



# A new green, ascorbic acid-assisted method for versatile synthesis of Au-graphene hybrids as efficient surface-enhanced Raman scattering platforms



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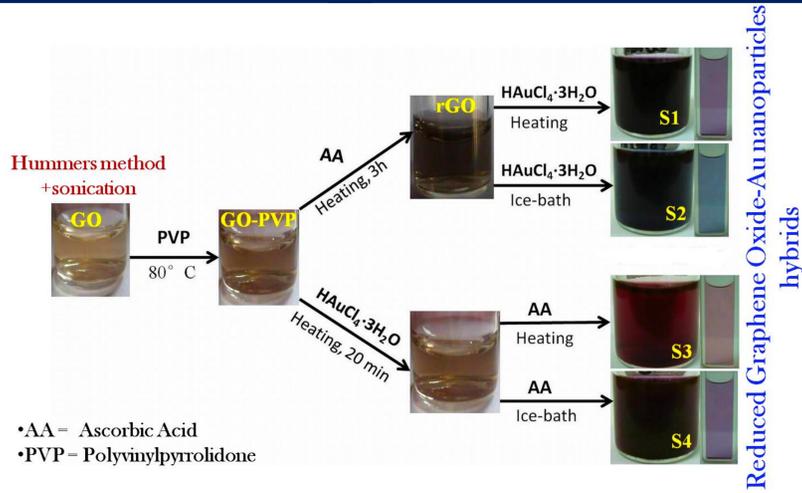
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Graphene, a monolayer of  $sp^2$ -hybridized carbon, arranged in a honeycomb lattice, has received considerable attention due to its unique two-dimensional (2D) structure and remarkable physical and chemical properties. Recently, a new class of graphene-based hybrid materials have aroused a great interest due to the novel properties resulted from combination of graphene with different nanomaterials (e.g. magnetic nanoparticles, noble metal nanoparticles). Many methods for Au-graphene hybrid material have been developed. However, two main challenges are still remain: to prevent the aggregation of hybrids by  $\pi$ - $\pi$  stacking between graphene nanosheets and to avoid toxic chemicals (e.g. hydrazine) for graphene and/or gold reduction.

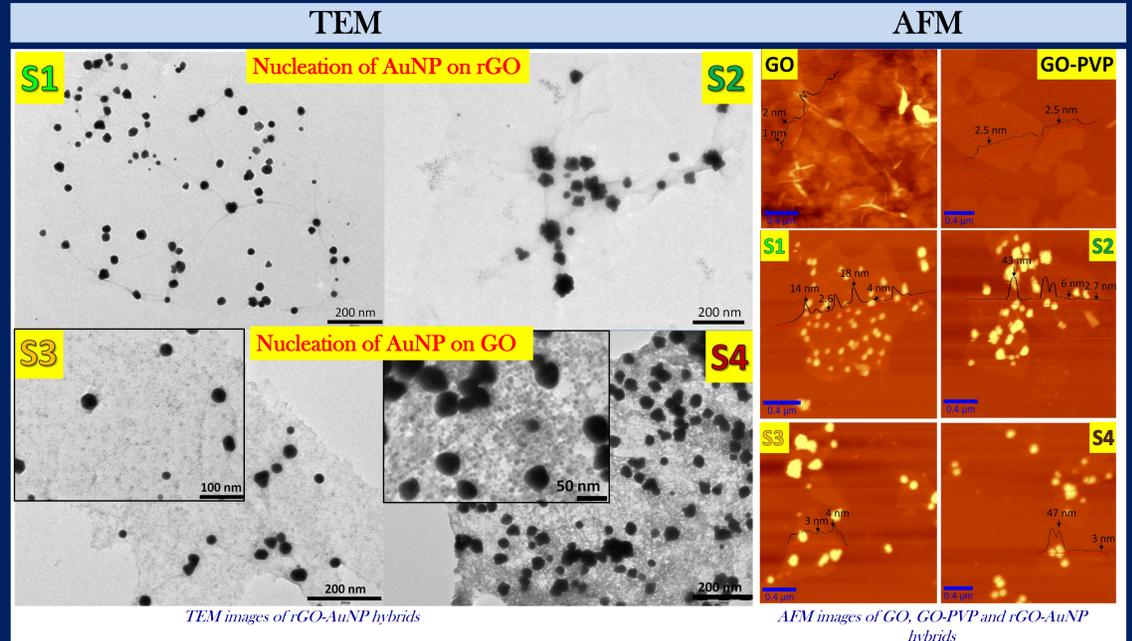
Here we explore a new green method for the synthesis of reduced graphene oxide-gold nanoparticles (rGO-AuNP) hybrids in aqueous solution that exploits the ability of ascorbic acid (AA) to operate as effective dual agent for both graphene oxide (GO) and gold ions reducing. Through careful investigation of the production of rGO-AuNP hybrids stabilized with polyvinylpyrrolidone (PVP), several versatile routes were devised with the aim to control the size, shape and distribution of AuNP anchored onto the graphene sheets as well as the degree of GO reduction. Particularly, when rGO is used as platform for Au ions nucleation, a relative sparse distribution of AuNP of size ranging from 20 nm to 50 nm is noticed. In contrast, when gold ions are added to the solution prior to any GO reduction, the density of large AuNPs is rather low relative to the uniformly packed small sized AuNPs (4-12 nm). The progress of GO reduction is explained by considering the contribution of the catalytic activity of AuNP and reaction temperature, besides the reducing activity of AA. Finally, a plausible mechanism for the nucleation and distribution of AuNP onto the graphenic surface is assumed, highlighting the significance of oxygen moieties. The green method developed here is promising for the fabrication of gold-graphene nanocomposites with tunable surface "decoration", suitable for surface-enhanced Raman spectroscopy (SERS).

## Experimental



•AA = Ascorbic Acid  
•PVP = Polyvinylpyrrolidone

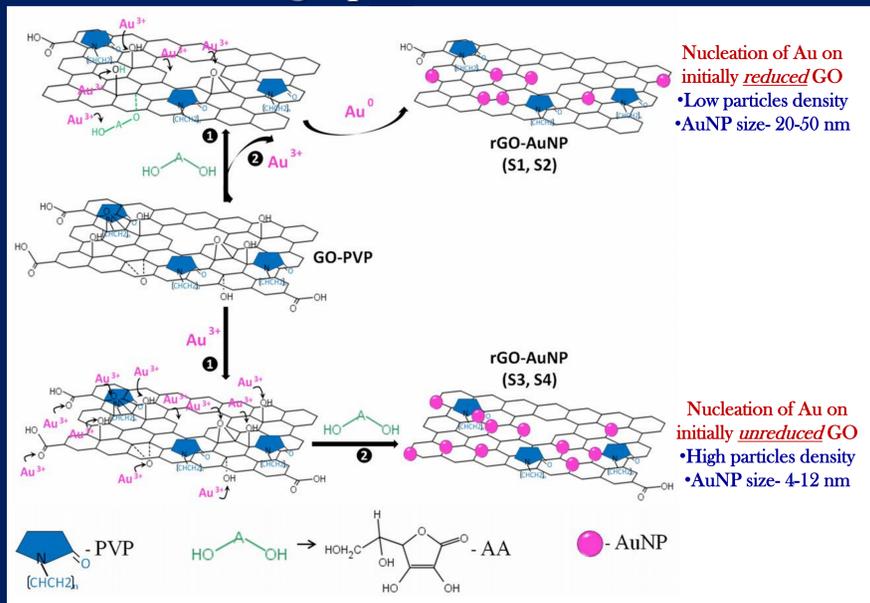
## Characterization



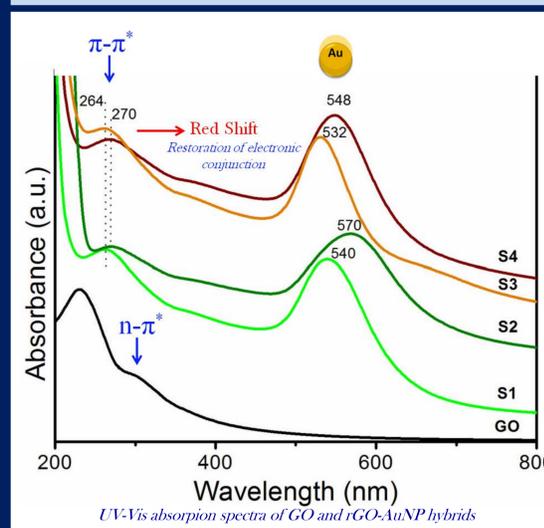
TEM images of rGO-AuNP hybrids

AFM images of GO, GO-PVP and rGO-AuNP hybrids

## Mechanism of AuNP nucleation on graphene sheets

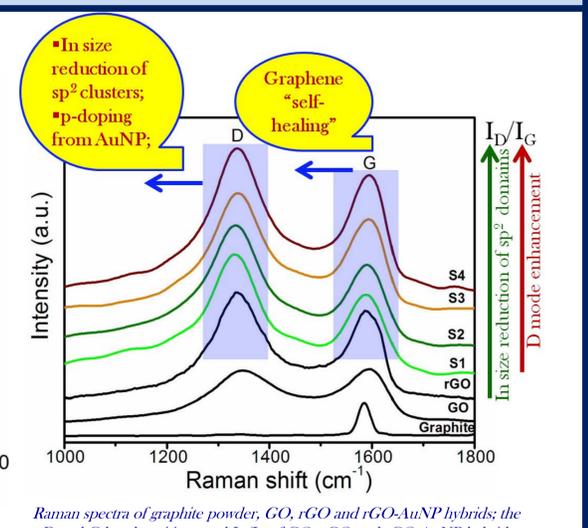


## UV-Vis



UV-Vis absorption spectra of GO and rGO-AuNP hybrids

## Raman



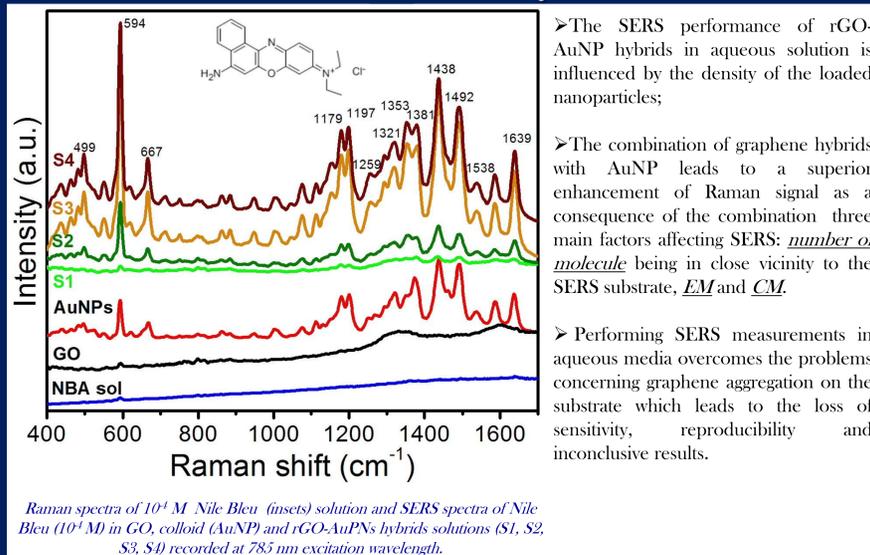
Raman spectra of graphite powder, GO, rGO and rGO-AuNP hybrids; the D and G band positions and  $I_D/I_G$  of GO, rGO and rGO-AuNP hybrids (the table).

Samples	D band ( $cm^{-1}$ )	G band ( $cm^{-1}$ )	$I_D/I_G$
GO	1348	1598	0.94
rGO	1336	1586	1.22
S1	1333	1589	1.70
S2	1335	1593	1.66
S3	1339	1597	1.39
S4	1338	1596	1.33

Confirms:

- the GO reduction;
- the successful formation and anchoring of AuNP on graphene plates.

## SERS study



Raman spectra of  $10^{-4}$  M Nile Bleu (insets) solution and SERS spectra of Nile Bleu ( $10^{-4}$  M) in GO, AuNP and rGO-AuNP hybrids solutions (S1, S2, S3, S4) recorded at 785 nm excitation wavelength.

The SERS performance of rGO-AuNP hybrids in aqueous solution is influenced by the density of the loaded nanoparticles;

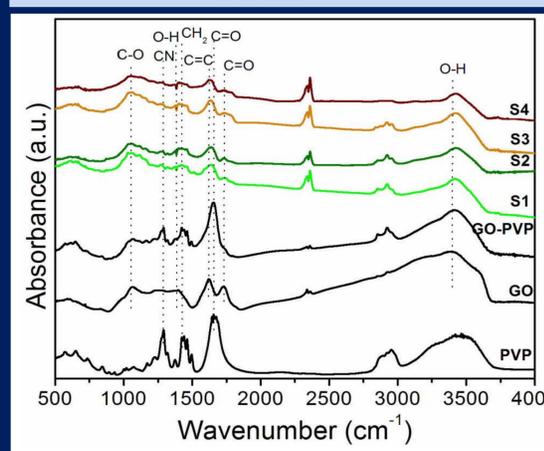
The combination of graphene hybrids with AuNP leads to a superior enhancement of Raman signal as a consequence of the combination three main factors affecting SERS: number of molecule being in close vicinity to the SERS substrate, EM and CM.

Performing SERS measurements in aqueous media overcomes the problems concerning graphene aggregation on the substrate which leads to the loss of sensitivity, reproducibility and inconclusive results.

## Conclusions

- We have showed a new, green and easy approach for the synthesis of aqueous stable rGO-AuNP hybrids;
- By changing the reaction conditions, we found that the sizes and densities of AuNP obtained onto rGO are highly sensitive to the chemistry of graphene derivatives surface prior to the Au ions source addition;
- The green method developed here is promising for the fabrication of gold-graphene nanocomposites with tunable surface "decoration", suitable for surface-enhanced Raman spectroscopy (SERS).
- The obtained rGO-AuNP hybrids are promising for biological studies.

## FT-IR

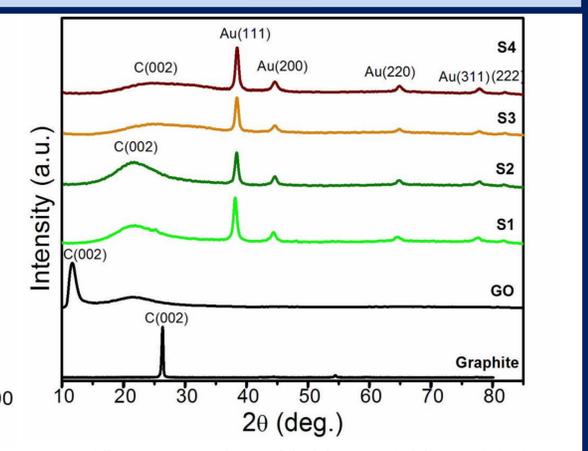


FT-IR spectra of PVP, GO, GO-PVP and rGO-AuNP hybrids

Confirms:

- the presence of oxygenated moieties on GO surface;
- the successful attachment of PVP;
- the GO reduction in all rGO-AuNP hybrid samples-the intensity of the peaks associated with oxygen groups decreases relative to GO.

## XRD



XRD diffraction patterns of PVP, GO, GO-PVP and rGO-AuNP hybrids

Confirms:

- the graphite exfoliation, GO formation and GO reduction:  $d(002)$  graphite - 3.4 Å
- GO- 7.6 Å
- rGO-AuNP-  $\sim 3.96$  Å and  $\sim 3.60$  Å.
- the successful formation of nano-crystals.

Zeta potential measurements =

- monitoring the changes of GO surface after chemical modification;
- Provide information about composite stability.

GO	GO-PVP	Zeta potential (mV)							
		Before $NH_3$ addition				After $NH_3$ addition			
		S1	S2	S3	S4	S1	S2	S3	S4
-40,2	-26,5	-23,2	-22,5	-27,6	-26,6	-33,8	-31,6	-32,9	-32,9