Covalent functionalisation of graphene-type materials under mild conditions for surface modification and polymer Grafting

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Grafting polymer brushes is a promising technique to tune the properties of graphene and related materials [1]. Here we demonstrate functionalisation routes for graphene-like materials [2], reduced graphene oxide (rGO) and graphene nanoplatelets (GNP), via Diels-Alder reaction [3] followed by esterification to decorate graphene with bromine groups or double-bond groups to grow polymer from the flakes. Both hydrophilic PMETAC and hydrophobic PMMA polymer were grown from functionalised graphene using both a 'graft through' method and SI-ARGET-ATRP (a 'graft from' method). XPS, TGA and zeta potential techniques were applied to determine the success of the grafting reaction on the functionalised graphene and to analyse the polymer content. The results reveal that the 'graft through' method has higher grafting efficiency than the 'graft from' method in terms of polymer content. Furthermore, we compare the two methods for growing polymer in detail through analysing the distribution of polymer chains by scanning electron microscopy (STEM-EDS) and nanoscale secondary ion mass spectroscopy (NanoSIMS). The decoration of graphene-like flakes with polymer brushes has the potential to greatly enhance the water- and/or solvent-stability of flake dispersions, induce strong surface charges in aqueous solution, as well as improving interfacial shear strength and dispersion in polymer composite matrices.

References

[1] Raphael Barbey, Chem. Rev. 109 (2009), 5437-5527
[2] Vasilios Georgakilas, Chem. Rev. 112 (2012), 6156−6214
[3] Santanu Sarkar, Materials today, 15 (2012) 276-285

Figures

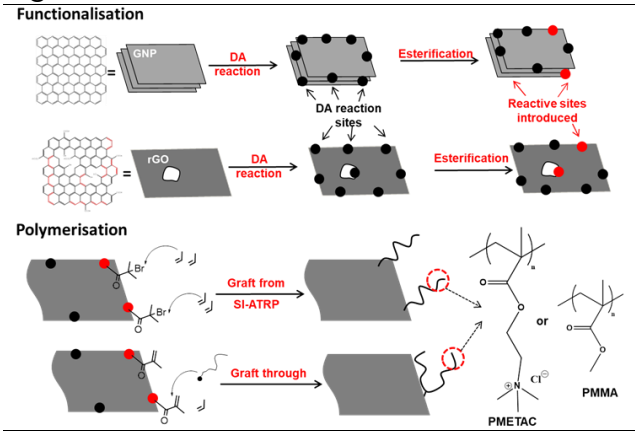

Figure 1: Overall process: first functionalise via Diels-Alder reaction and then induce reactive sites for growing polymer by esterification and polymerisation from functionalised graphene by both 'graft from' method and 'graft through' method with two types of polymer

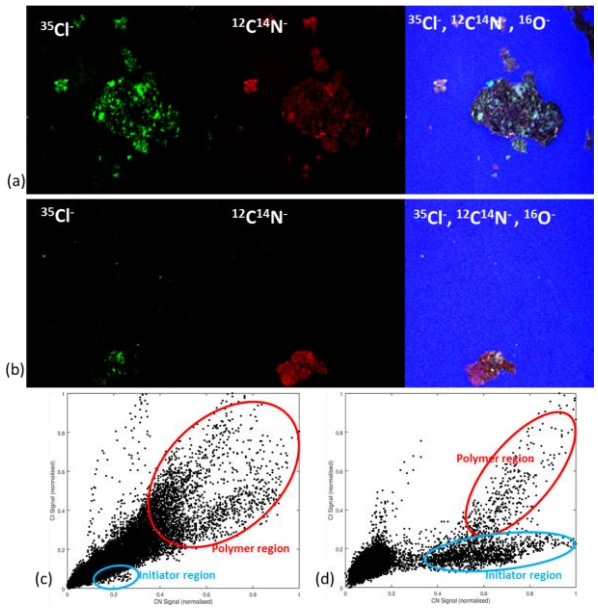

Figure 2: NanoSIMS ion maps showing $^{35}Cl^-$ (Green), $^{12}C^{14}N^-$ (red) and a colour merge image showing ($^{12}C^{14}N^-$: red; $^{16}O^-$: blue; $^{35}Cl^-$: green) of (a) GNP-MA-DB-P ('Graft through' method) and (b) GNP-MA -DB-P ('Graft from' method) ; $^{12}C^{14}N^-$ intensity versus $^{35}Cl^-$ intensity (normalised to 1) of (b) GNP-MA-DB-P and (c) GNP-MA-Br-P