

On-site Gas Sensing by Surface-Enhanced Raman Scattering

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Abstract:

Ag nanorods coated with an ultrathin HfO₂ shell (AgNRs@HfO₂) were prepared for the synthesis of a versatile, robust, and easily recyclable surface-enhanced Raman scattering (SERS) substrate. This substrate maximizes the high melting point of HfO₂ shell and thus ensures the plasmonic efficiency of AgNRs. Therefore, it possesses extraordinary thermal stability and SERS activity, which could act as a reusable and cost-effective SERS detector. After SERS detection, the regeneration of AgNRs@HfO₂ was achieved by annealing the substrate within several seconds. This procedure led to the thermal release of adsorbed molecules and resulted in a refreshed substrate for subsequent measurements. The composite substrate maintained its SERS efficiency well during multiple “detection–heating” cycles, exhibiting good stability and recyclability. Furthermore, in addition to revealing the feasibility of SERS sensing in liquids, AgNRs@HfO₂ also provided continuous real-time monitoring of gas targets at ultralow concentrations. This work provides a robust and renewable SERS sensor with advantages of high sensitivity, stability, cost effectiveness, and easy operation, which can be implemented for both aqueous and gaseous analyte detection and is thus an intriguing candidate for practical applications in environmental, industrial, and homeland security sensing fields.

Key words: Surface-enhanced Raman scattering, Ag nanorods, localized surface plasmon resonance, trace level detection, gas sensing.

Introduction

Surface-enhanced Raman scattering (SERS) is a powerful spectroscopic technique in biomolecule sensing, environmental monitoring, and detection of hazardous substances, etc. Due to localized surface plasmon resonance (LSPR) [1] of metallic nanostructures, SERS offers ultrasensitive and nondestructive sensing of trace analytes. Nevertheless, given that SERS substrates are generally made of noble metals (e.g., Au, Ag, and Cu), the costly preparation and disposable property of metallic substrates seriously obstruct the universality of SERS analysis. In addition, gas sensing is an important part of SERS applications, so it is desired to fabricate sensitive gas sensors.

In this study, a novel AgNRs@HfO₂ SERS platform with Ag nanorods coated by an ultrathin and uniform HfO₂ layer was developed. AgNRs@HfO₂ exhibits superior sensitivity and high-temperature robustness, and could thus function as a reusable and cost-effective SERS detector. After SERS measurement, the regeneration of AgNRs@HfO₂ was achieved by

thermal annealing the substrate within several seconds, in which way the adsorbed molecules were removed completely and conveniently. Notably, the composite platform can not only be exploited for SERS determination in aqueous solutions but also shows great potential for *in situ* gas sensing with ultralow concentrations.

Characterization of AgNRs@HfO₂

Slanted AgNRs were prepared by glancing angle deposition (GLAD) technique in an electron-beam system. The HfO₂ layers were then coated onto the as-prepared AgNRs via atomic layer deposition (ALD) approach. Figure 1 shows the SEM and TEM images of AgNRs coated with an HfO₂ shell of ~1.6 nm. AgNRs were well-separated, and the ultrathin HfO₂ shell wrapped the AgNRs uniformly.

Thermal stability of AgNRs@HfO₂

To achieve a “thermally cleanable” SERS sensor, its high-temperature stability must be assessed first. For bare AgNRs, their structures were damaged at a relatively low temperature of ~100 °C [2] and, according, they were not

feasible for high-temperature sensing or thermal cleaning. On the other hand, benefiting from the high melting point of HfO_2 , the coated substrate maintained well its morphology at temperatures as high as $400\text{ }^\circ\text{C}$. This stable AgNRs@HfO_2 substrate offers us a reliable means to thermally clean it without structure destruction, endowing it with great potential as a renewable SERS detector.

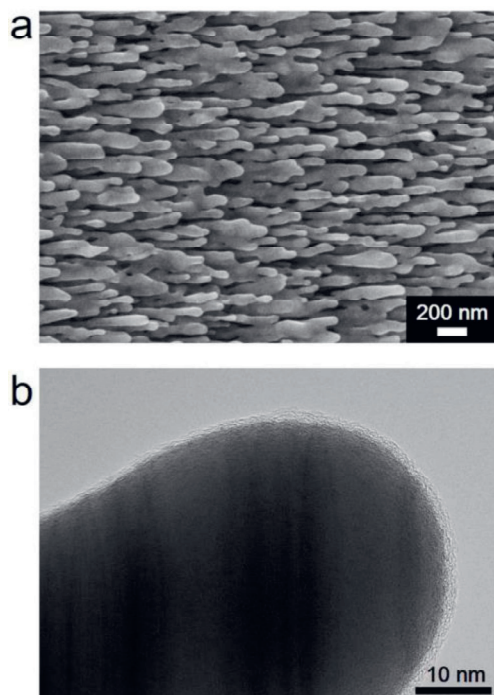


Fig.1. (a) SEM and (b) TEM images of AgNRs@HfO_2 substrates with shell thickness of $\sim 1.6\text{ nm}$.

Recyclable SERS detection of vapor-phase molecules

Figure 2a shows the schematic for SERS detection of 2-naphthalenethiol (2-NAT) gas molecules using AgNRs@HfO_2 substrate. N_2 was utilized as the carrier gas to transport 2-NAT from solution to SERS substrate, and Raman spectra were obtained *in situ*. Figure 2b shows the Raman spectra of 600 ppb 2-NAT and its Raman intensity changes at 1379 cm^{-1} within 100 min. The SERS signals increased gradually and reached saturation afterwards, demonstrating the feasibility of AgNRs@HfO_2 for trace gas sensing. After Raman detection, the AgNRs@HfO_2 substrate was annealed on a hot plate at $200\text{--}300\text{ }^\circ\text{C}$ for a few seconds. Figure 2c shows the Raman intensity variations of 600 ppb 2-NAT at 1379 cm^{-1} peak during the repetition of “vapor exposure-thermal cleaning” cycles on the substrate. AgNRs@HfO_2 exhibited almost no degradation in SERS sensitivity after multiple measurements, and the composite could regenerate rapidly and completely after annealing.

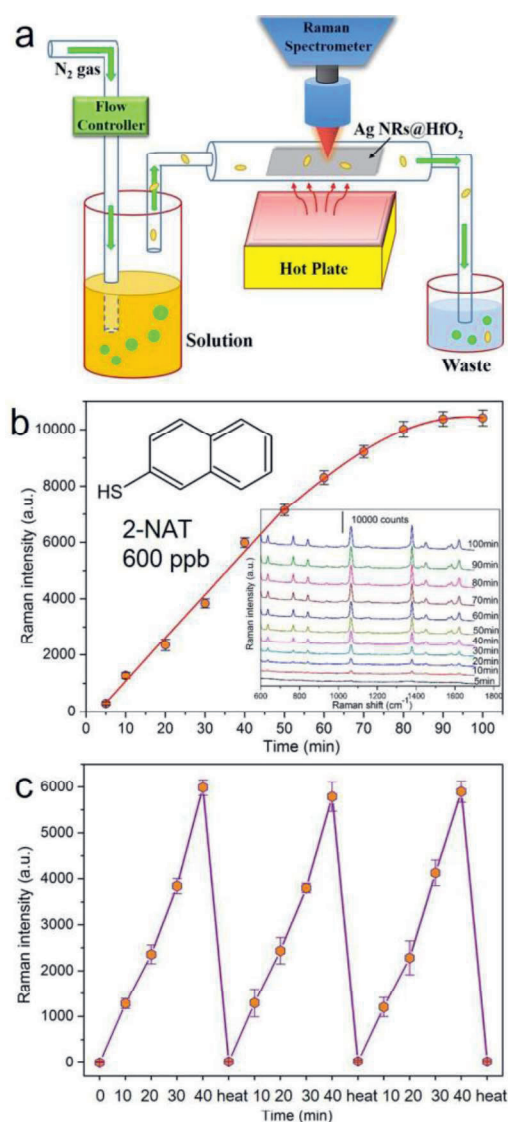


Fig.2. (a) Schematic of the gas sensing device; (b) SERS spectra and the 1379 cm^{-1} peak intensity of 2-NAT on the AgNRs@HfO_2 substrate as a function of gas flow time; (c) 1379 cm^{-1} peak intensity variations of 2-NAT during the repetition of “vapor exposure-thermal cleaning” cycles on the substrate.

Conclusion

This work leads to the development of efficient, robust and renewable SERS sensors that provide continuous, real-time monitoring of vapor-phase analytes at concentrations down to a ppb molecular level. The AgNRs@HfO_2 substrate provides an exciting platform for rapid and *in situ* determinations of gas samples from realistic environments, e.g., explosives, volatile organic compounds and chemical warfare agents.

References

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