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ORIGINAL ARTICLE

Screening for malachite green contamination on live fish skin with chewing gum based viscoelastic SERS sensor

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Abstract

Malachite green (MG), a prohibited but still found antimicrobial in aquafarm and during live fish shipping, is a hot target in food safety screening. Herein, a novel chewing gum based flexible SERS (G-SERS) sensor was proposed for rapid sampling and detection of MG on live fish skin. The whole analysis takes <5 min, while the limit of detection for MG is 0.73 pg. Different from other reports, MG contaminated live fish was monitored daily with the G-SERS sensor, during which the fish was firstly raised in 0.5 ppm MG solution for one day, followed by freshwater for a week. It was found that the SERS signal of residue MG on fish skin could still be seen even on the sixth day, roughly the sale cycle of live fish in a marketplace. Furthermore, the method was also applied for MG screening on the skin of fish purchased from a supermarket and a local street marketplace. MG was found on some fishes from the latter but not from the former, which was cross-validated by LC-MS, suggesting MG risks still exist in smaller marketplaces. This work demonstrated the feasibility of using the flexible SERS sensor for onsite food safety screening.

Keywords: Food safety monitoring, Malachite green, Live fish, SERS, Gum

1. Introduction

In recent years, formulated feeds (containing antibiotics, antifungal drugs, and other pharmaceuticals), pesticides and disinfectants have been widely used in aquaculture [1]. It may raise some serious concerns on the safety of seafood [2]. For example, antibacterials have been frequently detected in fish products [3,4], which is known to cause environmental and health issues (e.g., antibiotic resistance for bacteria [5]). Malachite green (MG), a good antibacterial but with potential carcinogenicity, mutagenicity, and teratogenicity, is prohibited in many countries [6,7]. In fact, it is one of the regulated inspection items for aquatic products globally because it is still used illegally owing to its low cost and high effectiveness, particularly in developing countries [8]. What's worse, the culture of pursuing live fish in countries like China has put a lot of stress on the supply chain, which could lead to the abuse of MG to improve the survival rate during live fish shipping, and hence presents the MG exposure risk right on the dinner table [9]. Therefore, onsite MG screening on live fish during shipping or in the market is very important to ensure food safety.

The primary analytical methods to detect MG include high-performance liquid chromatography (HPLC) [10] and liquid chromatography-tandem mass spectrometry (LC-MS) [6], which have high

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detection accuracy. Nevertheless, at least two issues are related to these methods. For one, the time frame from the aquafarm to the dining table (shipping plus sales cycle) is usually short (roughly less than a week); for another, the culture of pursuing live fish demands local purchasing from the decentralized street marketplaces. The lengthy pretreatment procedure and bulky instruments could seriously compromise the safeguarding role of these methods. That is, when the (positive) test results came back, the fish had probably already gone on the dining table. Therefore, fast on-site screening of MG is very necessary, especially in countries like China, where there are many decentralized street marketplaces and has a strong traditional culture for live fish.

Surface-enhanced Raman scattering (SERS) is considered to be one of the most important molecular spectroscopic techniques and suitable for on-site analysis [11,12]. In fact, there are many reports about the detection of MG on seafood based on SERS [1,8,13–24]. Nevertheless, the effectiveness of the SERS methods remains to be verified. For example, MG in fish tissues could be detected with SERS [18,19,21,24], but it is not suitable for onsite screening. There are also groups who devoted to the sensing of MG on the live fish by applying MG solution directly onto the body of an aquatic product [8,14–16,20], or soaking the aquatic products into diluted MG solution [1,17,22,23]. However, neither of the exposing scenarios is the general practice of illegal MG use, which usually involves raising the fishes in ppm level of MG solution during shipping (up to 36 h), followed by raising them in freshwater before the sale [7,9]. MG residue (if any) will undergo degradation and dissolving with time (during the time in the market). The effectiveness of SERS for MG sensing in this real-life scenario has not been explored, though it is vital for MG contamination risk evaluation.

Chewing gum of which the main ingredient is gum Arabic can undergo a large deformation [25]. Thus, it has been used as a stretchable and foldable sensor for monitoring muscle and joint motions [26]. On the other hand, gum has high viscoelasticity which means good adhesion capacity to remove any residual contaminants (analytes) from a surface. Herein, chewing gum was used for the fabrication of a flexible, adhesive and sensitive hydrogel SERS sensor to detect MG on live fish. Citrate-reduced Ag nanoparticles (Ag NPs) were prepared and modified with various halogen anions, including I^-, Br^- and Cl^-. It was found that I^- could give the highest enhancement for MG. Thus, the Ag NPs–KI mixture was then mixed with the gum to form the SERS sensor. The preparation procedure was shown in Scheme 1. The sensitivity and recovery efficiency for analyte MG, viscoelasticity, shelf-life, and reproducibility of the prepared sensor were explored. Later, the G-SERS sensor was applied for the detection of MG on the fish body. In the process, the crucian carp was firstly raised in MG spiked water for one day, and then in freshwater for a week, the G-SERS sensor was used to monitor the residual MG on the fish body each day. Finally, the proposed method was applied to the screening of MG residues on the crucian carp purchased from a supermarket and a local street marketplace before verifying with results obtained from the standard LC-MS method.

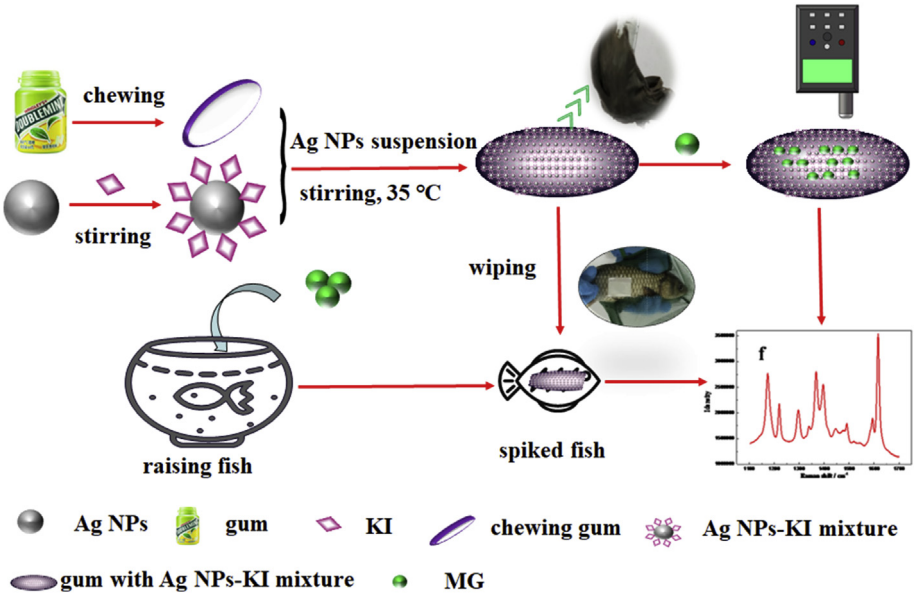
2. Material and methods

2.1. Reagents and materials

Silver nitrate (99%), sodium citrate (99%), Nile blue A (NBA), rhodamine 6G (R6G) and MG were supplied by Sigma–Aldrich (Shanghai, China). Potassium iodide, potassium bromide, potassium chloride, and ethanol were purchased from Shanghai Titan Scientific Co., Ltd, China. Doublemint® gum was obtained from a local supermarket. 18.2 MΩ cm water (Nanopure, Thermo) was used throughout the experiment.

2.2. Instruments

SERS measurements were performed on a customized Raman microscope equipped with Acton SP-2500i spectrograph (Princeton Instrument, US) and Pixis-100BR CCD (Princeton Instrument, US) in the whole experiment. A He–Ne laser (14 mW) was used in the experiments. Laser power 12×mW, 50 × objective, and 5 s integration time were used in the experiments. At least 10 spots on the same G-SERS sensor were examined. The Ag NPs was centrifuged in a centrifuge (Microfuge® 22 R, Beckman coulter, US) at 10,000 rpm for 10 min at 20 °C. The Ag NPs were characterized by a Field Emission Transmission Electron Microscope (TEM, JEM-2100 F, Japan), and the gum and G-SERS sensor by a scanning electron microscope (SEM, FEI Inspect F), respectively. The sampling recovery efficiency was determined by a UV–Vis spectrophotometer (UV–Vis, UV-4802H, China) at the wavelength of 614 nm. Liquid chromatography-mass spectrometry (LC-MS) measurements were performed on Shimadzu LCMS-8045 (USA).



Scheme 1. Schematic representation of the preparation and application of the G-SERS sensor.

2.3. Recommended procedures

2.3.1. Preparation of Ag NPs

Silver nitrate was used to prepare Ag NPs [27]. Briefly, 100 mL of $AgNO_3$ (5 mM) solution was heated to boiling with rapid stirring. 2 mL of 10% sodium citrate aqueous solution was added quickly, and the mixture was boiled for another 1 h. Finally, the solution was cooled to room temperature, denoted as 5 mM Ag NPs.

2.3.2. Preparation of G-SERS sensor

Firstly, gum was chewed for about 30 min [26]. It was then washed with ethanol and ultrapure water for about 5 min, respectively. Then, it was heated to 35 °C for 1 h to evaporate the excess amount of water from the gum. Meanwhile, a certain volume of 5 mM Ag NPs (the optimization was shown in "3.2. Optimization of the SERS Sensor") was centrifuged and the supernatant was removed. The remaining mixture in the centrifuge tube was about 100 μL. Then, 10 μL of 100 mM halogen ion solution was added to the 100 μL concentrated Ag NPs and the mixture was vortexed for 1 min. Immediately, the Ag NPs-halogen ion mixture was added to 0.3 g chewing gum, which was heated to 35 °C for another 30 min. The chewing gum was repeatedly folded and stretched during this period with a glass rod. The fabrication process involves no toxic chemicals.

2.3.3. SERS analysis

In this work, there were two protocols: (1) For optimization and characterization of the G-SERS sensor: 5 μL MG aqueous solution was dropped on about 0.1 g G-SERS sensor, which was subjected to SERS analysis after the solvent evaporated. (2) For the daily monitoring of the sensor: ten crucian carp (*Carassius carassius*) from the local supermarket were randomly divided into two groups: the experimental group and the control group. The control group was raised in a 75 L aquarium with tap water for a week. The experiment group was first exposed to 0.5 ppm MG aqueous solution [7] in another 75 L tank for one day and then raised in the tap water for a week (Fig. S1C) as well. In the process, water was changed daily and O_2 was supplied for both groups. The G-SERS sensor was used to stamp on the fish body (Fig. S1B) and then was analyzed on the Raman microscope daily for 6 days. Finally, MG on the crucian carp from 4 stalls in a street marketplace and a supermarket was monitored on the same day when purchased by this method, which was cross-validated by LC-MS approach [28] (supporting information).

2.3.4. Sample recovery efficiency (SRE) analysis

The SRE of the G-SERS sensor for MG was determined by a UV–Vis spectrophotometer [29]. Briefly, 20 μL of MG aqueous solution was dropped on a frozen fish. After 10 min, the G-SERS sensor was used to stamp on the fish body to recover the MG. Finally, the sensor was placed in a beaker filled with 10 mL of deionized water and sonicated for 20 min to extract the MG. The experimental conditions for the UV–Vis analysis can be found in Fig. S2.

3. Results and discussion

3.1. Preparation and characterization of the G-SERS sensor

The fabrication of the G-SERS sensor is very straightforward: citrate-reduced Ag NPs (Fig. 1A) were prepared and then modified with KI. Finally, the Ag NPs–KI mixture was doped in the gum to form the SERS sensor (Schemes 1 and S1A). The gum and G-SERS sensor were characterized by SEM, which were shown in Fig. 1B and C, respectively. It was clear that scattering NPs aggregates can be found in Fig. 1C. Besides, the color of the latter (the inset in Fig. 1C) became dark compared with the former (the inset in Fig. 1B), showing that gum was successfully doped with Ag NPs (Fig. 1C).

3.2. Optimization and characterization of the SERS sensor

Reports have shown that Ag NPs modified with iodide ion had a significant effect on the SERS signals of some analytes [30]. Herein, the same strategy was used to fabricate the G-SERS sensor through Ag NPs modified with KI. The SERS spectra in Fig. 2A showed the effect of KI on the signal of MG. It was found that the G-SERS sensor for the analysis of MG had an evident signal enhancement in the presence of gum, Ag NPs and KI. And the G-SERS sensor was found to have negligible interference with MG due to its clean Raman background. For MG, the major Raman peaks appeared at 1175, 1369 and 1618 cm^{-1} were ascribed to ring C–H in-plane bending (1175 cm^{-1}), N-phenyl stretching (1369 cm^{-1}) and ring C–C stretching (1618 cm^{-1}), respectively [31,32]. We also explored the effect of remaining halogen ions on SERS performance. The SERS spectra of MG on the G-SERS sensors in the presence of KCl, KBr, and KI were shown in Fig. 2B, respectively. It was found that G-SERS sensor fabricated with KI modified Ag NPs had the highest intensity. It's believed that I^- may change the shape of the silver surface in addition to inducing the aggregation to achieve a better signal [33]. Thus, we decide to use KI modified Ag NPs in the preparation of G-SERS sensor in the following experiment.

We then tried to optimize the concentration of I^- in the G-SERS sensor. To address this, 2–80 μL of 100 mM KI was mixed with 10 mL Ag NPs, and the mixture was mixed with 0.3 g gum for preparing the G-SERS sensor, respectively. The results were shown in Fig. 2C. Obviously, the signal of MG increased firstly and then decreased with the augment of the amount of KI. It was found that the G-SERS sensor mixed with 10 μL of 100 mM KI had the best SERS signal (at 1619 cm^{-1}). This is probably caused by Ag NPs over aggregation induced by excessive KI [30], which is known to be able to lower the SERS performance of given SERS sensor. Thus, 10 μL of 100 mM KI was used in the following experiments.

After optimizing the amount of I^-, the effect of Ag NPs concentration was then explored to get the optimal G-SERS sensor. In Fig. 2D, the SERS performance for MG at 1618 cm^{-1} was obtained with 0.3 g gum containing 3–25 mL of Ag NPs which was concentrated and modified with 10 μL of 100 mM KI, respectively. Apparently, the signal increased first and then gradually decline with the increase of Ag NPs. The best signal was achieved at the amount of 10 mL Ag NPs (before centrifuge). To be specific, lower concentration of Ag NPs can not produce sufficient SERS hot spots (Fig. S3A), resulting weaker SERS signal [34]. The increase of the SERS signal before 10 mL was explained by increased Ag NPs aggregates with the increased amount of Ag NPs [13]. However, at volume larger than 10 mL, over aggregation of Ag NPs (Fig. S3B) could happen, which is known to be inefficient in SERS peroformance [27].

In conclusion, the optimal procedure to fabricate the G-SERS sensor was as follows: 10 mL Ag NPs was concentrated and mixed with 10 μL of 100 mM KI, and the mixture was then added into 0.3 g gum.

3.3. Reproducibility and stability of G-SERS sensor

The optimal G-SERS sensor was compressed with a glass slide to form a flat surface for testing the reproducibility of the gum sensor. Briefly, 5 μL of 10 μM aqueous solution of MG was added onto the sensor. This experiment was repeated with 10 gum sensors, and ten SERS spectra were recorded from each gum. Fig. 3A showed the results of these experiments. The relative standard deviation (RSD%) was found to be 15% between different sensors and 9–25% within a single G-SERS sensor, which was comparable to other reports [27]. In order to test the shelf life of the G-SERS sensor, 3 g of the G-SERS sensor was prepared and sealed in fridge at 4 °C. And 0.1 g of the G-SERS sensor was cut and explored for its SERS performance each day for a week, respectively. Fig. 3B showed the variation of SERS intensity of MG at the peak of 1618 cm^{-1}. The RSD of signal intensities was found to be less than 11% for 8 days. Meanwhile, there was no significant difference in SERS performance of the G-SERS sensor in 8 days based upon the *t*-test (Table S1), confirming good

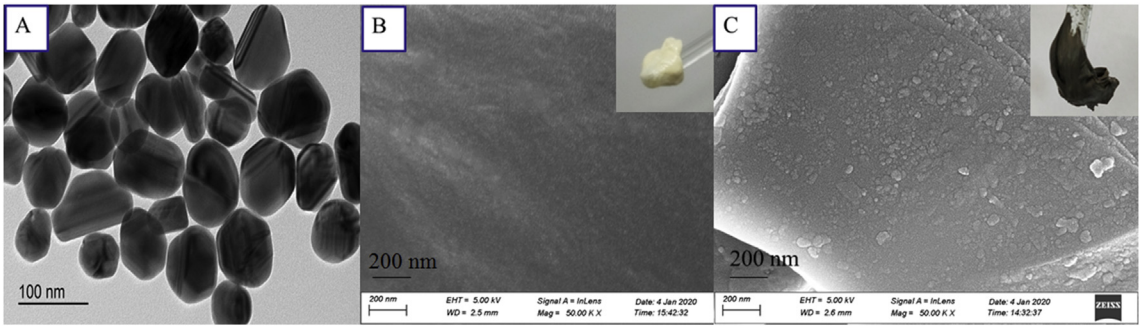


Fig. 1. TEM of Ag NPs (A), SEM images of gum (B) and G-SERS sensor (C). The insets in B and C are the photos of the gum and G-SERS sensor.

stability of G-SERS sensor. Hence, the G-SERS sensor has good reproducibility and stability.

3.4. LOD of the G-SERS sensor

To determine the SERS sensitivity, 5 μL of various concentrations of MG aqueous solution were added onto the G-SERS sensor. The results were shown in Fig. 3C. It is clear that the characteristic peaks of MG at 1175 cm^{-1} and 1618 cm^{-1} can still be identified even for 5 μL of 1 nM MG (1.82 pg). The linear relationship between SERS intensity I and MG concentration C at 1–500 nM was shown in Fig. 3D. The linear equation at 1618 cm^{-1} was $I_1 = 174.32C + 2107.90$ ($R^2 = 0.9362$). The RSD% at each concentration was found to be within 9.53–23.34%. The LOD was found to be 0.4 nM (0.73 pg). The linear equation at 1175 cm^{-1} was

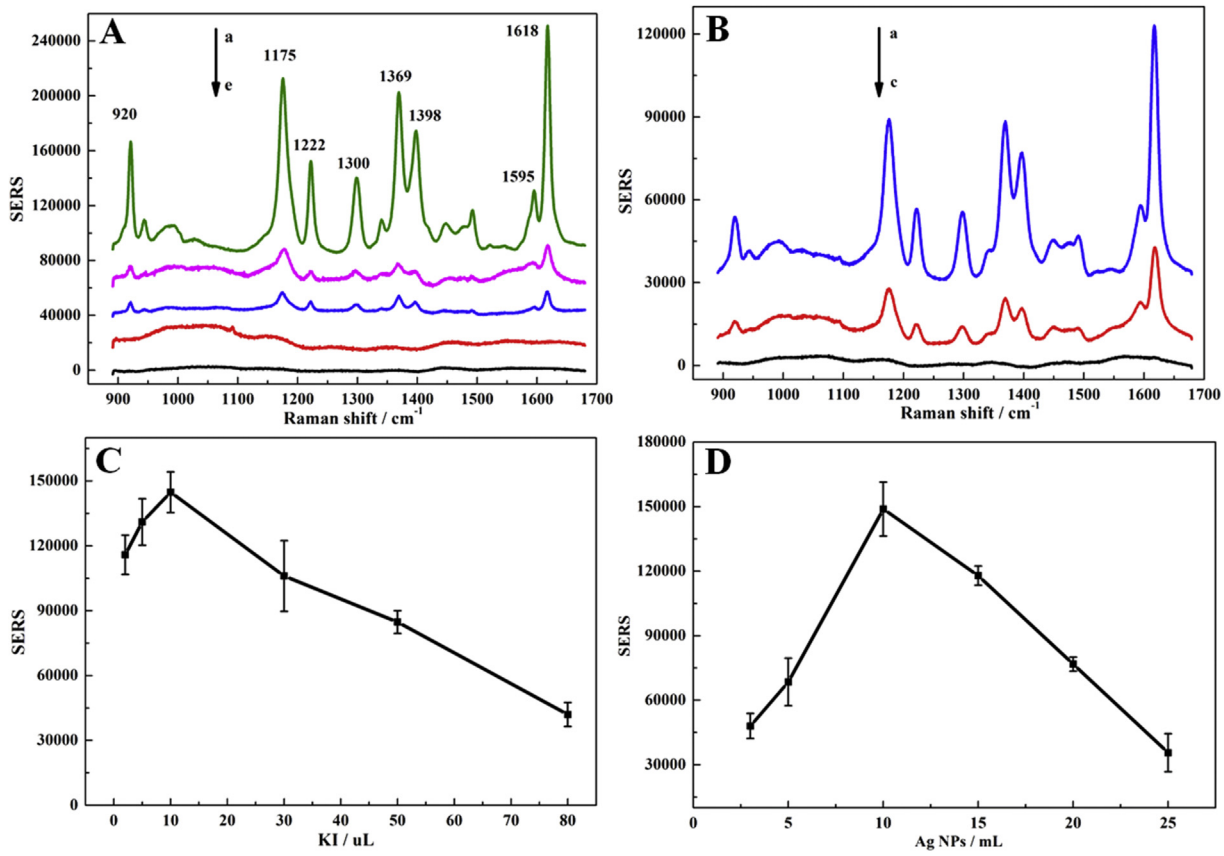


Fig. 2. A: The SERS spectra of MG with G-SERS sensor (a), MG with Ag NPs and gum mixture (b), MG with Ag NPs and KI mixture (c), MG with KI and gum mixture (d) and G-SERS sensor (e). B: The effect of halogen ions (10 μL 100 mM). Spectra (a) to (c) were KI, KBr and KCl, respectively. C: SERS performance of G-SERS sensor (0.3 g) modified with different KI: 2, 5, 10, 20, 30, 50, and 80 μL, respectively. D: SERS performance of G-SERS sensor modified with different amount of Ag NPs: 3, 5, 10, 15, 20, and 25 mL, respectively. 5 μL of 1 μM MG was used as the Raman probe. Laser power: 12 mW. Integration time: 5 s. Objective: 50 ×.

$I_2 = 126.19C + 1689.78$ ($R^2 = 0.9553$). The RSD% at each concentration was found to be 9.03–24.50%. To further prove its sensitivity, R6G and NBA were also examined, and the LODs were both 5 fmol (Fig. S4), indicating the G-SERS sensor had good sensitivity.

3.5. The sampling recovery efficiency (SRE) of the G-SERS sensor

We evaluated the SRE of MG on the fish by the G-SERS sensor (Fig. S2). The value was found to be 72.30%, showing that the G-SERS sensor had good recovery efficiency [35]. The possible reasons for the relatively low collection efficiency were the rough surface of the fish and the permeation of MG into the fish.

3.6. Detection of MG on the fish skin

Owing to the good flexibility, stability, and recovery efficiency of gum sensors, it could be applied for rapid, direct, and on-site detection of MG on the live fish. Briefly, the prepared G-SERS sensor was used to stamp on the live fish (Fig. S1B) each day, and the SERS spectra were recorded. The results from one of the fish were shown in Fig. 4A. It was found that the blank fish had no SERS features of MG, and the signal of MG on the spiked fish in tap water decreased with time. The peak of residual MG on the spiked fish at 1618 cm^{-1} and 1175 cm^{-1} on the sixth day in tap water still could be detected. We suspected that the signal of MG gradually decreased because some MG on the spiked fish partly converted to leucomalachite green (LMG) [36] and/or partly dissolved in water. The remaining results from other fish were shown in Figs. S5–S11. Note that the SERS signal of MG residue on fish skin could not be found with the G-SERS sensor after the seventh day, while it was still present in fish tissue (Table S2). This could be justified by the two sampling methods. The G-SERS is intended to monitor the MG residue on fish skin, while the LC-MS examines the fish tissue. Since the proposed G-SERS method is intended to safeguard any potential MG adulteration happening after leaving the farm and before the dining table, which is usually less than 1 week, we believe the proposed method is reliable.

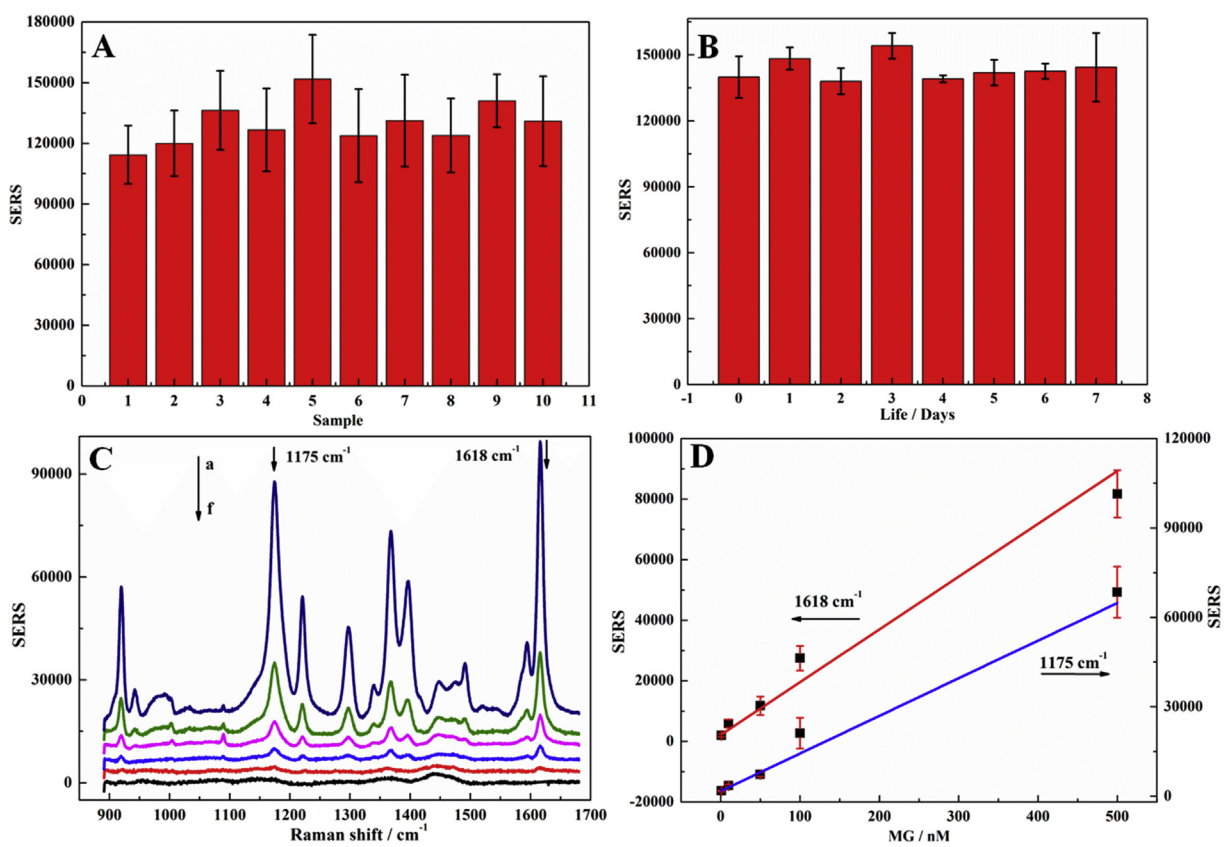


Fig. 3. A: Statistics of 10 G-SERS sensors obtained by using 5 μL of 1 μM MG as a Raman probe. B: Statistics of 5 μL of 1 μM MG aqueous solution on the G-SERS sensor corresponding to the signal variation every day in 8 days. 0 is that the sensor was prepared and used on the same day. C: The SERS spectra of different amount of MG: 500 (a), 100 (b), 50 (c), 10 (d), 1 (e), and 0 (f) nM, respectively. D: The plots of SERS intensity at characteristic peaks of 1175 and 1618 cm^{-1} with different concentrations of MG, respectively.

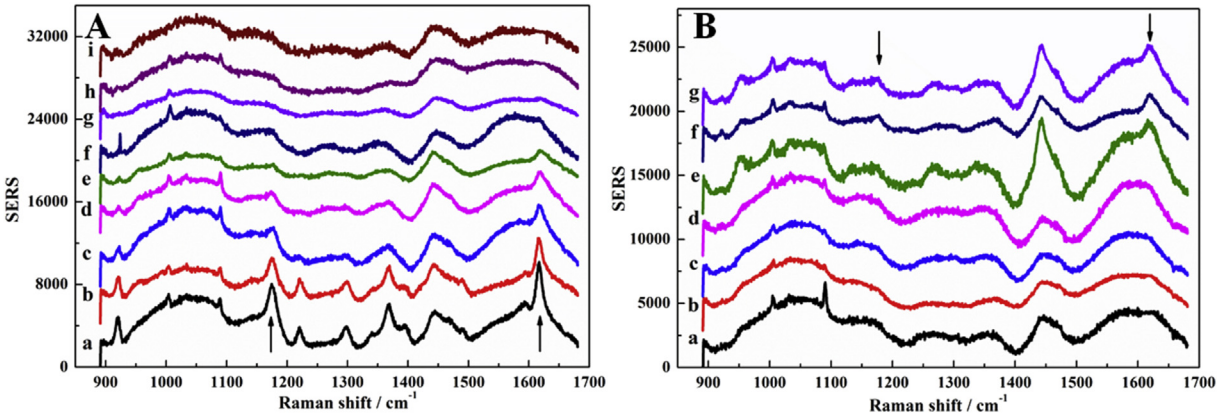


Fig. 4. A: The SERS spectra of MG on carp: crucian carp exposed to 0.5 ppm MG aqueous solution for 1 day (a), then raised in tap water for 1 (b), 2 (c), 3 (d), 4 (e), 5 (f), 6 (g) days, the blank fish (h) and G-SERS sensor (i), respectively. B: The SERS spectra obtained on live fish from a supermarket and a street marketplace: spectrum (a) was G-SERS sensor, spectra (b) to (c) were two crucian carp from the supermarket, and spectra (d) to (g) were four crucian carp from the same street marketplace (four stalls), respectively.

Table 1. Quantitative and confirmatory analysis of MG in fish by LC-MS.

Sample	LC-MS (LOD = 0.5 ug/kg)		SERS
	mean (ug/kg)	RSD (%)	
Street marketplace (stall 1)	50.30	1.14	Positive
Street marketplace (stall 2)	37.35	1.74	Positive
Street marketplace (stall 3)	28.28	2.75	Positive
Street marketplace (stall 4)	Not found	/	Negative
Supermarket 1	Not found	/	Negative
Supermarket 2	Not found	/	Negative

We finally applied the proposed method to detect MG on the live fish from the local supermarket and street marketplace (four stalls), the results were shown in Fig. 4B. It was found that the peak of MG on the fishes from the street marketplace at 1175 and 1618 cm^{-1} could be identified, while that from the supermarket could not. As shown in Table 1 and Fig. S12, LC-MS was used to quantify the amount of MG in the samples. The results coincided with the results of SERS analysis. In other words, the SERS method could be used to monitor MG contamination risks on live fish.

4. Conclusion

In conclusion, a novel dual functional gum based flexible SERS sensor (G-SERS) was proposed for monitoring MG contamination risks on live fish during shipping and in the marketplaces. The combination of iodide ion and chewing gum helps the signal enhancement on Ag NPs, making it possible for the detection of MG at 0.73 pg. The flexibility and viscoelasticity of the chewing gum make it possible for the direct sampling of a minute amount of MG on fish skin. To illustrate the effectiveness in food safety screening of the proposed G-SERS sensor, crucian carp was raised in 0.5 ppm MG solution for 1 day, and then in fresh water for another 6 days to mimic the live fish shipping and sale cycle, and monitored daily for the presence of MG. SERS signal of the residual MG on fish could be still found even after 6 days in fresh water. Crucian carp from the local supermarket and street marketplace was also screened and cross-validated with LC-MS. Positive results were found on some fishes from the local street marketplace, suggesting MG risks still exist in smaller marketplaces.

Conflict of interest

The authors of the manuscript declare that there is no conflict of interest regarding the publication of this study.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.38212/2224-6614.1057.

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