of quantum mechanics, has been introduced to metamaterial design to overcome the radiative loss problem and become a fascinating research topic.24,25 EIT is a well-known quantum interference effect that bases on extraordinary dispersive properties of an atomic medium in three-level atomic systems. This phenomenon leads to an extremely narrow band transparency window in the original absorption spectrum by dramatically changing the dispersion properties of the system. As EIT stems from coupled resonances, analogous effects can be realized using classical oscillator systems such as spring-mass or RLC oscillators (capacitance-inductance-resistance coupled oscillators). Thus, considerable attention has been paid to the EIT-like effect in plasmonic metamaterials, whose spectral response can be explained as being either the result of engaging “trapped mode” resonances or by the destructive interference between the so-called bright and dark mode resonances. These metamaterials can overcome the limitation and realize an EIT-like effect in normal environment where a significant difference in Q-factors or full width at half-maximum (fwhm) of the two resonance modes is required in developing the analogy to the EIT effect.26 Recently, research studies on EIT-like metamaterials have been performed by introducing a graphene layer in the metamaterials and achieve independent amplitude modulation of the transmission peaks in the THz regime.27−30

As a consequence, focusing on the high water cut oil—water emulsion, a method was introduced in this paper to detect the water content of oil—water emulsions using a THz metamaterial sensor. To gain the EIT-like effect, a planar symmetric metamaterial sensor was first designed and simulated without varying the lateral distance between the resonators. As the sensing performance of the metamaterial depends strongly on the relative spacing position between the two modes, the simulated transmission spectra with varying spacing distances were investigated to choose the optimum parameter for the designed sensor. It is shown that, because of the coupling strength modulation of the bright and dark modes, the sensing performance can be significantly impacted by the altering separation between the two modes. In addition, analyses of the electromagnetic responses with 5 μm thick oil—water emulsion overlayers on the selected metamaterial were made to demonstrate the sensing ability of water concentration. The THz transmission data illustrate the resonance shifting effects as water concentration increasing from 60 to 98%, from which the numerical expression used to predict the water content with high accuracy was then extracted. The results pave an avenue for THz metamaterials in terms of high water concentration sensing.

2. RESULTS AND DISCUSSION

The sensitivity (Δf/Δn) and Q-factors of the EIT-like metamaterial sensor, associated with the coupling degree between the radiative and dark modes, can be also determined by their spatial separation.24,35 Δf and Δn represent the shift of resonance frequency and the change of the refractive index resulted from the covering thin layers, respectively. Here, the transmission spectra of the designed metamaterial were simulated by displacing the U-shaped resonators (USRs) gradually from d = 0 to 40 μm as depicted in Figure 1a. It is clear that the coupling strength between the USR and I-shaped cut-wire (ICW) diminishes with the decreasing d, leading the fading EIT-like response to less transparency. When the USR moves downward from d = 40 to 10 μm, the transparency window gradually shrinks without a notable frequency shift. However, from d = 10 to 0 μm, the transparency window changes with a notable frequency shift. During the simulating, the surrounding environmental materials were selected as air (εair = 1) and oil (εair = 2.33), respectively, making Δε remain constant and thus sensitivity is proportional to frequency shifts (Δf) between the two surroundings. Then, the frequency shifts and the corresponding Q-factors were evaluated to explore the effect of d on the sensing parameters of THz metamaterials. The sensitivity of the metamaterials becomes higher first and then keeps stable when d increases from 0 to 40 μm. The Q-factors, rather, exhibit a downward tendency with an increase of d. Considering the abovementioned two parameters, metamaterial with d = 14 μm acted as the sensor to investigate the responses of oil—water emulsions in the next section.

A series of simulated THz transmission spectra of oil—water emulsions with high water cut for analysis have been shown in Figure 2. As the water content is gradually raised from 60 to 98%, the simulated EIT resonance is observed to shift lower in frequency because of the change in the dielectric constant and the corresponding Q-factors, rather, exhibit a downward tendency with an increase of d. Considering the abovementioned two parameters, metamaterial with d = 14 μm acted as the sensor to investigate the responses of oil—water emulsions in the next section.

The resonant frequency (f) with the covering emulsions can be calculated by $f = \frac{f_0(\epsilon_{\text{eff}}/\epsilon_0)}{(\epsilon_{\text{eff}}/\epsilon_0 - 1)^{1/2}}$ where $f_0$ is the resonant frequency without the target material while $\epsilon_{\text{eff}}$ and $\epsilon_0$ are the effective dielectric constants with and without the target material in the metamaterial sensor, respectively. The total effective dielectric constant can be given by $\epsilon_{\text{eff}} = \epsilon_1 + A\epsilon_0 + \epsilon_3$, which is made up of three parts: $\epsilon_1$ is the dielectric constant due to flux within the substrate, $\epsilon_0$ should be due to flux within the overlayer, and $\epsilon_3$ is the fringing flux in air where A is a scaling constant. Assuming $\epsilon_1$ and $\epsilon_3$ do not change by the
addition of the overlayer, then $f$ can be further given as:

$$f = f_0 \left( \frac{\varepsilon_1 + A\varepsilon + \varepsilon_3}{\varepsilon_1 + A\varepsilon_{air} + \varepsilon_3} \right)^{1/2}.$$ 

Thus, the red shift of the EIT peak is due to the increase of the ambient dielectric constant.

The extracted resonant frequencies $f$ at the transmission peak and dips from the FDTD (Finite-Difference Time-Domain) simulation results, as well as the corresponding emulsion water contents $\alpha$, for the characterized emulsions are shown in Figure 3a, indicating that the emulsions’ resonant frequencies can be characterized as functions of water concentration (solid line). Then, the water concentration of the oil–water mixture can be deduced from the resonant frequencies of the EIT peak as well as dips with the following formula

$$f = \left( a \times \varepsilon(\alpha) + b \right)^{-1/2},$$

where the corresponding values of $a$, $b$, $c$ for the predicting models built by the frequencies at transmission peak and dips are presented as a table in Figure 3a and all the correlation coefficients ($R$) exceeded 99.9%. Moreover, to verify the predicting accuracy of the model, the transmission spectra were simulated for emulsions with a water content range of 62–99%, from which the frequencies of EIT-like resonant peak and dips were derived. As indicated in Figure 3b, the predicted water concentrations were then calculated using the models built above and were listed as Table 1.

Meanwhile, the absolute errors of the approach are presented in Figure 3b as well, where the horizontal axis and the vertical axis represent the true water content in simulation and the water content predicted by the EIT-like metamaterial sensor, respectively. Agreement is shown between the predicting and the standard data with absolute errors less than 0.26, 0.41, and 0.24% for predicting models at $\omega_1$, $\omega_2$, and $\omega_3$ respectively. These data illustrate that THz EIT-like metamaterial has a higher detecting performance on comparing with the ultrasound method whose detection error is 0.5%.

The results demonstrate that the THz EIT-like metamaterial can work as an efficient sensor for high water concentration measurement of oil–water emulsions.

In order to understand the predicting models further, the distribution of induced currents at $\omega_1$, $\omega_2$, and $\omega_3$ are shown in Figure 4a. The ICW element is directly excited by the external field, whereas the USR is further excited by the near-field coupling of the ICW. The resonances of USR at $\omega_1$ and ICW at $\omega_3$ are caused by the interaction between the induced currents in the two coupling units. However, at the resonance $\omega_2$, both the USR and ICW are simultaneously excited because...
the current limitations imposed by the strong attenuation of THz waves by polar liquids.

3. CONCLUSIONS

In summary, because of the unique properties of metamaterials whose resonance frequencies are sensitive to the changes in permittivity in the surrounding environment, simulations of 5 μm thick oil–water emulsions containing 60–98% water were performed using THz metamaterial, whose Q-factors substantially reduce, whereas sensing sensitivity amplifies with increasing distance between the bright and dark modes. A red shift of the EIT-like resonant frequency is observed with increasing water volume for the 5 μm thick oil–water emulsion as the sample material. In addition, the resonance frequencies at the transmission peak and dips are on a downward trend with increasing water concentration of emulsions, which is closely related to the dielectric constant. The numerical expressions whose predicting absolute errors are less than 0.26, 0.41, and 0.24% in the actual water content range of 60–99% have been built about the resonance frequencies and particular water content at \( \omega_1 \), \( \omega_2 \), and \( \omega_3 \), respectively. The results verify the ability of this approach to accurately determine the water content of emulsions for high water cut emulsions without suffering large attenuation effects in water in the THz regime. Furthermore, the metamaterial could be potentially coupled with a microfluidic system for in situ sensing for oil–water two-phase flow.

4. METHODS

The THz metamaterial was first designed in this work. The dark mode is similar to a metastable energy level, which is necessary for the realization of an EIT medium in an atomic system.\(^{31,32}\) The EIT-like THz metamaterial consisting of a coupled symmetrical USR and ICW resonator has been proposed and designed as shown in Figure 5b, in which the coupling parameters \( a, b, w, m, l \) and \( t \) are 30, 50, 10, 17, 31, 90, and 5 μm, respectively. The results verify the ability of this approach to accurately determine the water content of emulsions for high water cut emulsions without suffering large attenuation effects in water in the THz regime. Furthermore, the metamaterial could be potentially coupled with a microfluidic system for in situ sensing for oil–water two-phase flow.

The transmission spectra of the designed EIT-like metamaterial and the coupling unit cells were simulated by CST Microwave Studio and are shown in Figure 5a. As expected, when a plane wave with its electric orientation parallel to the \( y \) axis normally irradiates on the metamaterials along the \( z \) axis, the 90° rotating USR (90-USR) and ICW are excited strongly by incident light and inspire a strong plasmon
whose coupling strength depends on the phase difference between the magnetic and the electric excited in the ICW.34

The media used in simulations were 5 μm thick oil–water emulsions whose water content ranged from 60 to 98%. The density and dielectric constant of water are 1000 kg/m³ and 78, respectively, whereas they are 920 kg/m³ and 2.33 for oil.

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**Notes**
The authors declare no competing financial interest.

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**REFERENCES**

(1) Song, Y.; Zhan, H. L.; Zhao, K.; Miao, X. Y.; Lu, Z. Q.; Bao, R. M.; Zhu, J.; Xiao, L. Z. Simultaneous characterization of water content and distribution in high water cut crude oil. *Energy Fuels* 2016, 30, 3929–3933.

(2) Borges, G. R.; Farias, G. B.; Braz, T. M.; Santos, L. M.; Amaral, M. J.; Fortuny, M.; Franceschi, E. D.; Dariva, C.; Santos, A. F. Use of near infrared for evaluation of droplet size distribution and water content in water-in-crude oil emulsions in pressurized pipeline. *Fuel* 2015, 147, 43–52.

(3) Fortuny, M.; Oliveira, C. B. Z.; Melo, R. L. F. V.; Nele, M.; Coutinho, R. C. C.; Santos, A. F. Effect of Salinity; Temperature; Water Content; and pH on the Microwave Demulsification of Crude Oil Emulsions. *Energy Fuels* 2007, 21, 1358–1364.

(4) Roshani, G. H.; Feghhi, S. A. H.; Mahmoudi-Aznaveh, A.; Nazemi, E.; Adineh-Vand, A. Precise volume fraction prediction in oil-water-gas multiphase flows by means of gamma-ray attenuation and artificial neural networks using one detector. *Measurement* 2014, 51, 34–41.

(5) Tang, T. B.; Lim, Y. M.; Aslam, M. Z. Detecting trace amount of water in crude oil with capacitance sensors. *Sensors*; IEEE, 2014; pp 2030–2033.

(6) Kestens, V.; Conneely, P.; Bernreuther, A. Vapourisation coulometric Karl Fischer titration: A perfect tool for water content determination of difficult matrix reference materials. *Food Chem.* 2008, 106, 1454–1459.

(7) Tripathi, M. M.; Hassan, E. B. M.; Yueh, F.-Y.; Singh, J. P.; Steele, P. H.; Ingram, L. L. Reflection-absorption-based near infrared spectroscopy for predicting water content in bio-oil. *Sens. Actuators, B* 2009, 136, 20–25.

(8) Ma, W.; Wang, Y.; Wang, J.; Wang, Y.; Wang, J.; Wu, S.; Wang, D.; Guo, W.; Li, Y.; Zhang, B.; Li, Z.; Liu, W.; Xu, G.; Xu, R. Measurement of water content in high water-cut oil-wells based on rayleigh scattering. *IOP Conf. Ser. Earth Environ. Sci.* 2017, 61, 012081.

(9) Lu, Z. Q.; Yang, X.; Zhao, K.; Wei, J. X.; Jin, W. J.; Jiang, C.; Zhao, L. J. Non-contact measurement of the water content in crude oil with all-optical detection. *Energy Fuels* 2015, 29, 2919–2922.

(10) Song, Y.; Miao, X.; Zhao, K.; Zhan, H.; Jiang, C.; Wang, D.; Xiao, L. Reliable Evaluation of Oil-Water Two Phase Flow Using a Method Based on Teraertz Time-Domain Spectroscopy. *Energy Fuels* 2017, 31, 2765–2770.
(11) Song, Y.; Zhao, K.; Zuo, J.; Wang, C.; Li, Y.; Miao, X.; Zhao, X. The Detection of Water Flow in Rectangular Microchannels by Terahertz Time Domain Spectroscopy. Sensors 2017, 17, 2330.

(12) Heyden, M.; Sun, J.; Funkner, S.; Mathias, G.; Forbert, H.; Havenith, M.; Marx, D. Dissecting the THz spectrum of liquid water from first principles via correlations in time and space. Proc. Natl. Acad. Sci. U.S.A. 2010, 107, 12068−12073.

(13) Kitagawa, J.; Ohkubo, T.; Onuma, M.; Kadoya, Y. THz spectroscopic characterization of biomolecule/water systems by compact sensor chips. Appl. Phys. Lett. 2006, 89, 041114.

(14) Castro-Camus, E.; Palomar, M.; Covarrubias, A. A. Leaf water dynamics of Arabidopsis thaliana monitored in-vivo using terahertz time-domain spectroscopy. Sci. Rep. 2013, 3, 2910.

(15) Guan, L.; Zhan, H.; Miao, X.; Zhu, J.; Zhao, K. Terahertz-dependent evaluation of water content in high-water-cut crude oil using additive-manufactured samplers. Sci. China: Phys., Mech. Astron. 2017, 60, 044211.

(16) Shelby, R. A.; Smith, D. R.; Schultz, S. Experimental verification of a negative index of refraction. Science 2001, 292, 77−79.

(17) O’Hara, J. F.; Singh, R.; Brener, I.; Smirnova, E.; Han, J.; Taylor, A. J.; Zhang, W. Thin-film sensing with planar terahertz metamaterials: sensitivity and limitations. Opt. Express 2008, 16, 1786.

(18) Tao, H.; Strikwerda, A. C.; Liu, M.; Mondia, J. P.; Ekmekci, E.; Fan, K.; Kaplan, D. L.; Padilla, W. J.; Zhang, X.; Averitt, R. D.; Omenetto, F. G. Performance enhancement of terahertz metamaterials on ultrathin substrates for sensing applications. Appl. Phys. Lett. 2010, 97, 261909.

(19) Wu, X.; Pan, X.; Quan, B.; Xu, X.; Gu, C.; Wang, L. Self-referenced sensing based on terahertz metamaterial for aqueous solutions. Appl. Phys. Lett. 2013, 102, 151109.

(20) Reinhard, B.; Schmitt, K. M.; Wolраб, V.; Neu, J.; Beigang, R.; Rahm, M. Metamaterial near-field sensor for deep-subwavelength thickness measurements and sensitive refractometry in the terahertz frequency range. Appl. Phys. Lett. 2012, 100, 221101.

(21) Miyamaru, F.; Kuboda, S.; Taima, K.; Takano, K.; Hangyo, M.; Takeda, M. W. Three-dimensional bulk metamaterials operating in the terahertz range. Appl. Phys. Lett. 2010, 96, 081105.

(22) Gu, J.; Singh, R.; Tian, Z.; Cao, W.; Xing, Q.; He, M.; Zhang, J. W.; Han, J.; Chen, H.-T.; Zhang, W. Terahertz superconductor metamaterial. Appl. Phys. Lett. 2010, 97, 071102.

(23) Singh, R.; Al-Naib, I. A. I.; Koch, M.; Zhang, W. Sharp Fano resonances in THz metamaterials. Opt. Express 2011, 19, 6312−6319.

(24) Jin, X.-R.; Lu, Y.; Park, J.; Zheng, H.; Gao, F.; Lee, Y.; Rhee, J. Y.; Kim, K. W.; Cheong, H.; Jang, W. H. Manipulation of electromagnetically-induced transparency in planar metamaterials based on phase coupling. J. Appl. Phys. 2012, 111, 073101.

(25) Wang, P.-Y.; Jin, T.; Meng, F.-Y.; Lyu, Y.-L.; Erni, D.; Wu, Q.; Zhu, L. Numerical investigation of nematic liquid crystals in the THz band based on EIT sensor. Opt. Express 2018, 26, 12318−12329.

(26) Zhang, S.; Genov, D. A.; Wang, Y.; Liu, M.; Zhang, X. Plasmon-induced transparency in metamaterials. Phys. Rev. Lett. 2008, 101, 047401.

(27) Xiao, S.; Wang, T.; Jiang, X.; Yan, X.; Cheng, L.; Wang, B.; Xu, C. Strong interaction between graphene layer and Fano resonance in terahertz metamaterials. J. Phys. D: Appl. Phys. 2017, 50, 195101.

(28) Xiao, S.; Wang, T.; Liu, T.; Yan, X.; Li, Z.; Xu, C. Active modulation of electromagnetically induced transparency analogue in terahertz metal-graphene metamaterials. Carbon 2018, 126, 271−278.

(29) Liu, T.; Wang, H.; Liu, Y.; Xiao, L.; Zhou, C.; Liu, Y.; Xu, C.; Xiao, S. Independently tunable dual-spectral electromagnetically induced transparency in a terahertz metal-graphene metamaterial. J. Phys. D: Appl. Phys. 2018, 51, 415105.

(30) Liu, T.; Wang, H.; Liu, Y.; Xiao, L.; Yi, Z.; Zhou, C.; Xiao, S. Active manipulation of electromagnetically induced transparency in a terahertz hybrid metamaterial. Opt. Commun. 2018, 426, 629−634.

(31) Harris, S. E. Electromagnetically Induced Transparency. Phys. Today 1997, 50, 36−42.

(32) Phillips, D. F.; Fleischhauer, A.; Mair, A.; Walsworth, R. L.; Lukin, M. D. Storage of Light in Atomic Vapor. Phys. Rev. Lett. 2001, 86, 783.

(33) Novo, C.; Gomez, D.; Perez-Juste, J.; Zhang, Z.; Petrova, H.; Reismann, M.; Mulvany, P.; Hartland, G. V. Contributions from radiation damping and surface scattering to the linewidth of the longitudinal plasmon band of gold nanorods: a single particle study. Phys. Chem. Chem. Phys. 2006, 8, 3540−3546.

(34) Liu, X.; Gu, J.; Singh, R.; Ma, Y.; Zhu, J.; Tian, Z.; He, M.; Han, J. Electromagnetically induced transparency in terahertz plasmonic metamaterials via dual excitation pathways of the dark mode. Appl. Phys. Lett. 2012, 100, 131101.

(35) Chen, C.-Y.; Un, I.-W.; Tai, N.-H.; Yen, T.-J. Asymmetric coupling between subradiant and superradiant plasmonic resonances and its enhanced sensing performance. Opt. Express 2009, 17, 15372−15380.

(36) Park, S. J.; Yoon, S. A. N.; Ahn, Y. H. Dielectric constant measurements of thin films and liquids using terahertz metamaterials. RSC Adv. 2016, 6, 69381−69386.

(37) Ming, L.; Cheng, X.; Zhang, L.; Dai, K. Measurement of Water Content of Petroleum by High Accuracy Interval Measuring Chip. International Conference on Computational & Information Sciences, 2012; pp 1171−1174.

(38) Zhao, Z.; Zheng, X.; Peng, W.; Zhang, J.; Zhao, H.; Luo, Z.; Shi, W. Localized terahertz electromagnetically-induced transparency-like phenomenon in a conductively coupled trimer molecule. Opt. Express 2017, 25, 24410−24424.

(39) Hanai, T.; Koizumi, N.; Goto, R. Dielectric Constants of Emulsions; Bulletin of the Institute for Chemical Research Kyoto University, 1962; Vol. 10, pp 348−350.

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