

## Magnetic films of metal-graphene-polymer nanocomposites

H. Takacs<sup>1,2</sup>, B. Viala<sup>1</sup>, C. Gourgon<sup>2</sup>, F. Duclairoir<sup>3</sup>, J.-H. Tortai<sup>2</sup>

<sup>1</sup>CEA, LETI, MINATEC Campus, Grenoble, France

<sup>2</sup>LTM-CNRS-UJF, CEA, LETI, MINATEC Campus, Grenoble, France

<sup>3</sup>CEA, INAC, Grenoble, France

17 rue des Martyrs, 38054 Grenoble cedex 9, France

[helene.takacs@cea.fr](mailto:helene.takacs@cea.fr)

### Abstract

Over the years components miniaturization has been a crucial objective in microelectronics resulting in the integration of most of the passive components. To go further, ultra-miniaturization of RF inductors and antennas is yet to be done because it runs up against the paradigm of a highly permeable material with zero macroscopic conductivity. Neither ferrites (too low permeability), nor ferromagnetic alloys (too conductive) meet this requirement. Therefore, a breakthrough is essential regarding the way of developing such material. Here, we are interested in metallic-nanoparticle-loaded polymers with enhanced soft magnetic properties from the bulk. Only metals such as Ni, Co, Fe and alloys (i.e. FeCo) can address high permeability in microwave region due to high natural saturation magnetization (1.6 – 2.2 T).

So far mainly ferrites-based nanocomposites (i.e. magnetic oxides) have been elaborated because most of chemistries are highly oxidizing. But magnetic oxides have too low magnetic properties at high frequency, mainly due to the diluted saturation magnetization (0.2 – 0.5 T) [1], [2], [3].

The objective of this work is to synthesize core-shell metallic commercial nanoparticles-based nanocomposites. Original dual core-shell schemes are investigated. First a graphene shell prevents oxidation of the metallic particle core (M/C). Then a (co)polymer ( $P_1$ ) shell insulates the graphene-coated metallic particles (M/C// $P_1$ ) and controls the inter-particle spacing at a nanometric scale. A second polymer ( $P_2$ ) can be used as an encapsulating matrix of the super beads (i.e.  $P_2$  can be  $P_1$  as well). Finally films of compacted metal-graphene-polymer (M/C// $P_1/P_2$ ) super particles are deposited on substrates by spin coating.

In this work, commercial <30nm> M/C nanoparticles of Co (from Sigma-Aldrich) are used.  $P_1$  consists in Pyrene-terminated Polystyrene with three different molecular weights (5.6, 26 and 355 kg.mol<sup>-1</sup>), while  $P_2$  is pure Polystyrene (molecular weight 35 kg.mol<sup>-1</sup>).

First ultra-sonication is used to break large aggregates of as-received commercial Co/C nanoparticles into small ones (~100nm). Then  $P_1$  is directly grafted on the graphene shell (Co/C// $P_1$ ). The super particles of Co/C// $P_1$  nanoparticles are further encapsulated with  $P_2$  which makes the whole nanocomposite cohesive (Co/C// $P_1/P_2$ ). Finally films of compacted Co/C// $P_1/P_2$  material are deposited on silicon substrates by spin coating.

The choice of using Pyrene-terminated Polystyrene as  $P_1$  is motivated by the presence of four aromatic cycles in Pyrene groups. Delocalized electrons can strongly interact with graphene sheet(s) surrounding NPs through  $\pi$ - $\pi$  stacking [4]. Pyrene groups are also known to fluoresce and are used as fluorescent labeling agent for biological applications [5]. Here the Pyrene fluorescence peak around 500 nm is used as a marker of grafting onto the NPs.

Sedimentation dynamics of the solutions has been studied first.  $P_1$ -grafting and further addition of  $P_2$  stabilize NPs and small aggregates, as can be seen on Figure 1 where relative area of integrated absorbance curves is plotted against sedimentation time, in the case of Co particles.

As can be seen on Figure 2,  $P_1$ -grafting (where  $M_w(P_1)=5.6$  kg.mol<sup>-1</sup>) can clearly be identified around typical 100 - 200nm aggregates which confirms the strength of  $\pi$ -interactions. Note that observation on single NP is difficult.

Figure 3 shows a cross-section of the film of Co/C// $P_1/P_2$  nanocomposite. For intermediate thickness (< 1 $\mu$ m), the films consist in a mixture of small aggregates and isolated NPs well dispersed inside the film volume. Such films of Co/C// $P_1/P_2$  nanocomposite exhibit a dominant soft ferromagnetic behavior at room temperature as shown on Figure 4 with moderate hysteresis ( $H_c$  of 23 Oe). The room temperature saturation magnetization is of 0.35T indicating a volume fraction of Co of about 20% from the bulk. The

relatively high anisotropy (i.e. suitable for high frequency use) may originate in chain-like arrangement of the Co NPs which is under investigation.

Finally, when considering thicker film (up to  $\sim 10\mu\text{m}$ ), soft magnetic properties somehow deteriorate because of the presence of residual large aggregates of big particles ( $\sim 100\text{nm}$ ) which remain trapped during spin-coating.

## Conclusion

Magnetic films of metal-graphene-polymer nanocomposites are synthesized by dispersing Co/C NPs in a PS matrix ( $P_2$ ). The graphene shell is successfully functionalized by grafting Pyrene-terminated PS ( $P_1$ ) via non-covalent interaction ( $\pi$  stacking). These first films of Co/C// $P_1/P_2$  consist in a mixture of small aggregates and isolated NPs well dispersed inside the film volume. Soft ferromagnetic-like behavior is observed at room temperature with a saturation magnetization of 0.35T indicating a volume fraction of Co of about 20%. Next steps will consist in increasing this number ( $\sim 40\%$ ) by varying the ratio of Co/C// $P_1$  super particles vs. PS ( $P_2$ ) in the solution.

## References

- [1] N. R. Jana, Y. Chen, and X. Peng, *Chemistry of Materials*, **16** (2004), pp. 3931–3935
- [2] Y. Wang, X. Teng, J.-S. Wang, and H. Yang, *Nano Letters*, **3** (2003), pp. 789–793
- [3] B. Frka-Petesic *et al.*, *Journal of Magnetism and Magnetic Materials*, **321** (2009), pp. 667–670
- [4] J. Liu, J. Tang and J. J. Gooding, *Journal of Materials Chemistry*, **22** (2012), pp. 12435–12452
- [5] J. C. Hicks *et al.*, *Chemistry of Materials*, **18** (2006), pp. 5022–5032

## Figures

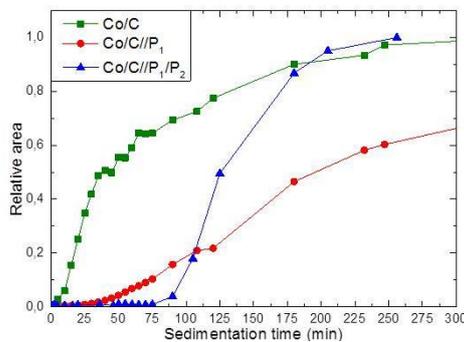


Fig. 1: Relative area of integrated absorbance curves vs. sedimentation time

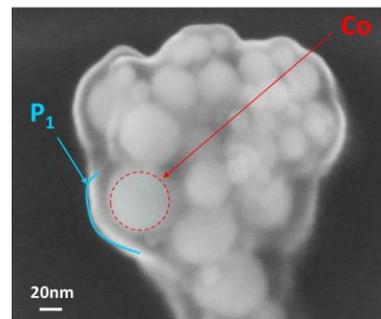


Fig. 2: SEM picture of an isolated  $P_1$ -coated Co/C aggregate

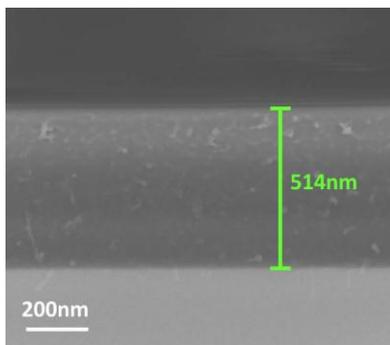


Fig. 3: SEM picture (cross-section) of Co/C// $P_1/P_2$  nanocomposite film

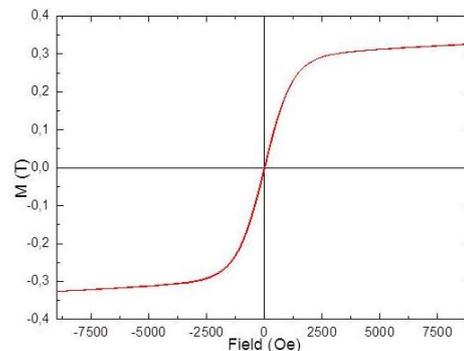


Fig. 4: Magnetic response of Co/C// $P_1/P_2$  nanocomposite film