Supporting Information

Non-covalent Functionalization of Graphene to Tune Its Band Gap and Stabilize Metal Nanoparticles on Its Surface.

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Figure S1. Adsorption and desorption isotherms of HIS on G at pH = 5.0

Figure S2. Species distribution vs pH for compound HIS in aqueous solution (0.1 M Me₄NCl) at 298.1 K. (HIS=H₃L)*
**Table S1.** Stability constants (log K) for the system HIS/H⁺ (0.1 M Me₄NCl, 298.1 K). (HIS=H₃L)*

| Equilibrium | logK  |
|-------------|-------|
| L³⁻ + H⁺ ⇌ HL²⁻ | 11.74(4) |
| HL²⁻ + H⁺ ⇌ H₂L⁻ | 7.32(1) |
| H₂L⁻ + H⁺ ⇌ H₃L | 6.83(1) |
| H₃L + H⁺ ⇌ H₄L⁺ | 3.160(9) |
| H₄L⁺ + H⁺ ⇌ H₅L²⁺ | 2.598(8) |

**Table S2.** Stability constants for the HIS/Cu(II) system in aqueous solution ([Cu(II])=10⁻³ M, [HIS]=10⁻³ M, 0.1 M Me₄NCl, 298.1 K). (HIS=H₃L)*

| Equilibrium          | logK  |
|----------------------|-------|
| Cu²⁺ + L³⁻ ⇌ [CuL]⁻  | 8.79(9) |
| Cu²⁺ + HL²⁻ ⇌ [Cu(HL)] | 7.35(6) |
| Cu²⁺ + H₂L⁻ ⇌ [Cu(H₂L)]⁺ | 6.69(4) |
| Cu²⁺ + H₃L ⇌ [Cu(H₃L)]²⁺ | 4.14(2) |
**Figure S3.** Species distribution diagram as a function of pH of the HIS/Cu(II) system in aqueous solution ([Cu(II)] = $10^{-3}$ M, [HIS] = $10^{-3}$ M, 0.1 M Me$_4$NCl, 298.1 K).

(HIS=H$_3$L)*

**Figure S4.** Adsorption isotherm of Cu(II) on G-HIS(0.47), obtained in water solution at pH = 5.0
Figure S5. Nitrogen adsorption-desorption isotherms of G and G-HIS(0.47)
Determination of G and G-HIS(0.47) proton isotherms

The proton isotherms of G and G-HIS were determined from a potentiometric titration of the solids in water suspension according to a previously reported procedure. The obtained surface charge profile of G (Figure S6a) shows positive charge surface at the lowest pH value (c.a. 2.5). This can be assigned to protonated water molecules, H$_3$O$^+$, as the carbon-oxygen functions on the G surface lack Brønsted basic character. It has been reported these water molecules interact with the basic arene centres, Cπ, of the sp$^2$ domains of graphitized activated carbons and CNTs. Moreover, it is also known that graphene surface tends to interact strongly with water.

The positive charge on G surface decreases as the pH increases in the 2.5-5.5 range. This is due to the neutralization of carboxylic acid groups. This process takes place through two well-differentiated steps corresponding to the protonation of the isolated carboxyl groups and those coming from disgregation of anhydrides. Two overlapped deprotonation processes in the 7.0-10.5 pH range are assigned to deprotonation of H$_3$O$^+$ surface groups and to the C-OH functions respectively.

On the other hand, it is seen in the Q vs pH profile of G-HIS(0.47) (Figure S6a) that the positive value of the surface-charge density at pH = 2.5, is higher than this of the bare G. Moreover, this plot also shows a steady decrease of positive charge in the pH range 2.5-9.5, sharper in the 7.2-9.5 pH range. This suggests the overlap of successive deprotonation processes.

The numerical SAIEUS procedure was applied to the proton isotherm of G-HIS(0.47) to determine the theoretical pKa values of the acidic functions of the G-HIS(0.47) surface (Figure S6b). Assuming the attachment of HIS on G takes place by a strong Cπ pyrimidine interaction, the net positive surface-charge at the initial pH (2.5), comes from both the Cπ-H$_3$O$^+$ groups (see above) and the carboxyl functions of HIS which remain partially protonated. Thus the peak of Figure S6b, at pKa = 2.6, corresponds to both the single carboxyl groups of G and the partly protonated carboxylate groups of HIS. After deprotonation of these groups, in the 2.5-3.5 pH range, the deprotonation of carboxyl functions coming from anhydride groups of G in the 3.6-5.0 pH range (pKa = 4.2) occurs. A peak at pKa = 5.9 is assigned to the neutralization of the protonated N$_\text{cyclic-imidazole}$ atoms. The amount of such groups was calculated by the peak integration, and the result is consistent with the amount of HIS attached to G (0.47 mmol·g$^{-1}$). The pKa value obtained
for the protonated N\textsubscript{cyclic-imidazole} of the molecules of HIS adsorbed on G is somewhat smaller than this group in the pure HIS in water (c.a. pKa = 7.8, see Figure S6b). This effect, which is similar to that observed when an analogous molecule was adsorbed on MWCNTs,\textsuperscript{3} is probably due to an elongated arrangement of the imidazole residues, which hampers to some extent the protonation of such groups. This arrangement is required to optimize the molecule-graphene stacking interactions (although this is somewhat limited by the polar character of the imidazole residues). A slightly asymmetric peak with a maximum at pKa 8.7 is assigned to the deprotonation of few C\textsubscript{x}-H\textsubscript{3}O\textsuperscript{+} groups (pKa = 7.8, see above), weak phenol groups of G and might also include partial deprotonation of the C(4)\textsubscript{pyrim}-NH\textsubscript{2} atom group (Figure S6b).

\textbf{Figure S6.} a) Proton isotherms of G and G-HIS(0.47); b) Distribution plots of acidic groups on G and G-HIS(0.47)
Figure S7. UV absorption spectrum of HIS

Figure S8. Plots of $(\alpha E)^{1/2}$ (indirect transitions) against the photon energy (E) for G, G-HIS hybrids and G-HIS-Cu(0)
Figure S9. HRTEM image of Pristine Graphene.

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