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A photoresponsive graphene oxide-C$_{60}$ conjugate

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An all-carbon donor-acceptor hybrid combining graphene oxide (GO) and C$_{60}$ has been prepared. Laser flash photolysis measurements revealed the occurrence of photoinduced electron transfer from the GO electron donor to the C$_{60}$ electron acceptor in the conjugate.

Owing to their remarkable electronic properties, the various allotropic forms of carbon have attracted an enormous attention in the field of materials science. For example, photovoltaic devices made with all-carbon thin films incorporating fullerenes, carbon nanotubes (CNTs) and graphene oxide, have shown promising efficiencies for light to electrical energy conversion. In this particular case, the all-carbon nanocomposites have been co-assembled in water to yield stable colloidal dispersions for thin film processing. On the other hand, covalent hybrid nanostructures combining fullerenes and CNTs, have been prepared and incorporated into photovoltaic or optical limiting devices. C$_{60}$ has been also grafted onto graphene surfaces. Interestingly, such conjugates, have shown enhanced nonlinear optical performances when compared to their individual components. In another example, graphene oxide (GO) has been decorated with both C$_{60}$ and Zn(II)-phthalocyanines (ZnPc).a

Recently, the electron-donating behaviour of few-layer graphene in covalent ensembles with electron-accepting phthalocyanines have been shown. Photophysical studies have revealed the occurrence of photoinduced electron transfer (PET) from the ZnPc donor to the C$_{60}$ acceptor suggesting that the GO scaffold is capable of mediating the electron transfer events involving the two other partners. The possibility to use GO as an electroactive component, namely as electron donor, in a GO-C$_{60}$ conjugate, remains an open question. To answer to this question, we now report the synthesis and the photophysical properties of a covalent GO-C$_{60}$ conjugate. Indeed, laser flash photolysis investigations revealed effectively the occurrence of PET from the modified GO sheets to the fullerene, thus demonstrating the possibility to develop covalent photoresponsive nanoconstructs exclusively based on carbon materials.

The preparation of the covalent graphene oxide-[60]fullerene conjugate (GO-C$_{60}$) is depicted in Fig. 1. The starting GO was purchased from Nanoinnova Technologies. It was then modified by 4-(trimethylsilyl)ethynylaniline via aryldiazonium salt reaction, to yield GO-TMS. Subsequent cleavage of the TMS groups with tetra-n-butylammonium fluoride (TBAF) gave GO-CCH. Finally, fullerene building block 1 was grafted onto the modified GO scaffold using the Cu-catalysed alkyne-azole cycloaddition (CuAAC) reaction under the conditions optimized for the grafting of fullerene-containing azide onto carbon nanohorns [CuSO$_4$•$n$H$_2$O, sodium ascorbate in N-methyl-pyrrolidone (NMP)] (see Electronic Supporting Information, ESI). The resulting GO-C$_{60}$ conjugate forms stable suspensions in solvents such as DMF, NMP and CH$_2$Cl$_2$ (Fig. S1). The GO-C$_{60}$ hybrid obtained was characterized by Fourier-transformed infrared spectroscopy (FT-IR), Raman spectroscopy, high-resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

As shown in Fig. 2, Raman spectroscopy ($\lambda_{exc}$ = 532 nm) of GO shows an intense tangential mode (G band) at 1585 cm$^{-1}$ and a disordered-induced peak (D band) at 1355 cm$^{-1}$. These signals are observed at 1588 cm$^{-1}$ and 1349 cm$^{-1}$ in the spectrum of GO-TMS. As a consequence of the functionalization, the I$_D$/I$_G$ ratio is slightly higher for GO-TMS (0.86) when compared to GO (0.73). The spectrum of GO-C$_{60}$ shows the signatures of all its constituents: (i) 1594 cm$^{-1}$ and 1355 cm$^{-1}$ (GO sheet),

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and (ii) 1486 cm⁻¹ (Ag(2) mode of C₆₀). It is worth noting that no further increase of the I₀/Iₓ ratio was observed when going from GO-TMS to GO-C₆₀-TMS, thus confirming that the cycloaddition reaction occurred onto the triple bonds of GO-CCH rather than directly onto the GO surface. The formation of GO-C₆₀ was also evidenced by XPS (Figs. S2-6, Tables S1-2). In particular, the high-resolution N 1s spectrum of GO-C₆₀ displays two components, (i) a major one at a binding energy of 399.9 eV, belonging to the two triazole N-atoms bound to C-atoms as nearest neighbors, and (ii) a minor one at 398.6 eV originating from the other remaining N-atom. In contrast, only one component is observed at 400.2 eV for azide 1. These observations unambiguously prove that the azide residue of fullerene 1 is no longer present, thus, confirming the formation of triazole rings during the reaction leading to GO-C₆₀. Based on the Nitrogen content, measured by XPS, it was estimated that one fullerene is present per 161 GO atoms. FT-IR spectroscopy (Fig. S7) further corroborated the results obtained by the previous techniques. Indeed, some of the diagnostic signals of precursor 1 were detected for GO-C₆₀. For example, the peaks around 2926 and 2855 cm⁻¹ assigned to C-H stretching vibrations of alkyl chains. Importantly, the characteristic signal of azide groups (2092 cm⁻¹) could not be detected for GO-C₆₀ confirming again the successful functionalization of GO-CCH via the CuAAC reaction.

HR-TEM shows that the morphology of GO-C₆₀ was constituted by large GO sheets with lateral dimensions of several microns (Figs. 1B and field emission scanning electron microscopy showing lateral dimensions over micron in Fig. S8). Importantly, electron diffraction in selected areas reveals the characteristic GO hexagonal patterns. Moreover, the structural feature of fullerene moieties grafted onto GO appears as circles with an inner diameter of ca. 0.7 nm in perfect agreement with the size of C₆₀ units (insets of Fig. 1B). Additional structural data were obtained by AFM investigations. Upon sonication of a suspension of GO-C₆₀ in CH₃Cl, (60 min) and drop-casting deposition on SiO₂, AFM revealed a layered material with typical heights in the range of 7-10 nm (Fig. S10). By increasing the sonication time, aggregation was further reduced leading to the observation of flakes with heights of ca. 4-6 nm (Figs. S9 and S11).

The areas of the layers observed for GO-C₆₀ are rather similar to those observed for the starting GO material thus showing that the morphology of GO has been maintained during its functionalization (Fig. S13).

The electrochemical properties of hybrid compound GO-C₆₀ were investigated by cyclic voltammetry (CV). For the sake of comparison, electrochemical measurements were also carried out with C₆₀ and 1. All the experiments were performed at room temperature in acetonitrile solutions containing tetra-n-butylammonium tetrafluoroborate (TBAF₄) as supporting electrolyte. The first reduction is observed at -0.60 and -0.67 V for C₆₀ and 1, respectively (Fig. S15). Interestingly, this reduction is observed at -0.53 V for GO-C₆₀ suggesting the existence of interactions between both moieties. A similar shift of the reduction potential has been already observed in a related carbon nanohorn-C₆₀ hybrid. Under similar conditions the reduction potential of GO appears at -1.36 V.
As typically observed for fullerene derivatives, compound 1 exhibits a weak emission at ca. 720 nm (Fig. 3A). This fluorescence signal is dramatically quenched in GO-C60, suggesting the occurrence of excited-state interactions between the two forms of carbon in the conjugate. In order to elucidate the quenching mechanism, laser flash photolysis experiments were carried out on GO-C60 in PhCN solutions (Fig. 3B). The results were compared to those obtained with compound 1 and GO (see ESI, Fig. S27). Upon 355 nm nanosecond laser excitation of a PhCN solution of GO-C60, the transient absorption spectra show a continuous absorption from 360 to 900 nm, peaking at 820 nm, as well as a continuous band from 1000 to 1200 nm. While the continuous absorption in the 400-800 nm region can be due to the combination of the spectra recorded for GO and 1, the most salient feature is the intense NIR absorption recorded for GO-C60.

The latter is ascribed to the absorption of fullerene radical anions. Similar transient absorptions have been recently observed in the NIR region upon PET in a modified GO derivative bearing C60 and ZnPc subunits. The temporal profile of the signals in the 360-900 nm zone was coincident but the signal decay in the NIR region was slower indicating the presence of long-lived transient species, namely C60•−.13 GO is thus acting as an electron donor, however the oxidized GO has no characteristic absorption bands in the visible region and the formation of GO•+ could not be monitored. It is also worth noting that no transient absorption was observed in the NIR region during control experiments using compound 1 in the absence of GO. Actually, the electron donor moiety generating C60•− must be GO and not the solvent.14 Finally, the occurrence of photoinduced intramolecular electron transfer in GO-C60 deduced from the transient absorption experiments with GO-C60 was further confirmed by bimolecular quenching experiments performed with mixtures of GO and C60 (see ESI, Figs S20 and S21).

In conclusion, CuAAC chemistry allowed us to efficiently conjugate two nanoforms of carbon and photoinduced electron transfer has been evidenced in the resulting GO-C60 nanohybrid. Therefore, GO-C60 nanoconjugates are appealing candidates for the preparation of all-carbon solar cells. Work in this direction is currently underway in our laboratories.

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Notes and references

9 For more information see: www.nanoinnova.com.


13. Detecting the building up of the fullerene anion was not possible as it is faster than the detection limit of the instrument.