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A piezoelectric magnetic molecularly imprinted surface sensor for the detection of Sudan I

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Magnetic nanoparticles that act as carriers of magnetic molecularly imprinted surface polymers (MMISPs) have been harnessed to produce a magnetic molecularly imprinted, piezoelectric surface sensor for the detection of Sudan I. The MMISP was characterized by ultraviolet and infrared spectroscopy as well as transmission electron microscopy. Test results show that this MMISP-modified piezoelectric sensor was effective at detecting Sudan I, with the sensor displaying perfect selectivity and high sensitivity, with a detection limit of 2 μg/L, and response time of 3.5 s. The reproducibility of the sensor was satisfactory due to $P > 0.05$, indicating that there is no statistical difference between the data obtained by the intra- and inter-batch methods. When applied to a real example, recovery testing indicated that the sensor effectively detected Sudan I in pepper.

1. Introduction

Sudan I is a type of azo dye that can produce carcinogenic metabolites when ingested. Consequently, it is prohibited in the food industry in accordance with the national standards of many countries. Unfortunately, there are still many organizations that use Sudan I in their products because it is inexpensive and provides excellent food color, despite being potentially damaging to human health. It is very important, therefore, to establish an accurate and reliable detection method for Sudan I. Current methods for the detection of Sudan I are based mainly on High Performance Liquid Chromatography (HPLC) techniques and purification by alumina chromatography. These methods are tedious, involve expensive equipment and are not suitable for real-time detection. Therefore, it is necessary to develop an efficient, sensitive, and cost-effective method for the analysis of Sudan I residues.

Recently, magnetic nanoparticles have become increasingly important in biology and biotechnology, with roles in MRI, targeted drug delivery, and the separation and purification of protein cores. Magnetic nanoparticles are also widely applied [1] in bioseparation owing to their small volumes and high surface to volume ratios. It has been established that modifications on the surfaces of magnetic nanoparticles provide key points and hot spots [2] for their application. Molecular imprinting [3–8] carried out on the surface of these magnetic nanoparticles has been shown to improve recognition [9,10] of specific molecules. For example, performing molecularly imprinted polymerization on the surface of magnetic nanoparticles (with the help of external magnetic fields) affords surface-modified magnetic nanoparticles that are able to separate and purify chemical substances [11] in a more convenient way. Now, sensors based on magnetic molecularly imprinted polymers (MMIPs) have been extensively reported. MMIPs act as sensitive sensor elements that can rapidly determine target molecules. Castillo et al. [12] attached MMIPs to fiber probes during the preparation of optical sensors. Jin et al. [13] modified electrode surfaces with MMIPs, which were used for electrochemical and quartz crystal microbalance analyses. Li et al. [14] prepared novel molecularly imprinted electrochemical sensor based Fe_3O_4 nanobeads for the detection of 17β-estradiol and achieved a detection limit of 0.819 nM. This sensor showed the highest selectivity and sensitivity among MMIP sensors. In this research, the magnetic molecular surface imprinting technique is applied to a piezoelectric sensor to prepare a new magnetic molecularly surface imprinted sensor that can be used to efficiently, accurately and rapidly detect Sudan I residues in pepper.

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2. Materials and methods

2.1. Materials

$FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, ethanol, aqueous ammonia (25%), isopropyl alcohol, tetraethyl orthosilicate (TEOS), methacrylic acid, acetone, ammonium persulfate, Sudan I, and ethylene glycol dimethacrylate (EGDE)were purchased from TCI Development Co., Ltd. Methanesulfonic acid (Chinese Medical Chemicals, Shanghai, China), triethoxyvinylsilane (TTS, Sigma-Aldrich, USA) and Sudan I (Chinese Medical Chemicals, Shanghai, China) were of analytical grade.

2.2. Methods

2.2.1. Preparation of magnetic surface molecularly imprinted polymer

Preparation of Fe_3O_4 Magnetic Nanoparticles. $FeCl_2 \cdot 4H_2O$ (1.72 g) and $FeCl_3 \cdot 6H_2O$ (4.72 g) were added into deionized water (80 mL), and the mixture was stirred intensely until the compounds dissolved. The system was flushed with nitrogen and heated to 80 °C, after which aqueous ammonia (10 mL) was slowly dropped into the mixture over 30 min, to give a thick black liquid. A permanent magnet was used to collect the black precipitate, which was washed using deionized water (4–6 times) to remove unreacted materials and impurities. After drying at 80 °C for 3 h, the Fe_3O_4 magnetic nanoparticles obtained were ready for further use.

Preparation of Fe_3O_4@SiO_2 [15]. The Fe_3O_4 magnetic nanoparticles, prepared above (300 mg), isopropyl alcohol (50 mL) and highly purified water (4 mL) were mixed together and sonicated for 15 min in an ultrasonic bath, after which ammonium hydroxide solution (5 mL), TEOS (2 mL) and polyethylene glycol (PEG) (0.2 g/mL, 1 mL) were added and the resulting mixture stirred constantly for 12 h. A permanent magnet was used to collect the product, which was subsequently washed with pure water (4–6 times). After drying at 80°, the obtained Fe_3O_4@SiO_2 was ready for further use.

Preparation of Sudan IMIP-Fe_3O_4@SiO_2. Fe_3O_4@SiO_2 (20 g) was suspended in methane sulfonic acid:water (1:1, v/v) for 24 h. The solid Fe_3O_4@SiO_2 was collected, washed with acetone (100 mL) and distilled water (200 mL) several times before drying at 80 °C, to afford the activated Fe_3O_4@SiO_2. Triethoxyvinylsilane (TTS) (30 mL) and the activated Fe_3O_4@SiO_2 (20 g) were added to a solution of ethanol in water (400 mL) ($V_{ethanol}$:V_{water} = 1:1) and allowed to react for 31 h. A permanent magnet was used to collect the obtained product, which was washed with ethanol and distilled water (3–4 times) to give TTS-Fe_3O_4@SiO_2. TTS-Fe_3O_4@SiO_2 (3 g), MAA (10 g), distilled water (200 mL) and ammonium persulfate (0.036 g) were added to a 500 mL round-bottom flask. After 7 h at 70 °C, the product was collected using a permanent magnet and repeatedly washed with ethanol and distilled water. The product and Sudan I (4 mmol/L, 99.3 mg) were dissolved in chloroform (100 mL) and the mixture was stirred by magnetic stirrer for 6 h under N_2 at 25 °C. The cross-linking agent, EGDE (0.4 mL) was added to the mixture, which was maintained at 50 °C for 8 h. The product was collected using a permanent magnet and then washed with methanol and a solution of ethanol and water in methanol ($V_{ethyl\ alcohol}$:$V_{methyl\ alcohol}$:V_{water} = 2:7:1), and dried at 60 °C.

The non-imprinted polymer was prepared in identical fashion with the exception that Sudan I was not added during the preparation process.

2.2.2. Preparation of the piezoelectric magnetic molecularly imprinted surface sensor

Two detection channels for the piezoelectric magnetic molecularly imprinted sensor were designed using piezoelectric crystals. The sensor circuits used the same parameters and were identical oscillating circuits. The piezoelectric crystal was modified using the magnetic molecularly imprinted polymer or the magnetic non-imprinted polymer to provide piezoelectric crystals for detection and reference purposes, respectively. The combination of the magnetic molecularly imprinted surface polymer and the materials to be tested affected the surface of the crystal, and was used to alter the frequency. A comparison against the reference piezoelectric crystal was carried out to allow for the content of Sudan I attached to the detection crystal to be calculated. This was achieved by a comparison of the frequency difference between the two circuits. During this process, the piezoelectric crystal was placed in a closed container free from external interference, which enabled more accurate results to be obtained. Fig. 1 depicts the schematic design

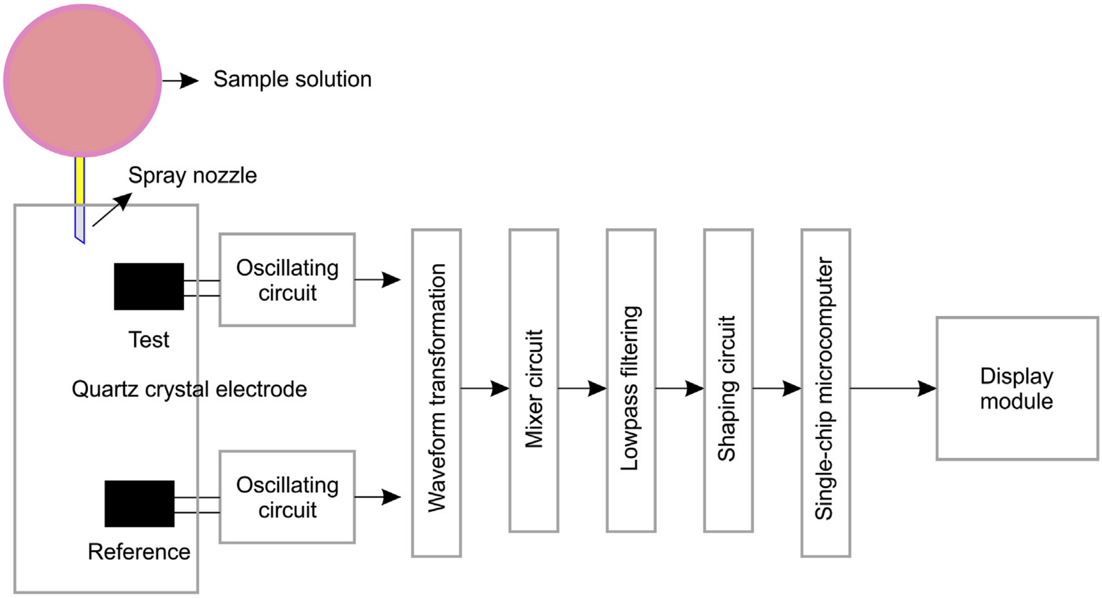

Fig. 1. Schematic diagram of the magnetic molecularly imprinted piezoelectric sensor.