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Ultrahigh sensitive metal-free SERS platforms by functional-groups

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ABSTRACT

Surface-enhanced Raman scattering (SERS) is a powerful molecule sensing technique with excellent identification via a specific Raman fingerprint. Nanometal-based SERS platforms that utilize plasmonic resonance mechanisms have high sensitivity, but have high cost and low stability. Ceramic-based SERS platforms that utilize chemical enhancement mechanisms have low cost and high stability, but have low sensitivity. In the present work, a high-sensitivity, low-cost, and stable sensing platform based on functional-group-enhanced Raman scattering (FGERS) is proposed and investigated. Functional groups (FGs), including carboxyls, carbonyls, and epoxides, formed on graphene oxide (GO) via the coupling effects of GO and ZnO under appropriate heat treatment or ultraviolet (UV) illumination. The key factors for the formation of FGs on GO are heat or UV energy, processing time, ZnO carrier type, and atmosphere composition. The optimized composites show a maximum enhancement factor that exceeds 10^5, the highest enhancement reported for dipole-induced local fields. The excellent detection performance of 10^{-10} M allows the potential fabrication of ultrasensitive, low-cost, and reliable platforms for molecule sensing. Moreover, the FG formation mechanisms can be employed to develop other composite FGERS systems.

1. Introduction

Surface-enhanced Raman scattering (SERS) is a powerful technique for sensing trace molecules. It has applications in the detection of food, drugs, explosives, and environment pollutants. Unlike chemical sensors based on electrochemical mechanisms, SERS identifies molecules based on a specific Raman fingerprint of a specific species. Many studies have demonstrated that SERS platforms employing noble metal nanoparticles (NPs) [1–8] or rough metal surfaces [9–12] exhibit excellent sensitivity due to abundant hot-spot-induced plasmonic resonance on the surface [13–19]. However, metal NPs easily aggregate, resulting in a decrease in the number of hot spots. Metal NPs are also apt to be oxidized, losing activation, which limits their practical applications. To solve these problems, several methods have been recently reported. For example, with tip-enhanced Raman scattering [20], substances on a substrate are probed using a nanoscale gold tip as a Raman signal amplifier. However, the Raman signals were rather weak, thus limiting its applications for molecule sensing. A shell-isolated approach [21] was proposed for protecting noble NPs from aggregation. Although ultrasensitive sensing was achieved, the strength of Raman signals significantly decreased with the thicknesses of the dielectric shells, and the ultra-thin shells are coated using expensive atomic layer deposition techniques. A high-sensitivity, stable, and low-cost SERS platform that does not use noble metals is thus in high demand.

On the other hand, another promising approach by utilizing molecule dipole-induced local electric fields to enhance Raman signals of trace species without using noble metals has attracted much attention very recently. To date, there have been several efforts devoted to producing molecular dipoles on the surface of graphene (Gr) or graphene oxide (GO) to improve sensing sensitivity. With the discovery of tunable SERS by reduction of GO [22], Huh et al. reported the employment of O_3/ultraviolet (UV) treatment to generate oxygen species on Gr [23] and obtained a high enhancement factor (EF) value of 1.5×10^4. CF_4 plasma was applied to induce C-F bonding on reduced GO [24], leading to a maximum EF value of 2×10^3. In addition, mild O plasma treatment was reported to yield oxygen species on graphene, enhancing the Raman signals of dyes [25] by several folds. We recently found that oxygen-containing functional groups (OFGs) can be formed via unique reactions by coupling ZnO and GO at a low temperature of 200 °C,with an EF value approaching 10^4 reached [26] without using expensive plasma-generating equipment or toxic O_3. How-

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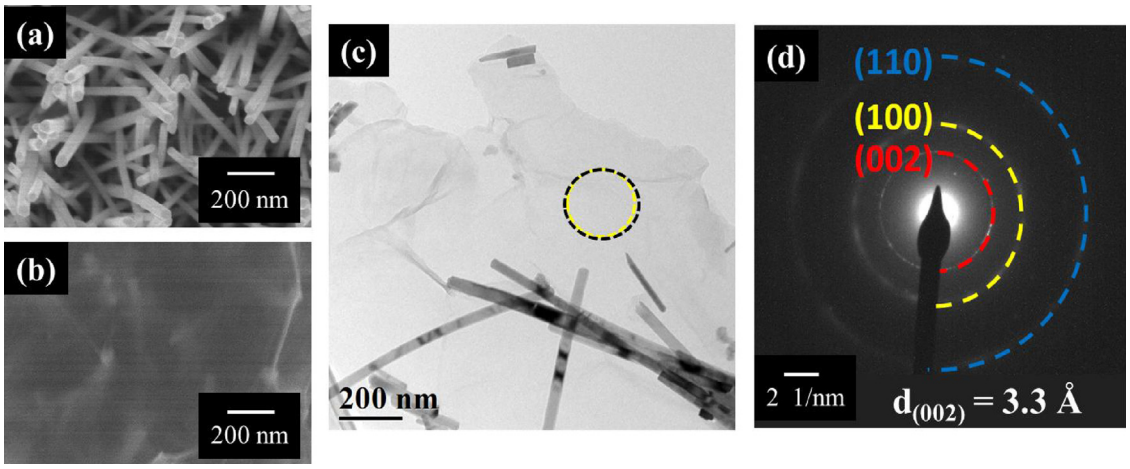

Fig. 1. SEM images of (a) ZnO NRs and (b) GO/ZnO composite after heat treatment at 200 °C for 2 h; (c) TEM bright-field image of GO and ZnO NRs from the GO/ZnO composite; (d) electron diffraction pattern of GO from region marked in (c).

ever, the OFG formation mechanisms are not fully understood. In the present study, to investigate these mechanisms, we designed a series of experiments to examine the key reaction factors for the formation of OFGs on GO/ZnO composites. The proposed theories are universal and can be applied to the development of other composite SERS systems. The optimized GO/ZnO composites based on functional-group-enhanced Raman scattering (FGERS) show a maximum EF value exceeding 10^5, the highest enhancement reported for dipole-induced local fields. The excellent detection performance for 10^{-10} M rhodamine 6G (R6G) allows the potential fabrication of ultrasensitive, low-cost, stable, and reliable SERS platforms for molecule sensing.

2. Experimental

2.1. Preparation of GO/ZnO nanocomposites

GO flakes (2.8 mg), prepared using Hummers' method [27],were dispersed in 500 ml of distilled water using centrifugal separation at 8000 rpm for 40 min. A small volume of 0.45 ml containing dispersed GO flakes was then dropped onto a $2 \times 2\,cm^2$ Si substrate covered with ZnO nanorod (NR) arrays, synthesized via chemical bath deposition (CBD) [28] and the substrate was dried at 60 °C for 5 min. The dropping/drying processes were repeated for 10 cycles to obtain a pristine GO/ZnO composite. For comparison, Sb-doped ZnO, as *p*-ZnO NR arrays, was also prepared via CBD, with antimony acetate solutions used as the sources of Sb dopant [29]. The *p*-type characteristics of Sb-doped ZnO were confirmed using thermoelectrical measurements. The GO/ZnO composites were subsequently subjected to heat treatment or 365-nm UV irradiation with a power density of $4.4\,mW/cm^2$ for various periods of time. Acetone vapor was introduced during heat treatment to investigate the effect of atmosphere composition. Acetone vapor with various concentrations was prepared by injecting specific volumes of acetone droplets into the chamber and allowing them to evaporate completely.

2.2. Characterization and SERS measurements

The nanomaterials were examined using field-emission scanning electron microscopy (FE-SEM; Hitachi 4800)for determining morphology and field-emission transmission electron microscopy (FE-TEM; Philips Tecnai G2 F20 FEG-TEM) for determining crystallography and microstructure characterization. The OFGs on the GO/ZnO samples were characterized using Fourier transform infrared spectroscopy(FTIR; Perkin Elmer Spectrum 100).

SERS measurements were performed with a Jobin Yvon LabRAM HR800 Raman spectrometer equipped with a 532-nm He-Cd laser as the excitation source. The laser power at the sample position was about 70 μW. Each of the samples for the SERS measurements was prepared by casting 10 μl of 10^{-6} M R6Gsolution on a $5 \times 5\,mm^2$ substrate, and then allowing the solvent (water) to evaporate. The area with molecules participating in the scattering process was determined by the diameter of the laser spot, which was around 1 μm in the experiments. To evaluate the EF values of SERS, the Raman signals of R6G were also acquired on a highly resistive flat Si wafer, which exhibits a negligible SERS effect, as a reference for comparison. Since the R6G signal is pretty weak on Si and ZnO, the R6G concentration is three orders higher than that used for GO and GO/ZnO substrates

3. Results and discussion

3.1. Morphology and microstructure of GO/ZnO composites

Fig. 1(a) and (b) shows the SEM plan-view images of the as-synthesized ZnO NR arrays and the GO/ZnO composites after 200 °Cheat treatment for 2 h. The average diameter of NRs is around 40 nm (Fig. 1(a)). The ZnO NRs were covered by GO flakes on the top of the GO/ZnO composite (Fig. 1(b)). Fig. 1(c) shows a TEM bright-field image of the same GO/ZnO composite and Fig. 1(d) shows the selected area electron diffraction pattern of the GO from the circle-marked region in Fig. 1(c). After the heat treatment, the morphology of ZnO NRs remained unchanged, but the d-spacing of the GO (002) planes decreased from 8.3 to 3.3 Å, indicating that a significant number of OFGs between adjacent carbon basal planes disappeared.

3.2. Effect of annealing temperature and time on formation of OFGs and SERS

Fig. 2(a) shows the FTIR spectra of the GO/ZnO composites without and with heat treatment at 200 °C for 1, 2, and 3 h (denoted as G/Z, G/Z-200/1, G/Z-200/2, and G/Z-200/3, respectively). The FTIR spectra show that all OFG signals increase to the maximum after annealing for 2 h (G/Z-200/2). This trend is opposite to the decreasing d-spacing values (TEM results in Fig. 1(d)),especially forcarboxyls, carbonyls, and epoxides. The results indicate that the OFGs intercalated between carbon basal planes were significantly