Gold nanoparticles-decorated single silver nanowire as an efficient SERS-active substrate*

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A novel surface-enhanced Raman scattering (SERS)-active substrate based on Au nanoparticles (AuNPs)-coated silver nanowire (AgNW) is obtained by an effective and simple method. The results show that the hybrid structures prepared by this method are powerful SERS-active substrates for the detection of malachite green (MG) molecules with the limit of 1 nmol/L. The excellent enhancing ability mainly comes from two kinds of hot spots. One is from the gaps among the adjacent AuNPs, and the other is the presence of zone between AuNPs and AgNW. In particular, the AuNPs-coated AgNW can be viewed through the objective of the confocal Raman spectrometer due to the length of the AgNW reaches microns, which can improve the repeatability of detection. Moreover, it is of great significance in research of SERS mechanism and application.

Document code: A **Article ID:** 1673-1905(2014)04-0241-3

DOI　10.1007/s11801-014-4068-9

Surface-enhanced Raman scattering (SERS) technique is a powerful analyzing and testing method for determining chemical information of molecules on metallic substrates. In recent years, it has attracted more and more attention because it can provide the fingerprint spectrum of probe molecule with very high sensitivity. The intensities of SERS spectra strongly depend on the material and structure of the SERS-active substrates. Up to now, Au and Ag nano-materials are the most used substrates. SERS-active hot spot can be generated at the gap between adjacent metal nanostructures due to the electromagnetic coupling effect. The detection of the trace even single-molecule level can be achieved due to the Raman signal of the probe molecule is greatly enhanced at the hot spots. Therefore, the construction of SERS-active substrate rich with hot spots has become one of the important subjects in SERS study.

The various substrates have been prepared, such as dimmer and aggregate of nanoparticles (NPs) and bundle of nanowires (NWs)[1-4]. NPs and NWs of Au and Ag are important class of SERS-active substrates because of their simple structure, easy preparation and high activity. AuNWs and AgNWs have a unique advantage, i.e., their length can reach micron level, making that the positioning measurement can be achieved by means of the objective of confocal Raman spectrometer. So SERS-active substrates-based single AuNW and AgNW have been prepared[5,6]. However, the individual NW also has an obvious drawback, namely, its enhancing ability is not good, which reduces their value of application. The design and preparation of SERS-active substrates based on NW with high activity have great significance and application prospect. For instance, Kim et al[7] have developed the AuNW-AuNPs conjugated system by biotin and biotin protein interaction, constructing hot spot structure between Au particles and NWs, to implement the trace detection of biotin protein. However, their preparation method is complex, and the variety of determination of the related substances is limited. Au-Ag bimetallic NWs with good enhancing ability were synthesized by using replacement reaction by Jiang's group[8]. Similarly, their method is unfavourable for application due to the low output. Self-assembly is developing fast in the field of nano-technology and has become the focus of scientific fields. It is widely used in the preparation of SERS substrates because it is simple and effective[9-12]. In this paper, AgNWs are prepared firstly, next the NWs are chemically modified using 1,6-hexanedithiol (HDT) molecules which act as coupling agent, and then AuNPs decorate on the AgNWs by self-assembly, resulting in the hybrid AuNPs-AgNW SERS substrates. Because the length of AgNW is up to micron level, it can be seen in the confocal microscope, which can implement the location measurement with good enhancement effect.

Malachite green (MG), which is a triphenylmethane dye, has been widely used in ceramics, textile, leather industry and paper industry. And it was also widely used in aquaculture, because it has good effect on the protec-

tion against fungal diseases and parasites of fish. However, MG was found to lead to organism distortion, fetal malformation, even cancer, so it has been banned in the food industry and aquaculture. However, some illegal traders still use MG because it is cheap and effective. Therefore, it is important to detect MG in food, especially in aquatic products. In this paper, MG is detected in aqueous solution by SERS using the as-prepared AuNPs-AgNW hybrids as substrate.

Silver nitrate ($AgNO_3$) chloroauric acid hydrated ($HAuCl_4 \cdot 4H_2O$), absolute alcohol, MG and sodium citrate were got from Beijing Chemical Reagent Company. 1,6-hexanedithiol (HDT), polyvinylpyrrolidone (PVP, with formula weight about 30 000), ethylene glycol (EG) and sodium sulfide were bought from J&K Scientific Ltd. All reagents were analytical grade and used without further purification.

AgNWs were synthetized according to the method reported in Ref.[13]. First, 0.15 g PVP was put into 10 mL Na_2S EG solution with concentration of 0.3 mmol/L, and stir the solution for mixing well. Next, 0.169 g $AgNO_3$ was added into another 10 mL EG and stirred for 5 min. Then, the $AgNO_3$ solution was mixed with the Na_2S solution, and the resulted mixed solution was poured into a 20 mL reaction kettle after stirring for 5 min. It was heated up to 160 °C and for 2.5 h, then cooled to room temperature naturally. AgNWs were obtained after centrifuging to remove EG and PVP, and dispersed into ethanol for further use.

HDT was dropped into the AgNW suspension with final concentration of 1×10^{-5} mol/L, stirring for 30 min to make it adsorb onto the surface of Ag fully. Then the functionalized AgNW was centrifuged three times to remove the free HDT. The dried functionalized AgNW was put into Au colloid and stirred for 30 min. AuNPs-AgNW hybrid substrate was achieved after three times of centrifugation and dispersed into water for use.

AuNPs-AgNW was dropped onto a rinsed Si wafer and dried naturally. And the substrate was immersed into the solution of the probe molecule for 30 min, then rinsed with distilled water, and dried in air before test. The Raman spectra were examined and recorded using a microscopic confocal Raman spectrometer (Horiba, HR800) with a 633 nm He-Ne laser as excitation source. The laser light was focused on a sample through a 100× objective. The Raman signals were recorded by a thermoelectrically cooled electron multiplying charge coupled device mounted on the spectrometer with a grating with 600 grooves per millimeter. Spectrometer was calibrated according to Si Raman peak at 520.7 cm^{-1} to ensure the measurement accuracy.

The absorption spectra were obtained on the Shimadzu 2550 spectrophotometer (Shimadzu, Japan). The samples were loaded in the standard quartz sample cell, and the length of light path was 1 cm.

AuNPs-AgNWs were dropped onto a rinsed Si wafer and dried in air for scanning electron microscope (SEM) measurement. The SEM images were taken on a Hitachi

S-4800 operated at 10 kV.

The morphology of the AuNPs-AgNW composite is examined by SEM, and the typical SEM images are shown in Fig.1. As shown in Fig.1(a), the diameter of the AgNWs ranges from 300 nm to 400 nm. And from the expanded image of AuNPs-AgNW shown in Fig.1(b), we can see that the diameter of AuNP is tens of nanometers. AgNW is decorated with a high density of AuNPs. And the distance of the AuNPs is only several nanometers, which is the ideal distance for the generation of hot spot due to electromagnetic coupling [14,15].
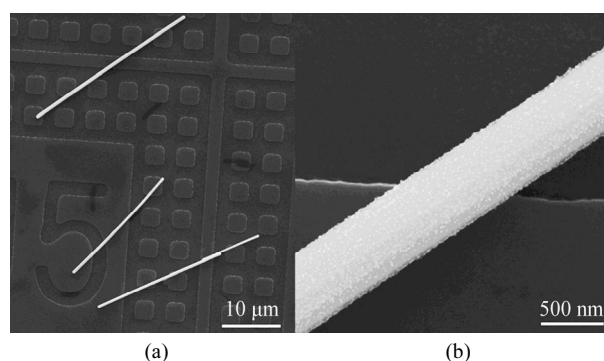

Fig.1 (a) SEM image of AuNPs-AgNW on Si wafer, and (b) the expanded image of AuNPs-AgNW

The ultraviolet-visible (UV-VIS) spectra of AgNW, AuNP and AuNPs-AgNW are shown in Fig.2, which characterize the property of surface plasmon resonance (SPR). As shown in Fig.2, the absorption peaks of AuNP and AgNW are at 520 nm and 400 nm, respectively, corresponding to the SPR peaks of AgNW and AuNP. For AuNPs-AgNW, there is a wide absorption band in the region from 400 nm to 700 nm, and the strongest peak is at 520 nm. This band is made up of three parts. And the part of shorter wavelength corresponds to the horizontal SPR peak of AgNW. The intensity of the band is weakened due to AgNW is coated by AuNP. The peak at 530 nm originates from the SPR of AuNP. The peak red-shifts relative to the SPR peak of AuNP suspension due to the smaller distance between the particles, which is verified by the SEM image as shown in Fig.1(a). Obviously, the absorption spectrum of AuNPs-AgNW composite is different from the direct sum of the absorption spectra of AuNP and AgNW, because the coupling between AgNW and AuNP leads to the new plasmon resonance[16]. As a result, there is a wide strong plasmon resonance absorption in the region from 400 nm to 700 nm. Considering the relationship of the excitation wavelength, SPR and Raman enhancement, we choose 632.8 nm He-Ne laser as excitation in experiment because the as-prepared AuNPs-AgNW substrate has a wide SPR range.

MG is selected as a probe molecule to verify the SERS-activity of the as-prepared AuNPs-AgNW substrate in this paper.

For the determination of MG, the as-prepared AuNPs-AgNWs were dipped into MG solutions with different

concentrations of 1 nmol/L, 10 nmol/L and 100 nmol/L, respectively. In 30 min, the AuNPs-AgNW hybrids were dropped on Si wafer for the achievement of the SRES spectra. As shown in Fig.3, the intensity of SERS spectra of AuNPs-AgNW and MG hybrids is increased with the increase of concentration. The main characteristic peaks of MG can be discriminated when the concentration is as low as 1 nmol/L, which shows that the limit of detection is 1 nmol/L. In video mode, AgNW can be observed under microscope as shown in Fig.4. Considering that the AuNPs-AgNW substrate is of easy preparation, good repeatability and stability, being located by optical microscope, it can be a very potential SERS platform in trace detection.
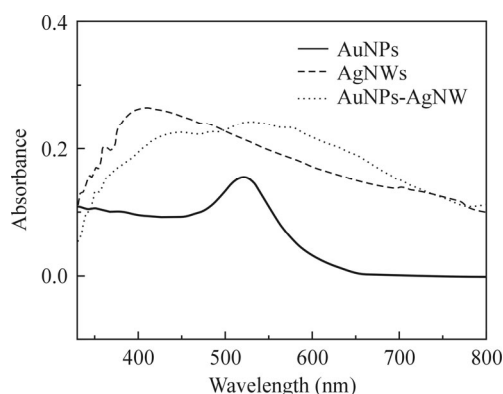

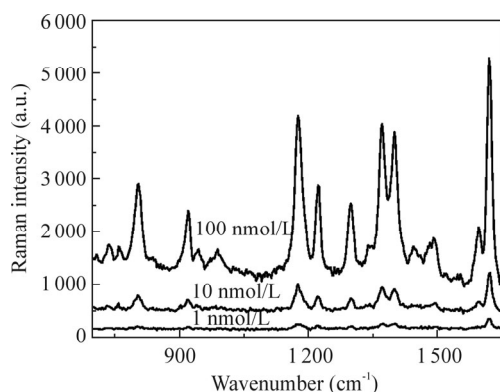**Fig.2 UV-VIS absorption spectra of AuNPs, AgNWs and AuNPs-AgNW hybrids**

Fig.3 SERS spectra obtained from AuNPs-AgNW hybrids with various MG concentrations

Fig.4 Optical image of the as-prepared AuNPs-AgNW

In this paper, a novel SERS-active substrate fabricated from single AuNPs-coated AgNW is prepared by coupling molecule HDT-assisted assembled method. The results show that the hybrid structures prepared by this method are powerful SERS-active substrates for the detection of MG molecules with high sensitivity. The limit of concentration is 1 nmol/L. The excellent enhancing ability mainly comes from the gaps among the adjacent AuNPs and the presence of zone between AuNPs and AgNW. Particularly, because the length of the AgNW reaches microns, the AuNPs-coated AgNW can be viewed through the objective of the confocal Raman spectrometer, which can improve the repeatability of detection. It is of great significance in research of SERS mechanism and application.

References

[1] Y. Sawai, B. Takimoto, H. Nabika, K. Ajito and K. Murakoshi, J. Am. Chem. Soc. **129**, 1658 (2007).

[2] K. D. Osberg, M. Rycenga, N. Harris, A. L. Schmucker, M. R. Langille, G. C. Schatz and C. A. Mirkin, Nano Lett. **12**, 3828 (2012).

[3] Y . Lu, G. L. Liu and L. L. P., Nano Lett. **5**, 5 (2005).

[4] S. J. Lee, A. R. Morrill and M. Moskovits, J. Am. Chem. Soc. **128**, 2200 (2006).

[5] I. Yoon, T. Kang, W. Choi, J. Kim, Y. Yoo, S. W. Joo, Q. H. Park, H. Ihee and B. Kim, J. Am. Chem. Soc. **131**, 758 (2009).

[6] T. Kang, I. Yoon, K. S. Jeon, W. Choi, Y. Lee, K. Seo, Y. Yoo, Q. H. Park, H. Ihee, Y. D. Suh and B. Kim, J. Phys. Chem. C **113**, 7492 (2009).

[7] T. Kang, I. Yoon, J. Kim, H. Hee and B. Kim, Chem.-Eur. J. **16**, 1351 (2010).

[8] N. L. Netzer, C. Qiu, Y. Y. Zhang, C. K. Lin, L. F. Zhang, H. Fong and C. Y. Jiang, Chem. Commun. **47**, 9606 (2011).

[9] Z. Q. Weng, H. B. Wang, J. Vongsvivut, R. Q. Li, A. M. Glushenkov, J. He, Y. Chen, C. J. Barrow and W. R. Yang, Anal. Chim. Acta **803**, 128 (2013).

[10] J. Fontana, J. Livenere, F. J. Bezares, J. D. Caldwell, R. Rendell and B. R. Ratna, Appl. Phys. Lett. **102**, 201606 (2013).

[11] QI Jian-xia, Journal of Optoelectronics·Laser **25**, 282 (2014). (in Chinese)

[12] TAN En-zhong, YIN Peng-gang and GUO Lin, Optoelectronics Letters **9**, 381 (2013).

[13] D. P. Chen, X. L. Qiao, X. L. Qiu, J. G. Chen and R. Z. Jiang, J. Colloid Interf. Sci. **344**, 286 (2010).

[14] C. J. Orendorff, A. Gole, T. K. Sau and C. J. Murphy, Anal. Chem. **77**, 3261 (2005).

[15] H. Wang, C. S. Levin and N. J. Halas, J. Am. Chem. Soc. **127**, 14992 (2005).

[16] O. Pena-Rodriguez and U. Pal, Nanoscale Res. Lett. **6**, 279 (2011).