



A colorimetric POCT mediated by poly(tannic acid)-capped AgNPs for the detection of hazardous H₂S: Applications in meat spoilage monitoring and halitosis diagnosis

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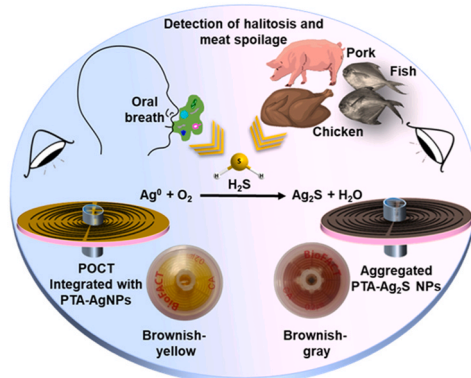
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HIGHLIGHTS

- The POCT device integrated with PTA-AgNPs enables lab-independent, on-site detection of H₂S.
- The POCT allows naked-eye detection of H₂S through a brown-yellow to brown-gray color change.
- The PTA-AgNPs nanoprobe exhibits high sensitivity toward H₂S.
- The method enables real-time colorimetric monitoring of meat freshness via H₂S detection.
- The sensor allows non-invasive breath analysis of H₂S for halitosis and clinical diagnostics.

GRAPHICAL ABSTRACT

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ARTICLE INFO

Keywords:

Poly(tannic acid)
Silver nanoparticles
POCT
Hydrogen sulfide
Halitosis

ABSTRACT

This study proposes a novel hydrophilic point-of-care testing (POCT) integrated with poly(tannic acid)-capped silver nanoparticles (PTA-AgNPs) designed to facilitate the naked-eye detection of hydrogen sulfide (H₂S) in food and human breath. We synthesize PTA-AgNPs using a handheld syringe filter by combining tannic acid, which serves as both a reducing and capping agent, with silver nitrate as the source of metal ions. Herein, a cellulose acetate syringe filter served as the substrate, facilitating the on-site surface dispersion of PTA-AgNPs. The PTA-AgNPs exhibit high stability, optical sensitivity, and selectivity, making them an effective probe for the spectrophotometric, colorimetric, and naked-eye detection of H₂S in both aqueous and gaseous media. Upon exposure to H₂S, the PTA-AgNPs underwent a visible color change from brownish-yellow to brownish-gray, attributed to the aggregation of PTA-AgNPs and the formation of silver sulfide nanoparticles. The calculated limit of detection is approximately 24.2 nM, while the limit of quantitation is 125 nM. Furthermore, we employ the POCT kits to monitor bacterial spoilage in protein-rich foods, such as fish, pork, and chicken, as well as for halitosis diagnosis by detecting H₂S in human breath. The POCT integrated with PTA-AgNPs shows potential as a

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<https://doi.org/10.1016/j.jhazmat.2025.138323>

Received 4 February 2025; Received in revised form 13 April 2025; Accepted 16 April 2025

Available online 16 April 2025

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convenient tool for developing practical biosensors to monitor bacterial growth in clinical, food industry, and environmental applications.

1. Introduction

In today's fast-paced world, the rapidly increasing demand has driven significant advancements in point-of-care testing (POCT) kits owing to their versatile applications in environmental monitoring, healthcare diagnostics, and food analysis [1,2]. Recent studies highlight the potential of paper-based platforms for rapid and on-site analysis with advances in microfluidic design and substrate-enhanced fluorescence, enabling sensitive detection of environmental and food contaminants [3,4]. Noble metal nanomaterials (NMNs) including those based on Ag, Au, Cu, Pt, and Pd have garnered significant attention in developing POCT kits due to their unique surface plasmon resonance (SPR) properties, enabling the manufacture of simple, cost-effective, and highly sensitive colorimetric detection platforms [5,6]. Silver nanoparticles (AgNPs) have strong plasmonic bands, yellow coloration, chemical stability, and high conductivity. These properties make them widely applicable in food storage, sensor development, and the textile industry [7,8]. However, spectroscopy-reliant AgNPs detection methods often depend on laboratory-based synthesis, costly instrumentation, and trained personnel, which limit their practicality for real-time or on-site applications. Recently, a promising alternative has emerged involving the regulation of AgNPs dispersions on solid substrates, facilitating the development of accessible and efficient POCT platforms for diverse naked-eye detection applications [9]. For example, Teengam et al. developed a multiplex paper-based colorimetric DNA sensor using pyrrolidyl peptide nucleic acid-induced AgNPs aggregation for the detection of MERS-CoV, MTB, and HPV oligonucleotides, while Zhang et al. reported a carbon dot-functionalized paper coupled with AgNPs composites as a sensor for hydrogen peroxide detection via SPR-enhanced energy transfer [5,6].

Hydrogen sulfide (H_2S) is a smelly, sulfur-containing gas that affects public health, harms the environment, and even causes food to spoil. It is also a major environmental pollutant contributing to acid rain and posing health risks such as liver damage, Alzheimer's disease, and Down syndrome [10–12]. The World Health Organization recommends the H_2S levels in drinking water must not exceed 0.05 mg/L [10–12]. In healthcare, the H_2S level in exhaled breath acts as an indicator of oral health issues, including halitosis and periodontal disease. Approximately 20 % of the population suffers from halitosis on a daily basis, while nearly 50 % experience it at least once in their lives [13,14]. In food chemistry, bacterial metabolism generates H_2S during the spoilage of protein-rich foods, such as seafood and meat. Sulfur-containing amino acids such as methionine, cysteine, and glutathione are degraded by anaerobic bacteria, including *Clostridium*, *Shewanella*, and *Desulfovibrio*, leading to the production of H_2S , which is the primary contributor to the foul odor of spoiled food [15,16].

Currently, few standard methods available for detecting H_2S include high-performance liquid chromatography [17], atomic absorption spectrometry [18], spectrofluorometry [19], cyclic voltammetry [20], ultraviolet-visible (UV-Vis) spectrophotometry [21], and portable gas chromatography (Oral Chroma) [22] are often very expensive, time-consuming, and equipment-dependent. Electrochemical techniques are also used for a sensitive and selective detection of acetone, ammonia, and H_2S in breath samples [23–25]. However, these methods are highly sensitive to environmental factors such as temperature and humidity, which can affect their accuracy and reliability. To overcome these limitations, we introduce a novel and user-friendly POCT kits integrated with poly(tannic acid)-capped AgNPs (PTA-AgNPs), fabricated directly on-site using tannic acid (TA) and silver nitrate (AgNO_3) within a cellulose acetate (CA) syringe filter. TA, a natural polyphenol, serves as both a capping and reducing agent due to its strong metal-ligand

interactions and antioxidant properties. The key innovation of present POCT kits ability to be prepared instantly on-site without laboratory support and its ability to detect H_2S through visible color changes make it ideal for a real-world, naked-eye, and on-site detection. This study offers significant contributions by providing a green, low-cost, and practical POCT kits for the detection of H_2S in both food and breath samples.

2. Materials and methods

2.1. Reagents and chemicals

Tannic acid ($\geq 98\%$), silver nitrate ($\geq 99.999\%$), gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.995\%$), and copper (II) chloride (CuCl_2 , $\geq 99.999\%$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). We purchased ethanol (EtOH), isopropyl alcohol (IPA), acetone (Ace), sodium hydroxide (NaOH), and hydrochloric acid (HCl) from Daejung Chemicals & Metals (Gyeonggi-do, ROK). Formamide (CH_3NO) was obtained from Junsei Chemical Co., Ltd. (Tokyo, Japan), while 2, 2, 2-trifluoroethanol (TFE), ammonia (NH_3), and methanol (MeOH) were purchased from Merck (Darmstadt, Germany). Toluene (PhCH_3), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), sodium sulfide (Na_2S), acetic acid (AcOH), N,N-dimethylformamide (DMF), disodium phosphate (Na_2HPO_4 , $\geq 98\%$), and monosodium phosphate (NaH_2PO_4 , $\geq 99\%$) were acquired from Sigma-Aldrich. A 0.2 M phosphate buffer solution with a pH range of 1–12 was prepared using NaH_2PO_4 and Na_2HPO_4 , with the pH adjusted using NaOH and HCl.

2.2. Synthesis of PTA-AgNPs

Scheme S1a illustrates the schematic procedure for the in situ synthesis of PTA-capped PTA-AgNPs using aqueous TA and AgNO_3 . Initially, 5 mL of 1 mM TA solution was added to a 25 mL glass vial. The pH of the solution was adjusted to 8.0 by the addition of 15 μL of 0.1 M NaOH, followed by stirring at 28 °C for 5 min at 500 RPM. A color change from colorless to light yellow indicated the successful self-polymerization of TA, resulting in the formation of poly(tannic acid) nanoparticles (PTA NPs). Subsequently, 5 mL of 5 mM AgNO_3 solution was added to the reaction mixture, which was further stirred under identical conditions (28 °C, 5 min, 500 RPM). The observed color change from light yellow to brownish-yellow confirmed the formation of PTA-AgNPs. The NaNO_3 by-product was removed by dialysis purification using deionized water.

The numerous hydroxyl groups in TA readily undergo oxidation, converting them into Quinone structures at a basic pH. The Quinone form of TA undergoes sequential reactions, including oxidation, decarboxylation, and aldehyde formation. These reactive intermediates facilitate crosslinking between near TA molecules via covalent bonding, leading to the formation of PTA NPs. The self-polymerization mechanism responsible for forming PTA NPs under basic conditions is depicted in Scheme S1b [26–28]. The PTA NPs act both as a non-toxic reducing agent and a stabilizing agent in combination with AgNPs [29,30].

2.3. Synthesis of PTA-AuNPs and PTA-CuNPs

PTA-capped gold nanoparticles (PTA-AuNPs) and PTA-capped copper nanoparticles (PTA-CuNPs) were synthesized following a similar protocol. Initially, 2 mL of 1 mM TA solution was added to a 25 mL glass vial. The pH of the solution was adjusted to 8.0 by adding 15 μL of 0.1 M NaOH, followed by stirring at 28 °C for 5 min at 500 RPM (Scheme S1a). Separate vials were used for the synthesis of PTA-AuNPs and PTA-CuNPs. To one vial, 2 mL of 5 mM HAuCl_4 solution was added, and to

the other, 2 mL of 5 mM CuCl_2 solution was introduced. Both mixtures were stirred under identical conditions (28 °C for 5 min). The appearance of a wine-red color in the HAuCl_4 -containing solution and a light yellow color in the CuCl_2 -containing solution indicated the successful formation of PTA-AuNPs and PTA-CuNPs, respectively (Scheme S1b). The resulting NaCl by-product was removed through dialysis purification using deionized water.

2.4. Instruments and characterization

Absorption spectral analysis was performed using a UV-visible/NIR spectrophotometer (V-770, JASCO, Hachioji, Tokyo, Japan) across a wavelength range of 200–800 nm to characterize the starting materials and nanoparticles (NPs). The UV-Vis absorption spectra were recorded using an Epoch microplate spectrophotometer (Sulim Science, Seoul, ROK) in the wavelength range of 300–700 nm for applications. High-resolution X-ray diffraction (HR-XRD) was performed using a SmartLab diffractometer (Rigaku Corporation, Neu-Isenburg, Germany) operating at 40 kV with Cu-filtered $\text{K}\beta$ radiation ($\lambda = 1.5406 \text{ \AA}$). The scan range was 10° – 80° with a scan speed of $2^\circ/\text{min}$. High-resolution transmission electron microscopy (HR-TEM) was performed using a JEM-F200 microscope (JEOL, Akishima, Tokyo, Japan) operating at an accelerating voltage of 300 kV. Fourier-transform infrared (FT-IR) spectra of the TA, PTA, and PTA-AgNPs were conducted using an FT-IR spectrometer (FT/IR-4700, JASCO, Hachioji, Tokyo, Japan).

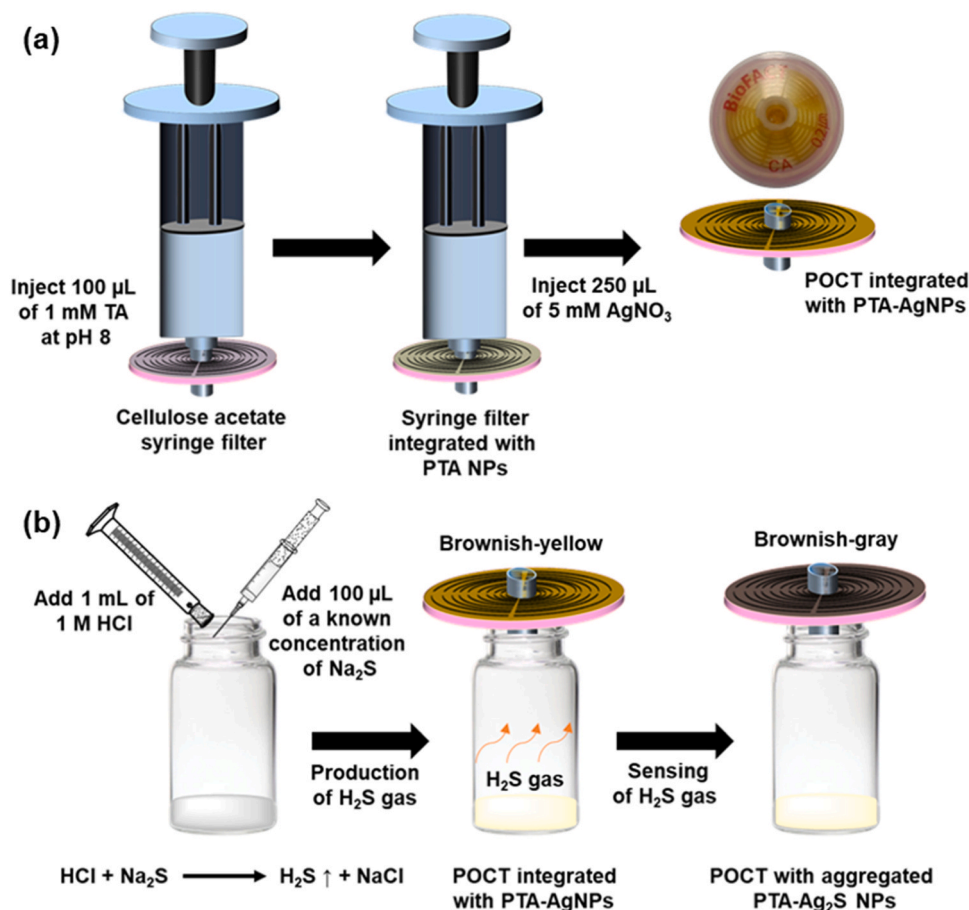
2.5. Spectrophotometric and colorimetric detection of H_2S in an aqueous medium

The H_2S was detected in the aqueous medium was performed by spectrophotometric and colorimetric methods as follows: 20 μL of purified PTA-AgNPs solution (15.4 nM) and 180 μL of phosphate buffer (pH 8) were sequentially added to a 300 μL 96-well microplate. Different concentrations of Na_2S were dissolved in H_2O to produce aqueous H_2S , which was introduced into the PTA-AgNPs solution. Variations in absorbance were monitored using a microplate reader after a 3 min incubation at room temperature (28 °C). A similar procedure was conducted using 2.5 mL centrifuge tubes, allowing for the visual observation of color changes in the solution. A linear relationship plot was constructed by plotting the concentration of H_2S against the relative absorbance values ($\Delta A = A_x - A_0$), where A_x is the absorbance of PTA-AgNPs in the presence of H_2S , and A_0 is the baseline absorbance of PTA-AgNPs in the absence of H_2S . The limit of quantitation (LOQ), or quantitation limit, is defined as the lowest concentration of H_2S that can be quantitatively determined with acceptable precision and accuracy [31]. The limit of detection (LOD) for H_2S was calculated using Eq. 1, where S denotes the standard deviation of the blank signal (PTA-AgNPs), and m represents the slope of the calibration curve.

$$\text{LOD} = 3S/m \quad (1)$$

2.6. In-situ preparation of POCT devices for naked-eye detection of H_2S in the gas phase

Scheme 1a depicts the on-site fabrication of the POCT integrated with PTA-AgNPs using a hand-held syringe filter. The CA syringe filters



Scheme 1. (a) Schematics representation of the fabrication of the point-of-care testing (POCT) integrated with poly(tannic acid)-capped silver nanoparticles (PTA-AgNPs). (b) Sensing of hydrogen sulfide (H_2S) gas using the POCT integrated with PTA-AgNPs.

(diameter: 0.25 mm) were obtained from BioFACT (Daejeon, South Korea). The process starts by injecting 100 μL of a 1 mM TA solution (pH 8) into a CA syringe filter using a hand-held syringe. Under these basic conditions, TA undergoes oxidation and self-polymerization, leading to the formation of PTA NPs on the CA filter. Subsequently, 250 μL of a 5 mM AgNO_3 solution was added to the PTA NPs-coated syringe filter. The PTA NPs serve as both reducing and stabilizing agents, facilitating the formation of AgNPs. Finally, the POCT integrated with PTA-AgNPs dried at room temperature (28 $^\circ\text{C}$) for 60 min.

A 10 mL glass vials used to generate H_2S gas, as outlined in Scheme 1b. The Na_2S solutions of varying concentrations were added to vials, each containing 1 mL of 1 M HCl. The reaction between HCl and Na_2S results in the production of H_2S gas. We assumed the Na_2S was fully converted to H_2S gas and the Na_2S concentration was considered equivalent to the H_2S concentration in each sensing analysis. After adding the Na_2S solutions, the vials were sealed with the POCT integrated with PTA-AgNPs. The H_2S gas interacts with the POCT integrated with PTA-AgNPs, inducing a visible color change. Similarly, POCT integrated with PTA-AuNPs and PTA-CuNPs was developed using a 1 mM TA solution (pH 8) applied to CA syringe filters with hand-held syringes. A 250 μL of HAuCl_4 solution was introduced into the syringe filter to fabricate the POCT integrated with PTA-AuNPs, while 250 μL mL of CuCl_2 solution was added to fabricate the POCT integrated with PTA-CuNPs.

2.7. Naked-eye detection of H_2S gas in real samples

Scheme S2a illustrates the naked-eye detection of H_2S in oral breath samples using the POCT integrated with PTA-AgNPs. Human breath samples were collected from three volunteers (two samples each) by exhaling mouth air into 200 mL Ziploc plastic bags. Using a 10 mL syringe, the breath air was collected from the Ziploc plastic bag and transferred through a POCT integrated with PTA-AgNPs. Additionally, H_2S was spiked into the second set of Ziploc plastic bags and used for detection. The color changes were observed after 3 min, indicating the levels of H_2S gas.

Scheme S2b illustrates the naked-eye detection of H_2S in fish, pork, and chicken samples using the POCT integrated with PTA-AgNPs. Fresh fish, pork, and chicken were purchased from a local market, transported in a clean environment and stored at 4 $^\circ\text{C}$. Approximately 2.5 g of each meat was placed in a glass vial and incubated at 37 $^\circ\text{C}$ for five days (d). The vials were sealed using POCT integrated with PTA-AgNPs and bacterial growth within the meat samples gradually produced H_2S gas. The presence of H_2S induces the aggregation of the POCT integrated with PTA-AgNPs, leading to a color change. The color changes of the POCT kits were photographed at intervals of 24 h to quantify the H_2S levels.

2.8. H_2S detection via smartphone RGB

Sections 2.5 and 2.6 describe the use of both PTA-AgNPs solution and a POCT integrated with PTA-AgNPs for detecting H_2S in liquid and

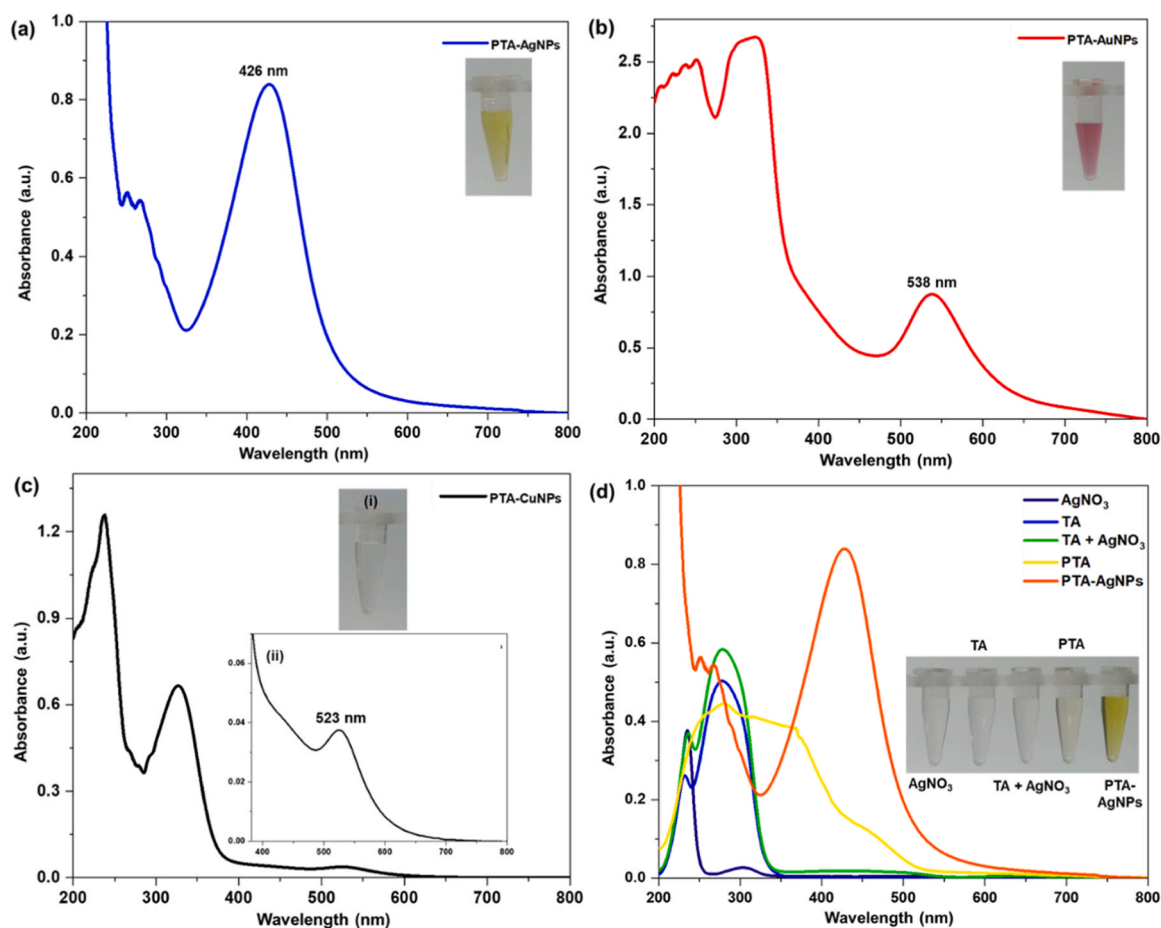


Fig. 1. Ultraviolet-visible (UV-Vis) spectra of (a) PTA-AgNPs, (b) poly(tannic acid)-capped gold nanoparticles (PTA-AuNPs), and (c) poly(tannic acid)-capped copper nanoparticles (PTA-CuNPs). Insets in (a) and (b) show the respective photographs. Inset in (c) i and ii show the photograph and magnified spectrum of PTA-CuNPs. (d) UV-Vis spectra of silver nitrate (AgNO_3), tannic acid (TA), and a mixture of TA with AgNO_3 , PTA, and PTA-AgNPs. Inset in (d) shows the corresponding photographs.

gaseous media. Different concentrations of H_2S were introduced into either the PTA-AgNPs solution or the POCT kits. Images of the resulting color changes were captured using an OPPO F15 smartphone equipped with a 48-megapixel camera. These images were used to analyze by Color Grab App (version 3.9.2, Loomatix) to collect RGB values. The H_2S concentration was subsequently estimated based on the changes in the RGB/R metrics.

3. Results and discussion

3.1. Absorption spectra of the PTA-AgNPs, PTA-AuNPs, and PTA-CuNPs

The synthesized PTA-AgNPs, PTA-AuNPs, and PTA-CuNPs solutions exhibit unique absorption spectra. As shown in Fig. 1a, the UV-Vis spectrum of the brownish-yellow PTA-AgNPs solution displays an SPR band at 426 nm. Fig. 1b illustrates the UV-Vis spectrum of the wine-red PTA-AuNPs solution, which exhibits an SPR peak at 538 nm. Fig. 1c and inset respectively show the UV-Vis spectrum of the PTA-CuNPs solution, with an SPR band at 523 nm and the appearance of the light-yellow solution. Notably, CuNPs are highly prone to rapid oxidation upon exposure to O_2 , which often leads to PTA-CuNPs aggregation. TA effectively acts as both a reducing and stabilizing agent for PTA-AgNPs and PTA-AuNPs. However, it is less effective in stabilizing PTA-CuNPs [32,33].

Fig. 1d presents the UV-Vis absorption spectra of AgNO_3 , TA, a TA and AgNO_3 mixture, PTA, and PTA-AgNPs. The spectrum of AgNO_3 shows an absorption peak at 234 nm, while the spectrum of TA exhibits maxima at 232 nm and 277 nm. The spectrum of the TA and AgNO_3 mixture shows peaks at 235 nm and 278 nm, while the spectrum of PTA exhibits peaks at 277 nm and 367 nm. Remarkably, when PTA was

combined with AgNO_3 to form PTA-AgNPs, an SPR band appeared at 426 nm. Only the PTA-AgNPs solution appears brownish-yellow, while the other solutions remain colorless. The formation of PTA-AgNPs was preliminarily confirmed by the appearance of the brownish-yellow color and the SPR band.

Similarly, Figure S1 presents the UV-Vis absorption spectra of HAuCl_4 , TA, a mixture of TA and HAuCl_4 , PTA, and PTA-AuNPs, with the corresponding solution photographs shown in the inset. The spectrum of yellow-colored HAuCl_4 displays absorption peaks at 246 nm and 293 nm. Upon mixing with TA, the yellow-brown HAuCl_4 -TA solution shows peaks at 231 nm and 286 nm, indicating interaction between the components. Figure S2 shows the UV-Vis absorption spectra of CuCl_2 , TA, a mixture of TA and CuCl_2 , PTA, and PTA-CuNPs, with the corresponding photographs also shown in the inset. The spectrum of colorless CuCl_2 exhibits a peak at 208 nm, while the CuCl_2 -TA mixture displays additional peaks at 208, 232, and 327 nm, reflecting complex formation. Notably, the absorption features and colors of these intermediate mixtures differ significantly from those of the final PTA-AuNPs and PTA-CuNPs, further confirming nanoparticle formation through distinct optical and visual changes.

Figures S3 and S4 present the UV-Vis spectra and photographs of freshly prepared PTA-AgNPs, captured over 80 d to evaluate nanoparticle stability. The PTA-AgNPs sample appears brownish-yellow and exhibits an SPR band at 426 nm. Remarkably, the PTA-AgNPs sample aged for 80 d maintains a consistent color, absorbance, and wavelength compared to the freshly prepared samples, indicating that the PTA-AgNPs remain stable for over 80 d.

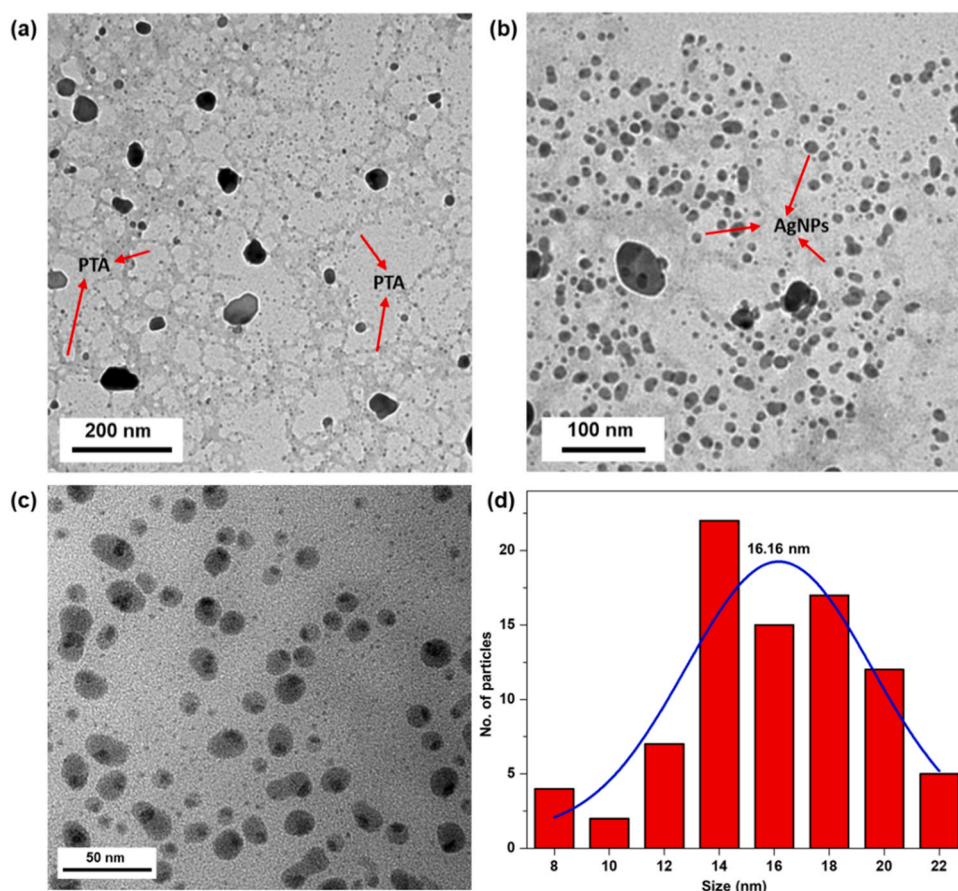


Fig. 2. High-resolution transmission electron microscopy (HR-TEM) images of the PTA-AgNPs at magnifications of (a) 200, (b) 100, and (c) 50 nm. (d) Particle size distribution histogram.

3.2. Morphology, shape, and size analyses of the PTA-AgNPs

Fig. 2a, b, c show HR-TEM images of the PTA-AgNPs at respective magnifications of 200, 100, and 50 nm. The synthesized PTA-AgNPs are observed as spherical, chain-linked PTA NPs and spherical, monodisperse AgNPs, as depicted in the HR-TEM images shown in Fig. 2a, b, c. Fig. 2d presents a histogram of the particle size distribution derived from the TEM images. The average diameter of the AgNPs is 16.16 nm, calculated using ImageJ software (National Institutes of Health, Bethesda, MD, USA) [7,34].

Fig. 3a displays the HR-XRD pattern of the PTA-AgNPs within the 20 range of 10°–80°. The crystalline nature and particle diameters of the AgNPs were determined using HR-XRD. Four prominent signals were observed at $2\theta = 38.12^\circ$, 44.3° , 64.45° , and 77.35° , corresponding to AgNPs and aligning well with the Joint Committee on Powder Diffraction Standards (JCPDS) card number 00–004-0783 (Fig. 3b). These four signals closely align with the JCPDS reference values and planes: 38.11° (111), 44.3° (200), 64.44° (220), and 77.4° (311), confirming the face-centered cubic (fcc) atomic arrangements and the well-ordered crystalline nature of the AgNPs [7,35].

XRD analysis reveals that the (111) plane of the PTA-AgNPs exhibits the highest intensity at 38.12° , with the calculated intensity ratio of the (111) to (200) planes being $3.7 > 1$. Hence, the crystal lattice arrangement is predominantly oriented along the (111) plane. The average diameter of the PTA-AgNPs was calculated using the full width at half maximum (FWHM) of the (111) plane and the Scherrer equation (Eq. 2)

[36].

$$D = (k\lambda)/(\beta \cos \theta) \quad (2)$$

The variables k , θ , β , λ , and D correspond to the Scherrer constant, the diffraction angle, the FWHM of the (111) plane, the X-ray wavelength, and the crystallite size of the AgNPs, respectively. The average diameter of the PTA-AgNPs was calculated to be 19.12 nm using Eq. 2. The size was consistent with the particle size observed using HR-TEM, which measured the particles to be approximately 16.16 nm in diameter. HR-TEM and HR-XRD confirm the nanoscale sizes, spherical morphologies, and fcc atomic arrangements, verifying the crystalline nature of the PTA-AgNPs.

3.3. Determination of the average number and molar concentrations of PTA-AgNPs

The average number of Ag atoms per nanoparticle was determined using HR-TEM and HR-XRD. The calculation was performed using Eq. 3 [37,38].

$$N = \frac{\pi \rho D^3}{6M} N_A \quad (3)$$

Fig. 2 presents the HR-TEM images of the PTA-AgNPs. As measured using the ImageJ software, the average diameter of the AgNPs (D) is 16.16 nm (16.16×10^{-7} cm). Assuming a spherical shape and uniform fcc structure based on the XRD pattern (Fig. 3), the average number of Ag atoms per NPs (N) is 130,284. This calculation utilizes the density of fcc Ag ($\rho = 10.5$ g/cm³), atomic mass of Ag ($M = 107.868$ g/mol), Avogadro's number ($N_A = 6.023 \times 10^{23}$), and $\pi = 3.14$. The molar concentration of the PTA-AgNPs was calculated using Eq. 4. [37,38]

$$C = \frac{N_T}{NVN_A} \quad (4)$$

The concentration of AgNPs (C) was calculated assuming the 100 % conversion of Ag⁺ to AgNPs. N , N_A , V , and N_T respectively represent the number of atoms per NPs (130,284), Avogadro's number (6.023×10^{23}), the volume of the reaction solution (in L), and total number of Ag atoms (0.002). Based on these parameters, the molar concentration of the PTA-AgNPs was calculated to be 15.4 nM

3.4. Vibrational spectral analysis of TA, PTA, and PTA-AgNPs

The FT-IR spectra of TA, PTA, and the PTA-AgNPs are shown in Figure S5. In the FT-IR spectrum of TA, several notable peaks were observed: the stretching vibrations of OH and CH were observed at 3317 and 2924 cm⁻¹, respectively. The peaks at 1706 and 1610 cm⁻¹ correspond to the C=O stretching vibration, while the stretching frequencies at 1528 and 1449 cm⁻¹ indicate the presence of aromatic carbon-carbon bonds, corresponding to C=C and C-C stretching vibrations, respectively. Additionally, phenolic C-O symmetric stretching was observed at 1328 and 1199 cm⁻¹ [39–43].

The FT-IR spectrum of PTA displays the characteristic functional groups of TA. It displays peaks at 3382, 2957, 1731, 1586, 1508, 1411, 1369, and 1203 cm⁻¹, representing OH, CH, C=O stretching, aromatic C=C, aromatic C-C bonds, and phenolic C-O, respectively. The intensities of the peaks at 3382, 1731, 1586, 1369, and 1203 cm⁻¹ differ from those in the spectrum of TA, indicating the formation of the polymeric PTA NPs. TA exhibits strong intramolecular hydrogen bonding due to its abundance of phenolic hydroxyl groups. During oxidative self-polymerization, the OH and C=O groups of TA participate in the formation of new covalent linkages, such as C-C and C-O-C bonds, resulting in a decrease in the number of free OH groups and a reduction in hydrogen bonding interactions. As a result, a distinct blue shift was observed in the O-H stretching vibration (Figure S5) [44–46]. The FT-IR spectrum of PTA-AgNPs reveals functional groups similar to those of PTA. The peaks at 3593, 2949, 1748, 1615, 1507, 1427, 1382,

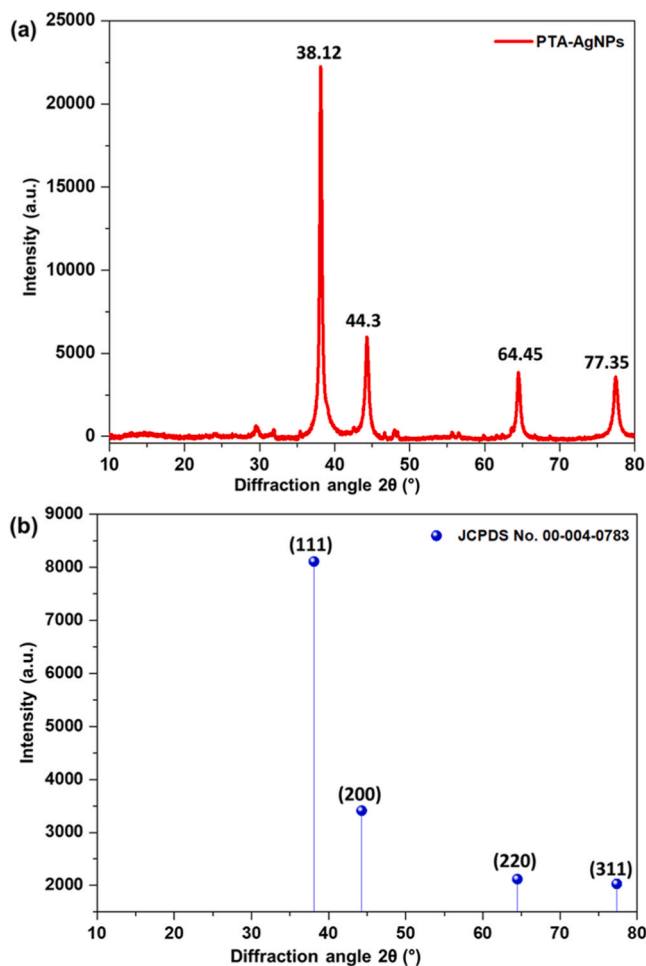


Fig. 3. (a) High-resolution X-ray diffraction (HR-XRD) pattern of the PTA-AgNPs. (b) Joint Committee on Powder Diffraction Standards (JCPDS) card for AgNPs (00–004-0783).

and 1228 cm^{-1} represent OH, CH, C=O stretching, aromatic C=C, aromatic C-C bonds, and phenolic C-O, respectively. Notably, the OH stretching frequency shifts from 3382 cm^{-1} in the spectrum of PTA to 3593 cm^{-1} , suggesting interactions between the OH groups and the surfaces of the AgNPs [39–43]. These interactions indicate that the phenolic OH groups serve as reducing, steric, and electrostatic stabilizing agents for PTA-AgNPs.

3.5. Optimization of reaction conditions: effect of pH, precursor concentration, synthesis time, and incubation time

Figures S6 and S7 present the UV–Vis absorbance spectra and corresponding images of the synthesized PTA-AgNPs across a broad pH ranges from 1 to 12. The SPR properties of the PTA-AgNPs are highly sensitive to the pH of the reaction medium, exhibiting distinct optical and morphological changes throughout the tested range. This pH-dependent behavior is primarily influenced by the protonation state and chemical reactivity of TA, which functions both as a reducing agent and a stabilizing agent during nanoparticle synthesis.

The synthesis conditions were optimized within the pH ranges of 1 to 7. In this acidic range, the SPR band intensity and the yellow coloration of the colloids were notably low, and increased only gradually. At very low pH levels of approximately 1 to 7, TA remains fully protonated, resulting in poor reducing and capping efficiency. Consequently, the formation of stable AgNPs is minimal, and those that do form tend to aggregate due to insufficient surface charge stabilization. This leads to the formation of weak or broadened SPR peaks in the UV–Vis spectra and a lack of yellow color. A significant change was observed at pH 8. Under mildly alkaline conditions, TA undergoes partial deprotonation, enhancing its ability to reduce silver ions and stabilize the resulting nanoparticles. At pH 8, the synthesized PTA-AgNPs exhibit the most intense SPR absorbance, characterized by a sharp, well-defined peak around 426 nm indicative of small, spherical, and monodisperse AgNPs. Correspondingly, the colloidal solution displays a yellow color and excellent dispersion stability. Beyond pH 8, however, a decline in SPR intensity was observed. In highly basic conditions ($\text{pH} > 8$), side reactions begin to dominate. These include the oxidation of silver ions to form insoluble silver oxide (Ag_2O), and the self-polymerization of TA under the influence of atmospheric oxygen. Such reactions reduce the availability of free TA for nanoparticle formation and compromise colloidal stability, leading to nanoparticle aggregation. While the formation of PTA NPs is favored in mildly basic environments ($\text{pH} > 8$), this condition not only ensures optimal stability for PTA-AgNPs but also provides a well-controlled environment for the polymerization of TA [47–49].

Figure S8 presents the UV–Vis spectral analysis of TA and AgNO_3 mixtures at varying volume ratios of 1:5, 5:5, and 5:1 mL. Among these, the 5:5 mL ratio exhibited the most prominent SPR band, indicating optimal nanoparticle formation at this concentration balance. Figure S9 illustrates the time-dependent UV–Vis spectral analysis of the TA and AgNO_3 mixture, monitored over intervals ranging from 2 to 20 min. The intensity of the SPR band increased steadily up to 10 min, after which it reached saturation, suggesting completion of nanoparticle formation. All synthesis were conducted under mildly alkaline conditions (pH 8), with the optimized parameters being a 5:5 mL volume ratio and a 10 min reaction time.

Figures S10 and S11 show the UV–Vis spectra and a bar diagram of PTA-AgNPs after the addition of a 0.744 μM H_2S solution, measured across incubation times ranging from 1 to 60 min. The absorbance was quenched during the initial 3 min of incubation, after which the absorbance of the SPR band remained stable from 3 to 60 min. Based on these results, we set the incubation time to 3 min and adjusted the pH to 8 for the detection of H_2S .

3.6. Spectroscopic and colorimetric detection of H_2S in solution using PTA-AgNPs

Fig. 4a shows the absorbance spectrum of the PTA-AgNPs suspension, which exhibits a peak in the SPR band at 426 nm. Initially, the addition of 0.125 μM H_2S to the PTA-AgNPs suspension resulted in a gradual reduction in the absorbance of the SPR band. With a further increase in H_2S concentration from 0.249 to 3.15 μM , the absorbance of the SPR band decreased significantly. These changes in the SPR band were attributed to the aggregation of the PTA-AgNPs, probably caused by the formation of silver sulfide nanoparticles (Ag_2S NPs) in the presence of H_2S . This process destabilizes the monodisperse AgNPs, leading to their aggregation [50–52]. The relative absorbance ($\Delta A = A_x - A_0$) of the sample of the PTA-AgNPs sample correlates with the H_2S concentration. Fig. 4b shows a linear relationship between the relative absorbance and the H_2S concentration, exhibiting excellent linearity with an R^2 value of 0.9831 over the concentration range of 0.125 to 3.15 μM . The linear relationship was used to determine the LOD and LOQ, which were calculated from the spectral data as 24.2 and 125 nM, respectively.

Fig. 4c presents a photograph of the PTA-AgNPs suspensions after the addition of H_2S at concentrations ranging from 0.125 to 3.15 μM . Initially, the PTA-AgNPs suspension appears brownish-yellow, gradually transitioning to brownish-gray as the H_2S concentration increases. The color change of the solution allows for naked-eye colorimetric detection of H_2S within the concentration range of 0.125–3.15 μM . In the naked-eye colorimetric detection of aqueous H_2S using the PTA-AgNPs, the LOQ was determined to be 1.72 μM .

In section 2.8 describes the protocol employed for H_2S detection via smartphone-assisted RGB analysis. Digital images used for RGB value observation (Fig. 4c) were acquired using an OPPO F15 smartphone with the Color Grab application. A representative screenshot of the Color Grab interface is presented in Figure S12, demonstrating the method for obtaining RGB values from images of PTA-AgNPs solutions. The quantitative relationship between H_2S concentration and the RGB/R ratio is plotted in Figure S13, exhibiting a strong linear correlation within the concentration range of 0.125–2.44 μM , with a correlation coefficient (R^2) of 0.9871. This result highlights the potential of smartphone-based on-site quantification of H_2S , using measurable changes in RGB/R.

3.7. Spectroscopic and colorimetric detection of H_2S using the PTA-AuNPs

Figure S14 shows the absorbance spectra of the PTA-AuNPs in the presence of varying H_2S concentrations in solutions (196 μM –1.07 mM), while Figure S15 shows the corresponding photographs. Initially, the SPR band of the wine-red PTA-AuNPs sample at 538 nm exhibits irregular changes in the absorbance upon the addition of H_2S solution, accompanied by a shift to a more intense red color. These inconsistent spectral changes and the unaltered red color shows the PTA-AuNPs unsuitable for spectroscopic and colorimetric detection of H_2S . Overall, the findings confirm that only the PTA-AgNPs function as reliable probes for H_2S detection using spectrophotometric and colorimetric methods.

The stability of PTA-AuNPs in the presence of H_2S solution is determined by the interactions between H_2S and the metallic surfaces of the AuNPs. This phenomenon can be explained by the findings reported by Park and Shumaker-Parry [53]. Dithiols act as molecular linkers, facilitating the connection of two AuNPs to form an aggregate. However, the sugar-like polymer structure of PTA with steric repulsion remarkably prevents aggregation during interparticle adsorption. Dithiol is too small for its sulfur atoms to simultaneously bind to different AuNPs. However, AuNPs remain stable as individual particles in solution, resulting in intraparticle adsorption of PTA-AgNPs.

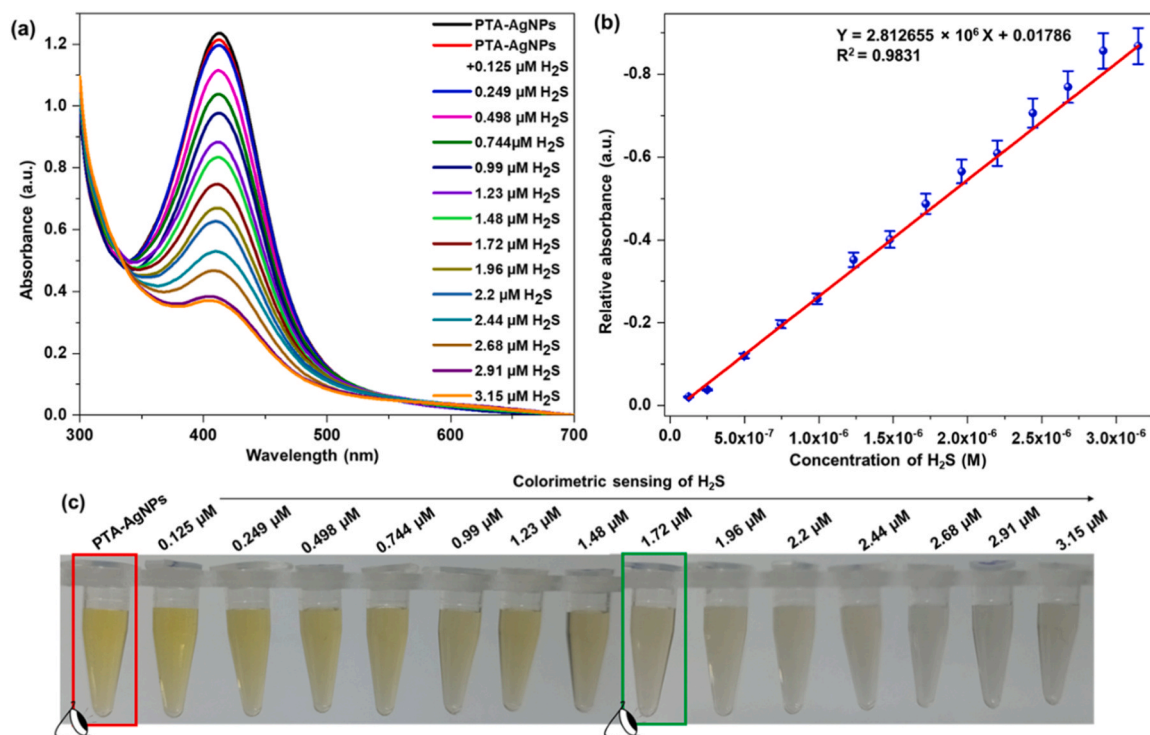


Fig. 4. (a) UV-Vis spectra of PTA-AgNPs in the presence of various concentrations of H_2S in solution (0.125–3.15 μM). (b) Linear relationship plot of H_2S concentration vs relative absorbance of the PTA-AgNPs. (c) Photographs of the PTA-AgNPs in the presence of various concentrations of H_2S in solution (0.125–3.15 μM).

3.8. Morphology, shape, and size analyses of the PTA-AgNPs in the presence of H_2S

Figure S16a shows an HR-TEM image of the PTA-AgNPs exposed to H_2S solution at a magnification of 200 nm, whereas figures S16b, c, and d show images at a magnification of 50 nm. Notably, aggregation of AgNPs was observed, likely induced by the formation of Ag_2S NPs in the presence of the H_2S solution. This process destabilizes the monodisperse AgNPs, leading to their aggregation. A comparison of bare PTA-AgNPs and aggregated Ag_2S NPs reveals that the aggregated particles exhibit an approximately 1.53-fold increase in size, reaching 24.87 nm. These findings demonstrate that the aggregation of PTA-AgNPs is a result of their interaction with H_2S .

Figure S17 presents the XRD pattern of the PTA-AgNPs after exposure to H_2S , indicating the formation of Ag_2S . Distinct diffraction peaks were observed at $2\theta = 38.12^\circ, 44.3^\circ, 64.45^\circ$, and 77.35° , corresponding to the characteristic planes of metallic Ag, consistent with those in Fig. 3. Additionally, new peaks were identified at $2\theta = 29.4^\circ$ (-121), 31.8° (-112), 44.3° (-231), 55.6° (-202), and 56.7° (-132), which align well with the standard JCPDS card No. 00-014-0072, confirming the presence of $\alpha\text{-Ag}_2\text{S}$ (acanthite phase). These results collectively confirm the coexistence of both PTA-AgNPs and Ag_2S phases in the sample [54,55].

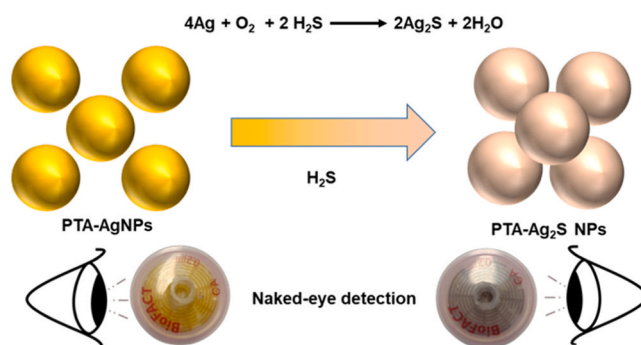
3.9. Absorbance spectra of TA and PTA in the presence of H_2S

Figure S18 shows the absorbance spectrum of the H_2S solution, with absorbance peaks at 253 and 309 nm. The inset in figure S18 shows an image of the colorless H_2S solution. Figure S19 shows the absorbance spectra of TA in the presence of H_2S solutions at varying concentrations (1.66–16.4 μM). The inset in figure S19 shows images of TA alone and TA with the addition of a 16.4 μM H_2S solution. The peaks of TA were observed at 229 and 281 nm and the solution appeared colorless. Upon adding H_2S solutions at different concentrations, the absorbance decreased, but no change was observed in the color of the solution. Figure S20 shows the relationship between H_2S concentration and the

absorbance of TA. The absorbance was not decreased consistently, indicating that TA was unsuitable for use as a H_2S sensor. Similarly, figure S21 shows the absorbance spectra of PTA in the presence of H_2S solution (1.66–16.4 μM), with peaks at 278 and 366 nm. The inset in figure S21 shows PTA (pale yellow) before and after the addition of the 16.4 μM H_2S solution. The absorbance of PTA decreases upon the addition of H_2S solution, but the color remains unchanged. Figure S22 shows the relationship between H_2S concentration and the absorbance of PTA, revealing inconsistencies and indicating that PTA is unsuitable as an H_2S sensor. Overall, TA, PTA, PTA-CuNPs, and PTA-AuNPs are unsuitable for use in H_2S sensing, whereas only the PTA-AgNPs are effective as H_2S sensors.

3.10. Sensing mechanism

Scheme 2 shows the proposed mechanism for sensing H_2S using the PTA-AgNPs probe. The HR-XRD patterns and HR-TEM images confirm that the PTA-AgNPs comprise spherical and monodisperse AgNPs (section 3.2). Additionally, the absorbance spectrum shows an SPR band



Scheme 2. Schematic representation of the sensing mechanism of the proposed assay.

at 426 nm and the solution exhibits a brownish-yellow (section 3.6). The interactions between the AgNPs and H₂S lead to the formation of the Ag₂S NPs, which precipitate out of the dispersion, with H₂O formed as a by-product. This phenomenon arises from a thermodynamically spontaneous reaction, driven by a significantly low Gibbs free energy (−40 kJ/mol). Silver demonstrates a strong chemical affinity for sulfur, and its high reactivity with both aqueous and gaseous sulfide ions is further underscored by the extremely low solubility product constant of Ag₂S (6.30×10^{-50}), indicating the formation of a highly stable compound [50–52]. The absorbance spectrum shows AgNPs aggregation, as evidenced by the quenching of the SPR band (section 3.6). HR-TEM and XRD further validate the formation of the Ag₂S NPs (section 3.8). Moreover, a visible color change from brownish-yellow to brownish-gray was observed (section 3.6). The sensitivity of the probe's color is influenced by the particle sizes of the PTA-AgNPs and directly correlates with the H₂S concentration detected.

3.11. Selectivity study

Figure S23a shows the absorbance spectrum of a PTA-AgNPs sample and its responses in the presence of various organic solvents, including EtOH, MeOH, Ace, NH₃, IPA, PhCH₃, AcOH, THF, CH₃NO, DMF, DMSO, TFE, and H₂S solution. The SPR band of the PTA-AgNPs sample was observed at 426 nm. When exposed to 0.698 mM (222-fold concentration) of organic solvents such as EtOH, MeOH, Ace, NH₃, IPA, PhCH₃, AcOH, THF, CH₃NO, DMF, DMSO, and TFE into PTA-AgNPs, the change in the absorbance spectrum was negligible. However, PTA-AgNPs in the presence of a 3.15 μM H₂S solution, the SPR band of the PTA-AgNPs sample was completely quenched indicating AgNPs aggregation.

Figure S23b shows a bar chart illustrating the changes in the relative absorbance of a PTA-AgNPs sample in the presence of various liquids, including EtOH, MeOH, Ace, NH₃, IPA, PhCH₃, AcOH, THF, CH₃NO, DMF, DMSO, TFE, and H₂S solution. The inset shown in figure S23b shows a photographic comparison of the PTA-AgNPs solutions in the presence of various organic solvents and H₂S solution. The addition of each solvent results in negligible changes in the relative absorbance and the brownish-yellow color of the PTA-AgNPs solution remains unaltered. However, upon adding the H₂S solution into PTA-AgNPs, the color of the PTA-AgNPs solution shifts from brownish-yellow to brownish-gray accompanied by a significant increase in relative absorbance. These results highlight the selective interactions between the PTA-AgNPs and H₂S solution, demonstrating the high specificity and potential of this sensing methodology for H₂S detection.

Figure S24 presents a bar chart illustrating the changes in relative absorbance of PTA-AgNPs upon exposure to a variety of potentially interfering gases including NH₃, sulfur dioxide (SO₂), and Ace, which represent common real-world gaseous interference. The inset image provides a photographic comparison between the color responses of bare PTA-AgNPs and POCT kits after exposure to each gas. Notably, the addition of NH₃, SO₂, and Ace induced negligible changes in the relative absorbance values, and the brownish-yellow color of both the PTA-AgNPs solution and POCT kits remained visually unchanged, indicating minimal non-specific interactions. These findings confirm the high selectivity of PTA-AgNPs toward H₂S even in the presence of interfering gases, thereby validating its potential for practical applications, especially in complex environments such as food spoilage monitoring where volatile organic compounds and atmospheric gases coexist.

3.12. Sensing of H₂S gas using the POCT kits

The preparation of the POCT kits is detailed in section 2.6. In this study, we modified syringe filter tubes with the PTA-AgNPs, PTA-AuNPs, and PTA-CuNPs using hand-held syringe filters. Figure S25 shows images of a CA syringe filter and POCT integrated with PTA-AgNPs, PTA-AuNPs, and PTA-CuNPs. The modified POCT kits exhibit distinct colors: brownish-yellow for PTA-AgNPs, wine-red for PTA-

AuNPs, and light yellow for PTA-CuNPs. To further analyze the POCT kits, three tubes were broken to collect the CA filter papers. The CA filter papers absorbance were measured using a 12-well plate and a microplate reader. Figure S26 shows the UV–Vis spectra of CA filters paper integrated with PTA-AgNPs, PTA-AuNPs, and PTA-CuNPs. The SPR bands were observed at 421 and 543 nm in the spectra of the CA syringe filters paper integrated with the PTA-AgNPs and PTA-AuNPs. Conversely, no significant absorbance was observed in the spectrum of the CA syringe filter papers integrated with the PTA-CuNPs. Among those of the three, the POCT integrated with PTA-AgNPs exhibited the most pronounced SPR and color making its suitable for use as an H₂S sensor in further studies.

The procedure for the fabrication of POCT kits and their application in H₂S gas sensing is detailed in section 2.6. Fig. 5 shows the POCT kits used for detecting H₂S gas in a 10 mL glass vial setup. Fig. 5a shows that H₂S gas was generated by reacting 1 M HCl with Na₂S solutions of various concentrations (0, 0.249, 0.99, 1.72, 2.44, and 3.15 μM). The color of the POCT kits initially appear brownish-yellow and gradually changes to brownish-gray as the concentration of H₂S gas increases. Fig. 5b shows clear top view of the POCT kits and color transition from brownish-yellow to brownish-gray due to the interactions between H₂S gas with the PTA-AgNPs. The LOQ of the naked-eye detection of H₂S gas using the POCT kits is 1.72 μM. Subsequently, the POCT kits were dismantled to collect the CA filter papers, as shown in Fig. 5c. These filter papers display the same color changes and were used for absorbance spectral measurements using a 12-well plate and a microplate reader. Figure S27 shows the UV–Vis absorption spectra of the CA filter papers exposed to H₂S gas. Initially, the SPR band was observed at 421 nm in the CA filter paper integrated with PTA-AgNPs without H₂S gas, but SPR band quenched as the H₂S gas concentration increased. These color changes and SPR quenching were attributed to the aggregation of PTA-AgNPs in the presence of H₂S gas. Thus, POCT integrated with PTA-AgNPs kit was effective for naked-eye H₂S gas detection and monitoring applications. Section 2.8 describes the smartphone-based protocol for H₂S detection via RGB analysis. Images (Fig. 5c) were taken to analysis RGB using an OPPO F15 smartphone with the Color Grab app. Figure S28 shows a screenshot of the app interface used to extract RGB values from POCT kits containing PTA-AgNPs. A strong linear correlation ($R^2 = 0.9255$) between H₂S concentration (0.249–315 μM) and the RGB/R is shown in Figure S29 demonstrating the smartphone with POCT potential for on-site H₂S quantification.

3.13. Repeatability and long-term stability assessment of PTA-AgNPs and POCT kits

The stability of PTA-AgNPs was previously assessed in section 3.1 and it has remained stable for over 80 d. Here, three independent batches of PTA-AgNPs were synthesized to assess repeatability and long-term stability. Figure S30 presents the UV–Vis spectra of freshly prepared PTA-AgNPs, as well as samples aged for 10 and 20 d. Each spectrum was recorded before and after the addition of 3.15 μM H₂S. The inset of Figure S30 shows the corresponding photographs of the solutions from each batch at different aging times. UV–Vis spectra across all three batches showed consistent peak wavelengths and SPR band absorbance, and the colorimetric response was visually similar, indicating high batch-to-batch repeatability. Furthermore, even after 20 d of storage, the PTA-AgNPs retained their ability to detect H₂S, demonstrating excellent long-term stability. Figure S31 shows photographs of the POCT integrated with freshly prepared, 10-d aged, and 20-d aged PTA-AgNPs, both before and after the exposure to 3.15 μM H₂S. The POCT devices exhibited consistent visual responses across all aging periods, further confirming the reproducibility and long-term stability of the PTA-AgNPs in a practical sensing platform.

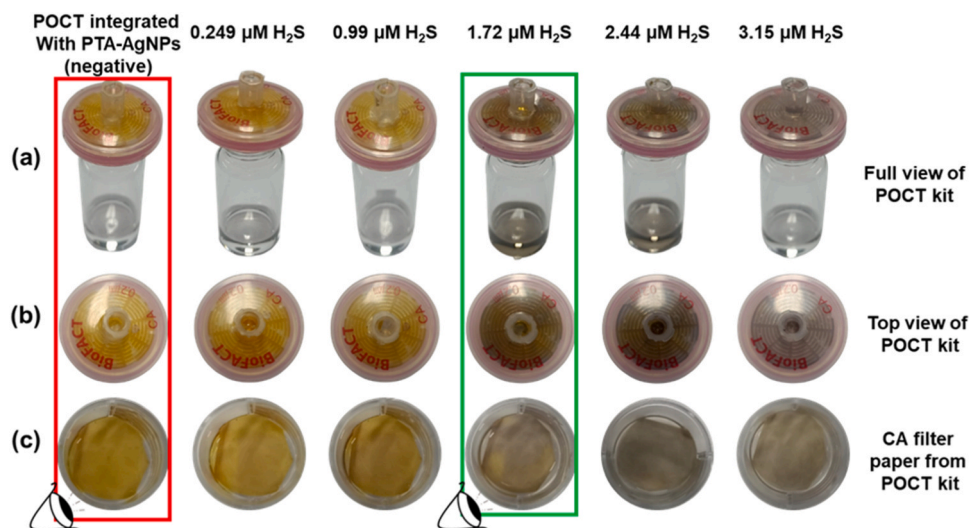


Fig. 5. (a) Photographs of the POCT kits integrated with PTA-AgNPs after the addition of 0.249, 0.99, 1.72, 2.44, and 3.15 μM H_2S gas into the glass vials. (b) Photographs of the H_2S gas-induced POCT integrated with PTA-AgNPs. (c) Photographs of the H_2S gas-induced cellulose acetate (CA) filter papers from the POCT kits.

3.14. Application in analyzing breath samples

The procedure and methodology of human oral breath sample collection and naked-eye analysis using the POCT integrated with PTA-AgNPs are given in section 2.7. The six POCT kits are shown in Fig. 6a, with their initial color observed as brownish-yellow. Fig. 6b shows the breath samples obtained from three volunteers via exhalation into 200 mL Ziploc plastic bags. Each volunteer provided two samples, one unaltered and the other spiked with H_2S gas at concentrations of 1.23, 1.72, and 2.2 μM . These breath samples were transferred to the POCT kits using 10 mL syringes. Fig. 6c shows the color changes of the POCT kits, with the first three kits displaying slight color changes due to the lower H_2S gas concentrations in the unaltered breath samples. Conversely, the last three kits exhibit more noticeable color changes to brownish-gray, correlating with the interactions between the spiked H_2S gas and PTA-AgNPs. The observed color changes indicate the capacities of the POCT kits for use in the on-site and naked-eye detection of various levels of H_2S gas in human breath samples. This method provides an effective approach for sensing H_2S gas, which can serve as indirect indicators of halitosis.

3.15. Application in analyzing fish, pork, and chicken

In section 2.7 describes the procedure for using the POCT integrated with PTA-AgNPs to analyze H_2S gas production in foods, including fish, pork, and chicken. A 2.5 g of fish was placed in a glass vial and maintained at 37 $^{\circ}\text{C}$ (Fig. 7a). The vial was sealed with a POCT integrated with PTA-AgNPs kits. Each day, bacterial activity in the fish produces H_2S gas, causing the aggregation of PTA-AgNPs within the POCT kit and resulting in a color change from brownish-yellow to brownish-gray. Fig. 7b shows the top view of the POCT integrated with the PTA-AgNPs kit with the fish, clearly displaying the progression of the color change that facilitates the detection of H_2S gas. Similarly, Fig. 7c shows 2.5 g of pork analyzed under the same conditions as the fish, with the vial sealed using a POCT kits. Over every day, bacterial growth within the pork produces H_2S gas causing a visible color transition in the POCT kits. Fig. 7d shows the clear top view of the POCT kits, revealing the progression of the color change from brownish-yellow to brownish-gray.

Finally, chicken (2.5 g) was evaluated under the same conditions (Fig. 7e). The top view of the POCT kits also reveals a gradual color change from brownish-yellow to brownish-gray as bacterial activity increases to produce H_2S gas (Fig. 7f). The POCT integrated with PTA-AgNPs kits were effective for on-site naked-eye detection of H_2S gas

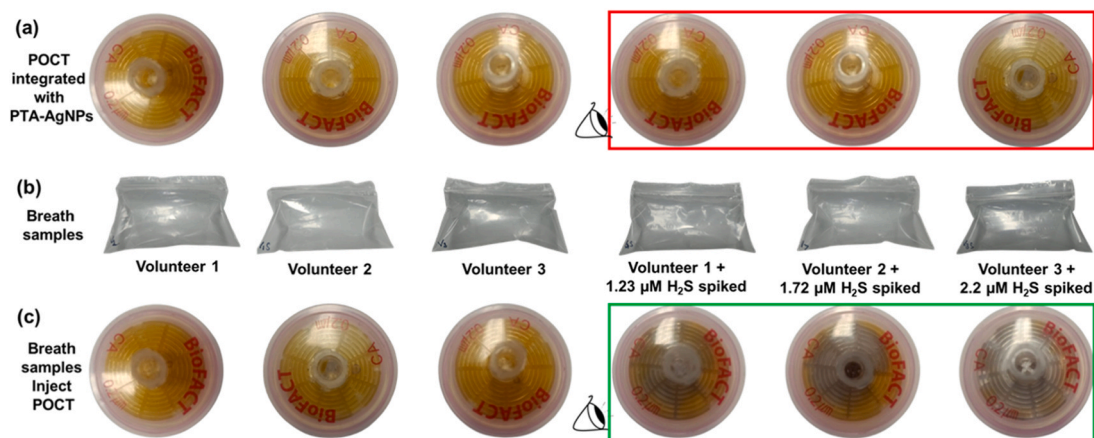


Fig. 6. (a) Photographs of the POCT integrated with PTA-AgNPs. (b) Photographs of breath samples from a volunteer. (c) Photographs of POCT integrated with PTA-AgNPs after the injection of H_2S gas breath samples.

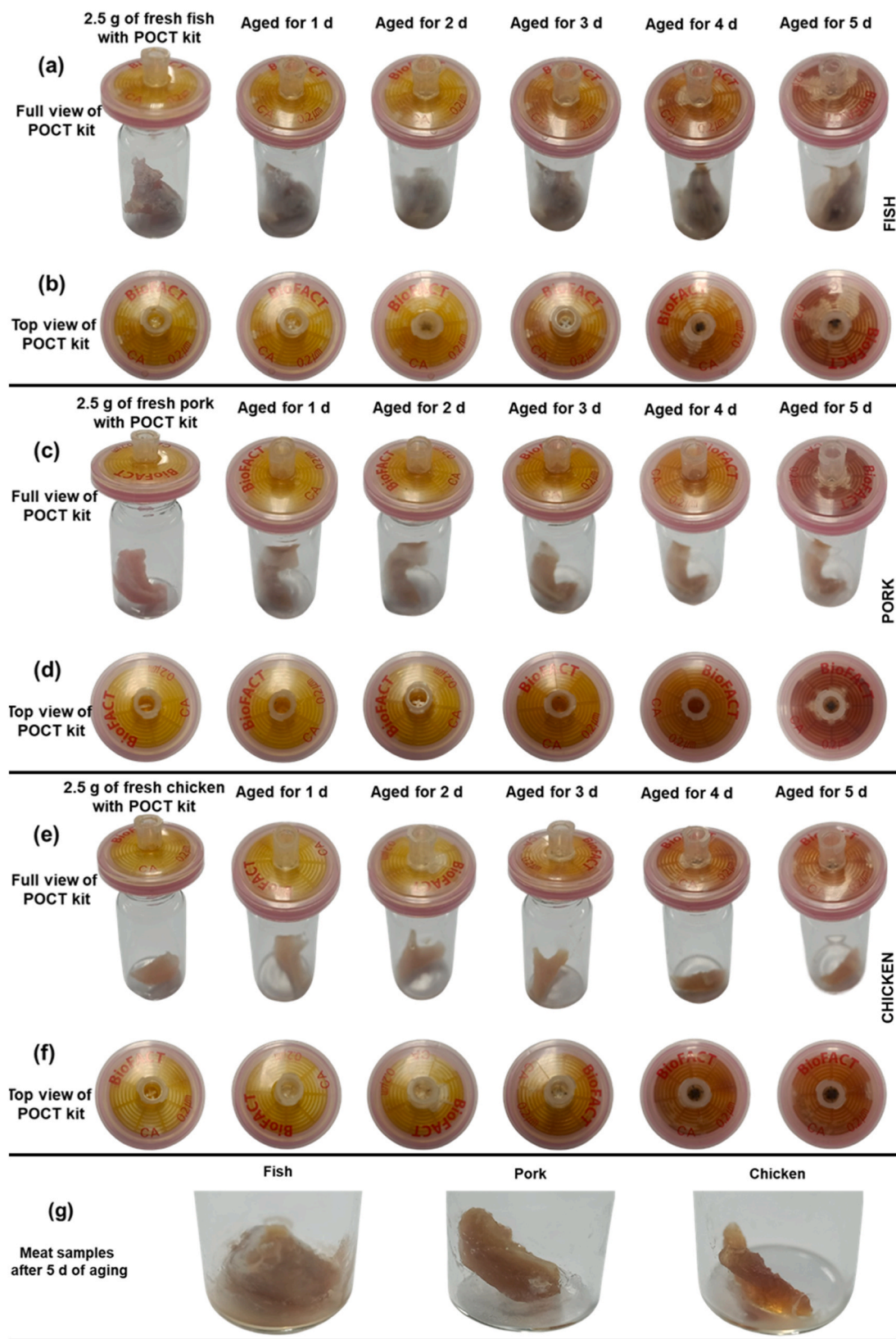


Fig. 7. (a) Full and (b) top view photographs of the POCT integrated with PTA-AgNPs used for the detection of H_2S gas in a fish sample at $37^\circ C$ across 1 to 5 d. (c) Full and (d) top view photographs of the POCT integrated with PTA-AgNPs used for the detection of H_2S gas in a pork sample at $37^\circ C$ across 1 to 5 d. (e) Full and (f) top view photographs of the POCT integrated with PTA-AgNPs used for the detection of H_2S gas in a chicken sample at $37^\circ C$ across 1 to 5 d. (g) Photographs of the meat samples after 5 d of ageing.

produced by bacterial activity in fish, pork, and chicken. The observable color change serves as a reliable indicator of bacterial contamination, enabling the rapid and efficient identification of unsafe meat products in food packaging and preservation systems. Fig. 7 g shows images of fish, pork, and chicken after ageing for 5 d, confirming bacterial growth in the gel-like samples derived from these meats.

Numerous colorimetric methods have been explored for detecting H₂S, including traditional lead acetate papers that darken upon exposure to H₂S due to the formation of brown/black lead sulfide. Jaiswal et al., developed a bismuth oxide (Bi₂O₃) nanorod-based colorimetric sensor that can reversibly detect trace amounts of H₂S in air and packaged food. The method utilizes the reaction of Bi₂O₃ with H₂S to form bismuth sulfide, resulting in a measurable color change [56]. Chen et al., employed gold nanorods (AuNRs) with horseradish peroxidase, where H₂S deactivates the enzyme and induces a multicolor response in rat brain microdialysis samples [21]. Zhao et al., (2017) introduced a dopamine-assisted AgNPs formation method in aqueous media, but the system lacked a solid support and was unsuitable for field deployment [52]. Shojaeifard et al., developed a dual-mode colorimetric and fluorometric sensor using copper nanoclusters and Cu²⁺ ions. However, copper-based sensors pose toxicity concerns and are limited to water-based analysis [57]. Similarly, Yu et al., (2022) used Ag-Fe nanotubes that reacted with H₂S to produce a visible change, but the system was not integrated into a practical POCT kits [58]. Core-shell Au@Ag nanoparticles reported by Liu et al., (2019) used SPR modulation for sulfide detection, but their synthesis is complex and lacks testing in real samples [59]. Advanced nanostructures such as triangular gold nanoplates (Wang et al.,) and Au/AgI dimeric particles (Zeng et al.,) showed good sensitivity, but these platforms require precise shape or dimeric control and have not been demonstrated in actual food or breath samples [60,61]. Key limitations of existing colorimetric H₂S sensors include (1) toxic or hazardous reagents (lead, copper, iron, organic chemical), (2) poor stability, (3) complex or costly nanostructures (Au@Ag core-shell prisms and alloyed Ag-Fe nanostructures), (4) only compatible with aqueous media, (5) lack of portability and on-site usability, and (6) narrow scope of real-world validation (Table 1).

Compared to previous reports, the present study demonstrates significant novelty for the following reasons: (1) first-time use of PTA as a green, dual-function reducing and capping agents for synthesizing stable AgNPs for H₂S sensing, (2) eco-friendly and biocompatible system,

avoiding toxic reagents like lead acetate and copper salts, and eliminating the need for enzymes or complex nanostructures, (3) on-site fabrication on a syringe filter allows easy use and portability as a POCT kit, (4) dual-phase compatibility allowing effective H₂S detection in both gaseous and aqueous media, (5) visible naked-eye color change from brownish-yellow to brownish-gray, (6) synthesis within 10 min under temperature conditions (28 °C), (7) optimal sensing conditions at pH 8 and 28 °C with quick response time as 3 min, (7) excellent analytical performance as linear detection range as 0.125 to 3.15 μM, LOD as 24.2 nM, LOQ as 125 nM, and (8) real-sample validation in food spoilage monitoring (fish, pork, and chicken) and halitosis detection (human breath) (Table 1). We emphasize that the PTA-AgNPs colorimetric POCT sensor provides an excellent trade-off between performance and practicality. While it may not replace all advanced electronic sensors, POCT benefits from its high sensitivity and unique chemical design, making it a practical choice for quick, on-site testing.

4. Conclusions

This study demonstrates an on-site fabrication and naked-eye detection system for H₂S gas based on a POCT kits integrated with PTA-AgNPs, developed as an optical probe. The introduced system integrated spectroscopy and colorimetric sensing in liquid-phase detection, as well as the naked eye sensing of gaseous H₂S using the POCT kits. The probe exhibited a color shift from brownish-yellow to brownish-gray upon exposure to H₂S in liquid or gas within the detection range of 0.125–3.15 μM, with the LOD and LOQ being 24.2 and 125 nM, respectively. The sensitivity of the probe was influenced by the particle size of the PTA-AgNPs. The mechanisms underlying the observed color changes and NPs aggregation were validated via UV-Vis spectroscopy, HR-XRD, and HR-TEM.

The key innovation of present POCT kits ability to be prepared instantly on-site without laboratory support, and its ability to detect H₂S through visible color changes-making it ideal for real-world, naked-eye, and on-site detection. The POCT kits exhibited versatility by reliably responding to the freshness levels of fish, pork, and chicken, and effectively detected H₂S gas in human breath samples, indicating its potential indirect halitosis diagnosis. This work advances the design of green nanomaterial-based sensors and broadens the application of naked-eye H₂S detection. It offers a low-cost and equipment-free solution for

Table 1

Comparison between the analytical performances of the nanomaterials used in this study with previously reported work based on the colorimetric sensing of H₂S in liquid and gas phases.

Sl. No.	Probes	Synthesis duration (min)/ temperature (°C)	Sensing medium	Color changes	Incubation time (min)/ pH/ temperature (°C)	Linear range (μM)	LOD/ LOQ (nM)	Real samples	Ref.
1	CTAB-AuNRs	750/30	Liquid	Pink to purple to green to reddish-brown	3/6.5/28	0.05–100	19/50	Rat brain	[21]
2	Dopamine-AgNPs	15/30	Liquid	Yellow to brown	20/N.A./28	3–40	300/3000	Fetal bovine serum	[52]
3	Bi ₂ O ₃	60/120	Gas	White to brown	3/N.A./26	30–1500	410/30000	Fish and chicken	[56]
4	Tannic acid-CuNCs	365/50	Liquid	Blue to brown	1/7.5/28	6–130	2000/6000	Rain, tap, spring, and wastewater	[57]
5	Ag-Fe NTs	490/80	Liquid, gas	Yellow to brown	N.A./N.A./28	2–100	N.A./2000	Broiler chicken	[58]
6	CTAB-Au@AgNPs	45/30	Liquid	Red-orange to blue-green	N.A./7.4/28	5–50	500/5000	N.A.	[59]
7	CTAC-AuNPLs	10/30	Liquid	Pink-red to purple-blue	20/3.4/60	0.02–1.5	10/20	River water	[60]
8	Au/AgI	15/95	Liquid, gas	Red to blue-green	30/7–10/28	5–100	500/5000	Tap and sewage water	[61]
9	PTA-AgNPs	10/28	Liquid, gas	Brownish-yellow to brownish-gray	3/8/28	0.125–3.15	24.2/125	Human breath, fish, pork, and chicken samples using the POCT kits	This study

N.A. Not available.

halitosis diagnosis and bacterial activity indication, particularly valuable in resource-limited settings. Future research may focus on improving selectivity in complex samples enhancing portability, and integrating wireless with smartphone-based sensing technologies.

CRedit authorship contribution statement

Maruthupandi Muniyandi: Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Lee Nae Yoon:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Data curation, Conceptualization.

Environmental implication

Bacterial hazards pose significant risks to food and aqueous systems, leading to spoilage and health concerns. Hydrogen sulfide (H₂S), a key indicator of bacterial activity and a harmful gas, was detected using a novel POCT integrated with poly(tannic acid)-capped silver nanoparticle (PTA-AgNPs). PTA-AgNPs were synthesized through a green and biodegradable chemistry route using tannic acid, a polyphenol, as both the reducing and capping agent, and silver nitrate as the metal ion source. The use of cellulose acetate, a biodegradable polymer, as the substrate further enhances the eco-friendliness and stability of the device. This sustainable method reduces reliance on hazardous chemicals and facilitates on-site manufacturing processes that are environmentally friendly and safer for both humans and ecosystems. In addition to its minimal environmental impact, the POCT kit developed in this study enables rapid and sensitive detection of H₂S present in meat and human breath, facilitating the real-time monitoring of bacterial spoilage and the detection of halitosis. These features highlight the broad potential for eco-friendly sensor technologies in food safety, healthcare diagnostics, and environmental monitoring.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korean Government (MSIT) (RS-2023-00208684) and also by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. RS-2021-NR060117).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2025.138323](https://doi.org/10.1016/j.jhazmat.2025.138323).

Data availability

Data will be made available on request.

References

- [1] Khan, A.R., Hussain, W.L., Shum, H.C., Hassan, S.U., 2024. Point-of-care testing: a critical analysis of the market and future trends. *Front Lab Chip Technol* 3, 1–15. <https://doi.org/10.3389/frlct.2024.1394752>.
- [2] Maruthupandi, M., Lee, N.Y., 2024. Point-of-care testing kit for the detection of hexavalent chromium by carbohydrazide-derived graphitic carbon nitride. *Chemosensors* 12, 180. <https://doi.org/10.3390/chemosensors12090180>.
- [3] Qin, X., Zhang, Z., Yang, T., Yuan, L., Guo, Y., Yang, X., 2022. Auto-fluorescence of cellulose paper with spatial solid phase dispersion-induced fluorescence enhancement behavior for three heavy metal ions detection. *Food Chem* 389, 133093. <https://doi.org/10.1016/j.foodchem.2022.133093>.
- [4] Qin, X., Liu, J., Zhang, Z., Li, J., Yuan, L., Zhang, Z., et al., 2021. Microfluidic paper-based chips in rapid detection: current status, challenges, and perspectives. *TrAC Trends Anal Chem* 143, 116371. <https://doi.org/10.1016/j.trac.2021.116371>.
- [5] Teengam, P., Siangproh, W., Tuantranont, A., Vilaivan, T., Chailapakul, O., Henry, C.S., 2017. Multiplex paper-based colorimetric DNA sensor using pyrrolidinyl peptide nucleic acid-induced AgNPs aggregation for detecting MERS-CoV, MTB, and HPV oligonucleotides. *Anal Chem* 89, 5428–5435. <https://doi.org/10.1021/acs.analchem.7b00255>.
- [6] Zhang, X., Chen, S., Zhuo, S., Ji, Y., Li, R., 2021. A carbon dots functionalized paper coupled with AgNPs composites platform: application as a sensor for hydrogen peroxide detection based on surface plasmon-enhanced energy transfer. *New J Chem* 45, 6025–6032. <https://doi.org/10.1039/d0nj05721e>.
- [7] Maruthupandi, M., Chandru, M., Rani, S.K., Vasimalai, N., 2019. Highly selective detection of iodide in biological, food, and environmental samples using polymer-capped silver nanoparticles: preparation of a paper-based testing kit for on-site monitoring. *ACS Omega* 4, 11372–11379. <https://doi.org/10.1021/acsomega.9b01144>.
- [8] Maruthupandi, M., Stairish, M.R.J., Sahila, S., Vasimalai, N., 2022. Ultrasensitive and selective detection of cadmium ions in hair, nail, cigarette and wastewater samples using disulfo-stilbenediamine capped silver nanoparticles. *J Mol Struct* 1269, 133798. <https://doi.org/10.1016/j.molstruc.2022.133798>.
- [9] Fu, Q., Wu, Z., Li, J., Wu, Z., Zhong, H., Yang, Q., et al., 2019. Quantitative assessment of disease markers using the naked eye: Point-of-care testing with gas generation-based biosensor immunochromatographic strips. *J Nanobiotechnol* 17, 1–10. <https://doi.org/10.1186/s12951-019-0493-z>.
- [10] World Health Organization, 1996. Hydrogen sulfide in drinking-water. In: *Guidel. Drink. Qual.*, second ed., 2. (https://cdn.who.int/media/docs/default-source/wash-documents/wash-chemicals/hydrogensulfide-bd.pdf?sfvrsn=2f03ad98_4).
- [11] Jornet-Martínez, N., Hakobyan, L., Argente-García, A.I., Molins-Legua, C., Campins-Falcó, P., 2019. Nylon-supported plasmonic assay based on the aggregation of silver nanoparticles: in situ determination of hydrogen sulfide-like compounds in breath samples as a proof of concept. *ACS Sens* 4, 2164–2172. <https://doi.org/10.1021/acssensors.9b01019>.
- [12] Maruthupandi, M., Thirupathi, D., Vasimalai, N., 2020. One minute synthesis of green fluorescent copper nanocluster: the preparation of smartphone aided paper-based kit for on-site monitoring of nanomolar level mercury and sulfide ions in environmental samples. *J Hazard Mater* 392, 122294. <https://doi.org/10.1016/j.jhazmat.2020.122294>.
- [13] Bollen, C.M.L., Beikler, T., 2012. Halitosis: the multidisciplinary approach. *Int J Oral Sci* 4, 55–63. <https://doi.org/10.1038/ijos.2012.39>.
- [14] Fernandes, D.L.A., Rolo, T.A., Oliveira, J.A.B.P., Gomes, M.T.S.R., 2009. A new analytical system, based on an acoustic wave sensor, for halitosis evaluation. *Sens Actuators B Chem* 136, 73–79. <https://doi.org/10.1016/j.snb.2008.10.037>.
- [15] Barton, L.L., Ritz, N.L., Fauque, G.D., Lin, H.C., 2017. Sulfur cycling and the intestinal microbiome. *Dig Dis Sci* 62, 2241–2257. <https://doi.org/10.1007/s10620-017-4689-5>.
- [16] Wu, G., Li, N., Mao, Y., Zhou, G., Gao, H., 2015. Endogenous generation of hydrogen sulfide and its regulation in *Shewanella oneidensis*. *Front Microbiol* 6, 1–12. <https://doi.org/10.3389/fmicb.2015.00374>.
- [17] Tang, D., Santschi, P.H., 2000. Sensitive determination of dissolved sulfide in estuarine water by solid-phase extraction and high-performance liquid chromatography of methylene blue. *J Chromatogr A* 883, 305–309. [https://doi.org/10.1016/S0021-9673\(00\)00381-2](https://doi.org/10.1016/S0021-9673(00)00381-2).
- [18] Afkhami, A., Khalafi, L., 2005. Indirect determination of sulfide by cold vapor atomic absorption spectrometry. *Microchim Acta* 150, 43–46. <https://doi.org/10.1007/s00604-005-0344-5>.
- [19] Vasimalai, N., Fernández-Argüelles, M.T., Espiña, B., 2018. Detection of sulfide using mercapto tetrazine-protected fluorescent gold nanodots: preparation of paper-based testing kit for on-site monitoring. *ACS Appl Mater Interfaces* 10, 1634–1645. <https://doi.org/10.1021/acsami.7b11769>.
- [20] Dilgin, Y., Kizilkaya, B., Ertek, B., Işık, F., Dilgin, D.G., 2012. Electrocatalytic oxidation of sulphide using a pencil graphite electrode modified with hematoxylin. *Sens Actuators, B Chem* 171–172, 223–229. <https://doi.org/10.1016/j.snb.2012.03.020>.
- [21] Chen, Z., Chen, C., Huang, H., Luo, F., Guo, L., Zhang, L., et al., 2018. Target-induced horseradish peroxidase deactivation for multicolor colorimetric assay of hydrogen sulfide in rat brain microdialysis. *Anal Chem* 90, 6222–6228. <https://doi.org/10.1021/acs.analchem.8b00752>.
- [22] Tangerman, A., Winkel, E.G., 2008. The portable gas chromatograph OralChromaTM: a method of choice to detect oral and extra-oral halitosis. *J Breath Res* 2 (6), 017010. <https://doi.org/10.1088/1752-7155/2/1/017010>.
- [23] Sun, M., Ding, K., Lu, Y., She, X., Chen, Y., Wang, M., et al., 2024. Two-dimensional p-n heterojunctions of black phosphorus nanosheet-sensitized α -MoO₃ nanoflake for low-temperature chemiresistive NH₃ recognition. *Microchem J* 207, 111911. <https://doi.org/10.1016/j.microm.2024.111911>.
- [24] Yu, C., Liu, J., Zhao, H., Wang, M., Li, J., She, X., et al., 2024. Sensitive breath acetone detection based on α -Fe₂O₃ nanoparticles modified WO₃ nanoplate heterojunctions. *IEEE Trans Instrum Meas* 73, 1–8. <https://doi.org/10.1109/TIM.2024.3440407>.
- [25] Zhao, H., Li, J., She, X., Chen, Y., Wang, M., Wang, Y., et al., 2024. Oxygen vacancy-rich bimetallic Au@Pt core-shell nanosphere-functionalized electrospun

- ZnFe₂O₄ nanofibers for chemiresistive breath acetone detection. *ACS Sens* 9, 2183–2193. <https://doi.org/10.1021/acssensors.4c00382>.
- [26] Sahiner, N., 2021. Self-crosslinked ellipsoidal poly(Tannic acid) particles for biomedical applications. *Molecules* 26 (14), 2429. <https://doi.org/10.3390/molecules26092429>.
- [27] Lee, B.P., Dalsin, J.L., Messersmith, P.B., 2002. Synthesis and gelation of DOPA-modified poly(ethylene glycol) hydrogels. *Biomacromolecules* 3, 1038–1047. <https://doi.org/10.1021/bm025546n>.
- [28] Allais, M., Mailley, D., Hébraud, P., Ihiwakrim, D., Ball, V., Meyer, F., et al., 2018. Polymer-free electrospinning of tannic acid and cross-linking in water for hybrid supramolecular nanofibers. *Nanoscale* 10, 9164–9173. <https://doi.org/10.1039/c8nr01067f>.
- [29] Ahmad, T., 2014. Reviewing the tannic acid mediated synthesis of metal nanoparticles. *J Nanotechnol* 204 (11), 954206. <https://doi.org/10.1155/2014/954206>.
- [30] Lopes, L.C.S., Brito, L.M., Bezerra, T.T., Gomes, K.N., Carvalho, F.A.D.A., Chaves, M.H., et al., 2018. Silver and gold nanoparticles from tannic acid: synthesis, characterization and evaluation of antileishmanial and cytotoxic activities. *Acad Bras Cienc* 90, 2679–2689. <https://doi.org/10.1590/0001-3765201820170598>.
- [31] Bretnall, A.E., Clarke, G.S., 2011. Validation of analytical test methods. *Sep Sci Technol* 10, 429–457. <https://doi.org/10.1016/B978-0-12-375680-0.00011-5>.
- [32] Tan, K.S., Cheong, K.Y., 2013. Advances of Ag, Cu, and Ag-Cu alloy nanoparticles synthesized via chemical reduction route. *J Nanopart Res* 15 (29), 1537. <https://doi.org/10.1007/s11051-013-1537-1>.
- [33] Sartho Immaculate Mercy, J., Vasimalai, N., 2023. Point-of-care sensor kit for on-site monitoring of creatinine in clinical samples using polyol functionalized gold nanoparticles by UV–visible spectrophotometry. *Microchem J* 193, 109173. <https://doi.org/10.1016/j.microc.2023.109173>.
- [34] Pucelik, B., Sulek, A., Borkowski, M., Barzowska, A., Kobielusz, M., Dąbrowski, J. M., 2022. Synthesis and characterization of size- and charge-tunable silver nanoparticles for selective anticancer and antibacterial treatment. *ACS Appl Mater Interfaces* 14, 14981–14996. <https://doi.org/10.1021/acsami.2c01100>.
- [35] Sanjoy, H., Aninda N, A., Md. A, G.Dr, Dr. Gimyeong, S., Dr. Muhammad, Z.H., 2021. Size-controlled facile synthesis of silver nanoparticles by chemical reduction method and analysis of their antibacterial performance. *ChemistrySelect* 6, 9714–9720. <https://doi.org/10.1088/0031-9112/8/7/008>.
- [36] Hirsch, P.B., 1957. Elements of X-ray diffraction. *Phys Bull* 8, 237–238. <https://doi.org/10.1088/0031-9112/8/7/008>.
- [37] Liu, X., Atwater, M., Wang, J., Huo, Q., 2007. Extinction coefficient of gold nanoparticles with different sizes and different capping ligands. *Colloids Surf B Biointerfaces* 58, 3–7. <https://doi.org/10.1016/j.colsurfb.2006.08.005>.
- [38] Mercy, J.S.I., Maruthupandi, M., Mamat, M.H.Bin, Vasimalai, N., 2022. Facile in-situ synthesis of biopolymer capped nano sized silver particles: smartphone aided paper-based selective detection of CYS and TC drugs in biological and drug samples. *J Clust Sci* 33, 1055–1067. <https://doi.org/10.1007/s10876-021-02035-2>.
- [39] Ullah, H., Qamar, S., Khan, F., Rahim, F., Shamim, A., Uddin, I., et al., 2019. Tannic acid based gold nanosensor for selective detection of Hg⁺² and pefloxacin. *J Ongoing Chem Res* 4, 24–31. <https://doi.org/10.5281/zenodo.3561139>.
- [40] Kim, N.E., Park, S., Kim, S., Choi, J.H., Kim, S.E., Choe, S.H., et al., 2023. Development of gelatin-based shape-memory polymer scaffolds with fast responsive performance and enhanced mechanical properties for tissue engineering applications. *ACS Omega* 8, 6455–6462. <https://doi.org/10.1021/acsomega.2c06730>.
- [41] Ecer, Ü., Zengin, A., Şahan, T., 2023. Fabrication and characterization of poly (tannic acid) coated magnetic clay decorated with cobalt nanoparticles for NaBH₄ hydrolysis: RSM-CCD based modeling and optimization. *Int J Hydrog Energy* 48, 23620–23632. <https://doi.org/10.1016/j.ijhydene.2023.03.125>.
- [42] Shabani, M., Khaleghi, M., Allahyari, F., Attar, F., Ahmadi, H.R., Roohani, M., et al., 2021. Tannic acid-modified tin oxide nanoparticle and aromatic polyamide: from synthesis to their application for preparation of safe p-PVC. *Polym Bull* 78, 1331–1352. <https://doi.org/10.1007/s00289-020-03160-0>.
- [43] Pantoja-Castro, M.A., González-Rodríguez, H., 2011. Study by infrared spectroscopy and thermogravimetric analysis of Tannins and Tannic acid. *Rev Latinoam Quím* 39, 107–112.
- [44] Rodig, O.R., 1963. Spectrometric identification of organic compounds. *J Med Chem* 6, 826–827. <https://doi.org/10.1021/jm00342a059>.
- [45] Socrates, G., 2001. Infrared and Raman characteristic group frequencies. Tables and charts. *J Raman Spectrosc* 347. (<http://doi.wiley.com/10.1002/jrs.1238>).
- [46] Jie, Wen, J., Xiaopeng, Zhang, Mingwang, Pan, Jinfeng, Yuan, Zhanyu, Lei, Z., Robust, A., 2020. Tough and multifunctional polyurethane/tannic acid hydrogel fabricated by physical-chemical dual crosslinking. *Polymers* 12, 239.
- [47] Zhao, Y., Xu, L., Kong, F., Yu, L., 2021. Design and preparation of poly(tannic acid) nanoparticles with intrinsic fluorescence: a sensitive detector of picric acid. *Chem Eng J* 416, 129090. <https://doi.org/10.1016/j.cej.2021.129090>.
- [48] Muirhead, D.L., Button-Denby, A., Smyth, C.M., Nelson, J., Callahan, M.R., 2020. Chemistry of Ionic Silver and Implications for Design of Potable Water Systems. 1–12. (<https://ntrs.nasa.gov/api/citations/20205004059/downloads/ICES-2020-522%20final%20for%20Strives.pdf>).
- [49] Bezuneh, T.T., Ofgea, N.M., Tessema, S.S., Bushira, F.A., 2023. Tannic acid-functionalized silver nanoparticles as colorimetric probe for the simultaneous and sensitive detection of aluminum(III) and fluoride ions. *ACS Omega* 8, 37293–37301. <https://doi.org/10.1021/acsomega.3c05092>.
- [50] Nguyen, M.L., Murphy, J.A., Hamlet, L.C., Lau, B.L.T., 2018. Ligand-dependent Ag₂S formation: changes in deposition of silver nanoparticles with sulfidation. *Environ Sci Nano* 5, 1090–1095. <https://doi.org/10.1039/c7en01240c>.
- [51] He, D., Garg, S., Wang, Z., Li, L., Rong, H., Ma, X., et al., 2019. Silver sulfide nanoparticles in aqueous environments: formation, transformation and toxicity. *Environ Sci Nano* 6, 1674–1687. <https://doi.org/10.1039/c9en00138g>.
- [52] Zhao, L., Zhao, L., Miao, Y., Liu, C., Zhang, C., 2017. A colorimetric sensor for the highly selective detection of sulfide and 1,4-dithiothreitol based on the in situ formation of silver nanoparticles using dopamine. *Sensors* 17, 1–13. <https://doi.org/10.3390/s17030626>.
- [53] Park, J.W., Shumaker-Parry, J.S., 2014. Structural study of citrate layers on gold nanoparticles: Role of intermolecular interactions in stabilizing nanoparticles. *J Am Chem Soc* 136, 1907–1921. <https://doi.org/10.1021/ja4097384>.
- [54] Blanton, T., Mixture, S., Dontula, N., Zdziszynski, S., 2011. In situ high-temperature X-ray diffraction characterization of silver sulfide, Ag₂S. *Powder Diff* 26, 114–118. <https://doi.org/10.1154/1.3583564>.
- [55] Hamed, M.S.G., Adedeji, M.A., Zhang, Y., Mola, G.T., 2020. Silver sulphide nanoparticles enhanced photo-current in polymer solar cells. *Appl Phys A Mater Sci Process* 126, 1–9. <https://doi.org/10.1007/s00339-020-3389-8>.
- [56] Jaiswal, M., Kumar, R., Tripathi, R.M., Nayak, R., Mittal, J., Choudhary, S., et al., 2023. Rapid and reversible detection of trace amounts of H₂S in air and packaged food using a biogenic bismuth oxide nanorod colorimetric sensor. *Sens Actuators B Chem* 38, 133395. <https://doi.org/10.1016/j.snb.2023.133395>.
- [57] Shojaeifard, Z., Hemmateenejad, B., Shamsipur, M., Ahmadi, R., 2019. Dual fluorometric and colorimetric sensor based on quenching effect of copper (II) sulfate on the copper nanocluster for determination of sulfide ion in water samples. *J Photochem Photobiol A Chem* 384, 112030. <https://doi.org/10.1016/j.jphotochem.2019.112030>.
- [58] Yu, J., Huang, M., Tian, H., Xu, X., 2022. Colorimetric sensor based on Ag-Fe NTs for H₂S sensing. *ACS Omega* 7, 44215–44222. <https://doi.org/10.1021/acsomega.2c05682>.
- [59] Liu, W., Li, Z., Jia, H., Zhang, L., He, W., Meng, Q., 2019. Shell surface sulfidation mediated the plasmonic response of Au@Ag NPs for colorimetric sensing of sulfide ions and sulfur. *Appl Surf Sci* 481, 678–683. <https://doi.org/10.1016/j.apsusc.2019.03.175>.
- [60] Wang, Q., Wang, Y., Guan, M., Zhu, S., Yan, X., Lei, Y., et al., 2020. A multicolor colorimetric assay for sensitive detection of sulfide ions based on anti-etching of triangular gold nanoplates. *Microchem J* 159, 105429. <https://doi.org/10.1016/j.microc.2020.105429>.
- [61] Zeng, J., Li, M., Liu, A., Feng, F., Zeng, T., Duan, W., et al., 2018. Au/AgI dimeric nanoparticles for highly selective and sensitive colorimetric detection of hydrogen sulfide. *Adv Funct Mater* 28, 1–10. <https://doi.org/10.1002/adfm.201800515>.