



Rapid and highly selective detection of formaldehyde in food using quartz crystal microbalance sensors based on biomimetic poly-dopamine functionalized hollow mesoporous silica spheres



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ABSTRACT

In this study, poly-dopamine functionalized hollow mesoporous silica spheres (PDA/HMSSs) are prepared and exploited as a sensing material for formaldehyde detection in food. The materials were characterized by small-angle X-ray diffraction, scanning electron microscope, transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectrometry, and nitrogen adsorption-desorption. The results show that PDA was successfully modified onto the surface of HMSSs. The PDA/HMSSs-based quartz crystal microbalance (QCM) sensors exhibited a low detection limit of 100 ppb, a remarkably rapid response (< 5 s), a short recovery (< 3 s), as well as excellent sensitivity due to available hollow space and accessibly radial channels. Based on enthalpy change ($\Delta H^\circ = -51.97$ KJ/mol) and the formation of C–N bonds, studying on the sensing mechanism revealed that weak chemisorption between PDA/HMSSs and formaldehyde played a significant role in the good specificity and reliability for formaldehyde detection. Furthermore, the as-prepared sensors were directly applied in measuring formaldehyde levels in shiitake mushroom, Chinese cabbage, *Litopenaues vannamei*, and broccoli, where rapid detections within 30 s were achieved with high sensitivity, reusability, and good selectivity.

1. Introduction

Formaldehyde has been widely used as an additive for preventing food spoilage, brightening the color, and enhancing the flavor [1–3]. However, people ingesting formaldehyde can develop irritation of the eyes and the upper respiratory tract, childhood asthma, allergic skin reactions, and even nasopharyngeal cancer and potentially leukemia [4]. In addition, it is considered carcinogenic by the International Agency for Research [5]. These facts pose a significant burden to consumers' health and cause substantial economic losses to our society. To date, notable efforts have been made in this field for formaldehyde detection, including spectrophotometry [6], fluorimetry [7], gas chromatography (GC) [8–10], and high-performance liquid chromatography spectrometry (HPLC) [11,12]. Nevertheless, these techniques suffer from various limitations, such as labor intensiveness, time-consuming processes, high cost, as well as the need for skilled operators. Consequently, a highly sensitive, easy-to-use, and low-cost analytical

approach based on chemosensors is a good alternative to provide more rapid and effective real-time monitoring of formaldehyde in food.

Quartz crystal microbalance (QCM) sensors, a miniaturized and portable platform, are regarded as a desirable approach to the rapid detection of toxic and harmful gases [13–15], which plays an essential role in many important research fields, such as environment pollutants sensing [16], disease diagnosis [17], pathogen detection [18,19], and food safety monitoring [20–22]. It is widely acknowledged that sensitivity, response/recovery time, selectivity, and stability are of great practical importance to evaluate the performance of QCM sensors [23]. Nevertheless, development of QCM sensors with ever-increasing sensitivity, shortened response and recovery time, and improved selectivity and stability remains a challenge. Previous studies have suggested that the gas sensing performance is strongly dependent on the specific surface area, microstructure, and surface functional sites of the gas-sensing materials [24,25]. Hollow mesoporous silica spheres (HMSSs) with large surface areas, highly permeable porous shells, and accessible

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interior space offer more advantages for facilitating gas diffusion and host–guest interactions [26,27]. With the same surface area, the sensitivity of HMSSs-based sensor is superior to their solid counterparts, the mesoporous silica spheres (MSSs). Radially oriented channels aligning perpendicular to the shell surface of HMSSs are favorable for molecular adsorption and release that promotes a shorter response/recovery time [28]. Tailoring the surface characteristics of HMSSs can greatly improve gas-sensing properties. In particular, easy surface functionalization of the mesoporous shells can be achieved by modifying with chemical species that provide specific interactions with target gas molecules, improving the sensitivity and selectivity of gas sensors [29]. Therefore, designing a simple and universal strategy to attach the chemical composites on the shell of the HMSSs is strongly demanded for practical application.

Recently, a straightforward and effective surface-modification technique based on the poly-dopamine (PDA) adhesive mechanism has attracted intensively research interest [30]. The advantages of PDA modification include: (i) this process does not require the time-consuming preparation of complex linkers, and is solvent-free and non-toxic, and (ii) PDA itself is regarded as a gas-sensing material due to the abundant functional groups such as catechol, amine, and imine, which provides a platform for chemical adsorption and leads to an enhancement in the selectivity. Consequently, we integrated PDA and HMSSs aiming to fabricate a novel material for improving the formaldehyde-sensing capacity. To the best of our knowledge, there have not been previous reports of HMSSs or PDA/HMSSs for the use as gas-sensing materials for formaldehyde detection. In this regard, a simple and facile fabrication method of functionalized HMSSs and its extending application in gas sensors is potentially significant.

In this paper, a series of PDA-functionalized HMSSs (PDA/HMSSs) with different decorations of amine group were prepared via a simple and facile process, and their gas-sensing properties were explored. The experimental results suggested that appropriate functionalization of amine groups remarkably improved the sensitivity and selectivity to formaldehyde. In contrast to PDA/MSSs, PDA/HMSSs-based sensors displayed a desired gas-sensing performance including the enhanced sensitivity as well as faster response and recovery (< 5 s). Besides, we combined in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and adsorption thermodynamics to reveal the sensing mechanism of PDA/HMSSs for formaldehyde molecules. Furthermore, the as-prepared sensors were applied directly in measurements of shiitake mushroom, Chinese cabbage, *Litopenaeus vannamei*, and broccoli. It proved that the as-developed approach was comparable with the conventional spectrophotometry method, further confirming the capability and reliability of the method for formaldehyde detection in food.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, 99%), ammonium hydroxide (25%), ethanol (200-proof), cetyltrimethylammonium bromide (CTAB), and formaldehyde were purchased from Sinopharm Chemical Reagent Co., Ltd. China. Hydrochloride dopamine (99%) was obtained from Sigma-Aldrich (USA). Deionized water was from a Milli-Q water ultrapure water purification system.

2.2. Synthesis of HMSSs

HMSSs were prepared via a surfactant-assembly sol-gel process using a Stöber reaction according to previously described protocol [28,31]. In a typical procedure, CTAB (0.15 g) was dissolved in 74 mL of ethanol/water mixed solution (23.75 mL, ethanol) containing ammonium hydroxide (0.25 mL, 25 wt%), and the mixture was heated to 35 °C under vigorous stirring. Afterwards, 1 mL of TEOS was rapidly

added into mixed solution. The vigorous stirring was continued for 24 h, and then the precipitates were collected by centrifugation, and extensively washed with ethanol. Thereafter, the product was dispersed into deionized water (240 mL) and incubated at 70 °C for 2 h. The white as-prepared products were collected by centrifugation, and washed with ethanol and deionized water. In order to extract the surfactant CTAB, the above-prepared materials were resuspended in ethanol solution (200 mL), to which a concentrated hydrochloric acid (37%, 1.5 mL) was added, and the suspension was refluxed at 80 °C for 24 h. Finally, the products were further treated at 550 °C in air for 5 h with a heating rate of 1 °C/min to remove the surfactant CTAB.

2.3. Preparation of PDA-functionalized HMSSs

For gas-sensing study, three types of PDA/HMSSs with different amine group contents were prepared by adjusting the concentration of dopamine in the reaction solution. Briefly, dopamine hydrochloride (0.07, 0.1, or 0.2 mg/mL) was dissolved in 50 mL of 10-mM Tris-HCl (pH = 8.5) buffer solution, and 50 mg of the above-prepared HMSSs were subsequently dispersed into the dopamine solution and ultrasonicated for 30 min. Afterwards, the mixture was stirred for 24 h at room temperature to generate PDA/HMSSs composite particles. Finally, the composite particles were centrifuged, washed with deionized water, and dried at 80 °C for 8 h. In the following discussion, the composite particles obtained from the dopamine solution (0.07, 0.1, and 0.2 mg/mL) were referred to as PDA/HMSSs-1, PDA/HMSSs-2, and PDA/HMSSs-3, respectively.

2.4. Materials characterization

The structural characteristics of the resulting mesoporous materials were determined by small-angle X-ray diffraction (SAXRD) analysis using a Bruker model D2 focus diffractometer equipped with copper anode to produce X-rays (30 kV, 10 mA). The morphology of samples was inspected using transmission electron microscope (TEM, JEM-2100F JEOL, Japan) operated at an acceleration voltage of 200 kV. Before measurement, the samples were ultrasonically dispersed in absolute ethanol and were then dropped on carbon film-covered copper grids for analysis. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM, Hitachi, Japan) at an accelerating voltage of 3 kV. Surface functionalization was recorded on a Nicolet iS5 Fourier-transform infrared (FT-IR) spectroscopy using KBr plates in wavelength range of 4500–400 cm^{-1} . X-ray photoelectric spectroscopy (XPS) experiments were carried out on an AXIS ULTRA DLD XPS system MONO Al Ka X-ray source (1486.6 eV). The XPS spectra were calibrated with respect to the C1s peak at 284.6 eV and deconvoluted according to Gaussian multi-peak fitting. The nitrogen adsorption-desorption isotherms of the samples were measured at -196 °C on a Quantachrome Autosorb-3 B volumetric adsorption analyzer. The specific surface areas and the pore size of the samples were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. For in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) studies, the IR spectra were recorded with a Nicolet iS5 FT-IR spectrophotometer, equipped with an in situ diffuse reflectance accessory. A liquid nitrogen-cooled Mercury-cadmium-telluride (MCT) detector was used and all the spectra were collected at a resolution of 4 cm^{-1} over the range of 4000–600 cm^{-1} . Before FT-IR measurement, the sample (30 mg) was placed in a sample cell and exposed to 30 ppm of formaldehyde vapor for 1–3 min. After that, the sample was rapidly placed into a ceramic crucible in the in situ chamber for testing. The scan was repeated six times, and the time interval was set as 1 min.

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