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Diels−Alder Chemistry of Graphite and Graphene: Graphene as Diene and Dienophile

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S *Supporting Information*

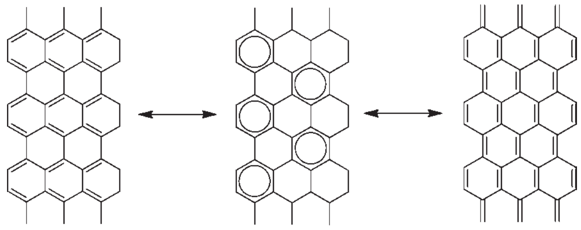
ABSTRACT: The zero-band-gap electronic structure of graphene enables it to function as either the diene or the dienophile in the Diels−Alder reaction, and this versatile synthetic method offers a powerful strategy for the reversible modification of the electronic properties of graphene under very mild conditions.

Graphene holds great potential as an electronic material because of its excellent transport properties, which derive from the unique Fermi surface and ballistic conductance;[1−4] however, the absence of an energy gap makes pristine graphene sheets unsuitable for use as the active element in conventional field-effect transistors. Three principal routes have been followed to engineer the necessary energy band gap into graphene: (1) formation of narrow ribbons (quantum confinement), (2) the use of bilayer structures, and (3) basal-plane chemical functionalization.[5−9]

While graphene is the thermodynamic reference for carbon and considered to be the prototypical stable benzenoid hydrocarbon, the absence of an energy gap makes graphene a viable target for organic chemical functionalization reactions, as the molecular HOMO−LUMO energy gap is a useful (inverse) index of chemical reactivity.[10] The thermodynamic stability of a molecule and the kinetics of its chemical reactions are usually held to be related,[10] and they are often considered in connection with Hammond's postulate.[11] Nevertheless, in this communication we demonstrate the facile reactivity of graphene in the Diels−Alder (DA) reaction; the fact that the conduction and valence bands of graphene touch at the Fermi level (Dirac point) allows the realization of reactions that require either diene or dienophile character in the graphene electronic structure, thereby demonstrating the accessibility of a number of canonical structures (Scheme 1).

We delineate the sensitivity of the chemistry to the choice of reaction conditions and the importance of kinetic control, which allow the realization of clean cycloaddition and cycloreversion reactions. Raman spectroscopy has been the primary analytical tool in the characterization of graphitic structures for many years, and this technique is known to be sensitive to the degree of defect sites introduced into the periodic graphene lattice[12,13] as well as the π-electron distribution.[14] It has recently been shown that Raman spectroscopy is a particularly sensitive method for monitoring basal-plane covalent chemical reactions in various forms of graphene,[7,15,16] and we have employed this technique to follow the progress of the Diels−Alder chemistry. We demonstrate cycloaddition and -reversion Diels−Alder chemistry with exfoliated graphene [XG, in either the solution-processed (XG_{sol}) or flake (XG_{flake}) form], epitaxial graphene (EG), and highly oriented pyrolytic graphite (HOPG) using representative dienes and dienophiles. The Diels−Alder transformation is a powerful reaction in organic chemistry that allows the saturation of conjugated sp^2-hybridized carbon atoms, and it has been extensively used in fullerene and carbon nanotube functionalization [see the Supporting Information (SI)].[17−24]

Scheme 1. Resonance Forms of Graphene: Graphene as Diene (1) and Dienophile (2)



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The Diels−Alder reaction of each form of graphene with the dienophile tetracyanoethylene (TCNE) was found to proceed at room temperature (Figure 1a; also see the SI) upon exposure of the graphene sample to a solution of TCNE in dichloromethane (DCM). In a typical reaction, a few drops of 1,4-dioxane were added to XG_{flake} supported on a Si substrate, after which a solution of TCNE in anhydrous DCM was added dropwise and the substrate kept at room temperature for 3 h under ambient atmosphere. The progress of the functionalization of the graphite and graphene samples was monitored by Raman spectroscopy: the spectra of pristine HOPG, few-layer graphene (FLG), and single-layer graphene (SLG, XG_{flake}) showed the characteristic G and 2D bands (Figure 1c), whereas the D, D′ and D+D′ peaks appeared in the spectra of the materials after reaction with TCNE (Figure 1d). The D band at 1345 cm^{-1} became the most prominent feature of the Raman spectrum in SLG (Figure 1b), and the 2D band was significantly

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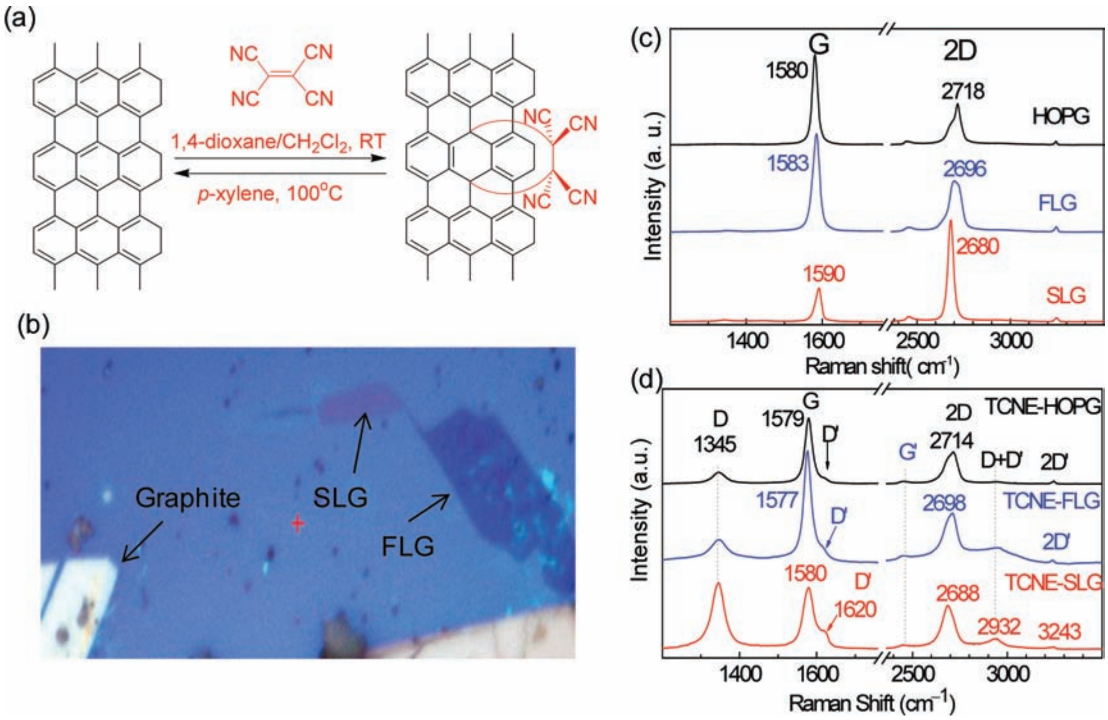


Figure 1. Room-temperature Diels–Alder (DA) reaction between graphene (diene) and tetracyanoethylene (TCNE, dienophile). (a) Schematic representation of the reaction. (b) Micrograph showing a large piece of HOPG, single-layer graphene (SLG), and few-layer graphene (FLG) on a Si substrate. (c, d) Raman spectra of HOPG, FLG and SLG (c) before and (d) after DA reaction with TCNE.

reduced in intensity; similar behavior was observed on nitrophenyl functionalization of XG and EG.[7] The D band is due to the A_{1g} breathing vibrations of six-membered sp^2 carbon rings and becomes Raman-active after the symmetry of the nearby lattice is reduced by the introduction of defects or functionality in graphitic materials; the ratio of the D- and G-band intensities (I_D/I_G) is a useful index of the degree of functionalization.[12,13] Although the IR spectra of the adducts showed very weak signals corresponding to the C–N stretch, the Raman peak at 2210 cm^{-1} in the TCNE–XG_{sol} adduct was assigned to this vibration (see the SI).

The formation of graphene adducts with maleic anhydride (MA) was found to be sensitive to the nature of the graphene sample and the reaction temperature. Examination of a variety of reaction conditions in conjunction with Raman spectroscopy of the products led to the following optimum temperatures for the MA reaction: HOPG, 120 °C (Figure 2a); XG_{sol}, 130 °C (see the SI); EG, 70 °C (see the SI). The reversibility of the process was also clear, as shown in Figure 2a. The reactivity of HOPG toward MA became apparent at 100 °C, and the extent of functionalization increased for temperatures up to 120 °C, as indicated by the intensity of the D band, which increased from $I_D/I_G = 0.12$ to $I_D/I_G = 0.63$ (Figure 2a). The presence of the MA functionality in the MA–XG product obtained at 130 °C was also observed in the IR spectrum (Figure 2b). A further increase in temperature led to products with a decreased amount of functionality because of the thermal instability of the DA adducts; the cycloreversion process was complete at 150 °C. Diels–Alder adducts of fullerenes were found to be stable up to temperatures of ~40 °C in solution but were much more thermally stable in the solid state.[25]

The use of graphite and graphene as dienophiles in the Diels–Alder reaction was investigated using 9-methylanthracene (Scheme 2; also see the SI) and 2,3-dimethoxy-1,3-butadiene (Figure 3a) as dienes. The DA chemistry leads to the simultaneous transformation of a pair of neighboring sp^2 carbons in the graphene honeycomb lattice into 1,2-sp^3 hybridized centers, which suggests that the DA chemistry should be effective in opening a band gap in graphene in much the same manner as has been demonstrated with metallic single-walled carbon nanotubes.[26]

After optimization, we observed that 9-methylanthracene (9-MeA) cycloadducts (Scheme 2) could be obtained in high yield ($I_D/I_G > 1$) by treating HOPG or XG_{sol} with a p-xylene solution of 9-MeA at 130 °C; the products were characterized with attenuated total reflectance (ATR) FTIR spectroscopy (see the SI), thus establishing the generality of the graphene DA reaction.

The formation of graphene adducts with 2,3-dimethoxy-1,3-butadiene (DMBD) was investigated by heating an EG substrate overnight in a ~0.15 M solution of DMBD in p-xylene at temperatures of 50, 90, and 120 °C under argon. After the reaction, the substrate was washed repeatedly with acetone and dried under a gentle flow of argon and then under vacuum for 2 h. The most efficient functionalization was achieved by heating EG at 50 °C in the absence of solvent with neat DMBD under an argon atmosphere for 3 h (Figure 3b; see the SI for other graphene reaction conditions and spectroscopic characterization). In Figure 3c, we compare the four-point resistances of pristine EG and the DMBD–EG adduct (neat reaction at 50 °C), and it can be seen that the room-temperature resistance of the functionalized sample was 60% larger and that the temperature dependence was activated (semiconducting). The temperature dependence of the resistance shown in Figure 3c indicates a change in the transport mechanism: EG exhibits a slight decrease in resistance with temperature and a crossover to metallic behavior below 110 K, whereas

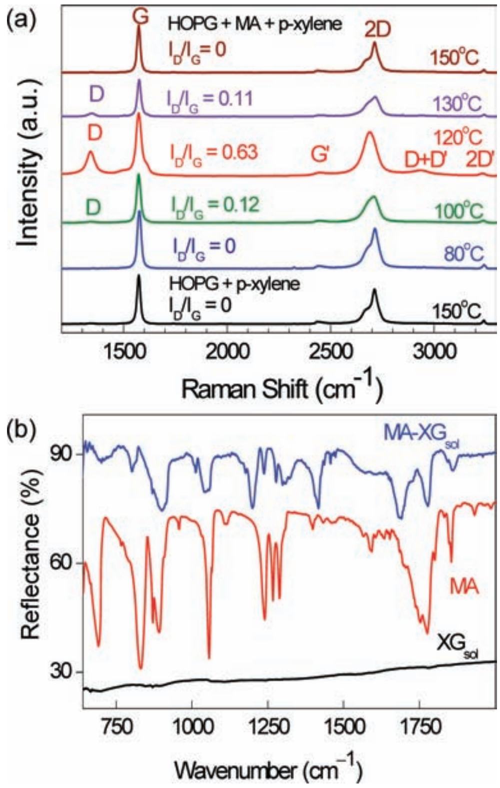
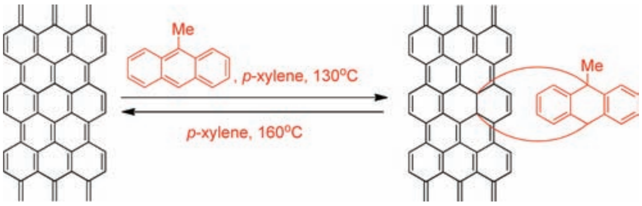


Figure 2. DA reactions of graphite and graphene (diene) with maleic anhydride (MA, dienophile). (a) Raman spectra of the reaction between HOPG and MA in *p*-xylene over the temperature range from 80 to 150 °C; the maximum amount of reaction was obtained at 120 °C, and the retro-DA reaction was complete at 150 °C. (b) ATR spectra of exfoliated graphene (XG_{sol}), MA, and the thermal DA adduct ($MA-XG_{sol}$) obtained by reaction of XG_{sol} with MA at 130 °C in *p*-xylene.

Scheme 2. Schematic of the Thermal DA Reaction between Graphene and 9-Methylanthracene



the DMBD−EG adduct shows nonmetallic behavior over the whole temperature range, characteristic of weak localization.[27,28]

In summary, we have shown the versatility of graphene as a Diels−Alder substrate and its ability to function as either the diene or the dienophile (Scheme 1). As a result of the scope of Diels−Alder chemistry and the dual nature of the reactivity of graphene, dienophiles and dienes with a wide range of modifiable chemical functionalities can be employed, providing a platform for postgrafting modification of graphene. The covalent functionalization of graphene via Diels−Alder reactions is a simple and efficient approach for reversibly engineering the band structure and conductivity of graphene for electronic and optical applications.

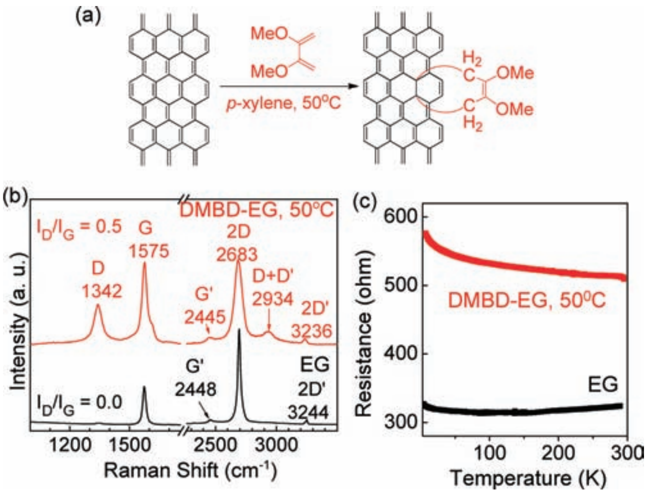


Figure 3. Thermal DA reaction between graphene (dienophile) and 2,3-dimethoxy-1,3-butadiene (DMBD, diene). (a) Schematic illustration of the DA reactions. (b) Raman spectra of pristine epitaxial graphene (EG) and the DMBD−EG adduct (50 °C, neat reaction). (c) Temperature dependence of the resistances of pristine EG and the DMBD−EG adduct (50 °C, neat reaction).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, Raman and IR spectroscopic data, and complete ref 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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