Carbon-nanotube films help to detect organic molecules with high sensitivity

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A novel surface-enhanced Raman-scattering substrate shows superior performance over its conventional planar counterpart thanks to a unique nanoporous nanostructure.

When light interacts with matter, photons become scattered in a number of ways. Some undergo a change of energy in a process known as inelastic (or Raman) scattering, which is used, for example, in studying materials. Because only very few photons (~1 in 10 million) are inelastically scattered, the Raman effect is normally quite weak, which complicates analysis. Surface-enhanced Raman scattering (SERS) provides a solution that increases the intensity of the Raman signal by several orders of magnitude. The enhancement effect is believed to be caused by surface-plasmon resonance, a phenomenon that greatly strengthens the local electric field. Many applications have demonstrated SERS as a sensitive detection technique, especially in identifying trace molecules from explosive materials, in which a vital role is played by the SERS substrate.

Ultrasensitive detection of molecules by SERS requires that the substrate possess a very large surface area. This enables adsorption of more molecules, contributing to the Raman signal, and abundant ‘hot’ sites of metal nanostructures, which enhance local electric fields. Conventional SERS substrates, which are obtained by electrochemically roughening metal foils, spraying metal colloids (dispersions of metal particles in solution) on a substrate, and fabricating nanostructures by lithography (stamping), are nearly planar and, thus, have limited surface area. If these planar surfaces were replaced by nanoporous surfaces with extensive surface area, more molecules could contribute to the SERS signal, thus further improving detection sensitivity.

Here we describe fabrication of a nanoporous surface by cross-stacking superaligned carbon-nanotube (SACNT) films, which are directly drawn out in a dry state from SACNT arrays. When two layers of SACNT films are cross-stacked, large...
numbers of square nanoholes form naturally, resulting in a 'CNT grid.' This grid can serve as nanoporous framework for adsorbing nanoparticles or gaseous molecules. Zero-dimensional silver (Ag) nanoparticles are automatically formed on the surface of 1D CNTs by electron-beam evaporation, leading to a unique nanoporous 0D@1D structure: see Figure 1(a). The resulting SERS substrate has a large surface area and densely packed metal nanoparticles that serve as hot sites for SERS.5

We employed rhodamine 6G (R6G) as a probe molecule. Figure 1(b) shows highly enhanced Raman peaks for R6G adsorbed on a Ag-CNT grid, which provides a higher SERS signal than a planar SERS substrate prepared by depositing Ag onto a silicon wafer. To optimize our SERS substrate for obtaining uniform nanoparticles with small gaps on the surface of CNTs, we inserted a buffer layer between the Ag and CNTs. We found that a buffer of amorphous silica (SiO\textsubscript{2}) greatly improves the uniformity of Ag nanoparticles. In this Ag-SiO\textsubscript{2}-CNT grid, Ag tends to form quasi-uniform spheres on the amorphous-silica layer around CNTs: see Figure 1(c) (inset). Under very weak laser irradiation (6\textmu W power), the Ag-SiO\textsubscript{2}-CNT grid provides nearly the same Raman intensity as the Ag-CNT grid. We also found that the Ag-SiO\textsubscript{2}-CNT grid provides a higher SERS signal than the planar SERS substrate.

This extraordinary Raman-enhancing capability can be used directly in ultrasensitive detection of trace molecules. For example, because the explosive TNT has very low vapor pressure, the ability to detect its vapor in trace analysis is very attractive. To prove the application of our SERS substrates in this field, we carried out preliminary experiments to detect ambient TNT vapor. We found that the adsorbed TNT molecules can be detected on the Ag-SiO\textsubscript{2}-CNT grid (see Figure 2). The peaks marked with stars could be used as a fingerprint for detecting TNT. In future, we plan to study the enhancement mechanism of SACNT-based SERS substrates in depth, to search for other buffer layers for greater enhancement, and to assemble SERS substrates into a real device to detect ambient explosive vapor.

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**References**

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