



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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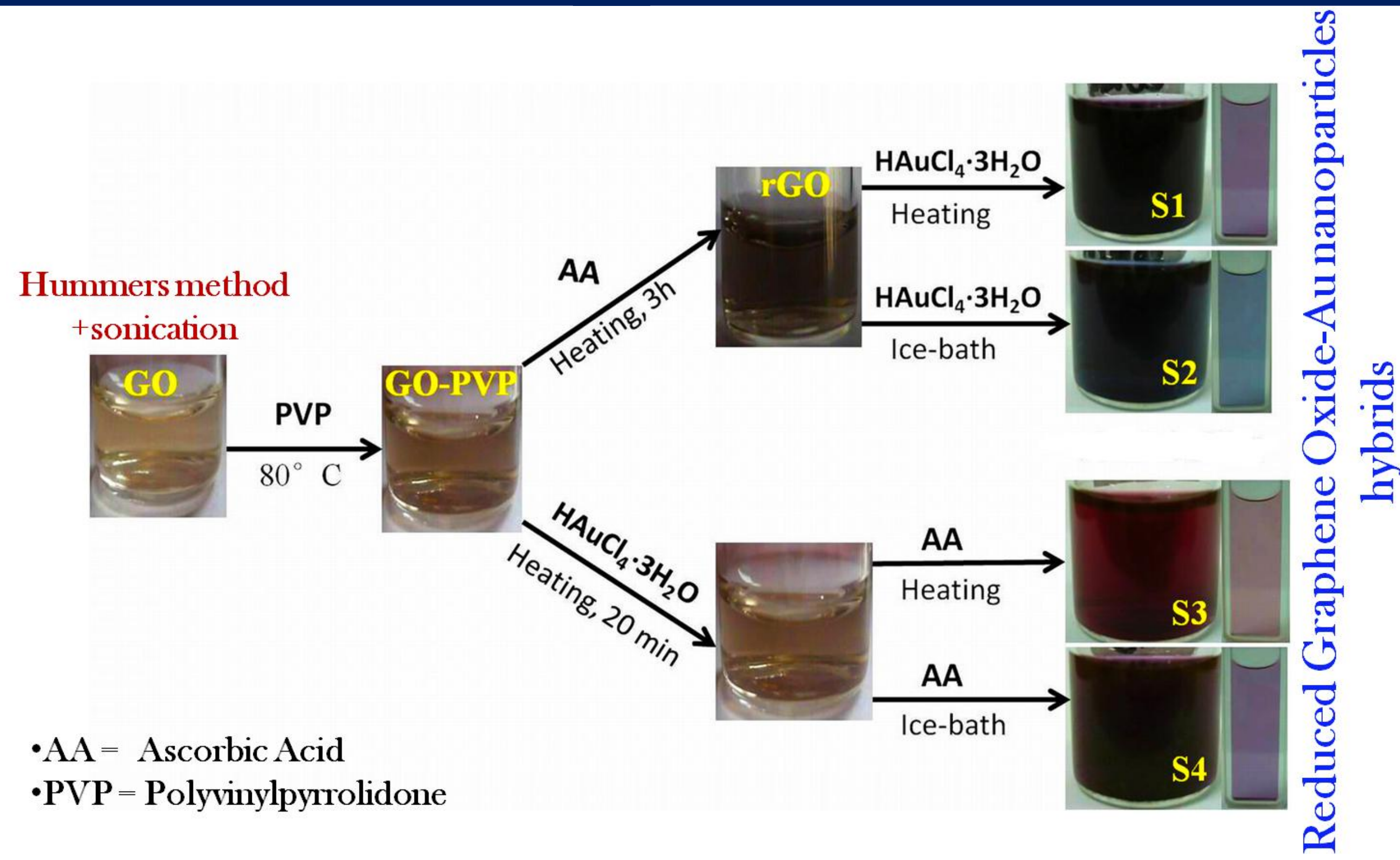
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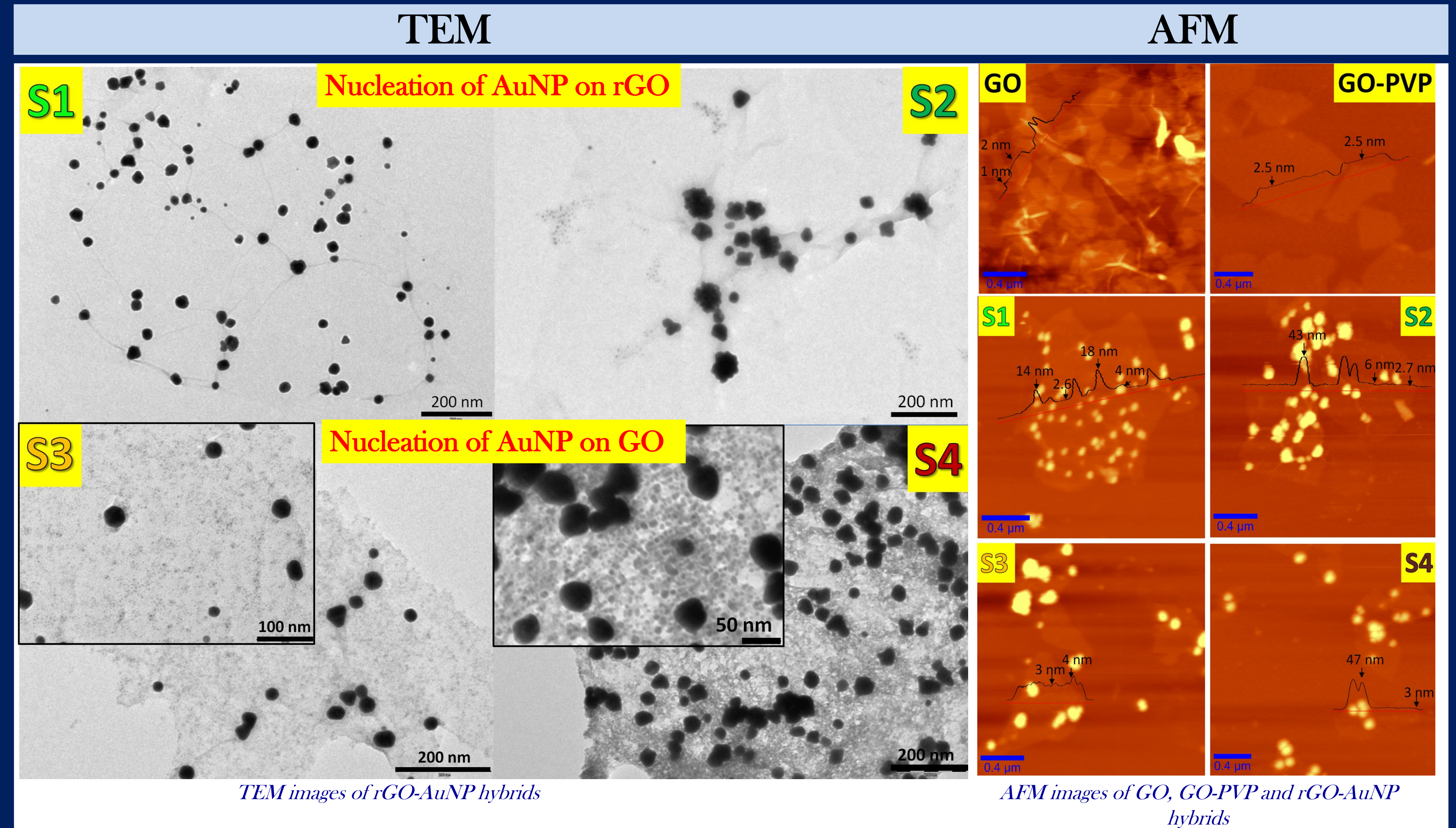
Graphene, a monolayer of sp^2 -hybridized carbon, arranged in a honeycomb lattice, has received considerable attention due to its unique two-dimensional (2D) structure and remarkable physical and chemical properties. Recently, a new class of graphene-based hybrid materials have aroused a great interest 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 π - π 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).

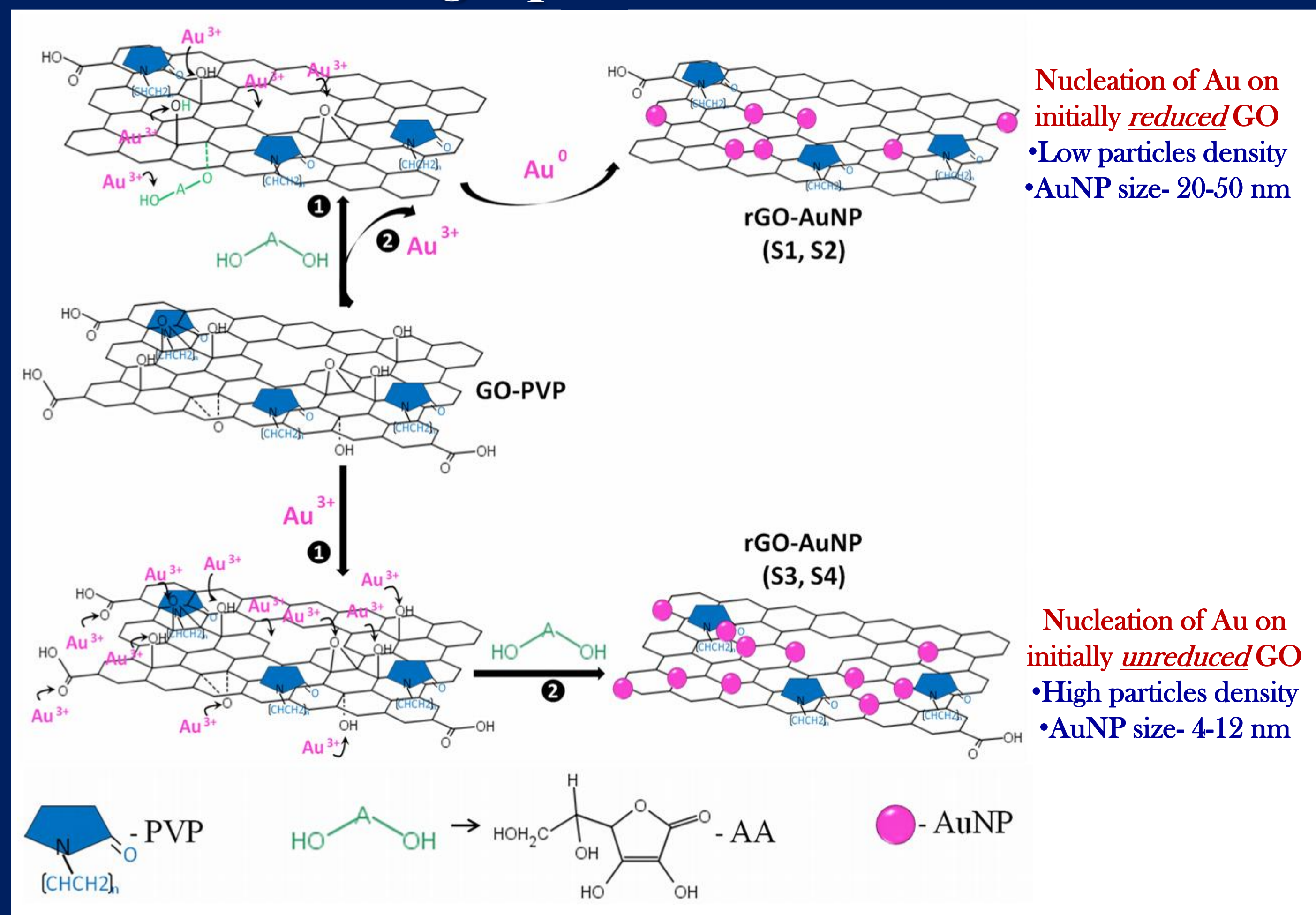
Experimental



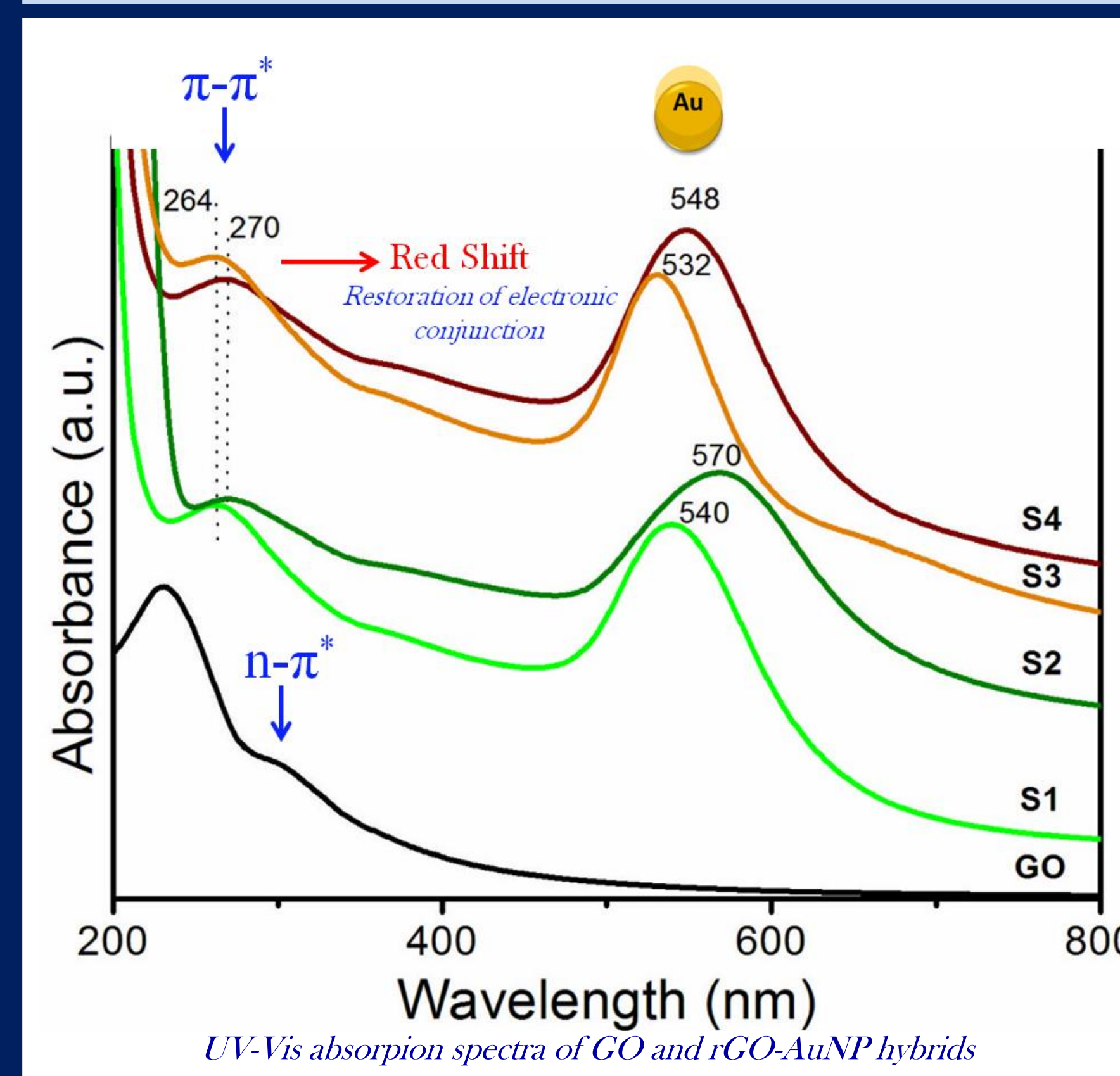
Characterization



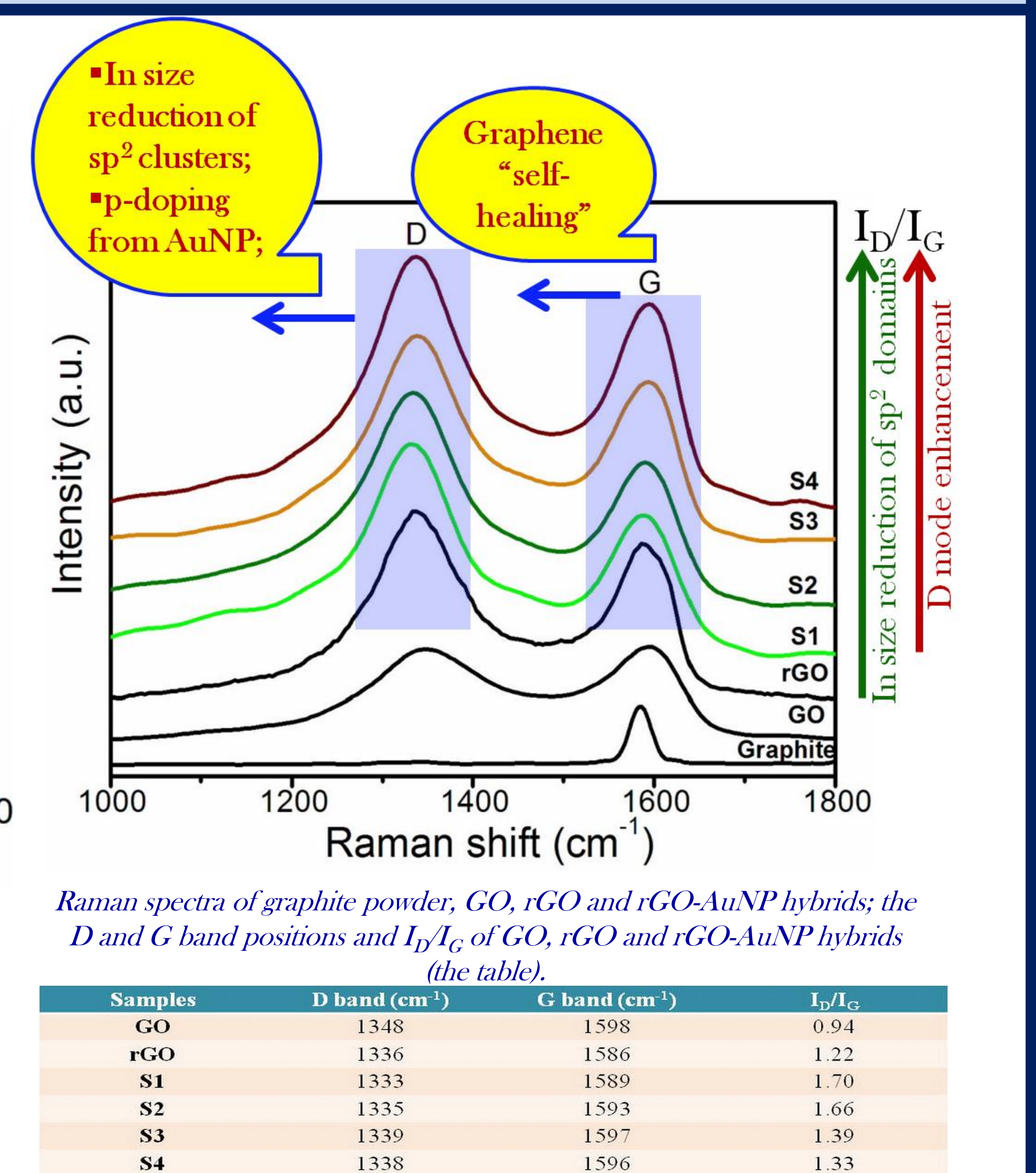
Mechanism of AuNP nucleation on graphene sheets



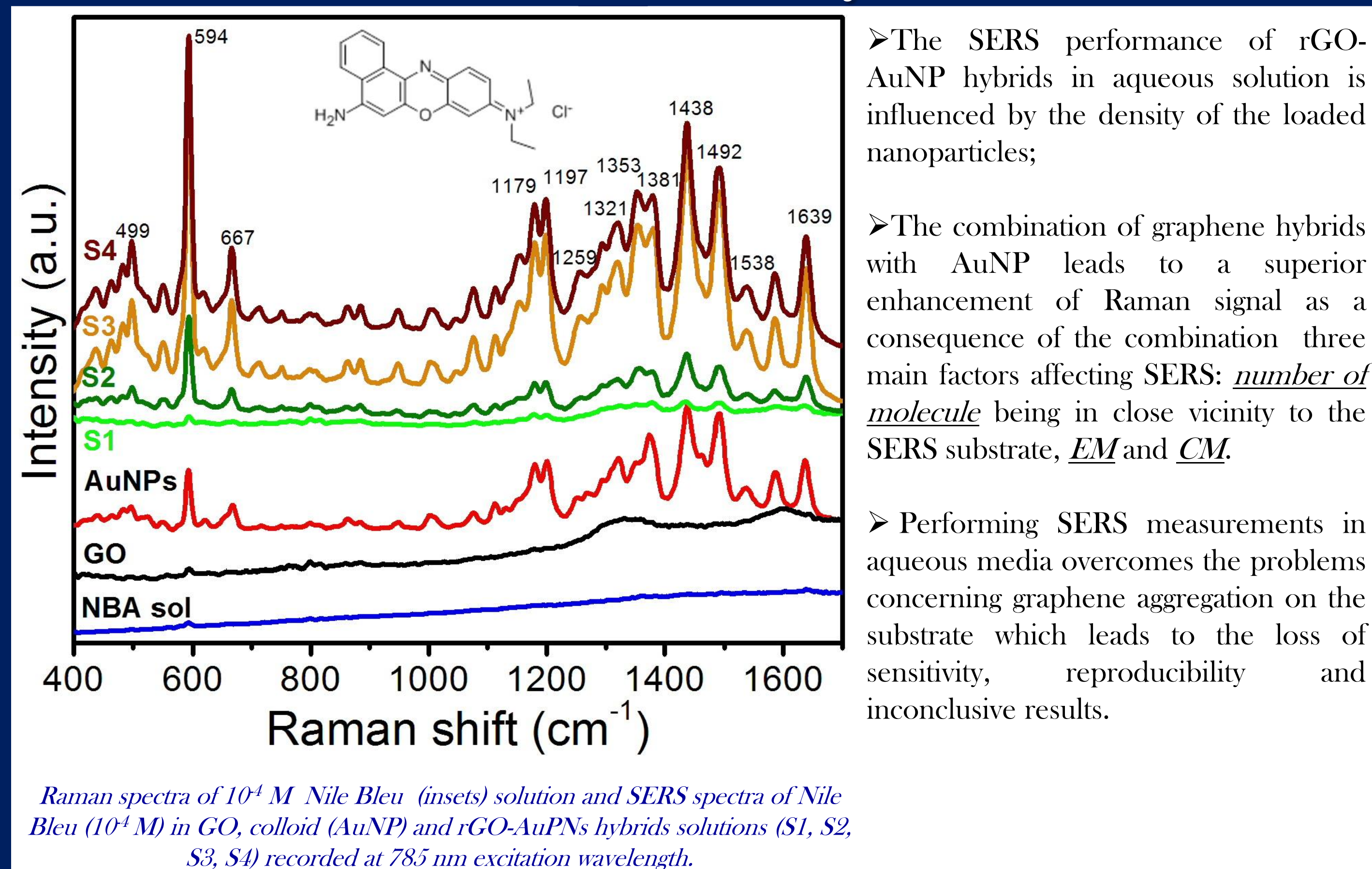
UV-Vis



Raman



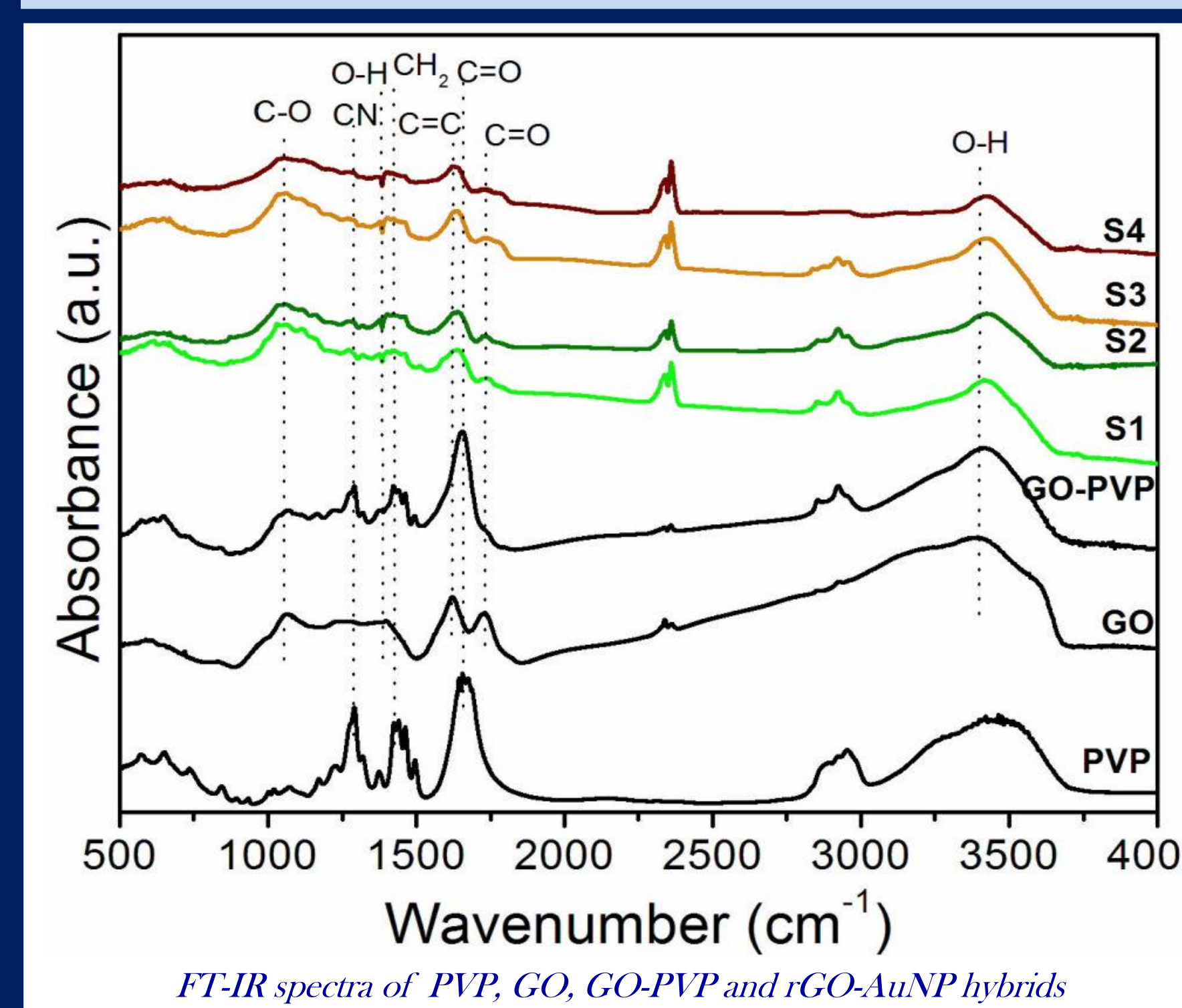
SERS study



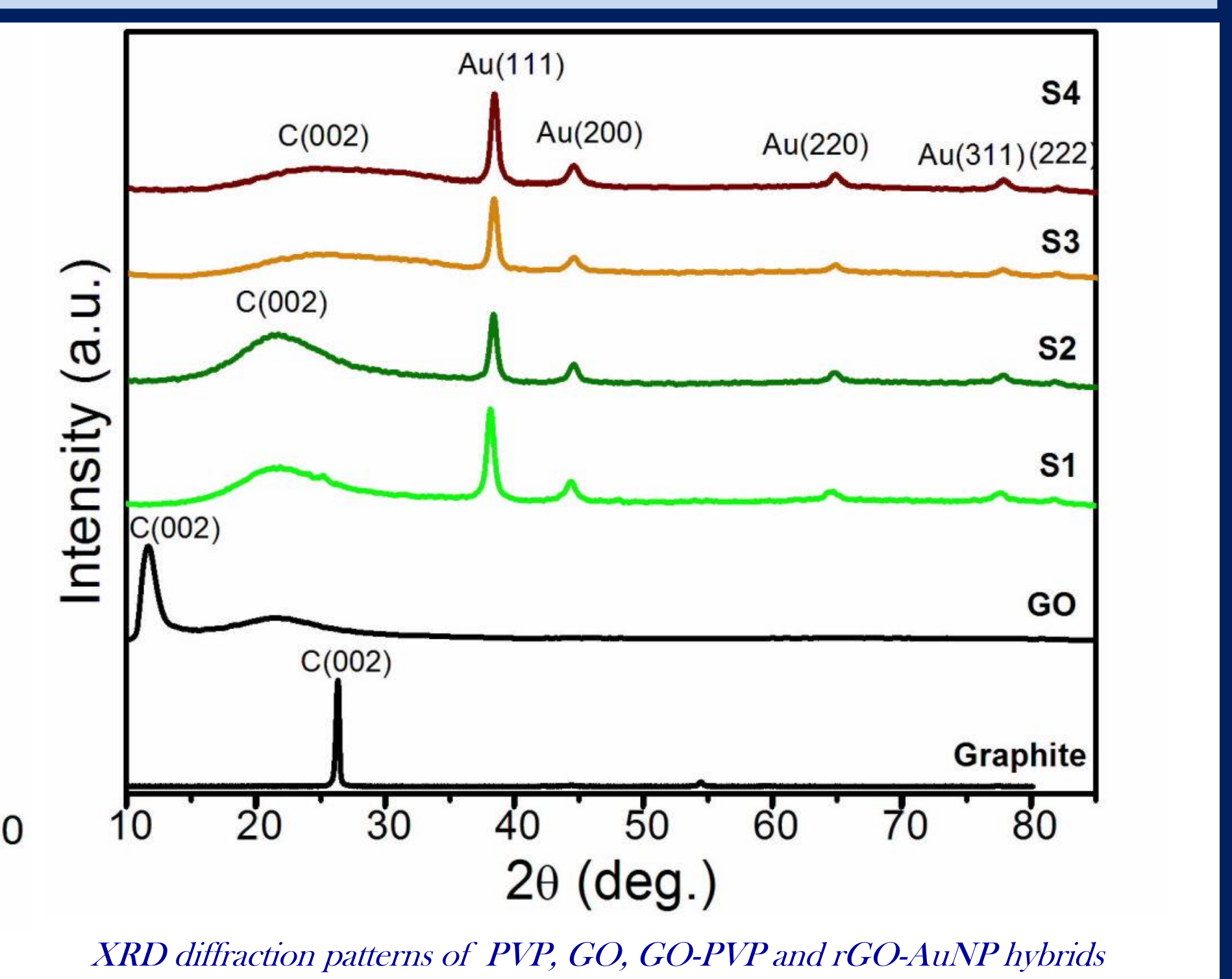
Conclusions

- 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



XRD



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.

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

Zeta potential measurements =

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