

Replies for the editor and reviewers

We appreciate for your kind comments on our paper. We have revised the manuscript by taking note of your comments. Corrected words and phrases have been highlighted through the manuscript to be recognized easily. Replies on reviewers' comments are given in below.

Reviewer #3

The aim of the paper is to fabricate silver films, on different types of substrates and with various deposition rates in order to test their SERS efficiency for R6G detection. The theme is appropriate for publication in this journal, but the manuscript lacks important information in presenting the results.

Strengths of the study: the experimental techniques are appropriate for the investigations.

Weaknesses of the study: mandatory improvements of the English; no assessment of the reproducibility of the films and their SERS efficiency; it lacks important information on the experimental conditions used to fabricate the films; no practical application envisioned for the obtained films.

Specific comments:

1. Row 10. Please rephrase the first phrase from the Abstract.

Thank you for your comment. We modified the sentence you mentioned as below:

Before: Oblique angle deposition for the fabrication of Ag nanorods was investigated.

After: The oblique angle deposition of Ag with different deposition rate and substrate was studied for SERS efficiency.

2. Row 22. Please add "s" to "substrate"

We modified the sentence you mentioned as below:

Before: The nanostructures of materials with SERS effect are synthesized and used as a substrate to detect the target analyte.

After: The nanostructures of materials with SERS effect are synthesized and used as substrates to detect the target analyte.

3. In the phrase "Sputtering [16, 17], solution method [18, 19], and electrochemical reaction method [20] were studied to control them." ref [16] only refers to deposition of Au films although the present manuscript is related to Ag deposition. Please explain the connection between the indicated

reference and the presented work.

We appreciate for your comment. The reference you mentioned was referred to do describe the diversity of SERS substrate manufacturing methods. To prevent the ambiguity, we changed the reference to another one that uses Ag.

Before: Merlen, A.; Gadenne, V.; Romann, J.; Chevallier, V.; Patrone, L.; Valmalette, J. C. Surface enhanced Raman spectroscopy of organic molecules deposited on gold sputtered substrates, *Nanotechnology* 2009, 20, 21

After: Sun, K.; Meng, G.; Huang, Q.; Zhao, X.; Zhu, C.; Huang, Z.; Qian, Y.; Wang, X. Hu, X., Gap-tunable Ag-nanorod arrays on alumina nanotip arrays as effective SERS substrates, *J. Mater. Chem. C* 2013, 1, 5015-5022

4. Please rephrase the phrase from row 22-row 23.

We rephrased the phrases.

Before: The SERS effect, which produces a strong scattering of the light signal of the target analyte, is caused by the combination of two effects. The first is the electromagnetic effect, localized surface plasmon resonance (LSPR), which refers to the amplification of the analyte signal by plasmon resonance on the surface of the nanostructured material (especially the metal). The second is the chemical effect. Amplification of the signal occurs by charge transfer between the SERS material and the analyte.

After: It is known that the SERS effect is caused by the following two effects. The first is the electromagnetic effect, localized surface plasmon resonance (LSPR), which refers to the amplification of the analyte signal by plasmon resonance on the surface of the nanostructured material (especially the metal). The second is the chemical effect. Amplification of the signal occurs by charge transfer between the SERS material and the analyte. The SERS effects of organic and inorganic semiconductor materials are largely dependent on the chemical effects.

5. Throughout the manuscript, th authors refer to the nanostructures as "nanorods", while in the title appears as "nano-columns". Please explain.

Thanks for the feedback. We used the word “column” in the title to refer to all the structures mentioned in this study. We modified the title to prevent ambiguity.

6. The authors deposit the films using oblique angle deposition; except Figure 1 where the deposition angle appears, nowhere in the experimental section can be found the deposition angle used.

Thank you for your comment. We added the details about the deposition angle in experimental section.

7. It is not clear how many samples were deposited. A table comprising all the samples, the substrates used, deposition rates, deposition time etc and other useful experimental details would bring a plus to the quality of the work.

We appreciate for your feedback. We added a table comprising all the samples as below:

Table 1. Sample treatment regarding deposition rates and substrates. **Experiment 1** is an experiment on the morphology of Ag depending on the deposition rate, and **Experiment 2** is an experiment on the morphology of Ag depending on the substrate. They are described in texts 3.1 and 3.2 respectively.

	Deposition rate (Å/s)	Substrate
Experiment 1	1.0	Si/SiO ₂
	1.7	Si/SiO ₂
	2.4	Si/SiO ₂
	3.1	Si/SiO ₂
	2.4	Sapphire
Experiment 2	2.4	Si/SiO ₂ /W
	2.4	Si/SiO ₂ /G
	2.4	P-Si/SiO ₂

8. Please explain the considerations on which the substrates were chosen.

We have picked the most commonly used Si/SiO₂ substrate. In addition to Si/SiO₂, we have selected substrates with various surface energy and wettability. We used graphene to observe the deposition tendency of Ag at low surface energies. We also used sapphire and tungsten to observe the Ag deposition tendencies at high surface energies. We also proceeded with O₂ plasma treatment to

determine the Ag deposition tendency at high wettability. We modified the experimental section to explain the reason that the substrates were chosen as below:

Before: The Si/SiO₂, sapphire, Si/SiO₂/Tungsten(W), Si/SiO₂/graphene(G), and plasma-treated Si/SiO₂(P-Si/SiO₂) were used for the substrates.

After: Various substrates were used to observe the tendency of Ag deposition according to the surface energy of the substrate. Si/SiO₂ most commonly used as a substrate and graphene(G) with lower surface energy were selected. Tungsten(W), sapphire, and O₂ plasma-treated Si/SiO₂(P-Si/SiO₂) were used as substrates with high surface energy (high wettability).

9. Row 45-row 46. Please rephrase.

We changed the sentence you mentioned as below:

Before: The deposition rates were 1, 1.7, 2.4, and 3.1 Å/s, and the base pressure was below 5×10^{-6} Torr. The Si/SiO₂, sapphire, Si/SiO₂/Tungsten(W), Si/SiO₂/graphene(G), and plasma-treated Si/SiO₂(P-Si/SiO₂) were used for the substrates.

After: The deposition rates were 1 Å/s, 1.7 Å/s, 2.4 Å/s, and 3.1 Å/s, and the base pressure was below 5×10^{-6} Torr. Various substrates were used to observe the tendency of Ag deposition according to the surface energy of the substrate. Si/SiO₂ most commonly used as a substrate and graphene(G) with lower surface energy were selected. Tungsten(W), sapphire, and O₂ plasma-treated Si/SiO₂(P-Si/SiO₂) were used as substrates with high surface energy (high wettability).

10. Why are the Tungsten and Copper intermediate layers used?

As mentioned in the answer to the previous question, we used tungsten because we expected tungsten to have high adhesion to Ag due to high surface energy. However, unlike predicted, there was no significant difference in the morphology of Ag deposited compared to Si/SiO₂. And we did not use copper as an intermediate layer.

11. Material and Methods section: please give detailed information about the magnetron sputtering deposition of tungsten layer.

Thank you for your comment. We added the experimental details as follows:

The sputtering was performed at 100W, 20 sccm of Ar flow, 10^{-6} Torr of base pressure, and at room temperature.

12. Regarding the SERS detection of R6G: a concentration of 10^{-4} M is pretty high for a SERS experiment. In a previous study published in 2012 (Wang et al, Appl Surf Sci 2012 <https://doi.org/10.1016/j.apsusc.2012.02.129>) using also a silver surface, a detection of 10^{-15} M concentration for R6G was possible. Please explain the choice of the 10^{-4} M concentration and if other lower R6G concentrations were tested using the fabricated silver films.

We appreciate for your feedback. We agree with you that low levels of R6G need to be analyzed. Many other papers, including the one you mentioned, detected very low concentrations of the analyte. However, in previous experiments, we found that the Raman signal decreased linearly with decreasing R6G concentration. Therefore, if we obtain a larger signal at the same R6G concentration, we expect to be able to analyze it to a lower concentration. We modified the following sentences in the text.

Before: Peaks corresponding to the spectrum of R6G were observed at 612, 776, 1189, 1314, 1363, 1511, 1599, and 1647 cm^{-1} , which are the same as the existing results. For the quantitative analysis, the SERS spectra of R6G adsorbed on the normally deposited Ag was obtained and the SERS intensities of the oblique angle-deposited Ag at 612 cm^{-1} were divided by the spectrum of it. As shown in **Fig. 2c**, the SERS efficiency of Ag substrate with the deposition rate of 1 Å/s and 1.7 Å/s (compared to the normally deposited Ag) were about 300 times. When the deposition rate was 2.4 Å/s , the SERS efficiency increased to about 850 times.

After: Peaks corresponding to the spectrum of R6G were observed, which are shown in **Table 2**. For the quantitative analysis, the SERS spectra of R6G adsorbed on the normally deposited Ag was obtained and the SERS intensities of the oblique angle-deposited Ag at 612 cm^{-1} were divided by the spectrum of it. As shown in **Fig. 2c**, the SERS efficiency of Ag substrate with the deposition rate of 1 Å/s and 1.7 Å/s (compared to the normally deposited Ag) were about 300 times. When the deposition rate was 2.4 Å/s , the SERS efficiency increased to about 850 times. It is reasonable to assume that R6G can be detected at lower concentrations because the intensity of R6G decreases linearly as R6G concentration decreases.

13. Please indicate the laser used, the exposure time, accumulations, laser power for the SERS measurements.

Thank you for your comment. We added some details about the SERS measurements as below:

The SERS measurement was carried out with 100 ppm (2.1×10^{-4} M) R6G solution and the Raman spectra were obtained by high resolution Raman spectrometer (HORIBA, Jobin Yvon, LabRam HR Evolution) with 633 nm He-Ne laser as excitation source, 1% of laser power, and the illuminating spot size was about 0.89 μ m in a diameter through a 100x objective. The acquisition time is 1s with 2 accumulation times.

14. What is the angle used for the SEM measurements? Please add it to the SEM experimental section.

Thank you for your comment. We added the information about the measurement angles we used at the SEM experimental section as follows:

The morphology of the Ag nanorods arrays were observed by FE-SEM (Hitachi S-4800) with top view and cross-sectional view.

15.No experimental parameters are given for the Ag deposition films. Please add to the Ag deposition section the deposition times, final thicknesses etc.

As you mentioned, we added the experimental parameters as follows:

The deposition times were 83 min, 49 min, 34 min, and 26 min, and the final thickness was 175.32 nm, 197.40 nm, 222.08 nm, and 285.71 nm, respectively.

16. Figure 2. What type of substrate/s have been used?

The substrate was Si/SiO₂. We added it to the caption in Figure 2.

17. Figure 3. What is/are the deposition rate/s?

The deposition rate was 2.4 Å/s. We added it to the caption in Figure 3.

18. Further information regarding the reproducibility of the Ag films should have been carried out. No information related to this is mention in the manuscript.

Thank you for your feedback. For the reproducibility, each SERS spectrum is an average of 5 spectra per sample. To prevent misreading, we added the following sentence to the text:

Five spectra of each sample were obtained and averaged.

19. Figure 4. What is/are the deposition rate/s?

Thank you for your comment. 30 nm of Ag was deposited, and the deposition rate was 2.4 Å/s. We added it to the caption in Figure.