

Synthesis of graphene-based nanocomposites as SERS substrates in biodetection

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The detection of biomarkers as genes and proteins of some pathologies like cancer should be made as early as possible to allow their treatment. Surface-enhanced Raman spectroscopy (SERS) is a technique capable of rapid label-free identification of small target analytes because of the high sensitivity, and the “fingerprinting” ability to produce distinct spectra from molecules with similar structure and function. In addition, the preparation of samples uses a minimum quantity of expensive reagents and takes much less time than other techniques such as polymerase chain reaction (PCR) or immunoassays[1].

Substrates used in SERS are typically composed by metal nanoparticles, in particular Ag and Au, due to the strong enhancement that may be induced in the Raman signal of surface adsorbed molecules. Graphene (Gra), a 2D monolayer of sp² bonded carbon atoms in a dense honeycomb crystal structure, may induce by itself a Raman enhancement effect on adsorbed molecules [2], also the association of noble metal nanoparticles and Gra can produce an effective SERS substrate, as we have demonstrated in a previous work [3].

Our aim is to produce noble metal/graphene nanocomposites in a controlled manner in order to fine-tune their SERS activity and make them specific to certain molecules identification and quantification. In this way, we aim to contribute to the development of manageable SERS sensors for the selective detection of biomolecules in targeted research.

In this communication we present results on the synthesis optimization of gold and silver/graphene nanocomposites towards SERS activity. The experimental procedures were modified to our purpose, by changing some parameters as metal and graphene oxide concentration and reduction agent composition.

Generally, HAuCl₄ or AgNO₃ were respectively added to graphene oxide (GO) aqueous suspensions and stirred for 30 minutes, in order to promote electrostatic interactions between the oxygen functional groups of GO and the metal ions. The reducing agent was then introduced and the reaction followed under different conditions. The reducing agent composition was varied according to the literature methods (Table). The *in situ* metal reduction allows the simultaneous metal nanoparticles formation on the graphene sheets surface and the reduction of graphene oxide, producing a uniform substrate.

The samples were then characterized by UV-visible, SEM and HRTEM. SERS spectra were recorded under the same conditions using thiosalicylic acid (SH) as analyte, in a Bruker RFS100/S FT-Raman spectrometer with a 1064 nm laser. Figure shows that methods 1 and 2 produce efficient SERS substrate.

We found that by changing the synthetic conditions it is possible to modulate the amount, size and morphology of the metal nanoparticles grown at the graphene sheet. Also interestingly was that the SERS signal depends on the reducing agent used.

References

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Table

Table– Methods used for Au and Ag nanocomposite synthesis.

<i>Method</i>	<i>Reducing agent</i>	<i>Composite</i>	<i>SERS signal</i>
1 ^[3]	Tri-Sodium citrate	AuGO1 AgGO1	yes yes
2 ^[4]	Glucose and aq. ammonia sol. (30 wt.%)	AuGO2 AgGO2	yes yes
3 ^[5]	DMSO (in substitution of DMF, literature)	AuGO3 AgGO3	no no
4 ^[6]	Ethylene Glycol	AuGO4 AgGO4	no no

Figure

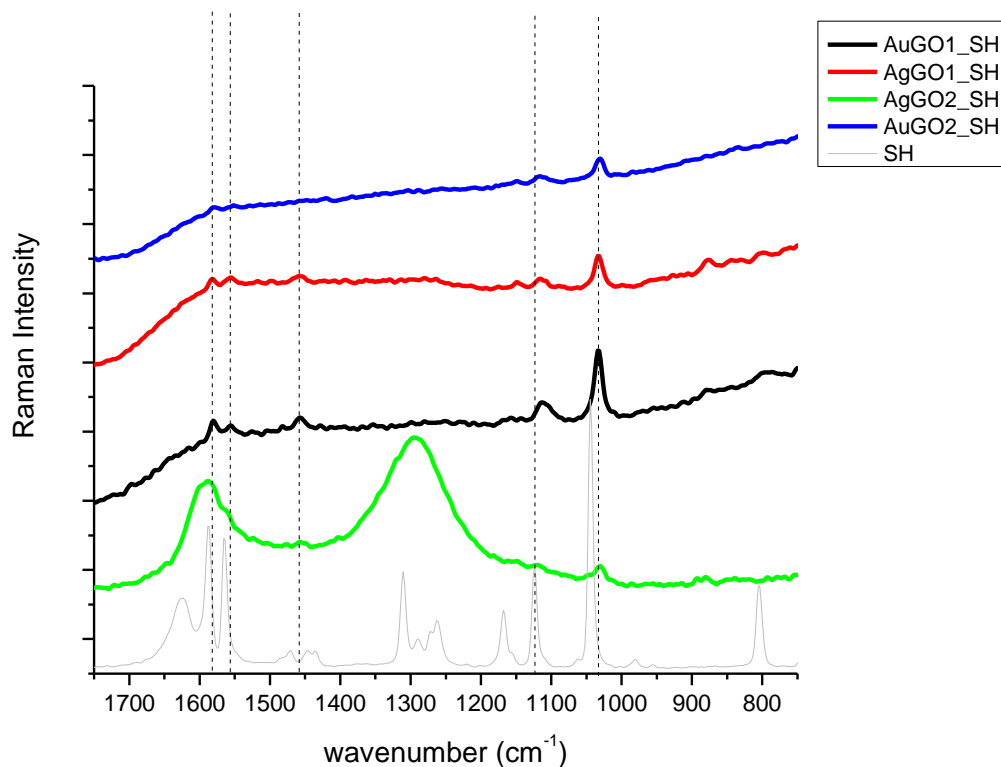


Figure – SERS spectra of thiosalicylic acid using the composites synthesized by method 1 and 2.

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