Food Chemistry 211 (2016) 300–305

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

A high-sensitivity terahertz spectroscopy technology for tetracycline hydrochloride detection using metamaterials

Jianyuan Qin, Lijuan Xie *, Yibin Ying

College of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou 310058, PR China

ARTICLE INFO

Article history:
Received 19 October 2015
Received in revised form 12 February 2016
Accepted 10 May 2016
Available online 11 May 2016

Keywords:
Terahertz
Metamaterials
Tetracycline hydrochloride
Detection

ABSTRACT

Antibiotic residues in animal-derived food due to their overuse in veterinary medicine will have potential adverse effects on human health. The rapid and accurate detection of these drugs is essential for ensuring human food safety. In particular, the current detection methods are usually limited by the low sensitivity or the tedious pre-treatment. Here we demonstrate that metamaterials operating at terahertz frequencies, acting as highly sensitive sensors, show promising potential for the detection of tetracycline hydrochloride (TCH). We were able to detect a trace amount of TCH, as small as 0.1 mg/L, which was about 10^5 times enhancement compared to the measurement of TCH on a silicon substance. Our study is likely to constitute an important step toward the detection of antibiotic residues in a food matrix.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Due to its broad spectrum activity and low production costs, Tetracycline (TC) has been widely used in animal husbandry as a veterinary antibiotic and an animal growth promoter (Schnappinger & Hillen, 1996; Sczesny, Nau, & Hamscher, 2003). However, the overuse of TC has resulted to the residue of this drug in food products, such as milk, meat, and eggs (Conzuelo, Gamella, Campuzano, Reviejo, & Pingarrón, 2012), which presented the risk of undesirable health effects for the consumers, such as allergic reactions, liver damage, and bacterial resistances (Capita & Alonso-Calleja, 2013; Jeon, Kim, Paeng, Park, & Paeng, 2008). To ensure food safety for the consumers, TC residue in food products need to be detected before consumption. In recent years, efficient methods such as liquid chromatography (Blasco, Di Corcia, & Picó, 2009), capillary electrophoresis (Ibarra, Rodriguez, Miranda, Vega, & Barrado, 2011), and immunoassays (Conzuelo et al., 2013) have been widely used to detect and quantify TC residues. These methods are sensitive and highly specific, but they are destructive and require tedious sample pre-treatment (Aga, O'Connor, Ensley, Payero, Snow, & Tarkalson, 2005; Cháfer-Pericás, Maquieira, & Puchades, 2010). Other methodologies based on spectroscopy analysis are non-destructive, but they suffer from the lack of sensitivity (Sivakesava & Irudayaraj, 2002). Therefore, there is an increasing need to develop novel techniques for rapid, sensitive, and non-destructive detection of TC residue in routine assays.

Recently, Terahertz time-domain spectroscopy (THz-TDS) has emerged as an attractive technique that enables the label-free detection on the chemical and biological compounds (Markelz, Roitberg, & Heilweil, 2000; McIntosh, Yang, Goldup, Watkinson, & Donnan, 2012). Eleven antibiotics commonly used in livestock production (Redo-Sanchez et al., 2011), three antibiotics in honey (Massaouti, Daskalaki, Gorodetsky, Kouloukldis, & Tzortzakis, 2013), as well as antibiotics in high-density polyethylene (Qin, Xie, & Ying, 2015) and in infant milk powder (Qin, Xie, & Ying, 2014) have been inspected by THz-TDS. The main issue that prevents the widespread use of THz-TDS in food control, despite its advantages, is the limited sensitivity. Given this problem, several routes (Debus & Bolivar, 2007; Lee, Lee, Kee, & Jeon, 2011; Nagel et al., 2002; Yoshida et al., 2007) have been proposed as THz signal amplification approaches to attain competitive sensitivity. Among them, metamaterials based on the extraordinary optical transmission (EOT) effect are of particular interest. Metamaterials, artificial materials consisting of periodically arranged, sub-wavelength elements, exhibit unique electromagnetic properties (Pendry, Schurig, & Smith, 2006; Shelby, Smith, & Schultz, 2001). Importantly, metamaterials have strongly localized and enhanced fields, enabling sensitive detection of extremely small amount of chemical and biological substances (Huang & Yang, 2011; Linden et al., 2004; Xu et al., 2011). Recently, metamaterials operating at THz frequencies have been used as transducers in biochemical sensing, which allow

---

* Corresponding author.
E-mail address: ljxie@zju.edu.cn (L. Xie).

http://dx.doi.org/10.1016/j.foodchem.2016.05.059
0308-8146/© 2016 Elsevier Ltd. All rights reserved.

the detection of micro-environmental variations with increasing sensitivity (Park et al., 2014; Reinhard et al., 2012; Tao et al., 2010).

Tetracycline hydrochloride (TCH) is cheap, stable, and has good oral absorption, thus it is widely used in veterinary medicine instead of TC. In our previous work, we gave full evidence to the feasibility of detecting TCH in high-density polyethylene (Qin et al., 2015) and in infant milk powder (Qin et al., 2014) using THz-TDS. However, the detection sensitivity suffered great limitation. We here focused our efforts mainly on improving the sensitivity of detecting TCH by using metamaterials. The metamaterials (Shu et al., 2011) used in our present work was a periodic array of circular apertures, which showed a transmission peak at ~0.43 THz. Fig. 1a shows a schematic of the THz metamaterials sensing of TCH. We measured the change in the spectra of the THz radiation transmitted through the metamaterials after the deposition of TCH. TCH located in the metamaterials induce a change in the dielectric properties of the metamaterials. As a result, changes in the transmission peak amplitude and in the transmission peak frequency could be observed. By using this metamaterials with THz-TDS, a trace amount of TCH, as small as 0.1 mg/L could be successfully detected, which was about 10^5 times enhancement of sensitivity compared to the measurement of TCH on a silicon substance.

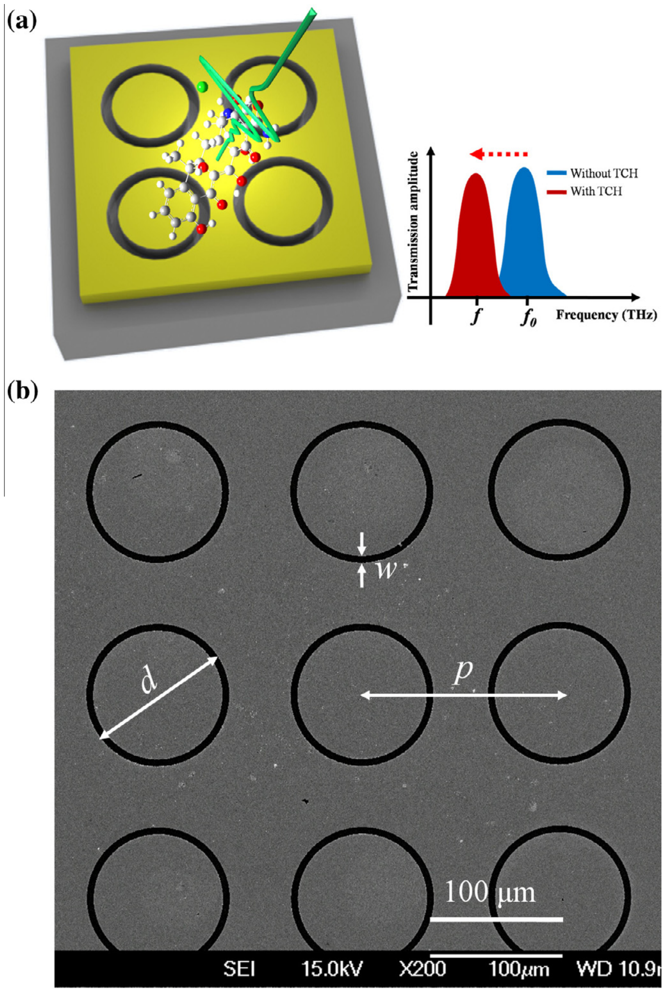

Fig. 1. (a) Schematic of the THz metamaterials sensing of TCH and (b) SEM image of the fabricated metamaterials with $p \sim 150$ μm, $d \sim 105$ μm, and $w \sim 5$ μm.

2. Materials and methods

2.1. Reagents and materials

Tetracycline hydrochloride (TCH, >98.5%) was purchased from Sangon Biotech (Shanghai, China). Pure water was obtained from a Milli-Q SP Reagent Water System (18 MΩ, Millipore, Billerica, USA). All of these chemicals and materials were used without further purification.

A series of TCH aqueous solutions with concentrations ranging from 0 to 10,000 mg/L (water, 0.01 mg/L, 0.1 mg/L, 1 mg/L, 10 mg/L, 100 mg/L, 1000 mg/L and 10,000 mg/L) were prepared by dissolving appropriate amounts of TCH powder in deionized water, and three replicates were prepared for each concentration.

The metamaterials used in our experiment consisted of an array of circular ring apertures deposited in a metal film (Shu et al., 2011). The circular ring apertures were prepared by using E-beam lithography on a 500-μm-thick high-resistivity silicon substrate. E-beam resist SU-8 was first deposited to define the pattern of circular ring apertures with period $p \sim 150$ μm, diameter $d \sim 105$ μm, and width $w \sim 5$ μm. Then a 100-nm-thick gold film was evaporated on the patterned resist, followed by a lift-off process. The scanning electronic microscopy (SEM) image of the fabricated metamaterials was showed in Fig. 1b, and the total size of the metamaterials was 4.8 mm × 4.8 mm.

2.2. Metamaterials simulations

Simulations for this metamaterials in the 0.2–0.8 THz were carried out using the 3D finite-difference-time-domain (FDTD) method (FDTD Solutions 8.11.315, Lumerical Solutions, Inc.) by applying periodic boundary conditions with lattice constant $p = 150$ μm. Gold components were modeled as perfect electric conductor. The aperture in a metal film on an intrinsic silicon substrate was excited by a normal-incidence broadband THz wave. The transmission spectrum and the electric field distribution of the aperture without any dielectric loading, as well as the spectral resonance of the aperture due to the dielectric loading (photoresist with refractive index = 1.6 in this case) with different thickness (thickness ranging from 0 to 4 μm in this case) were simulated.

2.3. Spectral measurements

All THz-TDS measurements were collected using a THz-TDS system (Z3-XL, Zomega Terahertz Corp.) in collimated transmission geometry at normal incidence. A photoconductive antenna was used for THz generation and an electro-optic ZnTe crystal was used for THz detection. A FemtoFiber pro NIR laser (pulse width of <100 fs at a repetition rate of 80 MHz) at 780 nm was used as a pump source (Lipscomb et al., 2012). The spot diameter of the THz pulse that focused on the sample was ~1 mm. All measurements were carried out at 25 °C (±0.1 °C), under the circumstance of a nitrogen purged container with the relative humidity less than 1% (±0.1%).

For sample deposition, a volume of 30 μL TCH aqueous solution was deposited on the metamaterials (or on the silicon substrate for comparison) and dried in nitrogen gas flow. A bare high-resistivity silicon substrate was used as the reference. Empty metamaterials referred to the metamaterials without depositing water or TCH aqueous solution onto its surface. Both the samples and reference were mounted at normal incidence to the THz beam for spectra collection. The metamaterials (or silicon substrate) coated with TCH were rinsed thoroughly with deionized water and dried in nitrogen gas flow after measurement. Then, a measurement for the clean and dry metamaterials (or silicon substrate) was taken

Download English Version:

https://daneshyari.com/en/article/7588537

Download Persian Version:

https://daneshyari.com/article/7588537

Daneshyari.com