Pinhole Effect on the Melting Behavior of Ag@Al$_2$O$_3$ SERS Substrates

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**Abstract**

High-temperature surface-enhanced Raman scattering (SERS) sensing is significant for practical detections, and pinhole-containing (PC) metal@oxide structures possessing both enhanced thermal stability and superior SERS sensitivity are served as promising SERS sensors at extreme sensing conditions. Through tuning the Al$_2$O$_3$ precursors’ exposure time during atomic layer deposition (ALD), Al$_2$O$_3$ shells with different amount of pinholes were covered over Ag nanorods (Ag NRs). By virtue of these unique PC Ag@Al$_2$O$_3$ nanostructures, herein we provide an excellent platform to investigate the relationship between the pinhole rate of Al$_2$O$_3$ shells and the melting behavior, high-temperature SERS performances of these core-shell nanostructures. Pinhole effect on the melting procedures of PC Ag@Al$_2$O$_3$ substrates was characterized in situ via their reflectivity variations during heating, and the specific melting point was quantitatively estimated. It is found that the melting point of PC Ag@Al$_2$O$_3$ raised along with the decrement of pinhole rate, and substrates with less pinholes exhibited better thermal stability but sacrificed SERS efficiency. This work achieved highly reliable and precise control of the pinholes over Al$_2$O$_3$ shells, offering sensitive SERS substrates with intensified thermal stability and superior SERS performances at extreme sensing conditions.

**Keywords:** Metal@oxide nanostructures, Pinhole shell, Thermal stability, Melting point, SERS

**Background**

High-temperature surface-enhanced Raman scattering (SERS) detection is a vital part for practical sensing, which can be employed for monitoring many in situ reactions, e.g., thermal crystallization [1], structural variations [2, 3], and chemical reactions [4, 5] at elevated temperatures. However, bare metal nanostructures suffer from the inherently low melting point [6, 7], which causes the morphological instability of nano-sized metal and as a result, may deteriorate their SERS performances at high temperatures [2–4, 8–10]. Lately, core-shell nanostructures of metal core covered with protective oxide layer have been proposed as good SERS substrates for high-temperature Raman sensing [2, 3, 5, 8–10]. For example, wrapping Ag nanorods (Ag NRs) with an ultrathin (~1.5 nm) but dense Al$_2$O$_3$ layer could make the substrate robust in morphology at 400 °C and stabilize its SERS efficiency [10]. Most recently, novel metal@oxide structures with pinhole-containing (PC) shells have drawn tremendous attention, which could not only increase the working temperature of SERS substrates moderately [10], but also exhibited even better SERS properties and broader application fields compared with metal@oxide substrates of compact shells [11, 12]. Accordingly, it is highly desired to synthesize PC metal@oxide structures as ideal SERS-active substrates as well as investigate and optimize their properties.

However, up to now, the accurate control and measurements of the oxide pinhole rate, as well as the comprehensive investigation of the melting procedures and thermal stability of PC metal@oxide substrates, have not been investigated in detail. In this regard, herein we introduced atomic layer deposition (ALD) technique to cover Ag NRs with Al$_2$O$_3$ shells (Ag@Al$_2$O$_3$) of different pinhole amount and experimentally analyzed the Al$_2$O$_3$ pinholes’ influence on the melting behavior of PC Ag@Al$_2$O$_3$ substrates. The pinholes can be readily tuned by varying the exposure time of Al$_2$O$_3$ precursors during ALD coating, and the pinhole rate was estimated using the Raman signals of acridine molecules on uncoated Ag NRs and PC Ag@Al$_2$O$_3$ substrates. The melting process of PC Ag@Al$_2$O$_3$ was monitored via their reflectivity...
variations during heating, and the melting point of different substrates was quantitatively calculated and compared. In addition, the SERS performances of PC Ag@Al₂O₃ substrates were tested after thermal treatment, demonstrating excellent stability and versatility of these SERS sensors.

Methods

Fabrication of Ag NRs

Slanted Ag NRs were prepared on Si (001) substrates by oblique angle deposition (OAD) technique in an electron-beam system (GLAD, Thermionics Inc.) with a background vacuum level of 10⁻⁶ Pa. During deposition, the incident angle between the surface normal of substrates and vapor flux was set at ~86°, with a deposition rate of ~0.75 nm/s. The NR growth finished at a thickness of 1000 nm read by a quartz crystal microbalance [10, 12].

Fabrication of PC Ag@Al₂O₃ Substrates

Al₂O₃ layers were coated onto the as-prepared Ag NRs in an ALD reactor (MNT-100, Wuxi MNT Micro and Nanotech Co.) at 50 °C. The Al₂O₃ precursors, i.e., trimethyaluminum (TMA; maintained at 150 °C) and water (maintained at 40 °C), were alternatively pumped into the reaction chamber using high purity N₂ (99.999 %, 15 sccm) as the carrier and purge gas. In order to synthesize Al₂O₃ shells with a different pinhole rate, only one ALD cycle was used on top of Ag NRs and the exposure time of TMA and water was simultaneously changed during coating [10, 12]. One complete reaction consisted of four steps: (1) TMA reactant exposure, 2/5/10/20/40/80/100 ms; (2) N₂ gas purging, 10 s; (3) water vapor exposure, 1/2/5/10/20/40/50 ms; and (4) N₂ gas purging, 20 s. These substrates are denoted hereafter as Ag@Al₂O₃/2, Ag@Al₂O₃/5, Ag@Al₂O₃/10, Ag@Al₂O₃/20, Ag@Al₂O₃/40, Ag@Al₂O₃/80, and Ag@Al₂O₃/100, respectively. (These numbers represent the TMA exposure time during ALD coating.)

Characterization of Ag NRs@Al₂O₃

The morphology and structures of Ag NRs and Al₂O₃ shells were characterized by scanning electron microscope (SEM; JEOL-JMS-7001F) and high-resolution transmission electron microscope (HRTEM; JEOL-2011). The melting process of these substrates was monitored in situ via their reflectivity variations upon annealing, using Optical Power Thermal Analyzer (OPA–1200).

SERS Detections

Acridine and 4-mercaptobenzoic acid (4-MBA) with different concentrations were dissolved into ethanol. SERS measurements were conducted by an optical fiber micro-Raman system (i-Raman Plus, B&W TEK Inc.). Before detection, all substrates were merged into different solutions for 1 h, washed thoroughly to remove the residual molecules, and dried naturally in air. Raman spectra were obtained using a 785-nm laser as the excitation source, with an excitation power of 150 mW and the data collection time of 10 s for each spectrum. For every sample, the spectrum was obtained by averaging the spectra obtained from five different areas of the SERS substrate.

Results and Discussion

Figure 1a, b shows typical top-view and side-view SEM images of Ag@Al₂O₃/10 substrate, from which one sees clearly that the slanted NRs are well-separated and ~700 nm in length. Figure 1c illustrates the HRTEM image of Ag@Al₂O₃/10 with a PC Al₂O₃ shell, which is sub-nanometer thick and uniformly wraps Ag NRs. To explore the relationship between the exposure time of ALD precursors and Al₂O₃ pinhole rate, we introduced acridine, a SERS probe molecule that can directly interact with Ag surface through pinholes and exhibit Raman signals, paving a reliable way toward the characterization of Al₂O₃ pinholes. One sees from Fig. 1d that the Raman spectra of 1 × 10⁻³ M acridine molecules [14, 15] showed up not only on uncoated Ag NRs but also on PC Ag@Al₂O₃ substrates with distinct TMA/water exposure time, indicating that all these substrates had PC shells with exposed Ag surface inside. Because of the saturation of 1 × 10⁻³ M acridine over uncoated Ag NRs (see Additional file 1: Figure S1), we further utilized the acridine spectra from different substrates to estimate the pinhole rate of Al₂O₃ shells, via dividing acridine Raman intensity at 1403 cm⁻¹ from PC Ag@Al₂O₃ substrates by that from uncoated Ag NRs. It is shown in Table 1 that the Al₂O₃ pinhole rate declined gradually with the increment of TMA/water exposure time, suggesting that longer exposure time provide better opportunity for TMA and water to react over Ag NRs. The pinhole rate ranges from ~18.0 to ~5.3 %, and further longer exposure time results in no obvious change of the pinhole rate.

Since optical property of nanostructures is sensitive to their morphology [16, 17], the melting procedures of PC Ag@Al₂O₃ substrates can be characterized in situ via their reflectivity changes upon annealing. Figure 2 thoroughly investigates the melting process and morphological changes of uncoated Ag NRs and Ag@Al₂O₃/10 at 50–350 °C (red line). Because melting occurs during a continuous process instead of at a specific point, to specifically and quantitatively characterize the melting point of different substrates, we define the melting point of reflectivity’s derivative (blue line) from each sample as their melting point, at which temperature the morphology of nanostructures changes most dramatically [18, 19]. For bare Ag NRs, the reflectivity began to change at ~120 °C and the obvious shape variation was observed at 150 °C, which would affect the efficiency of SERS substrates. The
structure distortion facilitated with increasing the annealing temperatures, and Ag NRs lost completely their shape after the melting point of ~197 °C, suggesting the instability nature of nano-sized Ag. As for Ag@Al₂O₃/10, the substrate maintained its shape at ~200 °C, and the melting point was as high as ~265 °C. It is particularly noted that although the morphology change of Ag@Al₂O₃/10 initiated at ~200 °C, the substrate kept partly the NR shape even at 350 °C, indicating the superior protection of Al₂O₃ shell. Figure 3 represents the SEM images of Ag@Al₂O₃/2, Ag@Al₂O₃/5, Ag@Al₂O₃/20, Ag@Al₂O₃/40, Ag@Al₂O₃/80, and Ag@Al₂O₃/100 after heating at 350 °C. It is observed that the substrates with less or smaller Al₂O₃ pinholes could keep better the nanorod shape and generate less fusion spots after annealing, indicating the pinhole rate’s effect on the thermal and morphological stability of these substrates. Furthermore, the melting point of various PC Ag@Al₂O₃ substrates as a function of their pinhole rate was quantitatively evaluated and depicted in Fig. 4. Remarkably, we found that their melting point increase monotonously with the decrease of pinhole rate, starting from 257 °C with ~18.0 % pinholes and reaching a maximum at 277 °C when the pinhole rate was ~5.3 %. These results clearly demonstrate that the Al₂O₃ coverage provides a useful opportunity to strengthen the thermal stability of Ag nanostructures, which also offers us a means to precisely control the melting point of PC Ag@Al₂O₃ substrates.

In the case of high-temperature SERS detection, 1 × 10⁻⁶ M 4-MBA [20, 21] was used to evaluate the SERS efficiency and thermal stability of PC Ag@Al₂O₃ substrates. Because SERS effect is highly localized and attenuates quickly away from metal surface [22, 23], a gradual decrement of 4-MBA Raman signals is observed with the decline of exposed Ag surface (see Fig. 5a). To be specific, the SERS intensity of 4-MBA on Ag@Al₂O₃/2, Ag@Al₂O₃/5, and Ag@Al₂O₃/10 with ~18.0 to ~10.7 % pinholes was about 80–70 % compared with that on uncoated Ag NRs. Further decrease of the pinhole rate led to a more dramatic drop of 4-MBA signals, which is consistent with the previous results of acridine molecules, except the fact that 4-MBA could interact not only with Ag surface but also with Al₂O₃ shells [24–27]. We should also mention that even though the SERS sensitivity of PC Ag@Al₂O₃ substrates

| Sample name | Pinhole rate (%) |
|-------------|-----------------|
| Ag NRs      | 100             |
| Ag@Al₂O₃/2  | 18.0            |
| Ag@Al₂O₃/5  | 14.9            |
| Ag@Al₂O₃/10 | 10.7            |
| Ag@Al₂O₃/20 | 7.9             |
| Ag@Al₂O₃/40 | 7.0             |
| Ag@Al₂O₃/80 | 5.5             |
| Ag@Al₂O₃/100| 5.3             |
decreased to some extent after ALD coating, all these sub-
strates with ultrathin Al$_2$O$_3$ shells and pinholes were highly
effective for trace analyte recognition [12].

To demonstrate the feasibility of PC Ag@Al$_2$O$_3$ sub-
strates for real-world applications, Ag@Al$_2$O$_3$/10 com-
bined with both high melting point and good SERS
activity was chosen to assess its high-temperature SERS
performances, utilizing uncoated Ag NRs as a reference.
It is observed from Fig. 5b that, when bare Ag NRs were
heated at 200–350 °C, due to their significant morpho-
logical changes, the SERS activity decreased about one
order of magnitude. On the contrary, although, at room
temperature (RT), the SERS intensity of 4-MBA on
Ag@Al$_2$O$_3$/10 was ~70 % in comparison with that on
uncoated Ag NRs, this substrate was extremely robust in
SERS performance at elevated temperatures. Approximately 5.5 times higher SERS enhancement was ob-
tained from Ag@Al$_2$O$_3$/10 compared with that from
bare Ag NRs when heated at 200 and 260 °C, indicating
the strongly improved SERS stability of PC Ag@Al$_2$O$_3$
substrates. At 300 and 350 °C, Ag@Al$_2$O$_3$/10 showed
moderate declines in SERS signals, which can be ex-
plained by its structure changes when exceeding its
melting point of ~265 °C.

Conclusions
In summary, we successfully synthesized PC Ag@Al$_2$O$_3$
nanostructures with controllable pinhole rate and
Fig. 4  

(a) The melting procedures and the extreme point of the reflectivity’s derivative from different PC Ag@Al₂O₃ substrates.

(b) The melting point of PC Ag@Al₂O₃ substrates as a function of their pinhole rate.
investigated in detail the relationship between the melting behavior of PC substrates and Al$_2$O$_3$ pinhole rate. Due to the unique structures of these substrates, the melting point of PC Ag@Al$_2$O$_3$ increased along with the decline of the Al$_2$O$_3$ pinhole rate. By coating protective Al$_2$O$_3$ layers over Ag NRs, the substrates could preserve their structures and SERS efficiency at temperatures higher than 250 °C. These PC Ag@Al$_2$O$_3$ substrates with a controllable pinhole rate exhibit great potential as advanced platforms for high-temperature SERS detections.

**Additional file**

**Additional file 1: Figure S1.** Raman spectra of $1 \times 10^{-6}$ M, $5 \times 10^{-7}$ M, $1 \times 10^{-7}$ M, and $1 \times 10^{-8}$ M acridine molecules from uncoated Ag NRs.

**Abbreviations**

4-MBA: 4-mercaptobenzoic acid; Ag NRs: Ag nanorods; ALD: atomic layer deposition; HRTEM: high-resolution transmission electron microscope; OAD: oblique angle deposition; PC: pinhole-containing; RT: room temperature; SEM: scanning electron microscope; SERS: surface-enhanced Raman scattering; TMA: trimethylaluminum.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

LM carried out the experiments. LM, YH, MH, JL, and ZZ participated in the design of the study. LM and ZZ conceived of the study and participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

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**Fig. 5** a Typical Raman signals of $1 \times 10^{-6}$ M 4-MBA molecules from uncoated Ag NRs and distinct PC Ag@Al$_2$O$_3$ substrates. b Normalized Raman intensity of $1 \times 10^{-6}$ M 4-MBA from uncoated Ag NRs and Ag@Al$_2$O$_3$/10 at various conditions, i.e., at room temperature (RT), and after annealing at 200, 260, 300, and 350 °C, respectively.
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