Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

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# Decoration of nanocarbon supports with magnetite nanoparticles: application to microwave-responsive metamaterials

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## 1. Reactants specifications

**Nanocarbon supports**

| Name | Specification | Company | Country |
|---|---|---|---|
| Multi-walled carbon nanotubes (MWCNTs) | NC3100 | Nanocyl | Belgium |
| Graphene oxide (GO) | - | Nanoinnova Technologies SL | Spain |
| Reduced graphene oxide (rGO) | - | | |
| Graphene nanoplatelets (GNPs) | TIMREX BNB90 | TIMCAL | Switzerland |

**Other reactants**

| Name | Specification | Company | Country |
|---|---|---|---|
| (3-aminopropyl)trimethoxysilane | 97% | Sigma-Aldrich | Germany |
| Iron (III) acetylacetonate | 97% | | |
| Iron (III) chloride hexahydrate | puriss. p.a., Reag. Ph. Eur., ≥99% | | |
| Thionyl chloride | ReagentPlus®, ≥99% | | |
| Triethylene glycol | ReagentPlus®, ≥99% | | |
| Etyhlene glycol | Spectrophotometric grade, 99+% | Alfa Aesar | Germany |
| Hydrazine monohydrate | 99+% | | |
| Iron (II) chloride tetrahydrate | Reagent grade, 99% | | |
| Polyethylene glycol 2000 | - | | |
| Tetraethoxysilane | 99.9% | | |
| Tetramethylammonium hydroxide | 25% w/w aq. soln., 99.9999% | | |
| Polyethylene glycol 400 | Synthesis grade | Merck | Germany |
| Ethanol | Technisolv | VWR | Belgium |
| Hydrochloric acid | AnalaR NORMAPUR | | |
| Nitric acid | 65%, AnalaR NORMAPUR | | |
| Sodium Hydroxide | AnalaR NORMAPUR | | |
| Toluene | AnalaR NORMAPUR | | |

## 2. Covalent linkage of functionalized core-shell nanoparticles and graphene oxide acyl chloride derivative (COV).

The nature of the linkage existing between the graphenic surface and the silica-coated MaNPs in a COV nanocomposite was characterized by XPS. As can be observed in Figure 1, the $N_{1s}$ photopeak can be fitted with two components located at binding energies of 402 eV and 399 eV which are attributable to an (C=O)-NH-C amide bond [1] or to an amine's N-$H_2$ [2], respectively. Furthermore, according to this analysis, the amide component is more abundant, given that its contribution to the $N_{1s}$ peak area is approximately 74%.

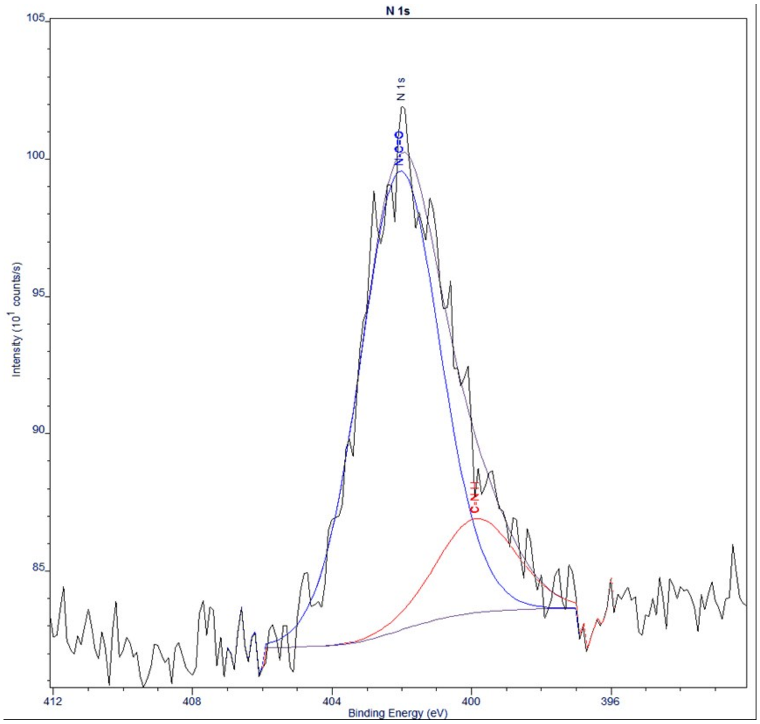


**Figure S1**- XPS spectra (N1s peak) of a COV product. The peak can be fitted with two components attributable to an (C=O)-NH-C amide bond (blue) or to an amine's N-$H_2$ (red).

The formation of the amide bond was also detected when fitting the nanocomposites' $C_{1s}$ peak (see Figure 2). Before the reaction, GO's $C_{1s}$ peak is fitted with five components: Carom, C-(C,H), C-O, C=O/O-C-O and (C=O)-OH. On the other hand, when analysing the COV nanocomposite, an additional component attributable to an (C=O)-NH-C amide bond is required in order to fit the peak shoulder located around 288 eV [3].

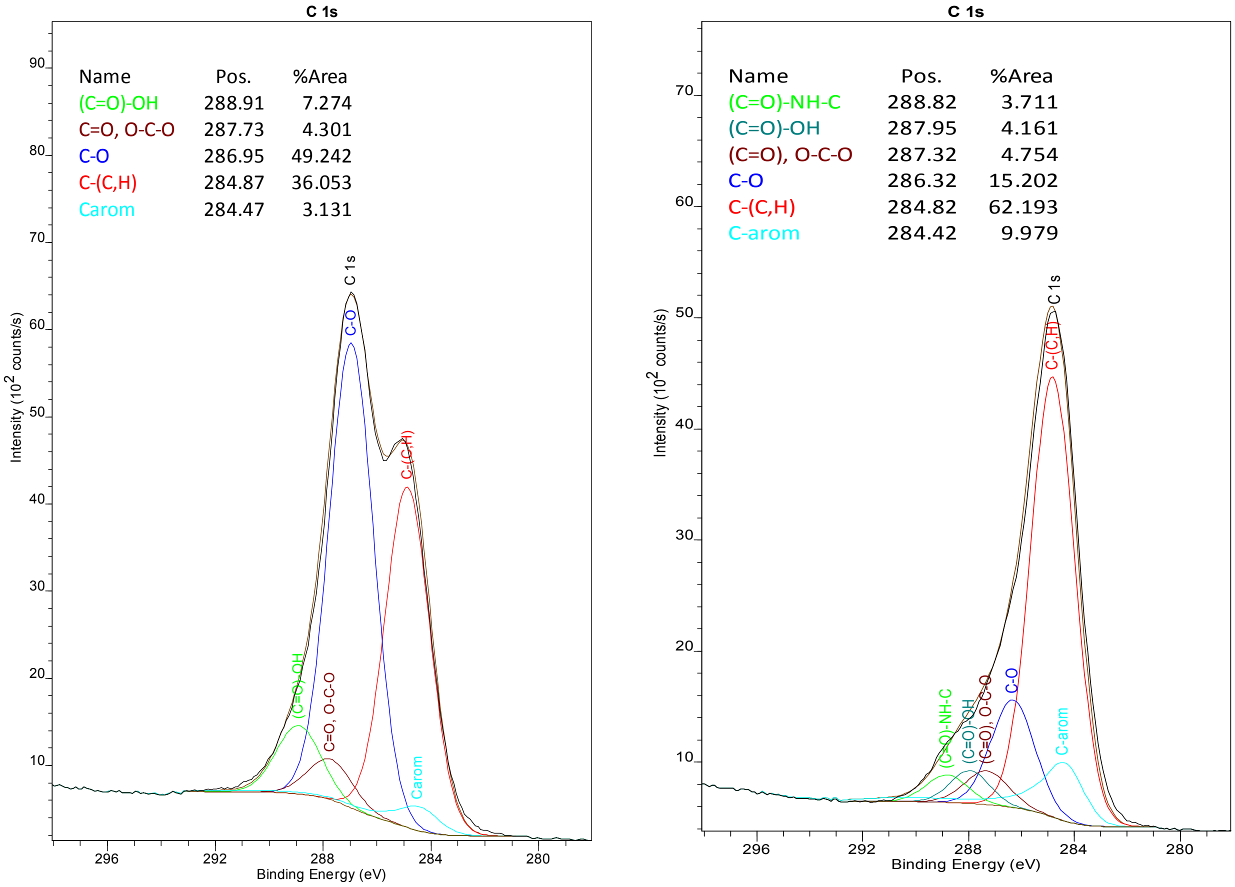


**Figure S2** XPS spectra of GO (left) and the COV nanocomposite product (right).

## 3. TEM images of tethered core-shell nanoparticles

TEM inspection of the M@Si product, prior to its functionalization and covalent linkage to an acyl-modified GO support, proves that magnetite nanoparticles have been effectively covered with a thin silica layer.

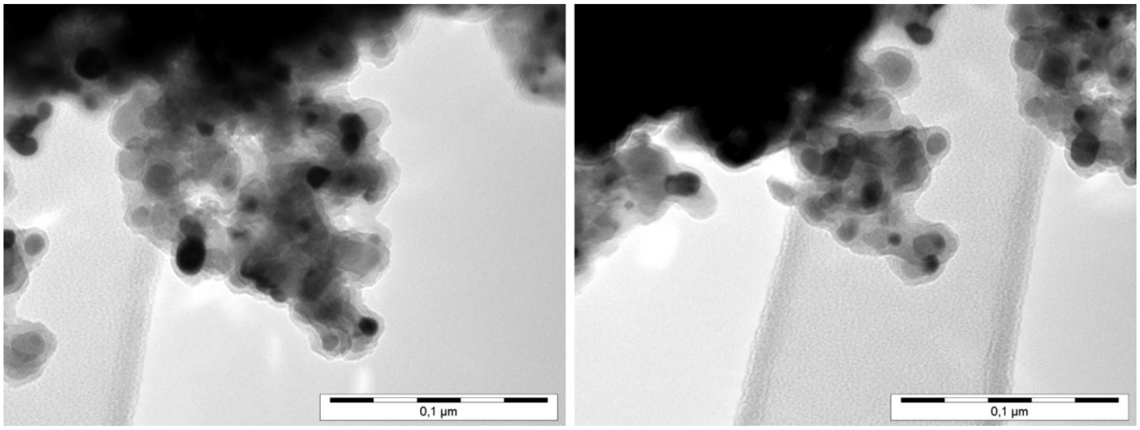
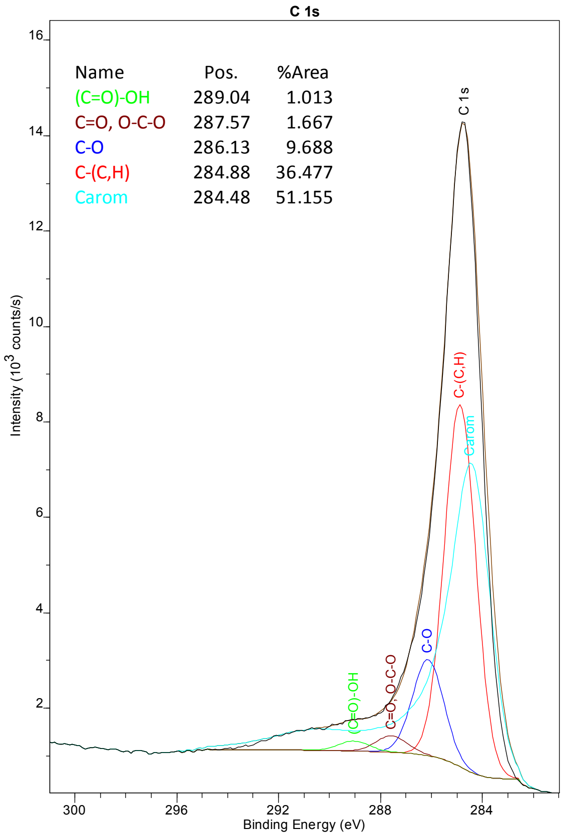
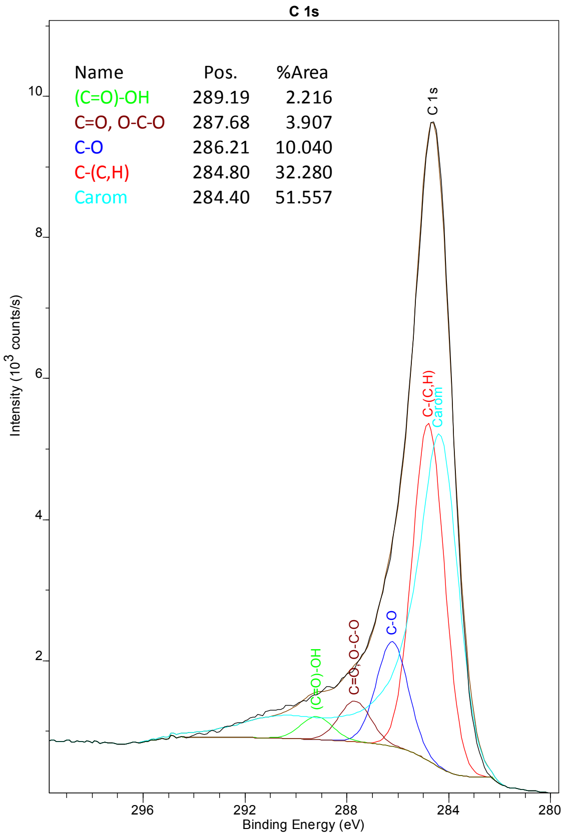


**Figure S3** – TEM images of the M@Si core-shell nanoparticles. Darker magnetite nanoparticles of different sizes and morphologies can be observed, surrounded by a light-grey thin shell of silica.

## 4. Oxygenated functions abundance in the different graphenic supports as determined by XPS.

XPS was performed on the different starting nanocarbon supports. The $C_{1s}$ peak was fitted using aromatic (C-arom), alkyl ($\underline{C}$-(C,H)), alcohol ($\underline{C}$-O), carbonyl/ether ($\underline{C}$=O, O-$\underline{C}$-O) and acyl (($\underline{C}$=O)-OH) components. The quantification of the different components' contribution to the $C_{1s}$ peak area indicate that the total amount of oxygenated functions decreases in the order: GO>rGO>GNPs (see Figure 3).





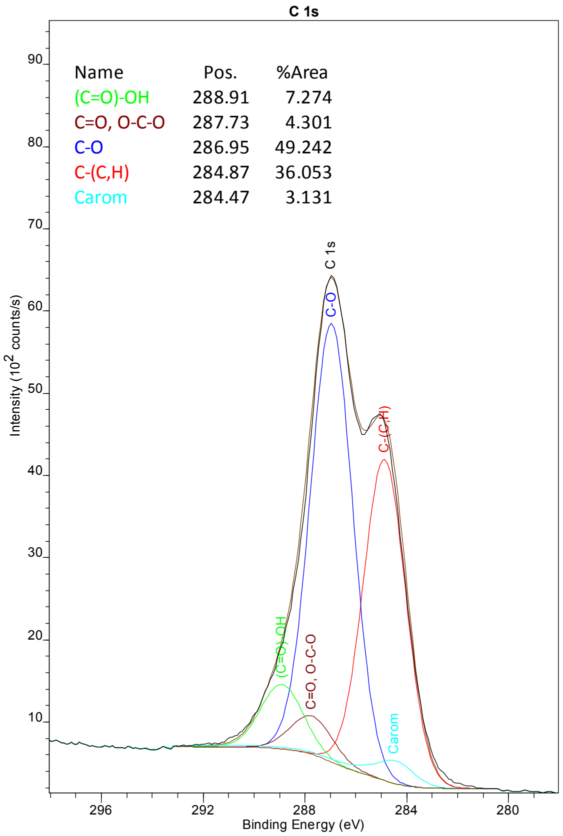


**Figure S3** XPS spectra for the C1s peak of a) GNPs (top, left); b) rGO (top, right) and c) GO (bottom, left).

## 5. TGA analysis of a series of samples synthesized by the SOLV-A method.

SOLV-A method was used to produce 750 mg of a MaNPs@GNPs (50% intended Fe/GNPs loading rate (LR)). The used autoclave vessel capacity is limited to 250 mL, thus being insufficient to synthetize this amount in a single experiment. The nanocomposite was therefore produced in 3 separate batches. TGA analyses performed on each batch show that the amount of loaded MaNPs is extremely similar from one batch to the other.

| MaNPs@GNPs (Timcal) LR (% w/w) as determined by TGA | | | |
|---|---|---|---|
| | **B1** | **B2** | **B3** |
| **%Fe (% w/w)** | 29.1 | 29.3 | 28.7 |

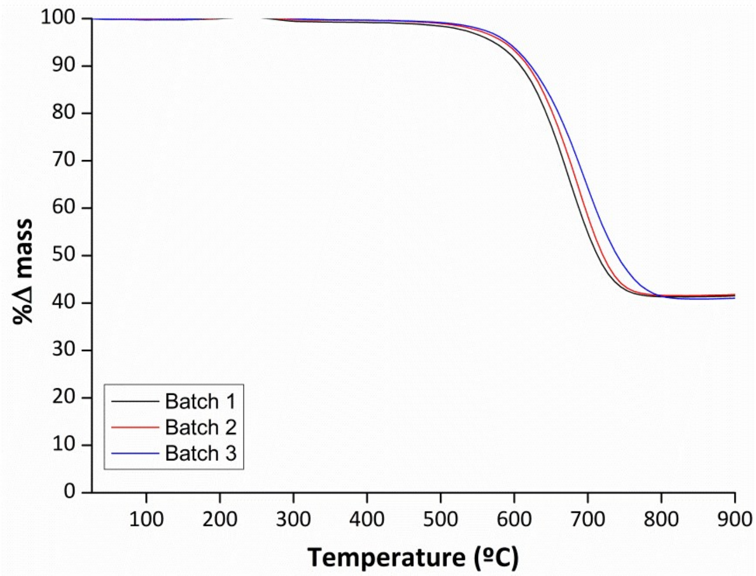


**Figure S4** Thermograms for the thermal decomposition under air of the different MaNPs@GNPs batches produced with the SOLV-A technique.

## 5. References

1. D.N. Hendrickson, J.M. Hollander and W.L. Jolly, *Inorg. Chem.,* 1969, **8**(12), 2642-2647.
2. E.T. Kang, K.G. Neoh, X. Zhang, K.L. Tan and D.J. Liaw, *Surf. Interface Anal.*, 1996, **24,** 51-58.
3. P.G. Rouxhet and M.J. Genet, *Surf. Interface Anal.*, 2011, **43**, 1453-1470.