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Full Length Article

A simple fabrication of plasmonic surface-enhanced Raman scattering (SERS) substrate for pesticide analysis via the immobilization of gold nanoparticles on UF membrane

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ABSTRACT

In this study, we developed a facile fabrication method to access a highly reproducible plasmonic surface enhanced Raman scattering substrate via the immobilization of gold nanoparticles on an Ultrafiltration (UF) membrane using a suction technique. This was combined with a simple and rapid analyte concentration and detection method utilizing portable Raman spectroscopy. The minimum detectable concentrations for aqueous thiabendazole standard solution and thiabendazole in orange extract are 0.01 μg/mL and 0.125 μg/g, respectively. The partial least squares (PLS) regression plot shows a good linear relationship between 0.001 and 100 μg/mL of analyte, with a root mean square error of prediction (RMSEP) of 0.294 and a correlation coefficient (R^2) of 0.976 for the thiabendazole standard solution. Meanwhile, the PLS plot also shows a good linear relationship between 0.0 and 2.5 μg/g of analyte, with an RMSEP value of 0.298 and an R^2 value of 0.993 for the orange peel extract. In addition to the detection of other types of pesticides in agricultural products, this highly uniform plasmonic substrate has great potential for application in various environmentally-related areas.

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1. Introduction

Food safety is one of the most interesting topics nowadays. Over the last 50 years, a number of developments in food science and technology have led to the discovery of many new substances with useful functions for food processing [1]. However, substances such as toxic pesticides are used during crop cultivation and post-harvest processing, leading to widespread consumers' concern on the issue of food safety. Pesticides are present in food as a result of their usage in any phase of production, processing, packaging, or storage. Therefore, the use of pesticides is strictly controlled by related agencies by stipulating the maximum residue limits (MRL) for pesticides in foods. Presently, chromatography, mass spectroscopy-based techniques, and immunoassay are commonly used to analyze thiabendazole (TBZ) residues in agricultural products. Nonetheless, chromatography and mass spectroscopy-based techniques tend to be costly, time-consuming, and require sophisticated sample preparation as well as highly trained personnel to operate the instrument [2,3]. Meanwhile, immunoassay has also been used to rapidly analyze pesticides but it often lacks sensitivity and reproducibility [4,5]. Recently, much interest has been given to surface-enhanced Raman spectroscopy (SERS) as a rapid, simple, and sensitive detection method for analyzing complex food matrices [6,7]. SERS is a technique combining the use of Raman spectroscopy and nanotechnology. Raman spectroscopy, a vibrational spectroscopic technique, has become a widely used experimental method for molecule identification and structural characterization of various compounds. It provides rich structural information content, so-called molecular "fingerprint", with a short spectra collection time that usually lasts for only a few seconds [8]. One of the most investigated areas in SERS application is the rapid detection of pesticides in the skin of fruits or vegetables with minimum or no sample preparation, involving the use of various SERS-activated substrates such as silver-coated gold bimetallic nanoparticles [3], gold-coated nanosubstrates [9], silver colloids [10], silver dendrite [7], imprinted polymer grating [11], and commercial tape decorated with gold nanoparticles [12]. Other studies that were performed to improve SERS activity have focused on modifying the surface of the substrate through nanomaterials and nanostructures synthesized using sophisticated techniques, which include lithography, a high-temperature process, and a number of chemical syntheses [13–15]. The use of SERS with these types of substrates is limited by the low reproducibility of the response [16].

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In addition, the concentration of the sample solutions is another challenging problem. In many cases, samples are dropped onto the substrate plate, and left to dry [17,18]. However, when drying on a solid surface, the nanoparticles (NP) tend to be randomly aggregated; therefore, the signals are extremely inconsistent from one spot to another [19].

In order to resolve these problems, some novel methods such as magnetic concentration [20,21], centrifugation concentration [22,23], and microfluidic channel [24,25] have been developed. In addition, loading of nanoparticles on the membrane were generally performed by chemical treatment [26–28]. Nevertheless, these methods are complex and time-consuming. Herein, we introduce a simple and rapid fabrication method for SERS substrate by physical adsorption of gold nanoparticles (AuNPs) on hydrophilic polytetrafluoroethylene membrane. Some researchers showed that loading of silver nanoparticles (AgNPs) with aggregating salt on the membrane by syringe filter system for detection of malathion and melamine [29], AgNPs-containing samples [30], and ferbam and ampicillin [31]. Another research showed that loading of AgNPs by filtration cell under a pressure to confirm bio-fouling [9]. In this study, we used a depressed suction technique to fabricate gold nanoparticles (AuNP)-immobilized Ultrafiltration (UF) membrane, along with a sample concentration method. The depressed suction technique is simple, favorable to high volume of samples, has prolonged stable and possibility to connect sample concentration with concentration procedure continuously. A UF membrane has rough and nano-sized pores, which facilitate the physical immobilization of NPs and surface plasmon resonance. It can also be highly stable to organic solvent and can be applied to purification procedures. In order to test this method, we selected TBZ as a target substance. TBZ is widely used to control a variety of fruit and vegetable diseases such as mold, rot, blight, and stain that are caused by various fungi during transportation and long term storage. Moreover, TBZ is also used as a preservative. For example, it is a common ingredient in the waxes that are applied to the skin of citrus fruits [32]. In the case of citrus fruits (grapefruits, oranges, lemons, limes, and mandarins), the European Union (EU) has set the MRL of TBZ at 5 mg/kg [33]. In general, TBZ is of low acute toxicity; however, it has been classified to be likely carcinogenic at doses that are high enough to cause disturbance of the thyroid hormone balance [34]. Consumers may be exposed to residual TBZ through agricultural products, which necessitates the analysis of TBZ content in agricultural products. In this study, we carried out TBZ analysis utilizing a highly uniform SERS substrate and a rapid sample concentration method via a simple suction technique.

2. Materials and methods

2.1. Chemicals and reagents

Gold (III) chloride trihydrate was obtained from Wako (Tokyo, Japan), trisodium citrate was obtained from Kanto Chemical (Tokyo, Japan), and thiabendazole (TBZ) was obtained from LKT Laboratories (Tokyo, Japan). Hydrophilic polytetrafluoroethylene (PTFE) membrane with a pore size of 0.1 μm was obtained from Flon Industry (Tokyo, Japan). All organic solvents were of pesticide analysis grade and obtained from Wako (Tokyo, Japan). Ultrapure water was used in all experiments.

2.2. Synthesis of Au NPs

Gold nanoparticles were synthesized via the chemical reduction of chloroauric acid with sodium citrate based on the work of Frens and they exist as spherical particles [35]. Briefly, 50 mL of aqueous $HAuCl_4$ solution (0.4 mM) was heated to 100 °C in an oil bath under vigorous stirring for 30 min. After adding a pre-determined amount of trisodium citrate (1% w/w) into the solution, the mixed solution was refluxed for 20 min until the solution's color became wine red. The AuNPs' size was determined by the amount of trisodium citrate used. The resultant solution gradually cooled to room temperature under stirring.

2.3. Sample preparation

TBZ standard solutions were prepared by dissolving TBZ powder in water to give final concentrations of 0.01, 0.1, 1, 10, and 100 μg/mL (ppm). Meanwhile, the orange peel extract solution was prepared as follows. Oranges were purchased from a local supermarket in Ehime, Japan. The selected fruits were uniform in size and were not washed to retain their original conditions. Firstly, the orange peel was carefully cleaned with soft paper and the final concentrations of TBZ powder in ethanol were fixed at 50, 100, 500, and 1000 μg/mL (ppm). Next, each orange peel was spiked with ten spots of the respective TBZ solutions (measuring 50 μL per spot to give a total of 500 μL TBZ solution per orange) and dried for 3 h under ambient conditions. The concentration of TBZ on the surface of each orange (weight of orange is 200 g) became 0.125, 0.25, 1.25, 2.5 μg/g respectively. Subsequently, the TBZ-contaminated oranges were put into polyethylene unipacks and 50 mL of pure water was added into each bag. The unipacks were vigorously shaken by hands for 5 min to ensure the sufficient recovery of TBZ from the orange peel. The extract was then used as an analyte solution for the analysis of TBZ-contaminated orange peel.

2.4. Fabrication of SERS substrate

Gold nanoparticles were physically immobilized on the UF membrane using a suction technique, followed by drying. 0.1 μm of hydrophilic PTFE membrane was used for this study. Before performing the experiments, we investigated several different types of membranes. AuNP colloids' permeation velocity was extremely slow using low pore size (below the pore size of 0.05 μm) and hydrophobic membranes. In contrast, AuNP colloids easily passed through high pore size membranes (*i.e.*, pore size of 0.1 μm). All suction procedures were conducted under a constant operating pressure of −90 kPa using a V-500 vacuum pump (Büchi Labortechnik AG, Flawil, Switzerland). Firstly, the UF membrane was placed in a suction apparatus, before adding 100 μL of AuNP colloids onto the UF membrane under suction. The mechanical suction was left for another 3 min after the AuNPs were completely immobilized on the UF membrane to facilitate drying. AuNPs are inexpensive, easy-to-prepare, stable, and could provide ideal SERS enhancement effects as demonstrated in many previous studies [5,36].

2.5. Concentration of TBZ solution

The TBZ solutions were concentrated and fixed on the AuNP-immobilized SERS substrate using a suction technique. A 50 μL volume of TBZ solution was added to the AuNP-immobilized UF membrane SERS substrate, which was placed in a suction apparatus under suction (−90 kPa). Using this simple process, the TBZ solution was concentrated and was quickly bound to the SERS substrate at the same time. The SERS peaks of TBZ on the SERS substrate can be directly obtained by portable Raman spectroscopy. In order to examine how much TBZ were concentrated on the AuNPs coated membrane, we analyze SERS signal of a filtrate of 100 ppm of TBZ by the suction method again and there was no signal. It means that concentration of the filtrate were less than 0.01 ppm which is the lowest detectable concentration (LOD).

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