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Conformation-dependent surface-enhanced Raman scattering of graphene oxide/metal nanoparticle hybrids

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Graphene oxide (GO)/Ag nanoparticle (NP) hybrids are obtained by in situ reduction of Ag NPs on GO sheets. In this letter, the influence of the conformation of GO sheets on the surface-enhanced Raman scattering (SERS) effect of GO/Ag NPs is investigated by covalently grafting folic acid (FA) molecules onto graphene sheets. SERS measurements are conducted in aqueous solutions with different pH values. Data show that the SERS signals of FA are pH dependent, consistent with the morphological changes of GO sheets.

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Graphene oxide (GO) is a novel, one-atom-thick, two-dimensional carbon network containing carboxylic acid groups at the sheet edges, as well as hydroxyl and epoxy groups on the graphite plane. GO is receiving considerable attention because of its excellent physical and chemical properties, as well as potential applications in energy, electronics, sensors, and biomedicine[1-4]. GO has recently become a promising support for anchoring and dispersing various metal and metal oxide nanoparticles (NPs), such as Pt, Pd, Ag, Au, and Fe3O4[5-8]. Among the many exciting applications of GO, the use of GO/NP composites as efficient and ultrasensitive surface-enhanced Raman scattering (SERS) substrates is particularly interesting. SERS-active metal (Au or Ag) NPs have been successfully assembled onto GO sheets by in situ chemical reduction or electrostatic adsorption[9-12]. GO/metal NP hybrids exhibit ultra-high SERS activity, in which GO serves as a template to enrich target molecules, thereby enhancing the presence of analytes around metal NPs[9].

GO can be well-dispersed in an aqueous solution because of the negatively charged oxygen-containing functional groups on graphene sheet[13]. Whitby et al. [14] have demonstrated that the morphology of GO sheets dramatically changes depending on the pH of a solution, which can be attributed to the ionization of O groups under various ionic environments. At low pH values, GO seems to agglomerate as flat sheets, whereas flaky structures tend to wrinkle and star-like morphologies form at higher pH values. Therefore, the SERS effect of GO/metal NP hybrids may be influenced by the conformational changes of GO sheets at different pH values.

To validate this hypothesis, a SERS study on folic acid (FA) at different pH values was carried out in the present work using GO/Ag NP composites as SERS substrates. In our previous work[15], we have illustrated that the non-covalent adsorption of aromatic molecules on GO sheets is significantly influenced by pH, eventually resulting in different GO-based SERS effects. To eliminate the SERS signals caused by the distinct de-
Fig. 1. Fabrication of FA-GO/Ag NPs.

Fig. 2. (a) UV-VIS spectra and (b) Raman characterization of GO (A), FA-GO (B), and FA-GO/Ag NP (C) solutions at pH 7. (c) FT-IR spectra of GO, GO-PVP, and FA-GO-PVP. (d) TEM image of FA-GO/Ag NPs.

distributed onto the surface of graphite sheet.

In this strategy, GO acts as a bridge between FA molecules and Ag NPs; thus, strong SERS signals of FA can emerge from interstitial sites in FA-GO/Ag NPs consisting of coupled Ag NPs, namely, hotspots. The SERS response of FA-GO/Ag NPs is observed in citric acid–phosphate buffer solutions at various pH values. Raman spectra were collected with a Renishaw inVia confocal Raman spectrometer equipped with a 514.5-nm laser (0.5 mW) and an integration time of 30 s. Figure 3 describes the SERS spectra of FA (1 μmol/L) induced by Ag NPs (Fig. 3(a)) and the Raman spectra of FA-GO/Ag NPs (Fig. 3(b)) in citric acid–phosphate buffer solutions with different pH values. The SERS spectra of FA are drastically influenced by pH, indicating that the Raman scattering event on dissociative Ag NPs or on GO-Ag NPs is pH controlled. However, the two events seem to be totally different.

To further investigate the difference between Ag NP-induced SERS spectrum and the SERS spectrum generated from FA-GO/Ag NPs in response to pH, the relative intensities of the four pair of Raman peaks were plotted on Fig. 4. A Raman shift sometimes occurs in the SERS spectrum induced by Ag NPs probably because of the instability of Ag NPs in citric acid–phosphate buffer solutions. For example, the strong peak at 1185 cm⁻¹ at low pH values red shifts to 1179 cm⁻¹ when at pH 5. By contrast, the SERS spectral pattern of FA induced by GO/Ag NPs is stable with a negligible frequency shift. Furthermore, gradually enhanced Raman signals are observed in the FA-GO/Ag NP-induced SERS spectra. Only very weak Raman peaks are observed in the SERS spectrum at pH 3. The intensities of the four bands significantly enlarge with increased pH, especially the phenyl ring deformation mode at 1505 cm⁻¹. However, no regular changes are found in the normalized intensities of the corresponding peaks induced by Ag NPs as a function of pH.

A mechanism of conformational changes of the GO sheet is proposed to explain the gradually enhanced SERS signals of FA induced by GO/Ag NPs (Fig. 5). Under acidic conditions, a few Ag NPs disperse on the flat graphene sheet, resulting in weak SERS signals of FA. The isolated Ag NPs aggregate on the wrinkled GO sheet under alkaline environments, facilitating the formation of SERS hotspots. The folded structures also allow the NPs and probes to be in close proximity, and then the strong Raman enhancement of FA emerges. To confirm the structural changes, TEM images of FA-GO/Ag NPs were acquired under acidic (pH 3) and alkaline conditions (pH 14). Figure 6 shows that the color of FA-GO/Ag NP colloids changes from straw yellow at pH 3 to brown at pH 14, consistent with previously reported color changes of GO colloids[14]. The TEM image of FA-GO/Ag NPs under an acidic condition shows a flat graphite sheet onto which irregular Ag NPs are deposited (Fig. 6(a)). However, the membranous structure...
Fig. 5. Probable mechanism underlying the pH-dependent SERS effect of GO/Ag NPs.

becomes folded at pH 14, which leads to the overlapping of Ag NPs on GO sheet (Fig. 6(b)). The wrinkling of FA-GO/Ag NP sheet at high pH values can facilitate the SERS event between Ag NPs and FA, thereby causing strong SERS signals (Fig. 3(b)).

In conclusion, GO/Ag NP hybrids covalently functionalized with FA are obtained by \textit{in situ} reduction of Ag NPs on GO surface using PVP as reductant and stabilizer. The hybrids exhibit highly sensitive and reproducible pH-dependent SERS responses within pH 3.0 to 8.0, which can be attributed to the conformational changes of GO sheet.

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