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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Graphene, a monolayer of sp²-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 has emerged, 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 hybrid by 3D 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-aqueous 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 reduction. Through careful investigation of the production of GO-AuNP hybrid stabilized with polyvinylpyrrolidone (PVP), several reaction routes were devised with the aim to control the size, shape, and distribution of AuNP nucleated onto the graphene sheets as well as the degree of GO reduction. Particularly, when GO 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 AuNPs (4-14 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 graphene surface is assumed, highlighting the importance 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).

Characterization

FT-IR

Absorbance (a.u.)

Wavenumber (cm⁻¹)

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

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

XRD

Intensity (a.u.)

20 (deg.)

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

Conclusions

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 AuNPs leads to a superior enhancement of Raman signal as a consequence of the combination of these main factors affecting SERS: number of analyte molecules; close to surface to the SERS-active sites.

Performing SERS measurements in aqueous media overcomes the problem of graphene aggregation on the substrate which leads to the loss of sensitivity, reproducibility and stability.

We have shown a new, green and easy approach for the synthesis of aqueous stable rGO-AuNP hybrid.

By changing the reaction conditions, we found that the sizes and densities of AuNP obtained onto GO 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 biologicals.

References:

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