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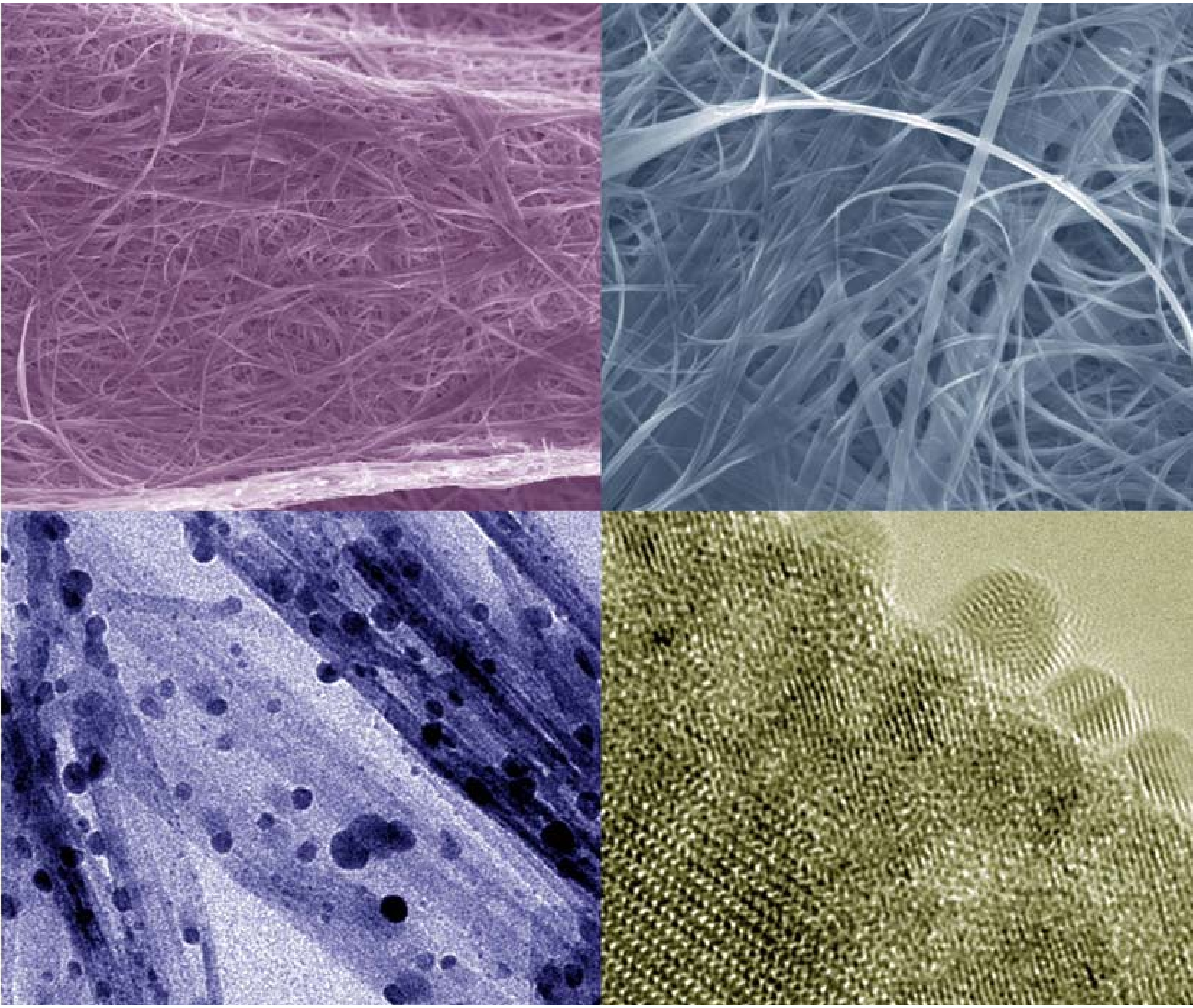

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FEATURE ARTICLE

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An ultrasensitive method: surface-enhanced Raman scattering of Ag nanoparticles from β-silver vanadate and copper†

Ming-Wang Shao,*[ab] Lei Lu,[a] Hong Wang,[a] Sheng Wang,[a] Ming-Liang Zhang,[b] Dorothy-Duo-Duo Ma[b] and Shuit-Tong Lee*[b]

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Ultrasensitive surface-enhanced Raman scattering signals of four typical analytes were observed on Ag nanoparticles from β-silver vanadate and copper, even though the concentrations of these analytes were as low as 1×10^{-16} M (Rhodamine 6G or crystal violet) and 1×10^{-15} M (trinitrotoluene or bovine serum albumin).

Surface-enhanced Raman spectroscopy (SERS), resulting in strongly increased Raman signals from molecules, was discovered by Fleischmann and Hendra.[1] It is a useful technique with an increase of Raman signals by a factor of 10^6 to 10^8 depending on the preparation of the nanometre sized metallic structures (typically Ag and Au)[2,3] and has wide application in various fields.[4,5]

Various methods have been employed to prepare such metals, such as vapor deposition,[6] chemical reactions,[7,8] lithography[9] and an ion-beam-sputtered technique,[10] which are all labeled as important and valuable. Yet, there is still a need to improve the sensitivity and reproducibility.

Herein, a unique approach to prepare a SERS substrate is proposed by utilizing copper and silver vanadate as raw materials.

Silver vanadates are important materials owing to their ionic properties and their application as cathode material in lithium ion batteries. β-$AgVO_3$ is a stable phase and a typical silver vanadate. Its ionic properties are highly dependent on the composition, size, shape, crystal structure and surface properties of the product.[11,12] In this work, silver nanoparticles were obtained using copper and β-$AgVO_3$ as reactants, which demonstrated ultrasensitivity in the SERS detection of four different analytes.

AgNPs were prepared *via* a mechanochemical method[13] through the reaction between β-$AgVO_3$ nanoribbons and Cu foil.

In this study, a hydrothermal method was employed to synthesize silver vanadate nanoribbons (SVNs). The SEM image (Fig. 1a) reveals that the SVNs are generally ultralong with lengths up to 100 μm. Fig. 1b displays a high-magnification SEM image of the nanoribbons. The width and thickness of the nanoribbons are about 200 nm and 20 nm, respectively.

When SVNs reacted with copper foil *via* a mechanochemical method, they grew freshly-produced silver nanoparticles *in situ*. The TEM image (Fig. 1c) shows the SVNs were almost completely covered with Ag nanoparticles with an average diameter of 15 nm. The HRTEM image of an Ag nanoparticle (Fig. 1c, inset) reveals the clear (111) crystal plane, which indicates high quality of crystallinity. The HRTEM image of SVN covered with Ag nanoparticles (Fig. 1d) clearly manifests their crystal nature. The crystal lattice of SVN may be indexed as (401) and (−203) crystal planes.

Several typical analytes were selected as models to demonstrate the performance of this substrate in SERS because they are important and have been well-characterized by SERS.

When 25 μl 1×10^{-16} M Rhodamine 6G (Rh 6G) methanol solution were added, the SERS which is shown in Fig. 2a was collected. There exist the spectral features of Rh 6G: the peak at 1184 cm^{-1} is associated with C–C stretching vibrations, 1313, 1363, 1509, 1574 and 1650 cm^{-1} with aromatic C–C stretching vibrations.[2,14,15] The surface enhancement factor is

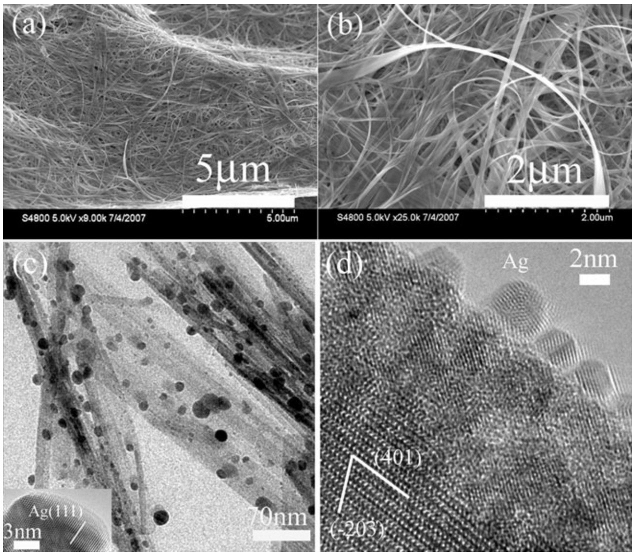

Fig. 1 (a) Low-magnification FESEM image and (b) high-magnification FESEM image of β-$AgVO_3$ nanoribbons; (c) TEM image of SVNs covered with Ag nanoparticles and HRTEM image of Ag nanoparticles showing (111) diffraction plane; (d) HRTEM image of SVN covered with Ag nanoparticles.

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[a] *Anhui Key Laboratory of Functional Molecular Solids, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, P. R. China. E-mail: mwshao@mail.ahnu.edu.cn; Fax: +86-553-3869303; Tel: +86-553-3869303*
[b] *Center of Super-Diamond and Advanced Films (COSDAF), Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon Tong, Hong Kong SAR, China. E-mail: apannale@cityu.edu.hk*

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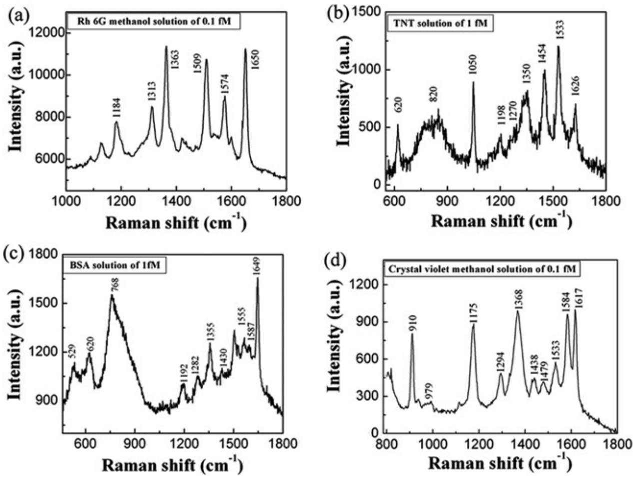

Fig. 2 SERS spectra on individually immobilized Ag nanoparticles: (a) 1.0×10^{-16} M Rh 6G methanol solution; (b) 1.0×10^{-15} M TNT solution; (c) 1.0×10^{-15} M BSA solution; and (d) 1.0×10^{-16} M CV methanol solution.

estimated as 10–11 orders of magnitude. These peaks are strong though the concentration of Rh 6G is much lower than the detection limits previously reported.[2]

The detection and identification of trace trinitrotoluene (TNT) is a problem of great practical interest. The SERS of this method may possess the sensitivity required for such applications.[16] The ring breathing mode at *ca.* 1050 cm^{-1}, together with the –NO$_2$ deformation mode near 1350 cm^{-1} and the bands at 1270 cm^{-1}, can be used as a "fingerprint" for the detection of TNT. There are other peaks, which are quite in accordance with the previous reference.[17] Fig. 2b demonstrates that these three SERS bands can be detected in concentration ranges down to 1×10^{-15} M.

Bovine serum albumin (BSA) is a globular water-soluble protein whose primary structure (66267 Da) is known.[18] Many vibrational bands of BSA have been assigned to vibrations of secondary structure and functional groups. Fig. 2c is the SERS of 1.0×10^{-15} M BSA solution. The peak at 529 cm^{-1} belongs to disulfide bond and that at 768 cm^{-1} to C–S bond, those at 620, 1192 and 1587 cm^{-1} to Phe, 1282, 1555 and 1649 cm^{-1} to amide, 1355 and 1430 cm^{-1} to CH$_2$ vibration.[19,20]

Crystal violet (CV) is a substance important as a molecular probe.[21] SERS of CV has been studied by several groups. Probably Jeanmaire and van Duyne[22] reported the first resonance surface Raman spectrum. Others studied it on silver electrodes,[23] silver films[24] and silica gel.[25] Fig. 2d is the SERS of 1.0×10^{-16} M CV methanol solution. The peaks at 910, 979, 1175, 1294, 1368, 1438, 1479, 1533, 1584 and 1617 cm^{-1} are in accordance with the reported values,[26] further confirming the ultrasensitive Raman signal of Ag modified SVNs.

Generally, it is agreed that more than one effect contributes to the enhancement effect, referred to as a large effective SERS cross-section: an electromagnetic effect associated with large local fields due to resonances occurring in the microstructures on the metal surface, and a chemical effect involving a scattering process associated with chemical interaction between the molecule and the metal surface. The electromagnetic effect is believed to be a few orders of magnitude more than that due to the chemical effect. According to Garcia-Vidal and Pendry's model, the smaller metallic particles give higher enhancement but the enhancement is almost the same if the particles' diameter is less than 15 nm.[27] In this work, Ag nanoparticles with an average diameter of 15 nm play an important role in the ultrasensitivity.

The β-silver vanadate might also play a key role in such an ultrahigh enhancement factor. As β-silver vanadate is a layered compound, the Ag nanoparticle might shift to a proper location because the laser beam is focused strongly on an extremely small object,[28,29] which is favorable to the surface-enhanced factor.

In conclusion, a new and universal method for preparing a substrate for surface-enhanced Raman spectroscopy with ultrasensitive detection is proposed. The diameters of the silver nanoparticles are 15 nm on average. By applying this method, strong SERS signals were obtained with concentrations of Rh 6G, TNT, BSA and CV down to 1×10^{-16}, 1×10^{-15}, 1×10^{-15} and 1×10^{-16} M respectively. This ultrasensitive SERS might facilitate the measurement of a wider range of analytes at lower concentration and with a short detection time.

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