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Electronic Supplementary Information

A General Method for the Fabrication of Graphene-Nanoparticle Hybrid Material

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Experimental section

Synthesis of PFPA-SNP

PFPA-functionalized SNPs were synthesized following a slightly modified protocol of our previous work.[1] To prepare SNPs, a solution of anhydrous ethanol (34 mL), TEOS (2.80 mL) and NH_4OH (6.25%, 2.80 mL) was vigorously stirred at room temperature for at least 24 h to give the Stöber solution. A solution of PFPA-silane[2] in toluene (19 mL, 12.5 mM) was added directly to the Stöber solution, and the solution was stirred overnight at room temperature and then refluxed at 78 °C for 1 h. The product was purified by centrifugation and re-dispersion by sonication for 3 times in 200-proof ethanol and 3 times in acetone to afford PFPA-SNP.

Synthesis of PFPA-AuNP

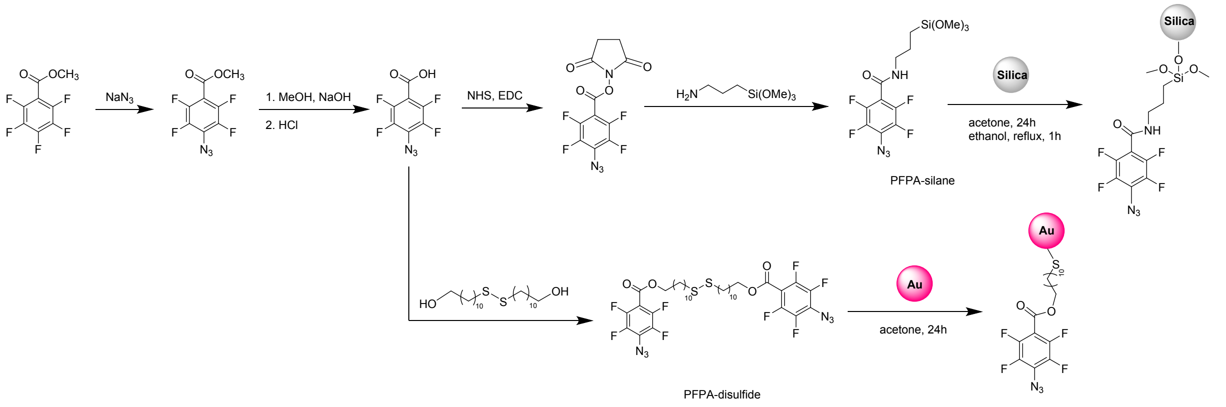
AuNPs were synthesized using the citrate reduction method as reported previously.[3] All glasswares were washed in aqua regia (3:1 conc. HCl/conc. HNO_3) and rinsed thoroughly with D.I. water. An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.2 mM) was heated to boil, and an aqueous solution of sodium citrate (1% w/v, 1.8 mL) was added. The resulting solution was then stirred vigorously overnight. 11,11'-Disulfanediylbis(undecane-11,1-diyl)bis(4-azido-2,3,5,6-tetrafluorobenzoate (PFPA-disulfide) was synthesized following a previously reported procedure.[3] A solution of PFPA-disulfide in acetone (1.7 mM, 5 mL) was added to the AuNP solution and the resulting solution was stirred at room temperature for 18 h. The solution was centrifuged at 8000 rpm for 10 min, and the precipitate was re-dissolved in acetone (100 mL). The solution of PFPA-disulfide in acetone (1.7 mM, 5 mL) was added again and the solution was stirred overnight. The solution was centrifuged at 8000 rpm for 7 min and the precipitate was redispersed in acetone (100 mL). The washing, centrifugation, and re-dispersion were repeated for 3 times, and the final product, PFPA-AuNP, was stored in acetone (100 mL) at room temperature.

Synthesis of Graphene-Nanoparticle Conjugates

A suspension of FLG flakes in DCB (3 mL, 0.3 mg/mL) was mixed with a suspension of PFPA-SNP or PFPA-AuNP in acetone (3 mL, 0.3 mg/mL). The mixture was irradiated with 450 W medium pressure Hg lamp (Ace Glass Inc., Vineland, NJ, USA) for 30 min under ambient condition. A 280-nm long-path optical filter was placed on top of the samples during irradiation. The resulting reaction mixture was then washed with DCB and centrifuged. This was repeated for 3 times, followed by washing and centrifugation with acetone for 3 times. For graphene prepared by mechanical exfoliation and the CVD graphene, the sample was immersed in a suspension of PFPA-SNP or PFPA-AuNP in acetone, and was irradiated for 30 min under the same conditions as described above. The samples were then washed with acetone for 3 times in a sonication bath, and were dried under vacuum for 24 h. Two control experiments were carried out. In one experiment, PFPA-SNPs and PFPA-AuNPs were treated with FLG flakes, mechanically exfoliated graphene or CVD graphene under the same conditions except no UV irradiation was applied. In another control experiment, SNPs and AuNPs without PFPA functionalization were treated with FLG flakes under the exact the same experimental condition as PFPA-SNPs and PFPA-AuNPs. FLG samples and controls were imaged on a TEM (Philips, EM400T) with an accelerating voltage of 100 kV. Samples prepared from mechanically exfoliated graphene and CVD graphene were examined using SEM (JEOL, JSM 7401F).

XPS analysis

The XPS system is a Vacuum Generators Escalab MK II x-ray photoelectron spectrometer equipped with a dual Mg/Al x-ray source and with a 150 degree spherical sector electron energy analyzer operated in constant analyzer energy mode. The vacuum level during XPS analysis was at 1×10^{-9} torr. Survey and core level spectra were collected at pass energy of 100 eV and 50 eV, respectively. All spectra were referenced to the C1s binding energy position of adventitious carbon taken at 285.0 eV.



Scheme S1. Synthesis of PFPA-SNP and PFPA-AuNP.

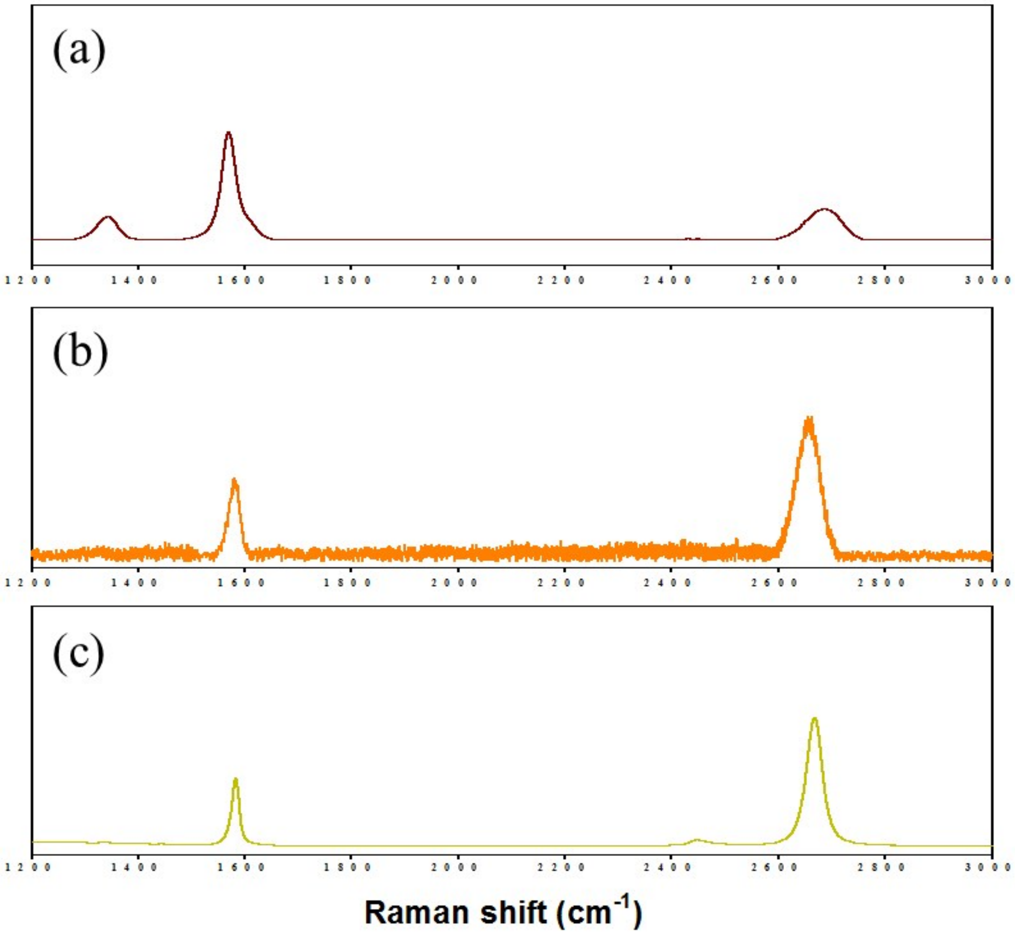


Fig. S1 Raman spectra of (a) FLG flakes, and graphene prepared by (b) CVD and (c) mechanical exfoliation.

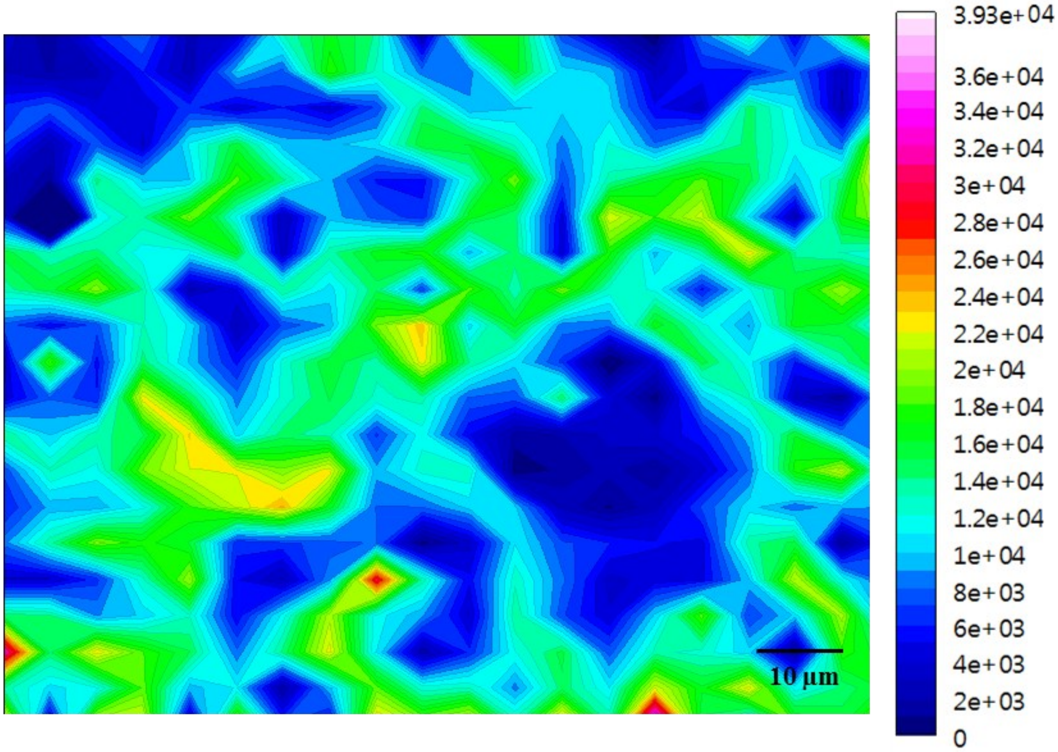


Fig. S2 The 2-D Raman map of the G band mode of CVD graphene. The blue areas do not have any graphene layer.

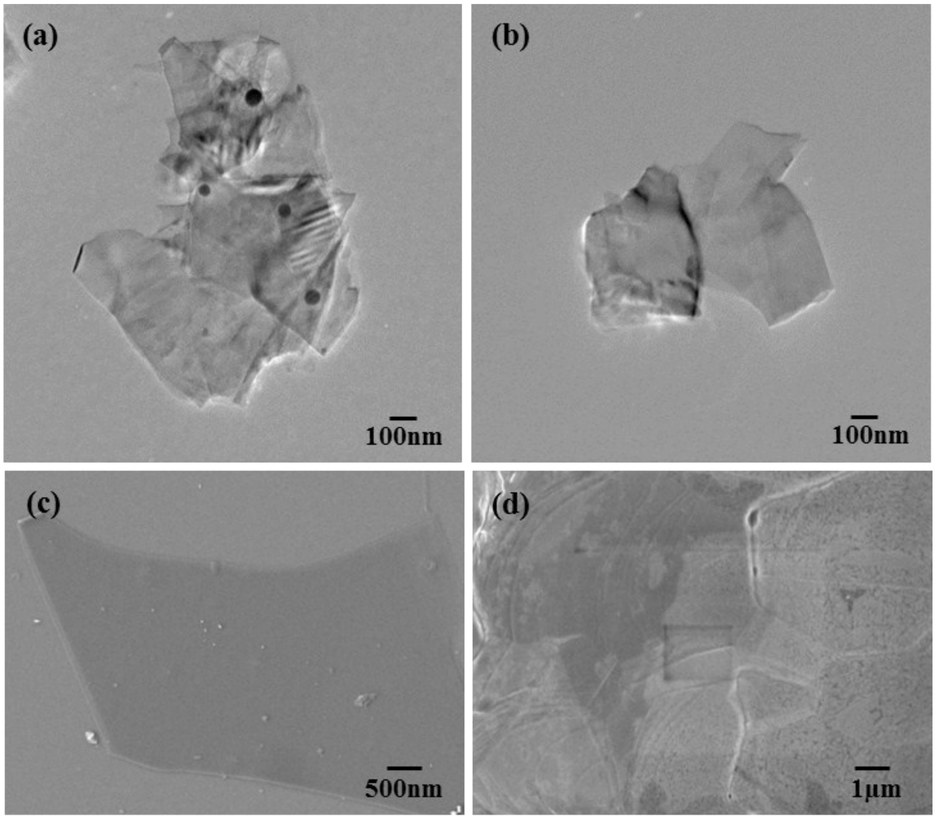


Fig S3 Electron microscopy images of control samples. (a) PFPA-SNPs treated with FLG flakes without UV irradiation. Unfunctionlized SNPs treated with (b) FLG flakes, (c) mechanically exfoliated graphene, and (d) CVD graphene.

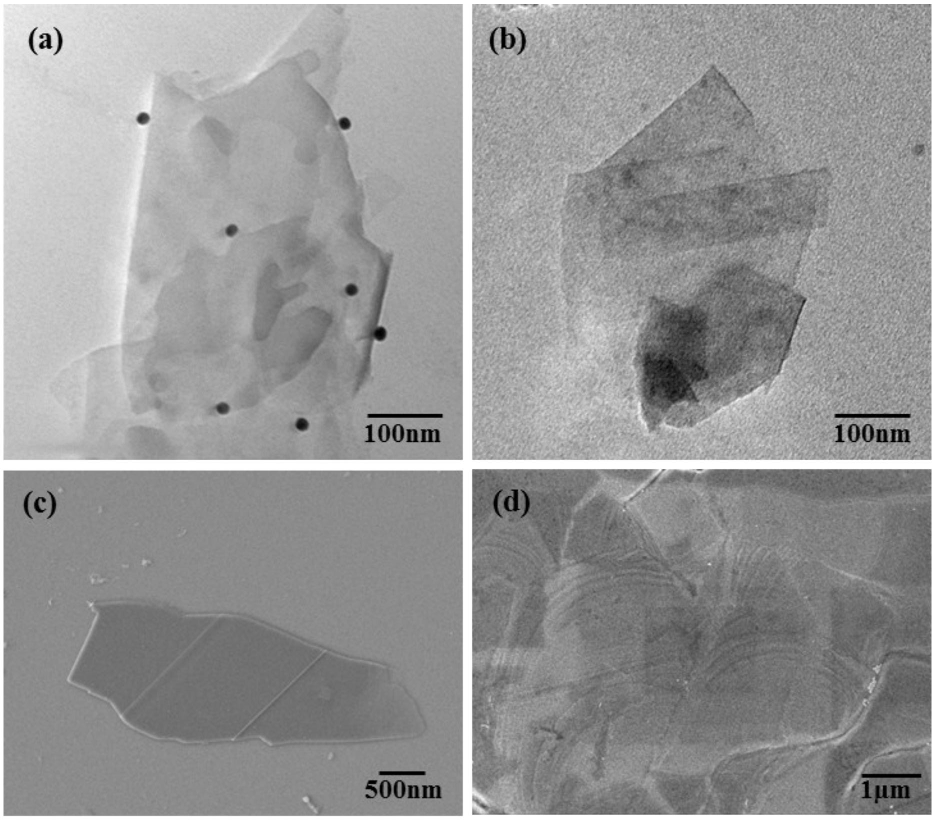


Fig S4 Electron microscopy images of control samples. (a) PFPA-AuNPs treated with FLG flakes without UV irradiation. Unfunctionlized AuNPs treated with (b) FLG flakes, (c) mechanically exfoliated graphene, and (d) CVD graphene.

References

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