Synthesis of GO/Au/Ag Nanocomposite with Excellent Surface Enhanced Raman Scattering Effect

Yongqiang Yang¹, Ling Wang²#, Qinsheng Wang¹* and Yan Zhang²*

¹National Graphene Products Quality Supervision and Inspection Center (Jiangsu), Jiangsu Province Special Equipment Safety Supervision Inspection Institute·Branch of Wuxi, Yanxin Road 330, Wuxi 214174, P.R. China
²School of Material Engineering, Shanghai University of Engineering Science, Shanghai 201620, P.R. China

# Yongqiang Yang and Ling Wang contributes equally to this work.
*Email: wqs@wxtjy.com; yanzhang@sues.edu.cn

Abstract. In this work, a nanocomposite (GO/Au/Ag) containing graphene oxide (GO) and Au/Ag nanoparticles was fabricated by in situ reduction for improved manipulation of their SERS effect. The uniform dispersion of Au/Ag nanoparticles were successfully generated on GO. Rhodamine 6G (R6G) as a Raman probe was used to investigate the SERS effect. Owing to the synergistic effect of the high localized surface plasmon resonance of Au/Ag, and chemical enhancement of GOs, the Raman intensities of R6G on GO/Au/Ag is several times as high as that on Au/Ag or GO/Au. GO/Au/Ag nanocomposites showed excellent Raman enhancement and appeared to be a kind of valuable material with potential application in SERS detection.

1. Introduction
Surface-enhanced Raman scattering (SERS) has attracted attentions in recent years. It not only characterize the internal structure of materials, but also has the advantages of traceless detection, and is widely used in biology, medicine, and environmental testing [1-3]. Noble metals such as Au, Ag, and Cu are used as SERS substrates with electromagnetic enhancement mechanism (EM), due to their localized surface plasmon resonance (LSPR) effect [4]. Au nanoparticles (Au NPs), in particularly, are used as SERS substrate with good catalytic activity, optical properties, and biocompatibility [5, 6]. However, metal nanoparticles do not capture well for some probe molecules, resulting in a failure to significantly enhance Raman signals [6]. Owing to the excellent chemical and physical performances, graphene and its derivatives have drawn extensive attentions [7-11]. In recent years, graphene and graphene oxide (GO) have been proved to be an excellent SERS substrate [12, 13]. Yu et al. showed that the Raman enhancement of GO was stronger than that of graphene [14]. It has also shown that the SERS activity of GO was promoted via chemical enhancement mechanism (CM), due to the charge transfer between GOs and the molecules [15]. Thus, in this work, Au/Ag nanoparticles and GO nanocomposite (GO/Au/Ag) was synthesized. Taking advantage of SERS effect of Au/Ag and GO, GO/Au/Ag was demonstrated to be an excellent SERS substrate for detecting R6G molecules. Thus, the composite has great potential in analytic field.
2. Experiments

2.1 Materials
HAuCl$_4$ (99.9 %), AgNO$_3$ (99.99%), L- ascorbic acid (AR, 99.7%), chitosan (BR), and rhodamine 6G (95%) were bought from Aladdin Industrial Co. Ltd (Shang Hai, China). Graphene oxide (GO) was prepared based on our earlier works. Ultrapure water (18.2 M Ω cm) were made use in all experiments.

2.2 Synthesis of GO/Au/Ag
GO/Au/Ag nanostructure was synthesized by in situ reduction. Briefly, the mixture containing 435 μl HAuCl$_4$ solution (10 mM) and 18 ml ultrapure water was stirred. Then, 100 μl chitosan (10 mg/ml) was added. After stirring for 1 min, 72 μl AgNO$_3$ solution (5 mM) and 1 ml GO (2 mg/ml) were added, respectively. 400 μl L-AA (0.1 M) was immediately added in the mixture and kept stirring for 3 h. Finally, the solution was centrifuged at 15000 rpm for 10 min at least 3 times to separate the solid precipitation, and GO/Au/Ag thus obtained.

Au/Ag, GO/Au, and GO/Ag nanostructures were synthesized by the same method except the absence of GO, AgNO$_3$, and HAuCl$_4$, respectively.

2.3 Characterizations
The morphologies were characterized by scanning electron microscopy (SEM, Zeiss Ultra 55). UV-vis spectroscopy was carried out by a N5000 UV-Vis spectrophotometer, respectively. Raman spectra were measured using Raman spectrometer (Hobiba scientific) with a 532-nm laser.

3. Results and discussion
The surface morphologies of GO/Au/Ag, Au/Ag, GO/Au, and GO/Ag nanocomposites were elucidated using SEM. As depicted in Figure 1(a), GO sheets maintained their layer topography, and nanoparticles were generated on both sides of GO sheets. The average size of Au/Ag nanoparticles on GO sheets is ~40 nm with uniform size. Without GO sheets, Au/Ag particles was increased to ~80 nm, and agglomerated seriously (Figure 1 (b)). In Figure 1 (c, d), it can be seen that isolated Au nanoclusters or Ag nanoparticles were distributed on GO sheets. The average diameters of Au nanoclusters and Ag nanoparticles are about 90 nm and 15 nm, respectively. Compared with GO/Au/Ag, both the number of isolated Au nanoclusters and Ag nanoparticles on GO/Au and GO/Ag surface were decreased tremendously.

![Figure 1](image-url) Figure 1. SEM images of (a) GO/Au/Ag, (b) Au/Ag, (c) GO/Au, and (d) GO/Ag.
Figure 2. EDS spectra of (a) GO/Au/Ag, (b) Au/Ag, (c) GO/Au, (d) GO/Ag.

EDS were performed to carefully study samples’ chemical elements. In Figure 2(a), it can be found that C, O, Au and Ag four elements are existed, indicating that the GO/Au/Ag composite material has been successfully prepared. Figure 2(b) shows the presence of Au and Ag elements in Au/Ag composite. The presence of a small amount of C and O in Figure 2(b) may come from the pollution of vacuum system under electron microscope. It can be found that C, O, Au elements in GO/Au nanocomposite, and C, O, Ag elements in GO/Ag nanocomposite (Figure 2(c)). Combined with SEM results, a series of GO/ noble metal composites can be successfully synthesized by in-situ reduction method.

Figure 3. UV−Vis absorption spectra of (a) GO/Ag, (b) GO/Au, (c) Au/Ag, and (d) GO/Au/Ag.

Figure 3 shows UV−Vis absorbance spectra of GO/Au/Ag, Au/Ag, GO/Au, and GO/Ag. Two peaks at 226 nm and 409 nm are observed on UV−Vis spectrum of GO/Ag nanocomposite (Figure 3(a)), corresponding to the π−π* transition of aromatic C=C sp² domains of GO and present of Ag nanoparticles, respectively. Two major peaks at 234 nm and 643 nm are observed for GO/Au (Figure
3(b)). The red-shifted from 226 to 234 nm suggested the GOs were partially reduced and some aromatic structure was restored[[16]], and the peak at 643 nm was attributed to the presence of Au NPs, corresponding to LSPR effect of Au NPs [[17]]. For GO/Au/Ag composites, there are three major peaks at 222 nm, 437 nm, and 525nm, corresponding to the π-π* transition of aromatic C=C sp² domains of GO, the surface plasmonic resonance peak of the gold-silver nanoparticle, and Au nanoparticle, respectively. These results further indicated that GO/Au/Ag nanostructure was successfully synthesized.

![Figure 4. SERS spectra of R6G (5 ×10⁶ mol/L) on different substrates.](image)

**Table 1.** The relative Raman shift and enhancement factor for R6G (5×10⁻⁶ M) on various substrates

| Samples     | 614 cm⁻¹   | EF    | 773 cm⁻¹   | EF    | 1186 cm⁻¹ | EF    |
|-------------|------------|-------|------------|-------|-----------|-------|
| GO/Au/Ag    | -3         | 6.72×10⁴ | -1         | 2.60×10⁴ | -3        | 3.86×10⁴ |
| Au/Ag       | -3         | 2.28×10⁴ | -1         | 0.81×10³  | -3        | 1.20×10⁴ |
| GO/Au       | -4         | 1.43×10⁴ | -1         | 0.64×10³  | -4        | 0.91×10⁴ |
| GO/Ag       | -3         | 0.19×10⁴ | -1         | 0.08×10³  | -4        | 0.08×10⁴ |

In order to further explore the SERS performance of GO/Au/Ag nanocomposite, we used R6G to evaluate the SERS effect. As shown in Fig. 4, at 532 nm excitation, which is at the resonant wavelength excitation of R6G, the observed signal located at 614, 775, 1186, 1366, 1505 and 1650 cm⁻¹ which consistent with the previously reported R6G characteristic peak [18] can be identified in the spectra. The peaks of R6G molecule at 614 cm⁻¹, 775 cm⁻¹, and 1186 cm⁻¹ are attributed to Cx-Cx-Cx bending vibration on the Xanthene ring, Cx-H bending vibration, and Cx-Cx stretching mode, respectively. The peaks at 1366 and 1650 cm⁻¹ belong to Cx-Cx (X stand for xanthene rings) stretching vibration. The Raman signal on GO/Ag was very weak. Raman intensities of R6G on GO/Au substrate were similar to those on Au/Ag NPs. Owing to LSPR effect of Au and Ag, Ag/Ag composites as substrates exhibited SERS activities. Raman intensities of R6G on GO/Au/Ag were enhanced remarkably, and about 35, 5 and 3 times higher than that on GO/Ag, GO/Au, and Au/Ag. Furthermore, Raman shifts and the enhancement factor (EF) values are also calculated (Table 1). The Raman shifts on the substrates proved the strong interaction and charge transfer between R6G molecules and GO/Au, GO/Au, Au/Ag, and GO/Au/Ag substrates. The EF values of R6G on GO/Au/Ag were as large as 10⁻³~10⁴, and took the order of GO/Au/Ag> Au/Ag> GO/Au> GO/Ag. The EF values of R6G on GO/Au/Ag reached up 6.72×10⁴, indicating the GO/Au/Ag exhibited the largest SERS activity. As we known, GO with a large average size of sp² carbon domain and sufficient
oxygen functional groups can absorb much more molecules and induce a considerable local electric field under laser excitation, resulting in the SERS enhancement via resonant enhancement and chemical enhancement [13]. In the meanwhile, Au/Ag nanoparticles have SERS activity via EM. Owing to the synergistic effect of GO and Au/Ag, there was a significant increase in SERS activity of GO/Au/Ag nanocomposite, indicating that GO/Au/Ag composite was an excellent substrate for SERS detecting.

4. Conclusions
In summary, GO/Au/Ag nanocomposites were synthesized by in situ reduction. The products were characterized by SEM, EDS, and UV-vis. The results showed that Au/Ag NPs were uniformly distributed on GO sheets. Owing to the electromagnetic enhancement of Au/Ag nanoparticles and chemical enhancement of GOs, GO/Au/Ag nanocomposites exhibited excellent SERS activity and great potential in rapid SERS analysis.

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6. References
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