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Synthesis of Hyperbranched Azo-polymer-grafted Graphene Oxide Hybrid

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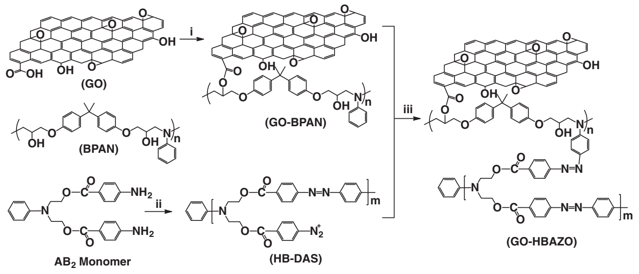
Hyperbranched azo-polymer-grafted graphene oxide (GO) hybrid was synthesized. Epoxy-based precursor polymer was first covalently attached to GO through an ester linkage. Then the hyperbranched azo-polymer-grafted graphene oxide hybrid can be obtained by azo-coupling reaction between the epoxy-based precursor-polymer-functionalized GO and hyperbranched diazonium salts under extremely mild conditions.

Graphene, the first isolated monolayer of carbon atoms arranged in a two-dimensional network, has attracted much attention due to its intrinsic properties, such as electrical transport capacity and intrinsic tensile strength.[1–4] As a traditional precursor for graphene, chemically derived graphene oxide (GO) has received increasing attention for its own characteristics.[5] The oxygen-containing functional groups such as carboxy, hydroxy, and epoxy groups on the basal plane or the sheet edge allow GO to interact with various materials to easily prepare functional hybrids and composites.[5–7]

It is well known that photochromic azobenzene derivatives exhibit diverse photoresponsive properties for their trans–cis photoisomerization upon light irradiation. On the basis of the photoisomerization, materials containing azobenzene chromophores show potential applications in areas such as holographic information storage, photoswitching, sensors, and many others.[8–12] Hyperbranched azo polymers with a highly branched backbone and a large number of terminal functional groups have received great attention during the past decade.[13,14] Hyperbranched azo polymers with different structures have been reported to show many interesting photoresponsive properties such as good surface relief grating properties and enhanced second-order nonlinear optical properties.[14–16]

Recently, GO containing low-molecular-weight azobenzene moieties (GO–AZO) has been reported to show some attractive properties such as tunable electronic properties.[17] The conductance of the GO–AZO film can be optically modulated by irradiating with UV light. We recently reported that graphene nanosheet grafted with azo polymer brushes prepared via a "grafting-from" approach could significantly increase the surface relief grating diffraction efficiency growth rate and the saturated level.[18] However, a study of the preparation of GO grafted with hyperbranched azo polymer has not appeared in the literature yet. Functionalizing GO with hyperbranched azo polymers can combine the interesting properties of graphene and the unique photoresponsive properties of hyperbranched azo polymers. In this paper, hyperbranched azo-polymer-grafted GO hybrid was synthesized. Precursor polymer (BPAN)[19] was first covalently attached to GO through an ester linkage. Then the hyperbranched azo-polymer-grafted GO hybrid can be obtained by azo-coupling reaction between the BPAN-functionalized GO and hyperbranched diazonium salts under extremely mild condition.



Scheme 1. Synthetic route of GO–HBAZO. Reaction conditions: (i) BPAN, DMF, r.t.; (ii) HOAc, H_2SO_4, $NaNO_2$, 0 °C, DMF; (iii) DMF, 0 °C.

Scheme 1 shows the synthetic route of hyperbranched azo-polymer-functionalized GO (GO–HBAZO). GO was prepared from natural graphite powder by a modification of Hummers method.[20] Sodium nitrate, sulfuric acid, potassium persulfate, phosphoric anhydride, and potassium permanganate were used as oxidants. After exhaustive washing with deionized water until the pH was 7, the resulting GO sheets were purified by dialysis for one week and finally were dried in air. Then GO powder was dispersed in dry dimethylformamide (DMF), and a solution of BPAN, *N*-ethyl-*N′*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl), and 4-dimethylaminopyridine (DMAP) in DMF were added, and the solution was stirred at room temperature for two days. The resulting GO–BPAN was filtered, and rinsed with DMF several times. An AB_2 monomer *N*,*N*-bis[2-(4-aminobenzoyloxy)ethyl]aniline was synthesized according to our previous report.[21] The hyperbranched azo polymer bearing peripheral diazonium groups (HB–DAS) was obtained through the azo-coupling reaction of above AB_2 monomer in DMF.[21] Then GO–BPAN and HB–DAS DMF solution were mixed in DMF and stirred for 3 days under 0 °C. The resulting GO–HBAZO was filtered, and rinsed with DMF several times. The exact experimental details are shown in the ESI.[22]

The UV–vis spectrum of GO–HBAZO in DMF is shown in Figure 1. The maximum absorbance of GO–HBAZO in DMF appears at about 484 nm, which is related to the π–π^* transition of the trans isomers of the azobenzene units. The spectrum shows typical absorption behavior of the pseudo-stilbene type of azo chromophores, which confirms the hyperbranched azo polymer has been successfully attached to the GO sheets.

The FTIR spectra of GO and GO–HBAZO are shown in Figure 2. For GO–HBAZO the new peaks at about 2960, 2872, and 2927 cm^{-1} can be attributed to the $-CH_3$ and $-CH_2-$ in the azo polymers. The strong peaks at 1600 and 1510 cm^{-1} can be attributed to the benzene rings of the polymer. The peak at 1716 cm^{-1} corresponds to the C=O stretching vibration of the aromatic ester bond. XPS was also used to confirm that the azo polymer has been attached to the GO sheets (Figure 3). The

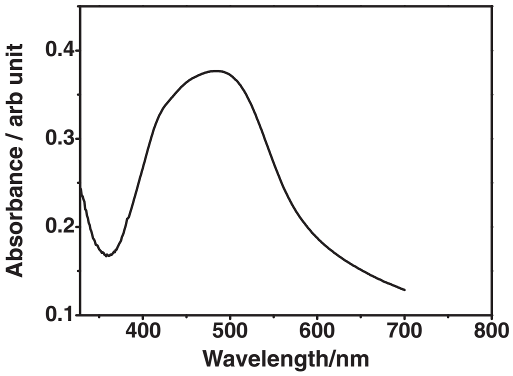


Figure 1. UV–vis spectrum of GO–HBAZO dispersed in DMF.

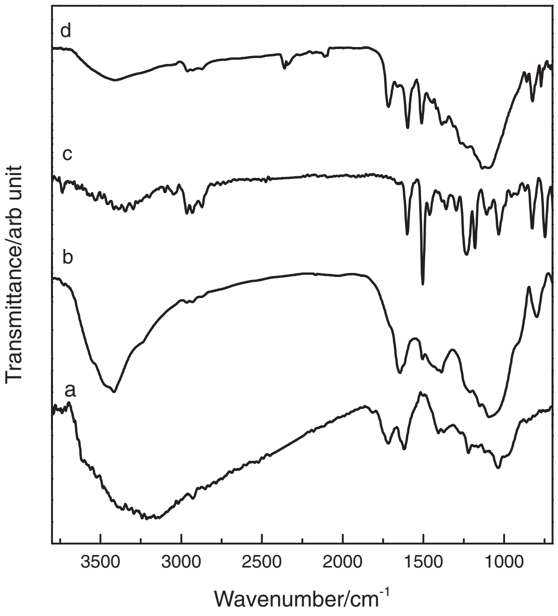


Figure 2. FTIR spectra of (a) GO, (b) GO–BPAN, (c) BPAN, and (d) GO–HBAZO.

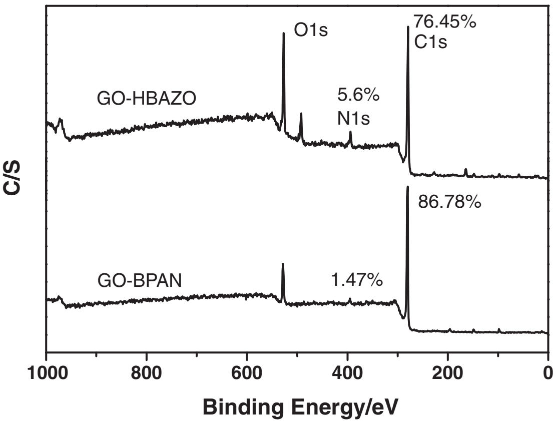


Figure 3. XPS survey scan of (a) GO–BPAN and (b) GO–HBAZO.

GO–BPAN and GO–HBAZO showed 1.47% and 5.6% nitrogen (atom %) respectively, whereas no nitrogen is detected for GO. Calculation results indicate the degree of functionalization is about 1 repeat azobenzene unit per 30 carbons of GO.

In summary, hyperbranched azo-polymer-graft graphene oxide hybrid was successfully synthesized. The resulting hybrid was characterized by UV–vis, FTIR, and XPS. The study of photoresponsive and conductive properties is in progress.

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