

SURFACE-ENHANCED RAMAN SCATTERING SENSOR BASED ON SELF-ASSEMBLED SILVER NANOPARTICLES FOR DETECTING ROTTEN EGGS**

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Eggs are nutritious food that can decompose to emit hydrogen sulfide (H_2S) gas when stored for a long time. We designed a surface-enhanced Raman scattering (SERS) sensor based on self-assembled silver nanoparticles (Ag NPs) to detect endogenous H_2S generated in rotten eggs. The Ag NPs were prepared using a reduction method to enhance the Raman signal of the probe molecule, 4-mercaptobenzoic acid. The prepared Ag-NP substrate exhibited an excellent Raman strength enhancement effect, good uniformity, and long-term stability. To explore the possibility of using a SERS platform in H_2S gas detection, a quantitative analysis with different H_2S concentrations was performed. The results showed a good linear relationship between the Raman intensity at 1073 cm^{-1} and various H_2S concentrations, and the H_2S detection limit was as low as $0.03\text{ }\mu\text{M}$.

Keywords: surface-enhanced Raman scattering, silver nanoparticles, hydrogen sulfide, rotten-egg detection, quantitative detection.

КР-СЕНСОР НА ОСНОВЕ САМОСОБИРАЮЩИХСЯ НАНОЧАСТИЦ СЕРЕБРА ДЛЯ ОБНАРУЖЕНИЯ ИСПОРЧЕННЫХ ЯИЦ

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Для обнаружения эндогенного сероводорода H_2S , образующегося в испорченных яйцах, разработан датчик на основе поверхностно-усиленного комбинационного рассеяния света (SERS) самособирающимися наночастицами серебра (НЧ Ag). НЧ Ag готовили с использованием метода восстановления для усиления КР-сигнала молекулы-зонда 4-меркаптобензойной кислоты. Приготовленная подложка НЧ Ag демонстрирует эффект усиления комбинационного рассеяния, однородность и долговременную стабильность. Для изучения возможности использования платформы SERS для обнаружения H_2S проведен количественный анализ с различными концентрациями H_2S . Показана линейная зависимость интенсивности комбинационного рассеяния при 1073 см^{-1} от концентрации H_2S с пределом обнаружения H_2S 0.03 мкМ .

Ключевые слова: поверхностно-усиленное комбинационное рассеяние света, наночастицы серебра, сероводород, обнаружение испорченных яиц, количественное обнаружение.

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Introduction. Eggs are an important and popular food in people's daily diet because they are nutritious and inexpensive [1]. According to the 2020–2021 China egg market's annual report, China's egg production in 2020 was 18.9 million tons, with an annual growth of 1.48%. As the storage time increases, eggs gradually start to deteriorate. Rotten eggs have reduced nutritional value and cause physical and economic losses to consumers [2]. Therefore, detecting rotten eggs during their processing, transportation, and sale can reduce the processing cost and protect consumers' rights. This will also promote the harmonious and stable development of the egg market [3].

Recently, several methods have been applied to detect the freshness of eggs [4]. Dong et al. employed a fiber probe to collect the near-infrared spectra of eggs in the equatorial region and established a prediction model using partial least-squares regression to evaluate the freshness of eggs [5, 6]. The Raman technique combined with a chemometrics method was used to monitor the freshness of eggs by scanning the eggshell [7]. A microwave spectrometric method based on a waveguide and network analyzer was developed for the non-destructive prediction of the freshness of eggs [8–10]. Yao et al. used the hyperspectral imaging technology to identify and grade the freshness of eggs nondestructively and rapidly [11–13]. Although these methods can be used for the nondestructive testing of the freshness of eggs, impurities and microorganisms attached to the shell can affect the accuracy of detection [14]. Moreover, in these methods, considerable effort is required to obtain sufficient samples and excellent algorithms for building prediction models. Therefore, the development of an easy and reliable sensor for detecting rotten eggs is urgently required.

Surface-enhanced Raman scattering (SERS) is a powerful vibrational spectroscopic technique that can provide rich analyte information with quantitative detection capabilities. Eggs decompose during the deterioration process and produce specific gases, such as H_2S [15]. Ahn et al. used Ag nanorods array SERS paper to detect endogenous H_2S in cancer cells [16]. SERS technology has attracted considerable attention in numerous detection fields, including biomolecular detection and chemical detection, because of the unique optical properties of metal nanoparticles and the molecular fingerprint information provided by Raman spectroscopy [17–19]. To the best of our knowledge, no report has been published on the screening of rotten eggs by detecting their endogenous H_2S using SERS technology.

We introduce a SERS method based on self-assembled Ag nanoparticles (NPs) to distinguish rotten eggs from fresh eggs by detecting endogenous H_2S in rotten eggs. The principle of this method is that Ag NPs react with H_2S to form Ag_2S , which reduces the SERS activity of Ag NPs [20–22]. The concentration of H_2S and the freshness grade of eggs can be determined by detecting the change in the Raman signal of the probe molecule 4-MBA [23–25]. The present report provides a novel strategy for the sensitive and quantitative detection of rotten eggs.

Experimental. Fresh eggs (Haugh Unit = 79.4) with the same production date were bought from the local supermarket (Hangzhou, China) and stored for different durations under the same storage conditions. Si (111) wafers (boron-doped) were purchased from Kaihua Shunchen Electronic Technology Co., Ltd. (Zhejiang province, China). Ultrapure water was obtained from a Milli-Q ultrapure (18.2 M Ω cm) system. All chemicals, including silver nitrate, ascorbic acid, trisodium citrate, citric acid, polyvinylpyrrolidone (PVP), sodium hydroxide, dichloromethane, *n*-hexane, and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), were reagent grade and purchased from technology companies.

Scanning electron microscopy (SEM) images were obtained using Nova Nano 450. Ultraviolet (UV)-Visible (vis) absorption spectra were collected using a UV-Vis spectrophotometer (TU-1901; PERSEE, Beijing, China). Raman spectra were obtained using a Raman spectrometer with a 50 $\times$ lens (LabRAM HR Evolution, Horiba). All detections were performed under a holographic grating of 600 g/mm. A He-Ne laser of 633 nm was used as the excited laser at room temperature. The integration time of the SERS spectrum was 5 s, and three scans were taken per spectrum.

A SERS sensor was built using a previously reported self-assembly method [26, 27]. The SERS detection of H_2S was performed according to Fig. 1 as follows. A solution of Na_2S was prepared in 100-mM phosphate-buffered saline (PBS, pH 7.4) as a H_2S donor [15, 28]. The corresponding H_2S concentration produced using this method was approximately one-third of the Na_2S concentration [17, 18, 29]. The standard solution (300 μL) at concentrations ranging from 0.1 to 30 μM was injected rapidly into 50-mL centrifuge tubes. A piece of the Si substrate with Ag NPs was immediately stuck inside the centrifuge tube's cover with the Ag-covered side facing down toward the solution. The Na_2S solution decomposed to produce H_2S that reacted with the Ag NPs to form Ag_2S for 2 h. The Ag-NP substrate was then removed and soaked in 4-MBA for 4 h. Subsequently, the substrate was dried at room temperature and characterized using Raman spectroscopy.

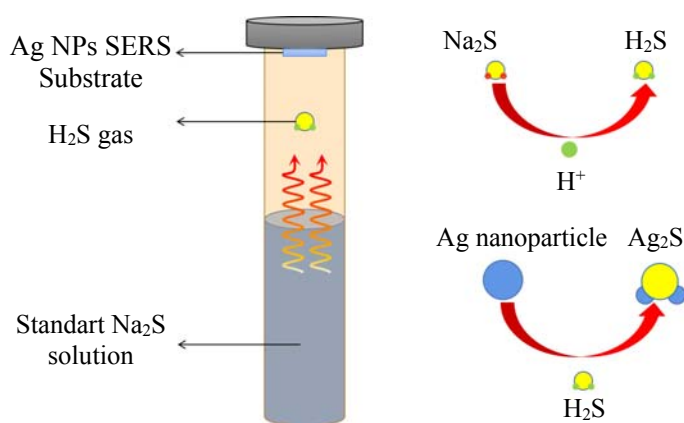


Fig. 1. Schematic of the SERS detection of H_2S based on self-assembled Ag-NP SERS.

Results and discussion. *Characterization of the Ag-NP substrate.* The self-assembled Ag-NP monolayer film coated onto a Si wafer was used as the Ag-NP substrate for detecting H_2S gas. The morphology and structure of the Ag NPs were characterized using field emission scanning electron microscopy (SEM) and ultraviolet and visible (UV) spectroscopy. Figure 2a presents the SEM image of the Ag-NP monolayer film on a Si wafer. The distribution of Ag NPs was observed to be uniform, with a mean diameter of $\sim 35\text{--}45\text{ nm}$. According to previous reports, the uniform spacing between the NPs on the substrate promotes outstanding uniformity [30–33]. Figure 2b presents the UV-Vis absorption spectrum of the Ag-NP solution. The absorption peak was observed at 402 nm , and the half-peak width was 63 nm , indicating a slight difference in particle size among the Ag NPs. The results of characterization were consistent with another study regarding the synthesis of Ag NPs, indicating that the Ag NPs were synthesized successfully [34].

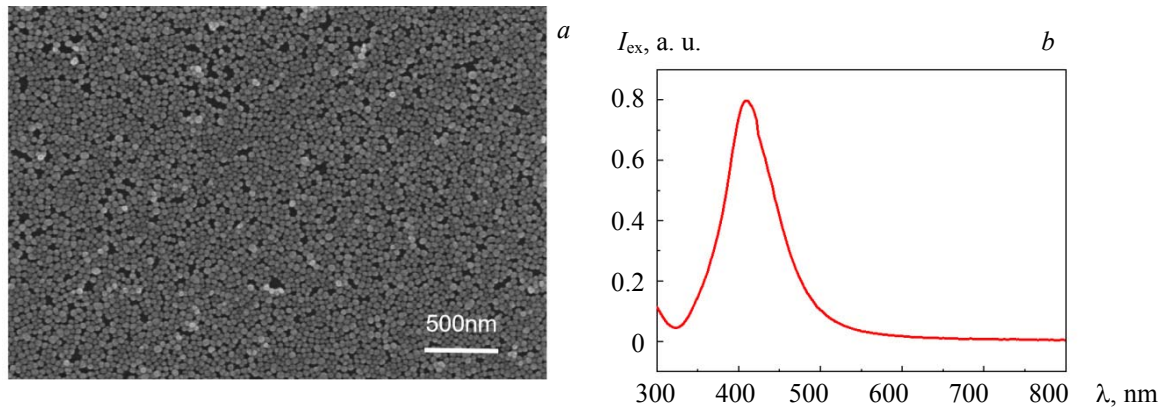


Fig. 2. (a) SEM image of Ag NPs on a Si wafer. (b) Ultraviolet-visible absorption spectrum of Ag NPs.

H_2S detection strategy. A validation experiment was performed to determine if H_2S gas could react with Ag NPs to form Ag_2S . Na_2S was used as the donor of H_2S in the experiment because it is difficult to store and transport H_2S gas. A control group was set up with the same amount of ultrapure water instead of the Na_2S solution, with the other experimental conditions unchanged [35]. Figure 3a shows the SERS spectrum of the 4-MBA (10^{-4} M) probe molecule adsorbed on the Ag NPs without the reaction that generates H_2S gas. The SERS spectrum displayed the characteristic peaks of Ag NPs. The peak at 1073 cm^{-1} was assigned to the C–S stretching vibration. The peak at 1582 cm^{-1} was attributed to the breathing mode of the aromatic ring. Figure 3b shows the SERS spectrum of the 4-MBA (10^{-4} M) probe molecule adsorbed on the Ag NPs after the reaction generating H_2S gas. The Raman intensity of the spectrum presented in Fig. 3b was lower than that shown in Fig. 3a. This shows that the H_2S gas generated from the Na_2S solution reacted with the Ag NPs, thereby reducing the SERS activity. Therefore, the qualitative experiment suggests that the SERS substrate based on self-assembled Ag NPs might be suitable for detecting H_2S gas.

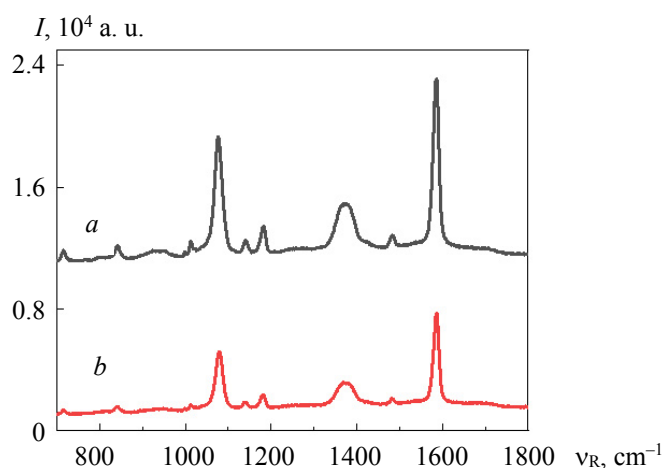


Fig. 3. SERS spectra of the 4-MBA (10^{-4} M) probe molecule adsorbed on Ag NPs (a) before and (b) after the reaction generating H_2S gas.

The uniformity and reproducibility of the SERS signals were evaluated by applying a point-by-point scanning method to a randomly selected large area ($20 \times 20 \mu\text{m}$) using 4-MBA as a probe molecule with a step size of $1 \mu\text{m}$ of Ag-NP substrate [36]. As shown in Fig. 4a, the obtained three-dimensional Raman spectrogram exhibited characteristic peaks of 4-MBA similar to those presented in Fig. 2, and the peak intensities were consistent. A statistical result was obtained by producing a relative SERS intensity map comprising 400 spectra of a randomly selected area on the Ag-NP substrate at 1073 cm^{-1} , as shown in Fig. 4b. Figure 4c presents the corresponding histograms for the SERS peak intensity. The results show that each point has a high ability to enhance the Raman signal of 4-MBA molecules and the Raman intensity of the peak was homogeneous. The calculated relative standard deviation (RSD) of the Raman intensity at 1073 cm^{-1} was 11.6%, suggesting that the prepared Ag-NP substrate might have good uniformity over a large area and may be a promising substrate for high-sensitivity and uniform SERS detection [37].

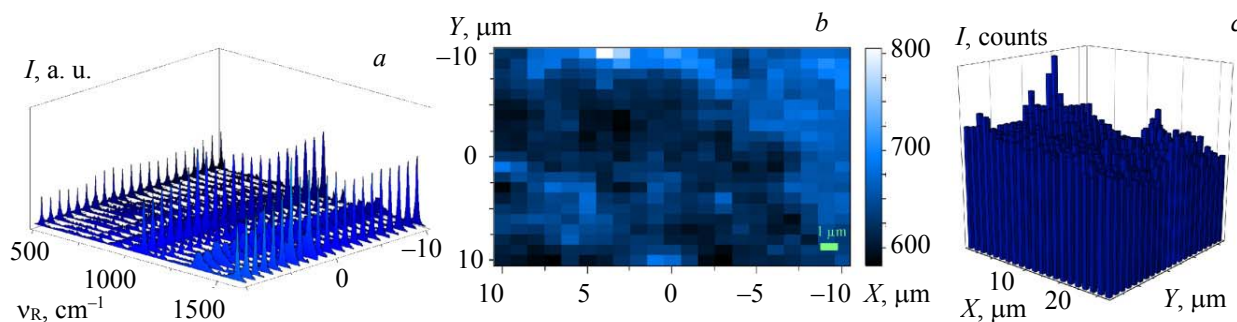


Fig. 4. (a) Three-dimensional SERS spectra of Ag NPs. (b) Relative SERS intensity map of a randomly selected $20 \times 20 \mu\text{m}$ area on Ag-NP substrate at 1073 cm^{-1} . (c) Corresponding histograms for the SERS peak intensity at 1073 cm^{-1} in the abovementioned mapping region.

Quantitative detection of H_2S . The previous section proved that the Ag-NP substrate could be used for the qualitative detection of H_2S gas. Nevertheless, the quantitative detection of H_2S is more important for evaluating the freshness of eggs in practical applications. The content of H_2S gas was determined quantitatively by filling eight $500\text{-}\mu\text{L}$ centrifuge tubes with the Na_2S solutions of different concentrations (0.1, 1, 5, 10, 15, 20, 25, and $30 \mu\text{M}$). According to the previous theoretical calculation, the corresponding content of H_2S produced was 0.03, 0.3, 1.67, 3.3, 5, 6.7, 8.3, and $10 \mu\text{M}$, respectively. The method described above was applied to the SERS measurement. Figure 5a shows the corresponding Raman spectra with different H_2S concentrations. The Raman signal decreased with increasing H_2S concentration. The change was analyzed further by plotting the Raman intensity at 1073 cm^{-1} as a function of the concentration of H_2S (Fig. 5b). The results show that the Raman intensity of 4-MBA decreased with increasing H_2S concentration. However, the rate of change of the Raman strength decreased when the H_2S concentration was greater than $3.3 \mu\text{M}$. This

result may be related to the saturation of H₂S in the Ag-NP substrate. The Raman intensity at 1073 cm⁻¹ was plotted as a function of the H₂S concentration within the range 0.03–3.3 μM (Fig. 5c) and 3.3–10 μM (Fig. 5d). The calibration curves show a good linear relationship between the Raman intensity at 1073 cm⁻¹ and various H₂S concentrations, and the detection limit was as low as 0.03 μM. The linear relationship coefficient was 0.99992 within the range 0.03–3.3 μM and 0.98895 within the range 3.3–10 μM. The linear variation indicates that the proposed SERS sensor is suitable for quantitatively detecting the H₂S-gas content. In particular, the substrate of this sensing platform is a dense monolayer film, which provides numerous “hot spots” for signal enhancement and results in high sensitivity. In addition, the proposed Ag-NP substrate is easy to store and carry and exhibits excellent performance in practical applications.

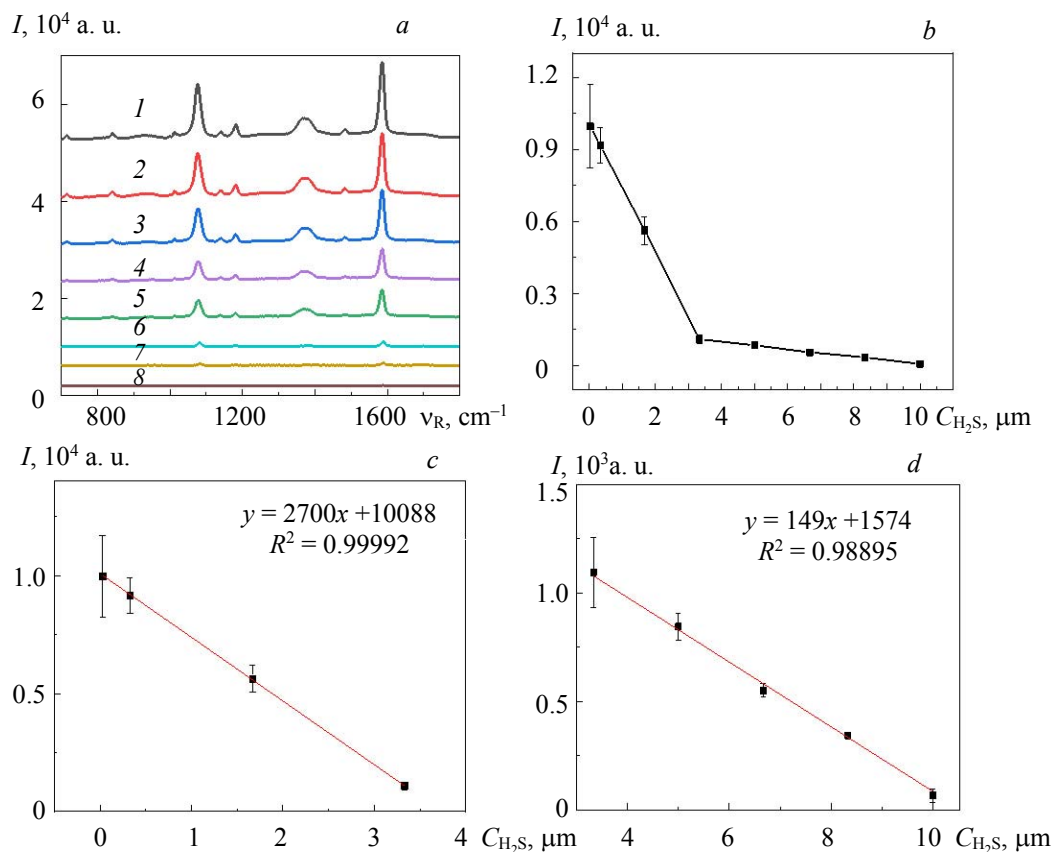


Fig. 5. (a) Enhanced Raman signals of 4-MBA molecule for Ag NPs reacting with different concentrations of H₂S: (1) 0.03, (2) 0.3, (3) 1.67, (4) 3.3, (5) 5, (6) 6.7, (7) 8.3, and (8) 10 μM. (b) Spectral intensity of the Raman spectrum of 4-MBA at 1073 cm⁻¹ with H₂S concentrations ranging from 0.03 to 10 μM. (c) Linear fitting within the H₂S concentration range 0.03–3.3 μM. (d) Linear fitting within the H₂S concentration range 3.3–10 μM.

Repeatability and stability. The repeatability and stability of the substrate are crucial to maintain its sensing properties. The repeatability of the Ag-NP SERS substrate preparation was evaluated by preparing five samples of Ag-NP substrates under different periods with the same preparation conditions. Figure 6a shows the Raman spectra of 4-MBA for the five samples prepared under different periods. Typical Raman bands were observed in the spectra. Figure 6b shows a histogram of the Raman intensity of the samples at 1073 cm⁻¹. The Raman intensity was similar in all five SERS samples, indicating that the prepared Ag-NP substrate has high repeatability. The SERS spectra of newly prepared Ag NPs and those stored in a dark environment at 4°C for 7 and 14 days were compared to determine the stability of the Ag-NP substrate. As shown in Fig. 6c, the intensity of the SERS spectra of the samples stored for different durations did not change drastically (97 and 96% of the initial response at 1073 cm⁻¹ for 7 and 14 days, respectively), suggesting that the proposed Ag-NP substrate has reliable stability [19]. Figure 6d presents a histogram of the Raman intensity of 4-MBA at 1073 cm⁻¹. The Raman intensity of 4-MBA decreased marginally with increasing

storage time. Ag NPs tend to agglomerate with time and decrease the SERS activity. The stability of the prepared Ag-NP substrate was attributed to the effective encapsulation of Ag NPs by PVP.

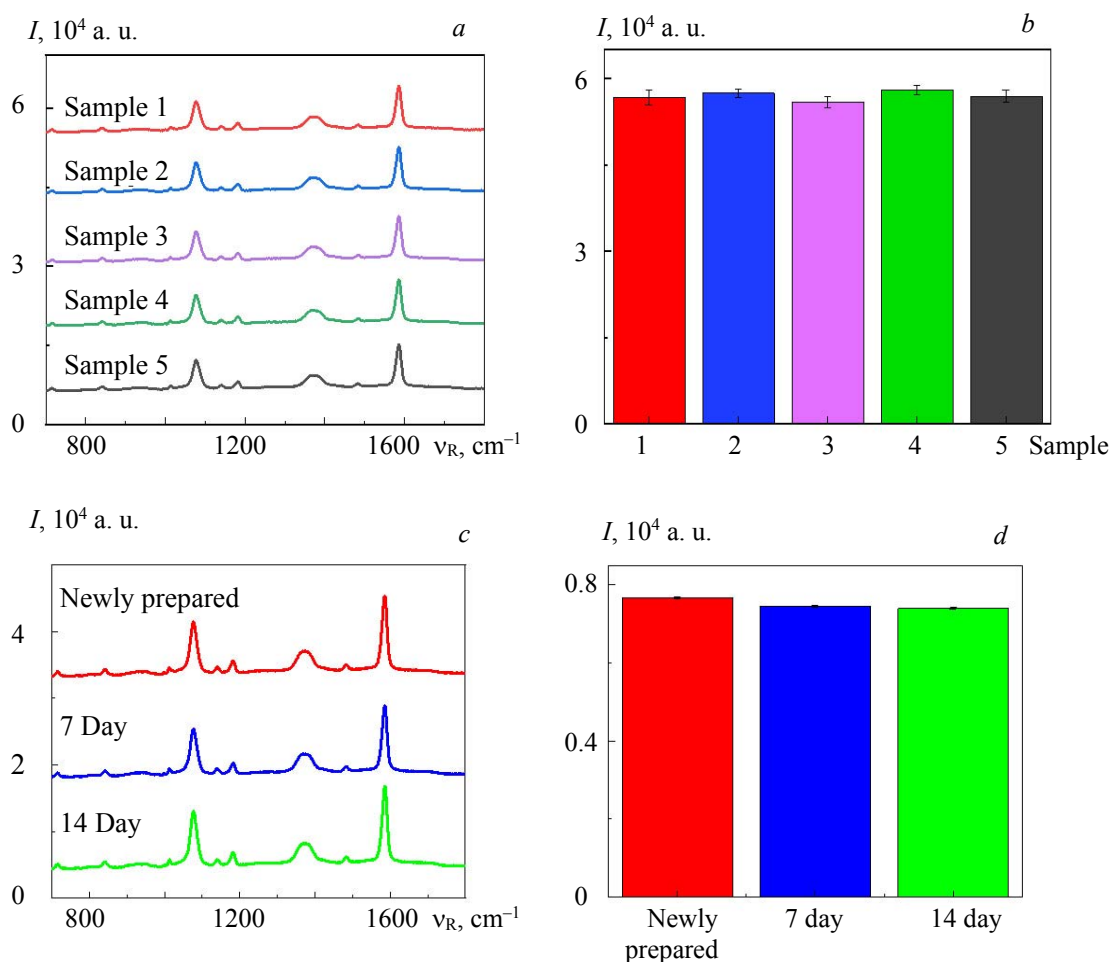


Fig. 6. (a) SERS spectra of 4-MBA under different preparation periods. (b) Histogram of Raman intensity of 4-MBA at 1073 cm^{-1} ; (c) SERS spectra of 4-MBA for the newly prepared substrates and the substrates stored for 7 and 14 days; (d) Histogram of the Raman intensity of 4-MBA at 1073 cm^{-1} .

Labeling experiment of real samples. The possibility of using the prepared Ag-NP substrate for practical application was assessed using eggs as real samples because eggs decompose and produce H_2S gas when stored for a long time. A labeling experiment was performed to eliminate interference factors in eggs during the experiment. A fresh egg albumen and yolk mixture (500 μL) was added into 300 μL of the standard Na_2S solution in 1-mL centrifuge tubes as an experimental set. A control set was prepared by mixing 500 μL of ultrapure water with 300 μL of the standard Na_2S solution. Two concentrations of the standard Na_2S solution (5 and 15 μM , corresponding to the H_2S concentrations of 1.67 and 5 μM , respectively) were prepared to prevent the contingency of the experimental results. Subsequently, SERS substrate was stuck inside the centrifuge tube's cover and the tube was sealed. After the reaction at room temperature for 2 h, the Ag-NP substrate was soaked in a 4-MBA solution (10^{-4} M) for 4 h and dried naturally at room temperature. SERS analysis was performed, and the results are shown in Fig. 7. The Raman intensity of the spectra at low H_2S concentration was considerably higher than that at high H_2S concentration. However, the Raman intensity of the spectra was similar in the experimental and control sets at the same H_2S concentration. In addition, the Raman peak positions did not shift. This indicates that the substances in eggs have no influence on H_2S detection, and the SERS sensor platform established in this work has the potential to detect rotten eggs.

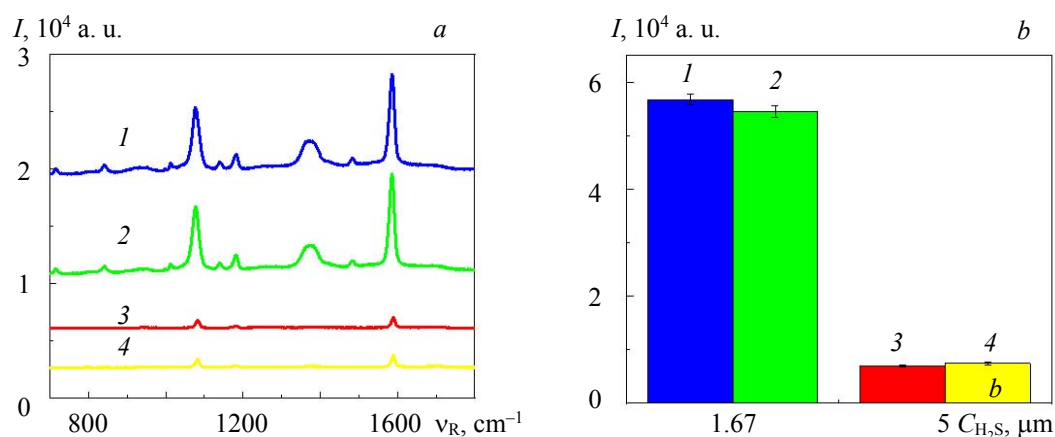


Fig. 7. (a) SERS spectra of 4-MBA of (1) fresh egg and H_2S (1.67 μM), (2) ultrapure water and H_2S (1.67 μM), (3) fresh egg and H_2S (5 μM), and (4) ultrapure water and H_2S (5 μM). (b) Histogram of the relative Raman intensity at Raman displacement (1073 cm^{-1}).

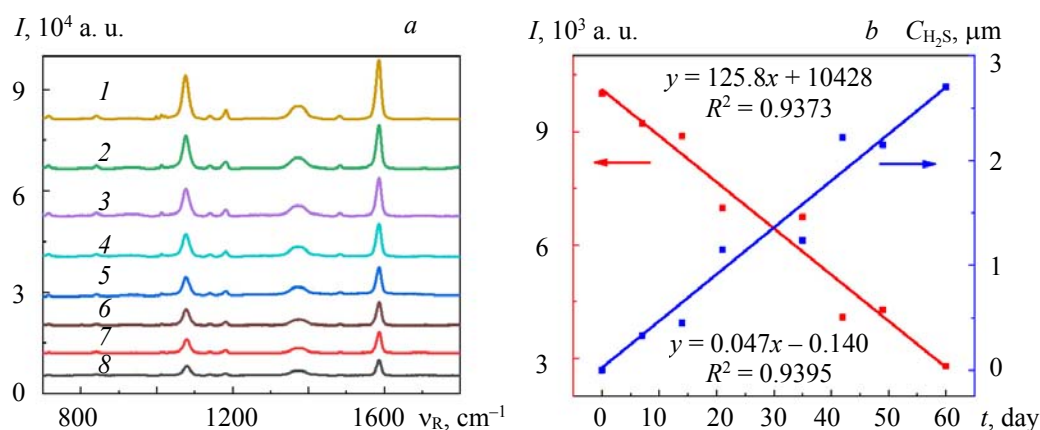


Fig. 8. (a) SERS spectra of 4-MBA of (1) fresh eggs and the eggs stored for (2) 7, (3) 21, (4) 28, (5) 35, (6) 42, (7) 49, and (8) 60 days. (b) Histogram of Raman intensity at Raman displacement (1073 cm^{-1}).

Detection of rotten eggs. To further verify the feasibility and functionality of the SERS sensor platform, fresh and rotten eggs with different H_2S concentrations were tested. The mixture of the fresh eggs and eggs stored for 7, 21, 28, 35, 42, 49, and 60 days were added to 50-mL centrifuge tubes. The centrifuge tubes were then sealed with SERS substrate stuck inside the centrifuge tube's cover, and the H_2S gas produced by the rotten eggs started to react with the Ag NPs for 2 h. Subsequently, the Ag-NP substrates were soaked in a 4-MBA solution for 4 h and dried naturally at room temperature. Finally, SERS analysis was performed. Figure 8a shows the SERS spectra of 4-MBA of fresh eggs and the eggs stored for 7, 21, 28, 35, 42, 49, and 60 days. The Raman peak positions of all the samples were the same, indicating that the conditions for Raman detection are appropriate. The amount of H_2S gas released to react with the Ag NPs increased with increasing egg storage time, weakening the Raman intensity. Figure 8b shows the Raman intensity and H_2S concentration as a function of egg storage time. Two sets of points could be fitted linearly with a regression coefficient of ~ 0.94 . The storage time of eggs could be estimated easily by measuring the Raman intensity at 1073 cm^{-1} . Hence, the proposed Ag-NP substrate based on self-assembled Ag NPs has a good ability to evaluate the freshness of eggs quantitatively in practical applications.

Conclusions. A SERS sensor based on self-assembled Ag NPs was designed to detect endogenous H_2S in rotten eggs. The proposed Ag-NP SERS substrate showed good uniformity, repeatability, and stability. The calculated RSD of the Raman intensity of 4-MBA molecules at 1073 cm^{-1} over a large area was 11.6%. Because H_2S gas reacts with Ag NPs, the SERS activity is reduced; qualitative and quantitative analyses were conducted to verify the feasibility of the experiment. The results showed a good linear relationship between the Raman intensity at 1073 cm^{-1} and the H_2S concentrations. The linear relationship coefficient was 0.99992 within the range 0.03–3.3 μM and 0.98895 within the range 3.3–10 μM . Real eggs were chosen

as experimental samples for demonstrating practical applications of the Ag-NP substrate because rotten eggs decompose and produce H_2S gas. A labeling experiment was performed to eliminate interference factors in eggs during the experiment. The experiment showed a linear relationship between the Raman peak intensity and the storage time of eggs. The freshness of eggs could be estimated by measuring the Raman intensity at 1073 cm^{-1} . Preliminary experiments demonstrated the potential of the Ag-NP SERS sensor for detecting rotten eggs in practical applications.

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