Composites & nanocomposites



Surface-enhanced Raman scattering on sandwiched structures with gallium telluride

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Received: 7 February 2020 Accepted: 22 April 2020

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ABSTRACT

Two-dimensional crystals-based surface-enhanced Raman scattering (SERS) substrates are a research hot spot in the realm of chemistry and biology. Herein, a novel hybrid substrate based on AuNPs/GaTe/Au-film is proposed and fabricated for SERS activity. Finite-difference time-domain numerical simulations demonstrate that the plasmonic coupling in the hybrid structure, particularly the LSPs coupling of AuNPs and Au-film, promotes an enhanced electric field and consequently, greatly enhances the Raman activity. Impressively, the enhancement factor of 3×10^5 and the limiting detection concentration of 10^{-14} M have been achieved for the rhodamine 6G molecules, which are equivalent to the best results achieved from the patterned graphene substrates. Due to its simple structure, cost-effectiveness, good uniformity, reproducibility, and stability, it is expected that such a SERS substrate will open up a new way toward the ultrasensitive detection of molecules.

Introduction

Owing to its surface sensitivity, the surface-enhanced Raman scattering (SERS) has emerged as a powerful spectroscopic technique that is widely employed in the ultrasensitive molecular analysis [1]. Generally, there are two mechanisms predominantly accountable for the enhanced Raman activity, i.e. the electromagnetic mechanism (EM) and the chemical mechanism (CM) [2]. The former is related to the resonant excitation of the surface plasmons (SPs), where the latter depends on the polarizability of the analyte molecule adsorbed on the surface of substrates. An ideal SERS substrate should meet the following requirements, i.e. high SERS activity, surface uniformity, stability and reproducibility, and cost-effectiveness; however, these requirements have not been fulfilled yet. The preparation of substrates is one of the key issues in SERS technology. The unordered substrates such as noble metal nanoparticles (NPs) [3], shell-isolated nanoparticles [4], nanorods

https://doi.org/10.1007/s10853-020-04729-w

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[5], and nanoporous gold [6] usually exhibit poor uniformity, stability, and reproducibility. On the other side, the ordered substrates, which are mainly periodic metal structures prepared via nanosphere lithography, nanolithography or nanoimprint [7–9], are limited by the process resolution. It is difficult to prepare sub-10 nm ordered structures to maximize the electromagnetic coupling.

Due to their unique physical and chemical properties, the advent of two-dimensional (2D) layered materials provided a new approach to prepare SERS substrates [10]. Due to the $\pi - \pi$ interaction between aromatic molecules and 2D materials, the aromatic molecules are efficiently adsorbed on the surface of 2D materials and hence detected sensitively [11, 12]. Moreover, the 2D materials-based substrates are usually uniform, stable, and reproducible [10]. Therefore, to make them ideal SERS substrates, the main attention should be devoted to the improvement in their detection capability. In this regard, various surface-decorating structures with different 2D materials have been put forward [12–15].

Graphene was extensively studied as a 2D SERS substrate and achieved the lowest detection limit of 10^{-14} M for R6G molecule, which is almost capable of detecting a single molecule [13]. However, the recent study showed that gallium telluride (GaTe) could exhibit a better SERS activity than grapheme [15]. It has been found that when GaTe and graphene were evenly decorated with AuNPs, the detection limit of R6G molecule on AuNPs/GaTe and AuNPs/graphene substrates was found to be 10^{-11} M and 8×10^{-7} M, respectively [15, 16]. Namely, the AuNPs/GaTe substrate has demonstrated a better SERS activity than the AuNPs/graphene substrate, which was ascribed to the higher density of AuNPs on the surface of GaTe resulting from its defect nature [17]. However, GaTe is rarely utilized for SERS application.

SERS effect is usually initiated on the 2D layered materials by decorating their top surfaces with metal nanoparticles, commonly with AuNPs. A strong electric field is generated due to localized surface plasmons (LSPs) at the interstitial sites of the AuNPs, which leads to the enhanced Raman signals [12, 16]. Besides the top surface decoration, the space underneath the 2D materials was also utilized to manipulate SPs and enhance the SERS capability [13, 18]. However, it is observed that the spaces of the top and bottom sides of the 2D layered crystals are seldom

utilized simultaneously. We expect that a sandwiched structure of metal/2D crystal/metal would further enhance the Raman scattering by virtue of the SPs coupling of the two metallic layers. Since the thickness of the 2D layer can be as thin as a few nanometers, it is feasible to utilize the spaces on both sides for a synergistic enhancement, which could lead to a significant improvement in the detection performance.

Herein, we present a hybrid structure of AuNPs/ GaTe/Au-film and demonstrate it for single-molecule detection activity. The limiting detection concentration of rhodamine 6G (R6G) is observed to be as high as 10^{-14} M, which is of the same order of the best result achieved from the patterned graphene substrates. When the hybrid structure is exposed to light, some photons illuminate the AuNPs on the surface and excite the LSPs in the NPs, while others pass through the GaTe and excite the LSPs on the underlying gold film. Then, the coupling of LSPs of both AuNPs and Au-film leads to an enhanced electric field on the GaTe surface and consequently enhances the Raman activity.

Results and discussion

Figure 1a shows the schematic of the AuNPs/GaTe/ Au-film hybrid structure prepared on the SiO₂/Si substrate. The corresponding scanning electron microscope (SEM) image is shown in Fig. 1b. As can be seen, the decoration of AuNPs on GaTe is uniform. For comparison, the InSe, WS₂, and graphene were used as a bottom layer instead of Au-film. Moreover, AuNPs/GaTe was also synthesized as a control. Figure 1c shows the normalized Raman spectra of the R6G molecule on few-layer GaTe, Au-film, the AuNPs/GaTe and the AuNPs/GaTe/Au-film, as well as graphene, InSe, and WS₂ used as the bottom layer. The signals on few-layer GaTe, Au-film, the AuNPs/GaTe, the AuNPs/GaTe/InSe, and the AuNPs/GaTe/WS₂ all magnify five times. From the intensity of Raman peak at 1652 cm⁻¹, the enhancement of AuNPs/GaTe/InSe and AuNPs/GaTe/WS₂ over AuNPs/GaTe is found to be ca. twofold. This enhancement is closer to the one reported in the graphene/WSe₂ structure, where chemical enhancement resulted from the electronic transfer between graphene and WSe₂ was dominant [14]. Thus, the enhancement of AuNPs/GaTe/InSe and AuNPs/



Figure 1 a Schematic of AuNPs/GaTe/Au-film. b SEM image of AuNPs/GaTe/Au-film. c Raman signals of 10^{-4} M R6G on different samples (slit width: 100 μ m).

GaTe/WS₂ over AuNPs/GaTe could be ascribed to the electronic transition between GaTe and InSe (WS₂). Similarly, AuNPs/GaTe/graphene exhibits a giant enhancement up to tens of fold over AuNPs/ GaTe. The enhancement of AuNPs/GaTe/Au-film is even much greater than that of AuNPs/GaTe/graphene. Raman peaks with a high signal-to-noise ratio can be observed in the spectrum of R6G on AuNPs/GaTe/Au-film substrates. High-intensity peaks of R6G around 1193, 1311, 1363, 1505, and 1652 cm⁻¹ are attributed to the out-of-plane C–H_x bending; the combination of C-H and N-H bending; the combination of ring stretching of C-C vibration, N–H bending, and C– H_x wagging, C–H bending; the combination of C-N stretching, C-H and N-H bending; and the combination of ring stretching of C-C vibration and C– H_x bending, respectively [19]. As a comparison, some feeble peaks are observed in the spectra of R6G on Au-film and AuNPs/GaTe. When collecting signals from molecules on GaTe, only a very feeble peak around 1652 cm^{-1} can be observed. The corresponding enhancement factor for R6G molecule is calculated to be 3×10^5 from the equation, i.e., enhancement factor = $\frac{I_{sers}}{I_{ref}} \times \frac{N_{ref}}{N_{vers'}}$ where I represents the intensity of R6G peak at 1652 cm⁻¹ and N the average number of adsorbed molecules [20]. The reference is the Raman spectrum of R6G molecule on GaTe.

To explore the plasmonic coupling effect in the AuNPs/GaTe/Au-film structure, we have conducted numerical simulations using a finite-different time-domain (FDTD) method. As shown in Fig. 2a, a layer of 3-nm-thick GaTe is sandwiched between Au-film

and AuNPs. The morphology of Au-film is not hypothetical but constructed from the atomic force microscope (AFM) image of Au-film, which is presented in Fig. 2b. Similarly, the morphology of AuNPs is constructed from the SEM image of the AuNPs/GaTe, which is presented in Fig. 2d. As can be seen from the top-down view of the configuration shown in Fig. 2e, the modeling of AuNPs is pretty good. Figure 2f-l shows the calculated absolute value of electric field (EF) magnitude |E| on different surfaces, including GaTe, Au-film, GaTe/Au-film, AuNPs/GaTe and AuNPs/GaTe/Au-film. The scale is the ratio of $|E|/|E_0|$, in which $|E_0|$ is the intensity of incident light. Since molecules are absorbed on the GaTe surface, the EF intensity on the GaTe surface is vital. Figure 2(f) reveals that no LSPs are excited on the upper surface of the bare GaTe. The EF intensity is around 0.6. As a result, the Raman signal of R6G on bare GaTe is very weak. Figure 2g reveals that LSPs can be efficiently excited on the Au-film. When covered by GaTe, the structure does not experience clear EF attenuation due to the good penetrability of fewlayer GaTe. Accordingly, the maximal EF intensity of GaTe/Au-film is around 1.2 compared to that of 1.1 for Au-film. For the case of AuNPs/GaTe, strong coupling occurs between upper AuNPs and the EF is enhanced at the interstitial sites of the AuNPs. The maximal EF intensity reaches 4.0 as shown in Fig. 2i, j. When combining AuNPs, GaTe, and Au-film in a 3D hybrid structure, the LSPs coupling of AuNPs and Au-film occurs. Resulted from the LSPs coupling, the maximal EF intensity reaches 6.0 on the GaTe upper surface as shown in Fig. 2k, l. Scaled as the fourth



Figure 2 a Cross-sectional view of the AuNPs/GaTe/Au-film structure for simulations. **b** AFM image of Au-film. **c** The corresponding line profile of A–B line in (**b**). **d** SEM image of AuNPs on GaTe. **e** Top-down view of the configuration. **f** EF intensity on the upper surface of the bare GaTe. **g** EF intensity on the Au-film surface which is shown in the white rectangle of (**b**). **h** EF intensity on the upper surface of GaTe in GaTe/Au-film

power of EF intensity in the electromagnetic mechanism, the SERS effect can thus be greatly increased [21].

The SERS effect of AuNPs/GaTe/Au-film can be tuned by the thickness of GaTe. Figure 3a depicts the

structure. **i** EF intensity on the upper surface of AuNPs/GaTe structure which is shown in the white rectangle of (**d**); the EF intensity in the xz plane is shown in **j** with a maximal $|E|/|E_0|$ ratio of 4.0. **k** EF intensity on the upper surface of AuNPs/GaTe/Au-film structure. The EF intensity in the xz plane is shown in **l** with a maximal $|E|/|E_0|$ ratio of 6.0.

normalized intensity of Raman peaks of R6G at 1652 cm^{-1} as a function of the thickness of GaTe, which corresponds well to the decay exponential function. Such results support the presumption that the SERS effect is mainly attributed to the enhanced

Figure 3 a Normalized intensity of Raman peaks of R6G at 1652 cm^{-1} as a function of the thickness of GaTe. b TEM image of GaTe film after 10-min exposure to the ambient atmosphere; c and d Raman signals around $1505 \text{ cm}^{-1} \text{ of } 10^{-10} \text{ M R6G}$ on substrates with different exposure times of GaTe and AuNPs/GaTe. e The normalized intensity of Raman peaks of R6G at 1652 cm^{-1} as a function of immersion time with different concentrations of R6G. (slit width: 500 µm).



electric field resulting from the LSPs coupling of AuNPs and Au-film [22]. To obtain the largest SERS effect, the GaTe layer on Au-film should be very thin; therefore, few-layered GaTe with thickness around 3-6 nm is employed in our experiments. However, few-layered GaTe could be susceptible to oxidation in the atmosphere due to its large surface-volume ratio and high reducibility. Figure 3b shows the transmission electron microscope (TEM) image of the fewlayered GaTe after being exposed for 10 min to the ambient atmosphere. A clear amorphous oxidation layer on the surface can be observed, indicating that the adsorption of molecules on GaTe could be greatly weakened. Moreover, the formation of AuNPs on the GaTe will also be affected by this amorphous oxidation layer. To characterize the influence of oxidation, five GaTe samples were prepared and exposed to the atmosphere for different time intervals (i.e., 0, 30, 60, 90, and 120 min, respectively). After the exposures, samples were immediately immersed in the HAuCl₄ solution for the 960 s to decorate the AuNPs on it. Raman peak at 1505 cm^{-1} for 10^{-10} M R6G on these substrates is shown in Fig. 3c. As expected, the intensity of the Raman signal weakens with the

increased exposure time. The Raman peaks of R6G around 1505 cm⁻¹ cannot be detected after a mere 120-min exposure. Similarly, Fig. 3d shows the oxidation analyses of the freshly prepared AuNPs (960 s)/GaTe samples. It is seen that the Raman signals are preserved much better, such that the peak around 1505 cm⁻¹ is still visible even after the 120-min exposure. Thus, we can suggest the following to avoid excessive oxidation: i. GaTe crystal should be kept under inert atmosphere; ii. AuNPs decoration should be conducted immediately after the transfer of a few-layered GaTe onto Au-film.

For SERS applications, the nanomaterials above the GaTe top surface are normally noble nanoparticles. In this regard, AuNPs is the best choice since it can slow the oxidation of GaTe film. Furthermore, AuNPs can be facilely decorated on the surface of GaTe when immersed in the HAuCl₄ solution, where the size and coverage of AuNPs increase with longer immersion time. The detailed relationship between morphology and immersion time has been provided in our previous paper [15]. Since the morphology of AuNPs obviously influences the SERS effect, the optimization of immersion time is essential for molecular

detection. Here, the Raman signals of R6G solution with a molecular concentration of 10^{-4} M, 10^{-7} M, 10^{-10} M, and 10^{-13} M are detected using AuNPs/ GaTe substrates (AuNPs/GaTe/Au-film substrates for 10^{-13} M), where the immersion times are 60 s, 120 s, 240 s, 480 s, 960 s, 1920s, and 3840 s, respectively. The normalized intensity of the Raman peaks of the R6G at 1652 cm⁻¹ is plotted as a function of immersion time in Fig. 3e, where the maximum intensity of the Raman signals of 10^{-4} M, 10^{-7} M, 10^{-10} M was achieved at 960 s immersion time, while that of 10^{-13} M was achieved with 240 s immersion time. The phenomenon can be explained by the change in AuNPs coverage. Figure 4a shows the maximal EF intensity on AuNPs/GaTe and AuNPs/ GaTe/Au-film substrates with different immersion times. As can be seen from the curve of AuNPs/ GaTe, a prolonged immersion time increases the plasmonic coupling between the top AuNPs. The same tendency is observed in the curve of AuNPs/ GaTe/Au-film, indicating that a stronger plasmonic coupling between the top AuNPs also benefits the enhancement of AuNPs/GaTe/Au-film substrate. Thus, the Raman intensity increases initially with longer immersion time. However, as R6G molecules are adsorbed on the GaTe surface, the decreased surface area of GaTe with higher AuNPs coverage shall counteract the gain from the former advantage, leading to the SERS saturation and eventual decrease. When the concentration of the target molecule is low, a higher GaTe area could benefit the detection. Thus, the immersion time of the 960 s suits the detection of molecules with high concentration, while the immersion time of 240 s suits the detection of trace molecules.

The synthesized AuNPs/GaTe/Au-film substrates were also immersed in R6G solution with varying concentrations for 20 min to explore their quantitative detection performance, which is an important issue in the SERS realm. As shown in Fig. 4b, Raman signals decreased with reduced concentration. The normalized intensity of Raman peak at 1652 cm⁻¹ is log–log plotted as a function of the concentration in Fig. 4c, which corresponds well to the Langmuir model for adsorption [23]. Distinct Raman signals can be observed for the R6G solution at a concentration as low as 10^{-14} M, which is much lower than the previously reported 10^{-11} M on AuNPs-GaTe substrates [15]. Only a few substrates could reach this limiting concentration [22, 24, 25]. To the best of our

knowledge, only the graphene/Au pyramids substrate exhibited the same limiting concentration in the 2D materials-based SERS substrates [13]. Yet, the preparation of the graphene/Au pyramids substrate is complex and expensive, impeding the massive application of the substrate. Other high-performance substrates such as the noble metal nanocavity arrays also share the same high-cost issues [7]. Moreover, the performance of the AuNPs/GaTe/Au-film substrates could further be enhanced with ordered nanostructures. Figure 4d, e shows the uniformity test of AuNPs/GaTe/Au-film substrate. Good uniformity can be observed among the areas with similar GaTe thickness. Figure 4f shows the reproducibility test of the substrate. Two samples with thick GaTe and two samples with thin GaTe were measured. It can be seen that when GaTe films have the same thickness, good reproducibility is promised. Figure 4g shows the stability test of the substrate. After exposing the structure to the atmosphere for two months, the Raman intensity of R6G on it remains at about 70%.

Conclusion

In conclusion, a novel self-assembled AuNPs/GaTe/ Au-film hybrid substrate for SERS activity was proposed and fabricated, which has demonstrated a superior detection capability for the aromatic molecules at lower fabrication cost. FDTD simulations demonstrated that the plasmonic coupling in the hybrid structure, particularly the LSPs coupling of AuNPs and Au-film, promotes an enhanced electric field, leading to the impressive SERS effect. The enhancement factor for R6G molecules was found to be as high as 3×10^5 . The corresponding limiting detection concentration of 10⁻¹⁴ M for R6G was reported, which is of the same order as the best performed patterned graphene substrates. Moreover, along with better uniformity and reproducibility, the oxidation of the GaTe was greatly hindered by the decoration of AuNPs on its environmentally exposed surface. With the superior detection performance, good uniformity, reproducibility, stability, and low cost, the novel AuNPs/GaTe/Au-film substrate could be significant in the practical applications of 2D materials-based SERS substrates.



Figure 4 a Immersion time-dependent maximal EF intensity on the surface of AuNPs/GaTe and AuNPs/GaTe/Au-film. **b** Normalized SERS spectra for R6G in varying concentrations on AuNPs/GaTe/Au-film substrates. The signals of the 10^{-10} M, 10^{-12} M, and 10^{-14} M magnify ten times. **c** Normalized intensity of Raman signals (1652 cm⁻¹) as a function of the concentration of R6G. The red dash line shows the Langmuir fit of data. The inset shows the Raman spectrum of the sample immersed in a 10^{-14} M R6G solution. **d** Seven spots evenly distributed on an

AuNPs/GaTe/Au-film substrate are chosen to measure the Raman spectra of R6G (10^{-4} M). The corresponding Raman signals are shown in (e). f Raman spectra of R6G (10^{-4} M) on four AuNPs/GaTe/Au-film substrates, two with thick GaTe and two with thin GaTe. g Raman signals of 10^{-4} M R6G on the Au NPs/GaTe/Au-film SERS substrate recorded for stability testing. The pink one was measured at the initial stage, while the blue one was measured after exposure to the atmosphere for two months. (slit width: 100 µm for (e), (f) and (g). 500 µm for (b)).



Experimental section

Preparation of AuNPs/GaTe/Au-film: Au-film (50 nm)/Ti film (5 nm) was evaporated on the SiO₂(300 nm)/Si substrate, in which the Ti film was employed to enhance the adhesion of Au-film. For the preparation of heterostructures, few-layer GaTe films were mechanically exfoliated from bulk crystal (99.999%, Aladdin) with scotch tape and transferred to PDMS film (Metatest). They were then transferred to Au-film through a transfer platform (Metatest, E1-T). For the AuNPs decoration, the GaTe films were immersed in 0.2 mg/ml HAuCl₄ (AR, Sinopharm Chemical Reagent Co., Ltd.) aqueous solution, and then they were rinsed with ethanol and dried with N₂.

Raman measurements: For the characterization of Raman activity, all of the hybrid structures (i.e., AuNPs/GaTe and AuNPs/GaTe/Au-film or InSe, WS₂, graphene) were immersed in 10^{-4} M R6G solution for 20 min, and after rinsing with ethanol and drying with nitrogen, the Raman spectra were measured under 532-nm continuous-wave laser excitation using an Andor SR-500i-B1 spectrograph. The power density of excitation was 0.38 mW/µm². The total exposure time was 5 s. The slit widths were provided in the captions of figures.

FDTD simulations: The mesh step of dx, dy was 1 nm, while that of dz was 0.1 nm. Periodic boundary condition was employed in x- and y-direction, and perfectly matched layer (PML) boundary condition was employed in the z-direction. A linearly polarized plane wave in the x-direction with a wavelength of 532 nm was used as a source, which is incident from the top of the model along the z-axis.

Funding

National Natural Science Foundation of China (U1737109, 11933006).

Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interest.

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