

Electronic Supplementary Information

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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Preparation of GO. Graphite oxide was synthesized according to Hummers and Offeman's method.¹ Concentrated H₂SO₄ (25 mL) was added in a 250 mL flask with graphite powder (1 g) at room temperature and vigorously stirred for 30 min. Subsequently, the flask was cooled in an ice bath and NaNO₃ (0.5 g) was added, followed by slow KMnO₄ (3 g) addition, by maintaining permanent stirring. The ice bath was then removed and the composite was warmed at 35°C and stirred for 2h. The mixture gradually thickened and become pasty and brownish grey in color. Afterward, 46 mL of distilled water was slowly added into the paste under continuous stirring (Attention! this causes violent effervescence and temperature increase). The diluted suspension (brown in color) is stirred for another hour (without supplementary increase in temperature). The suspension was further diluted by adding 140 mL of warm distilled water and treated with H₂O₂ (10 mL) to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate.¹ After 20 min of stirring, the resulted bright yellow suspension was filtered and the yellow-brown filter cake was washed with 300 mL of HCl (5%) (for metal ions removal) and warm water several times (6-8 times). The as obtained graphite oxide was further exfoliated in distilled water by sonication (2h) followed by centrifugation (30 min, 4000 rpm) for unexfoliated graphite oxide removal, until the resulting GO solution became completely transparent.

Control experiment: In order to highlight the role of PVP as stabilizer, 3 mL of GO (0.04 mg/mL) was heated and stirred with the same amount and concentration of AA as it was reported for previous samples, by keeping the experimental conditions used for S1 and S2 (e.g. temperature etc.) The reduced GO started to aggregate within 2 h, by contrast with GO containing PVP. This experiment was performed to check the presence and stabilizing abilities of PVP in the presented system.

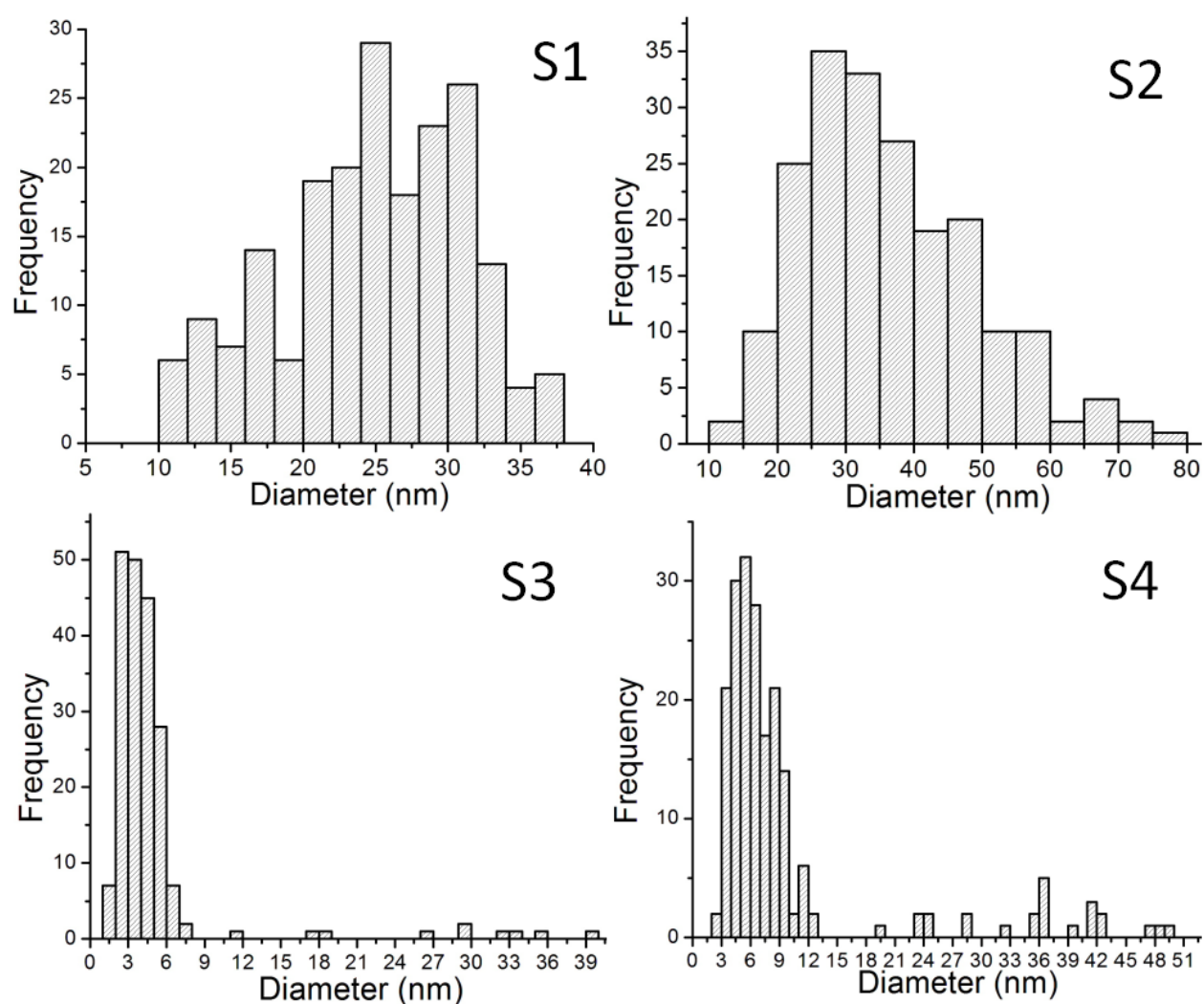


Fig. S1 AuNPs size distribution histograms of rGO-AuNP hybrids based on the statistic of 200 particles for each sample.

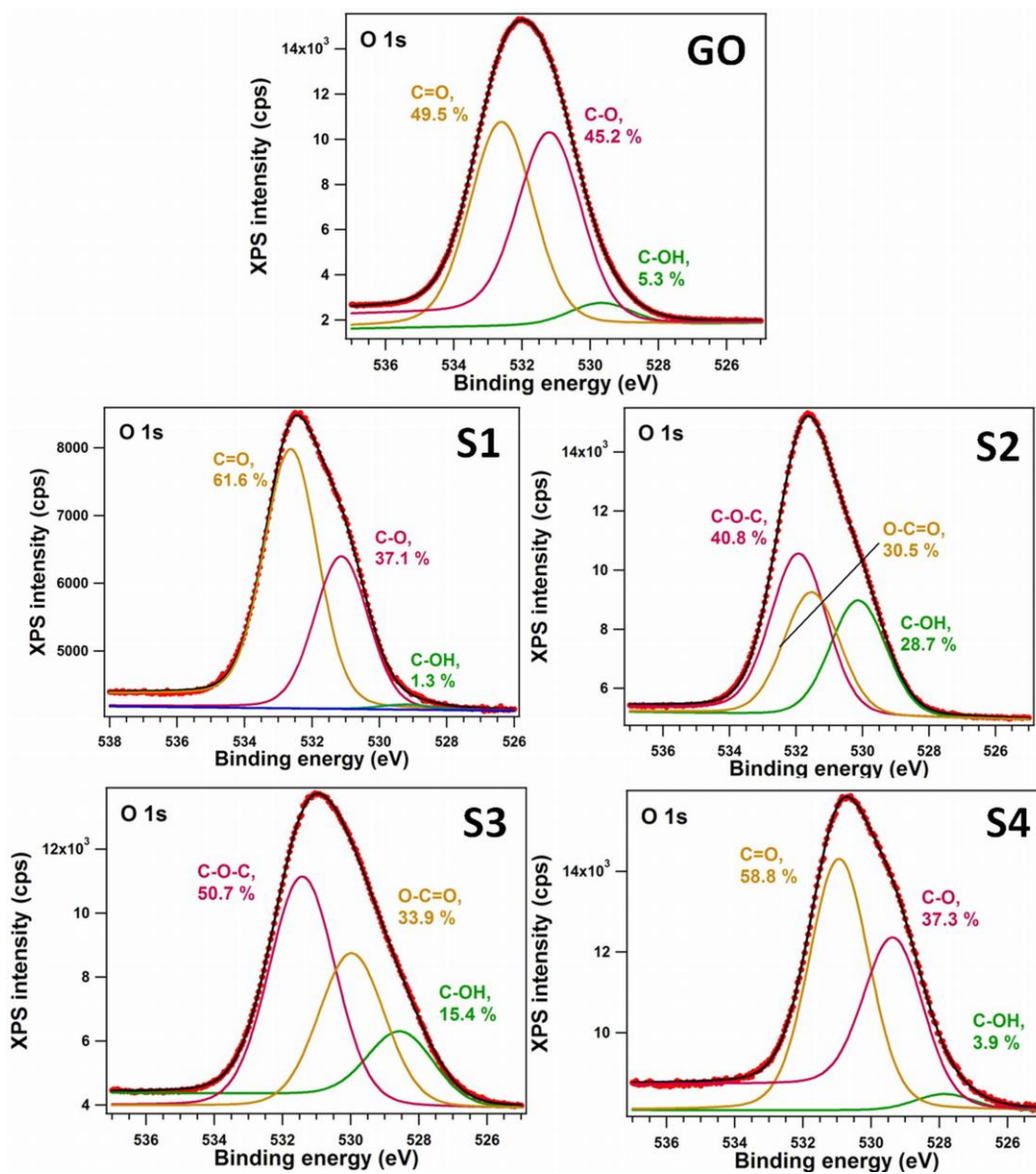


Fig. S2 O1s X-ray photoelectron spectra of GO and S1, S2, S3 and S4. Experimental data are red dots, the total fit is the full black curve, while curves with different colors represent individual components.

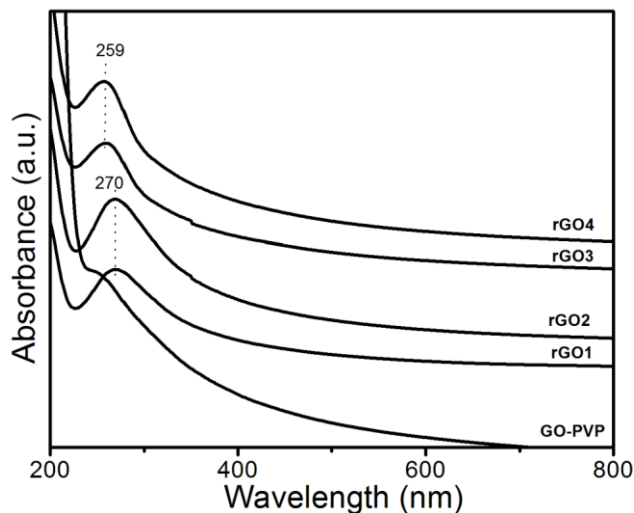


Fig. S3 UV-Vis absorption spectra of GO-PVP and rGOs.

SERS experiment: Nile Blue A (NBA) powder was dissolved first in water. Then, a certain amount of solution was added to the 0.04 mg/mL rGO-AuNPs solutions (S1, S2, S3, S4), GO (0.04 mg/mL) and standard colloid (citrate capped AuNP) solutions to obtain the concentration of 10^{-4} M. The mixtures were vigorously shaken and left for 2 h to reach the adsorption equilibrium for SERS detection in liquid environment. The laser excitation wavelength used for SERS recordings was 785 nm. All spectra were recorded in the same conditions in terms of laser power, integration time (10 sec) and environment. For SERS sensitivity test, the sample S4 was used: 350 μ l of S4 solution of the same concentration (\sim 0.04 mg/mL) were mixed with 150 μ l of NBA solution of different concentrations to the final concentration of NBA ranging from 10^{-4} to 10^{-9} M. The solutions were left 2 hours. The SERS spectra were recorded with 785 nm laser excitation, using the same laser power and integration time (10 sec x 3 accumulations per spectrum).

References

1. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.