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Facile synthesis of cellulose nanofiber nanocomposite as a SERS substrate for detection of thiram in juice

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ABSTRACT

There has been growing interest in the use of nanocellulose-based substrate for surface-enhanced Raman spectroscopy (SERS) applications. This study aimed to use cellulose nanofibers (CNF) to develop novel CNF-based nanocomposite as a SERS substrate. CNF were cationized with ammonium ions and then interacted with citrate-stabilized gold nanoparticles (AuNPs) via electrostatic attraction to form uniform nanocomposites. The CNF-based nanostructures were loaded with AuNPs that were firmly adhered on the CNF surfaces, providing a three-dimensional plasmonic SERS platform. A Raman-active probe molecule, 4-aminothiophenol, was selected to evaluate the sensitivity and reproducibility of CNF-based SERS substrate. The intensity of SERS spectra obtained from CNF/AuNP nanocomposite was 20 times higher than that from the filter paper/AuNP substrate. The SERS intensity map demonstrates good uniformity of the CNF/AuNP substrate. CNF/AuNP nanocomposites were used in rapid detection of thiram in apple juice by SERS and a limit of detection of 52 ppb of thiram was achieved. These results demonstrate that CNF/AuNP nanocomposite can be used for rapid and sensitive detection of pesticides in food products.

1. Introduction

Nanocellulose is a novel nanomaterial consisting of nano-structured cellulose that exhibits unique properties, including large surface area, high length-to-width ratio, high stiffness, and optical transparency. Among different types of nanocellulose, cellulose nanofibers (CNF) consist of crystalline regions of cellulose that are interconnected with each other through amorphous regions to form nanocellulose with length in micrometer range and width spanning from several nanometers to several hundred nanometers, as a result of strong inter-fiber hydrogen bonding (Abitbol et al., 2016; Ruiz-Palomero, Soriano, & Valcárcel, 2017). CNF has received much attention in recent years for the applications in material science, food packaging, and food analysis for chemical contaminants such as pesticides.

Thiram, a sulfur fungicide, has been widely used as a protective agent on food crops, vegetables, and fruits (Sharma, Aulakh, & Malik, 2003). Approximately 165,000 pounds of thiram are applied to 35,000 acres of strawberries, apples, and peaches annually in the U.S. (EPA, 2004). Thiram is slightly toxic by ingestion and inhalation and moderately toxic by dermal absorption (Sharma et al., 2003). Various analytical methods have been used for the determination of thiram, including chromatography, polarographic and voltammetric methods, and capillary electrophoresis (Sharma et al., 2003). However, these methods are time-consuming, labor-intensive, and require tedious sample pretreatment. Consequently, there is an increasing interest in developing rapid and sensitive methods with easy sample preparation for detection of thiram in foods.

Raman spectroscopy is a spectroscopic technology based on measuring molecular vibrations of analyte molecules. It can provide information about structural properties of molecules by capturing the signals from inelastic light scattering from the incident light on analytes (Cialla et al., 2012; Haynes, McFarland, & Duyne, 2005). Surface-enhanced Raman scattering (SERS) is a surface-sensitive technique that greatly enhances Raman scattering signals of analyte molecules adsorbed on roughened metal surface, which is being increasingly used in medical science, environmental monitoring, and food analysis (Craig, Franca, & Irudayaraj, 2013; Liu et al., 2015). Although the exact mechanism of SERS is not clearly understood, two theories have been widely accepted: electromagnetic and chemical enhancement. The electromagnetic enhancement is considered as the main contributor to the SERS in which the enhancement of Raman signals is due to the excitation of the localized surface plasmon resonance of nanoparticles

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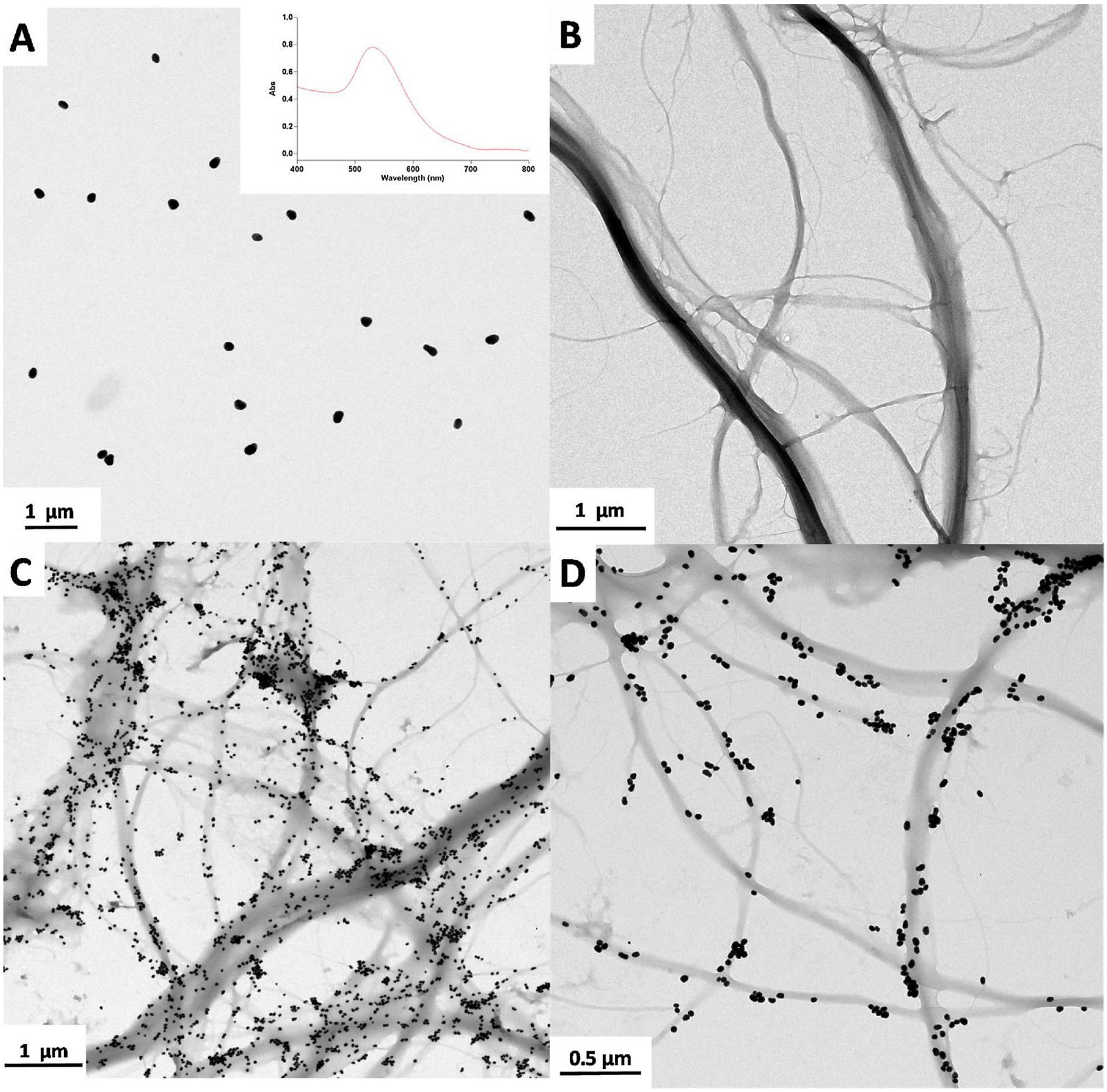

Fig. 1. TEM images at different magnifications of synthesized AuNPs (A); insert: UV–vis of AuNPs with a peak at 531 nm; unmodified CNF suspension (B); modified CNF coated with AuNPs (C & D).

Table 1
Zeta potential of different materials.

Materials	AuNPs	Original CNF	Modified CNF
ζ-potential (mV)	−3.94	−39.47	+14.77

stimulated by an incident light (Cialla et al., 2012). The regions of the intense local field enhancement are known as "hot-spots".

In general, the SERS detection is performed on a plasmon-active SERS substrate and its fabrication plays a key role in obtaining high SERS performance. Paper-based SERS substrates have been developed to take advantage of natural wrinkles and fibril structures of paper, thus allowing metal nanoparticles to be deposited and arranged on a paper to from large-area SERS "hot-spots" (Li et al., 2016; Wei & White, 2013; Zhang et al., 2012). However, the width of cellulose fibril of paper, which is a range of several to tens of micrometers, limits the SERS performance due to its inhomogeneous distribution of nanoparticles and low signal intensity.

To solve this problem, nanocellulose with lateral dimensions of less than 100 nm can be used to support higher loading of nanomaterials and improve homogeneity of the substrate. Our previous study developed CNF-based SERS substrate by placing gold nanoparticles (AuNPs) onto dried CNF sheet (Xiong, Chen, Liou, & Lin, 2017). However, this approach was largely based on gravity-assisted loading of AuNPs on CNF, which led to inhomogeneous distribution of AuNPs mainly on the surface layer of the CNF. To improve the sensitivity and reproducibility of SERS method, a novel approach was taken in this study to modify CNF with ammonium ions and allow them to interact with citrate-stabilized AuNPs, forming a uniform film with firmly adhered nanoparticles. This CNF-based nanocomposite provides a three-dimensional (3D) and highly porous structure as a plasmonic SERS substrate. In addition, the detection of thiram in apple juice was conducted by SERS coupled with CNF/AuNP nanocomposite. Multivariate statistical analysis was used to analyze the SERS spectral data.