Unusual functionalization of reduced graphene oxide for excellent chemical surface-enhanced Raman scattering by coupling with ZnO

Ruey-Chi Wang a,*, Ya-Chun Chen a, Shu-Jen Chen b,*, Yu-Ming Chang a

a Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 81148, Taiwan
b Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80778, Taiwan

ABSTRACT
A low-cost noble metal-free substrate comprised of annealed graphene oxide (GO)/ZnO composites is prepared to demonstrate an efficient chemical surface-enhanced Raman scattering effect. A high enhancement factor of about $10^4$, better than those reported for reduced GO (rGO)/Au and GO/Ag composites, is mainly attributed to the unusually abundant oxygen-containing groups generated on surface of rGO by coupling with ZnO nanoparticles at moderate temperature. High-resolution transmission electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy are employed to examine the evolution of ZnO as well as reduction and functionalization of GO after different heat treatments.

1. Introduction
Graphene is a novel carbon nanomaterial of a two-dimensional conjugated structure, offering unique electronic properties, and has been intensively studied for many applications, such as electronic devices [1], solar cells [2], photocatalysts [3], and sensors [4]. There has been growing interest in graphene-based surface-enhanced Raman scattering (SERS) substrates for bio-chemical sensing due to the high surface area and great electrical conductivity of graphene. For example, Au nanoparticle (NP)–graphene oxide (GO) [5] and Ag–graphene [6] composites were recently synthesized for chemical sensing and cell imaging by taking advantage of the electromagnetic enhancement of plasmonic metal NPs. In addition, an ultraviolet/ozone treatment [7] has been used to oxidize graphene and demonstrated an efficient improvement in SERS compared with pristine graphene, due to charge transfer-induced chemical enhancement. However, these high-performance SERS substrates usually need expensive noble metals to enhance plasmonic resonance or toxic O3 gas to activate graphene. It thus remains a challenge to fabricate low-cost graphene-based SERS substrates with excellent enhancement performance.

In this work, an excellent SERS substrate comprised of annealed low-cost reduced GO (rGO)/ZnO composites is firstly demonstrated. The morphologies, structures, and functional groups of the rGO/ZnO composites after different heat treatments show significant variations, indicative of strong reactions between rGO and ZnO. The high SERS enhancement factor (EF) of about $10^4$, even better than those reported for Ag/GO [8], Au/GO [5], Au/rGO [9], and Au/graphene [10] composites, is mainly attributed to the abundant oxygen-containing groups unusually generated on the surface of rGO by coupling with ZnO nanoparticles at moderate temperature, as seen in the Fourier transform infrared spectroscopy (FTIR) spectra. This work demonstrates the preparation of low-cost SERS substrates with excellent performance by reactions of...
2. Experiment

2.1. Preparation of rGO/ZnO composites

GO flakes were prepared following Hummers method [11]. The GO dispersion was prepared by dispersing 0.5 g GO flakes in 500 ml distilled water using centrifugal separation at a speed of 8000 rpm for 40 min. GO dispersion of 0.5 ml was then dropped onto a ZnO nanorod (NR)/Si substrate, synthesized by a hydrothermal route [12], and dried at 90 °C for 5 min. The dropping/drying processes were repeated for 10 cycles to obtain a pristine GO/ZnO composite. The prepared GO/ZnO composites were then annealed at temperatures of 100–400 °C for 1 h in air and cooled down to room temperature (RT) to transform them into various rGO/ZnO composites.

2.2. Characterization and SERS measurements

The as-prepared nanostructures were examined by field-emission scanning electron microscopy (FE-SEM) with a Hitachi 4800, X-ray diffraction (XRD) with a D/MAX-2500, field-emission transmission electron microscopy (FE-TEM) and energy-dispersive spectrometry (EDS) with a Philips Tecnai G2 F20 FEG-TEM for morphology, crystallography, microstructure, and composition characterization, respectively. The functional groups of the GO and rGO/ZnO samples were characterized by FTIR with a Perkin Elmer Spectrum 100. The thermogravimetric analysis (TGA) was performed with a TA, SDT-A600 thermogravimetric analyzer at a heating rate of 15 °C/min under nitrogen. About 15 mg GO and 0.24 mg rGO/ZnO powders were taken for measurement. The electrical properties were measured by depositing two Au electrodes on the rGO/ZnO composites and the current was measured at a fixed bias of 1 V. The gap between the electrodes was about 2 mm.

SERS measurements were performed with a Jobin Yvon LabRAM HR800 Raman spectrometer equipped with a 532 nm He–Cd laser as the excitation sources. 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 Rhodamine 6G (R6G) in ethanol, dropping this on a 5 × 5 mm² substrate, and then allowing the solvent to evaporate. The size of the area of molecules participating in the scattering process is essentially determined by the diameter of the laser spot (1 μm). To evaluate the EF values of SERS, the Raman intensity of R6G was also acquired on a highly resistive flat Si wafer as the reference for comparison, which exhibits a negligible SERS effect.

3. Results and discussion

3.1. Morphologies, microstructures, and crystal structures of the rGO/ZnO composites

Based on the SEM results, the morphologies of the GO/ZnO composites show significant variations after annealing at different temperatures. Fig. 1(a) and (b) show the SEM images of the ZnO NRs and GO/ZnO composites before annealing, respectively. The GO flakes are uniformly attached to the surface of the NRs. After annealing at 150–200 °C for 1 h, the GO flakes were transformed into film-like structures, and small dots of lighter contrast were generated on the films, as shown in Fig. 1(c) and (d). As the annealing temperature was increased, the dots gradually enlarged and aggregated, as shown in Fig. 1(e) and (g).

Fig. 1 – SEM images of as-prepared (a) ZnO NRs and (b) GO/ZnO composites; GO/ZnO composites annealed at (c) 150 °C, (d) 200 °C, (e) 250 °C, (f) 300 °C, and (g) 400 °C for 1 h.
the EF values of the rGO samples annealed at different temperatures do not show obvious difference. In addition to the peak at 1190 cm\(^{-1}\), other main vibrational modes of R6G were also compared (see Fig. S2 and Table S1 of the Supplementary materials), and the EF values for other peaks are also around 10\(^6\). Since the electrical conductivities of substrates are critical for physical SERS effects, the electrical properties of the rGO/ZnO samples with different annealing temperatures were measured and shown in Fig. 9(d). At a fixed bias of 1 V, the current increases with the annealing temperature from RT to 400 °C. It appears that the physical effects are not responsible for the strong SERS effects of the rGO/ZnO sample annealed at 200 °C. On carefully checking the peak positions of R6G on different substrates, including Si, ZnO NRs, and GO/ZnO composites annealed at different temperatures, we found that there is only negligible shift (see Table S2 of the Supplementary materials). Therefore, the enhancement mechanism should not be the effect of charge-transfer or chemical bonding between R6G and functional groups on rGO [7,18] because the above mechanisms will affect the geometrical or electronic structure of the adsorbed molecules, leading to significant spectral shifts [19]. Therefore, the enhancement may be attributed to the local electric field on molecules generated by the highly electronegative oxygen-containing functional groups under the laser excitation from their strong local dipole moments [20]. In the work, we adopted the dropping [21,22] rather than soaking [20,23] method to prepare SERS samples, so the number of molecules per unit area should be identical irrespective of the morphologies of the nanostructures changed with different annealing temperatures because the samples were all fully covered by the drops. Although the signal of R6G on the annealed rGO/ZnO composites is not pretty high, the EF value is estimated by comparing the respective signal intensity per molecule under the same parameters of SERS measurements. Because the number of R6G molecules on the rGO/ZnO samples is only one thousandth of that on the Si substrate by considering the difference in concentration, the high EF value of 10\(^6\) is derived. By testing some R6G solutions with different concentrations, we can know the lowest R6G concentration on the annealed ZnO/rGO sample that all the main Raman peaks still can be detected is about 10\(^{-8}\) M (see Fig. S3 in the Supplementary materials). This work demonstrates that rGO could be effectively functionalized by coupling with ZnO at moderate temperature, which leads to excellent chemical SERS effects for bio-chemical sensing applications.

4. Conclusion

This work presents a novel and efficient SERS substrate based on low-cost rGO/ZnO composites. The high EF value, about 10\(^4\) for R6G, is mainly attributed to the unusually abundant oxygen-containing groups generated on rGO by coupling with ZnO at a moderate temperature. The SEM, TEM, and XRD results show numerous ZnO NPs were generated on the surface of rGO, and the d-spacing of GO gradually decreased after the annealing treatments. Unusually, the functional groups of rGO/ZnO increased significantly, in contrast to the behavior of GO powders, after annealing at 150–200 °C, indicative of the functionalizing of the rGO surface, even if the d-spacing decreased. This evolution could be attributed to the coupling of rGO with ZnO, and the generated abundant functional groups enhanced the chemical SERS effects due to the local electric field created under the laser excitation by their strong local dipole moments. This work thus demonstrates an efficient method to functionalize rGO for excellent SERS effects, which is promising for low-cost bio-chemical sensing applications.

Acknowledgement

This work was supported by the National Science Council of Taiwan under the Grant (NSC100-2221-E-390-009-MY3).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.12.110.

REFERENCES


