

Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets

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Abstract

A number of functionalized graphite oxides were prepared by treatment of graphite oxide (GO) with organic isocyanates. These isocyanate-treated GOs (*i*GOs) can then be exfoliated into functionalized graphene oxide nanoplatelets that can form a stable dispersion in polar aprotic solvents. Characterization of *i*GOs by FT-IR spectroscopy and elemental analysis suggested that the isocyanate treatment results in the functionalization of the carboxyl and hydroxyl groups in GO via formation of amides and carbamate esters, respectively. The degree of GO functionalization can be controlled via either the reactivity of the isocyanate or the reaction time. When used with functionalized isocyanates, the described methodology allows for the elaboration of graphene oxide nanoplatelets with different surface functional groups.

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1. Introduction

Graphite oxide (GO), an oxygen-rich carbonaceous layered material, is produced by the controlled oxidation of graphite [1–3]. Each layer of GO is essentially an oxidized graphene sheet commonly referred to as graphene oxide [4]. Based on recent studies [5–10], GO consists of intact graphitic regions interspersed with sp³-hybridized carbons containing hydroxyl and epoxide functional groups on the top and bottom surfaces of each sheet and sp²-hybridized carbons containing carboxyl and carbonyl groups mostly at the sheet edges. Hence, GO is hydrophilic and readily disperses in water to form stable colloidal suspensions [4,11–13].

We have long been interested in developing and using graphene-based nanoplatelets as a well-dispersed filler for

a broad range of polymer composites. As such, we suspect that GO would serve as an excellent precursor to a variety of graphene-based nanofillers if it could be completely exfoliated in a wide range of media. In our hands, GO readily exfoliates in water under a mild ultrasonic treatment to produce transparent dispersions that are stable for at least months at concentrations of 1 mg/mL [14]. Atomic force microscopy (AFM) shows that these dispersions contain graphene oxide nanoplatelets of ~1 nm uniform thickness [14]. However, since GO is hydrophilic, its direct exfoliation into non-aqueous solvents is not favored. This behavior can presumably be attributed to the strong interlayer hydrogen bonds between the oxygen functional groups of adjacent graphene oxide layers in GO. Unlike water, organic solvents are unable to penetrate the interlayer spaces of GO and disrupt these hydrogen bonds, which in turn prevents their exfoliation. If the density of the hydrogen bond donor groups, such as hydroxyls, is decreased via chemical functionalization, the graphene oxide layers would become less hydrophilic and the strength of interlayer hydrogen bonding will be attenuated,

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possibly allowing for exfoliation in organic solvents. Such functionalization of graphite oxide has been shown to be possible by Lerf et al., who prepared and studied a number of chemically modified graphite oxide derivatives [7]. In addition, Matsuo et al. successfully carried out the silylation of butyl amine-intercalated graphite oxide [15,16]. However, the exfoliation behavior of such chemically modified graphite oxides has never been studied.

We report herein the synthesis of chemically modified GO derivatives via treatment of graphite oxide with aryl and alkyl isocyanates. We also demonstrate, for the first time, that such chemical treatment dramatically alters the exfoliation behavior of graphite oxide and allows for the complete exfoliation of GO into individual chemically derivatized graphene oxide sheets to be achieved in organic solvents.

2. Experimental

2.1. Materials and methods

Graphite oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30 μm) by the Hummers [2] method and dried for a week over phosphorus pentoxide in a vacuum desiccator before use. 4-Isocyanatobenzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure [17]. All other isocyanates were purchased from Sigma–Aldrich and used as received. All solvents were HPLC grade and were purchased from Fisher Scientific. Anhydrous *N,N*-dimethylformamide (DMF) was obtained from a Dow-Grubbs solvent system installed by Glass Contours (Laguna Beach, CA) [18]. All manipulations with this solvent were performed using standard Schlenk techniques.

A Fisher Scientific FS60 ultrasonic bath cleaner (150 W) was used in the preparation of stable dispersions of functionalized graphite oxides. AFM images were taken on an AutoProbe CP/MT Scanning Probe Microscope (MultiTask; Veeco Instruments). Imaging was done in non-contact mode using a V-shape “Ultralever” probe B (Park Scientific Instruments, B-doped Si with frequency $f_c = 78.6$ kHz, spring constants $k = 2.0$ – 3.8 N/m, and nominal tip radius $r = 10$ nm). All images were collected under ambient conditions at 50% relative humidity and 23 °C with a scanning raster rate of 1 Hz. AFM images were obtained by depositing dispersions of functionalized graphite oxides on a freshly cleaved mica surface (Ted Pella Inc., Redding, CA). Dynamic light-scattering (DLS) measurements were performed on a Brookhaven Instruments Corp. photon correlation spectrometer (BI-200 SM goniometer) fitted with a Brookhaven Instruments BI-9000AT digital correlator and a 300-mW argon ion laser at 514 nm. The scattering angle used was 90°. A refractive index-matching bath of filtered decalin (0.2 μm) surrounded the scattering cell, and the temperature was fixed at 25 °C. Correlation data were fitted using the method of cumulants [19] to the logarithm of the correlation function, yielding the diffusion coefficient, D . The hydrodynamic diameters (d) of the nanoparticles were calculated using D and the Stokes–Einstein equation ($D = k_B T / 3\pi\eta d$, where k_B is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and d is the diameter of the particle). The polydispersity factor of the nanoparticles, represented as μ_2/Γ^2 , where μ_2 is the second cumulant of the decay function and Γ is the average characteristic line width, was calculated by the cumulant method. CONTIN algorithms were used in the Laplace inversion of the autocorrelation functions to confirm particle size distributions. All analyses were performed with the supplied instrument software. For the DLS measurements, the stable dispersions of phenyl isocyanate-treated GO were prepared at 1 mg/mL and then diluted 1000 times. FT-IR spectra (KBr) were collected with a Thermo Nicolet Nexus 870 instrument and the spectral features were assigned using the KnowItAll Informatics System

Academic Edition 5.0 software (Bio-Rad Laboratories, Inc.). Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

2.2. Preparation of isocyanate-treated graphite oxides (*iGOs*)

In a typical procedure, graphite oxide (50 mg) was loaded into a 10-mL round-bottom flask equipped with a magnetic stir bar and anhydrous DMF (5 mL) was then added under nitrogen to create an inhomogeneous suspension. The organic isocyanate (2 mmol) was next added and the mixture was allowed to stir under nitrogen for 24 h. (In the case of solid isocyanates, both the isocyanate and graphite oxide were loaded into the flask prior to adding DMF.) After 24 h the slurry reaction mixture was poured into methylene chloride (50 mL) to coagulate the product. The product was filtered, washed with additional methylene chloride (50 mL), and dried under vacuum.

3. Results and discussion

In stark contrast to the parent GO, our isocyanate-treated GO (*iGO*) does not disperse at all in water. However, it swells and, after a brief ultrasonic treatment, readily forms stable colloidal dispersions in polar aprotic solvents such as DMF, *N*-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), and hexamethylphosphoramide (HMPA). Other less polar solvents, such as tetrahydrofuran (THF), acetone, methylene chloride, and toluene, or common polar protic solvents, such as methanol and ethanol, do not disperse the *iGO* materials. Fig. 1 shows the dispersions of the parent GO in DMF (left), phenyl isocyanate-treated GO in water (middle), and phenyl isocyanate-treated GO in DMF (right), at 1 mg/mL concentration. The vials with parent GO in DMF and phenyl isocyanate-treated GO in water contain visible precipitates, indicating poor dispersion.

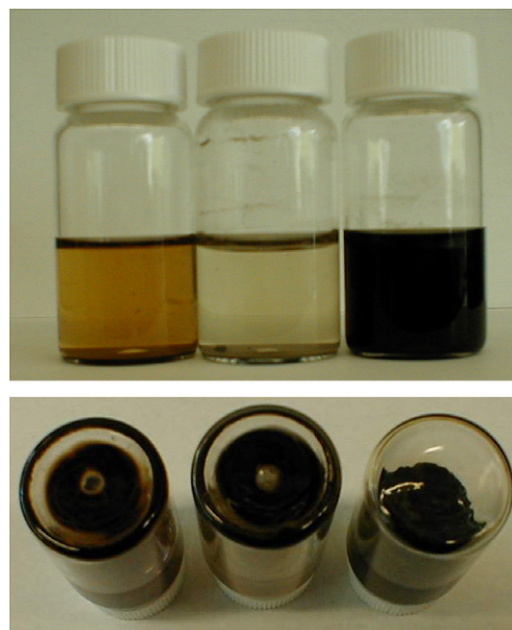


Fig. 1. Vials containing dispersions (1 mg/mL) of GO in DMF (left), phenyl isocyanate-treated GO in water (middle), and phenyl isocyanate-treated GO in DMF (right). The top image shows the dispersions 24 h after preparation. The bottom image shows the inverted dispersions with the precipitate clearly shown on the bottom of the left and middle vials.

On the other hand, the dark brown dispersion of the phenyl isocyanate-treated GO in DMF contains no visible precipitate and is stable for weeks.








The treatment of GO with organic isocyanates can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides [20] or carbamate esters [21], respectively (Fig. 2a). The chemical changes occurring upon treatment of GO with isocyanates can be observed by FT-IR spectroscopy as both GO and its isocyanate-treated derivatives display characteristic IR spectra. Fig. 2b illustrates the changes occurring in the FT-IR spectrum of GO upon treatment with phenyl isocyanate (for FT-IR spectra of all *i*GO derivatives see Electronic Supporting Information (ESI)). The most characteristic features in the FT-IR spectrum of GO are the adsorption bands corresponding to the C=O carbonyl stretching at 1733 cm^{-1} , the O–H deformation vibration at 1412 cm^{-1} , the C–OH stretching at 1226 cm^{-1} , and the C–O stretching at 1053 cm^{-1} [5,8,12]. Besides the ubiquitous O–H stretches which appear at 3400 cm^{-1} as a broad and intense signal (not shown), the resonance at 1621 cm^{-1} can be assigned to the vibrations of the adsorbed water molecules, but may also contain components from the skeletal vibrations of un-oxidized graphitic domains [5,22,23].

Upon treatment with phenyl isocyanate, the C=O stretching vibration at 1733 cm^{-1} in GO becomes obscured by the appearance of a stronger absorption at 1703 cm^{-1} that can be attributed to the carbonyl stretching vibration of the carbamate esters of the surface hydroxyls in *i*GO. The new stretch at 1646 cm^{-1} can be assigned to an amide carbonyl-stretching mode (the so-called Amide I vibrational stretch). The new band at 1543 cm^{-1} can originate from either amides or carbamate esters and corresponds to the coupling of the C–N stretching vibration with the CHN deformation vibration (the so-called Amide II vibration) [24]. Significantly, the FT-IR spectra of *i*GOs do not contain signals associated with the isocyanate group ($2275\text{--}2263\text{ cm}^{-1}$), indicating that the treatment of GO with phenyl isocyanate results in chemical reactions and not mere absorption/intercalation of the organic isocyanate.

Assuming that the formation of the carbamate esters via the reaction of the isocyanate with the surface hydroxyls is the exclusive reaction pathway, the carbon-to-nitrogen atomic ratio in *i*GO can be used to calculate an approximate functionalization degree. Table 1 shows calculated degrees of functionalization for different *i*GO expressed as the number of graphene carbons per one incorporated carbamate ester unit. We note that these calculated numbers comprise the lower limits of functionalization; for exclusive amide formation, the calculated functionalization degrees would be higher since there is a loss of carbon (as carbon dioxide) from the isocyanate reagent (Fig. 2a, the chemical pathways shown in the right oval) [25].

The extent of functionalization with different isocyanates appears to correlate with their relative reactivities. For example, for the sterically hindered *tert*-butyl isocyanate, one carbamate unit is incorporated for every 20 graphene carbons (Table 1, entry 2), while for the more reactive 4-acetylphenyl isocyanate there is one carbamate

Table 1
Calculated functionalization degrees for different isocyanate-treated GOs

Entry	Isocyanate ^a	Graphene-C/N ratio
1		15.7 (8.7 ^b)
2		20
3		16
4		18.3
5		12.4
6		7.6
7		16.1

^a Reaction conditions: GO (50 mg), and isocyanate (2 mmol) in anhydrous DMF (5 mL), 24 h.

^b Reaction time was 7 days.

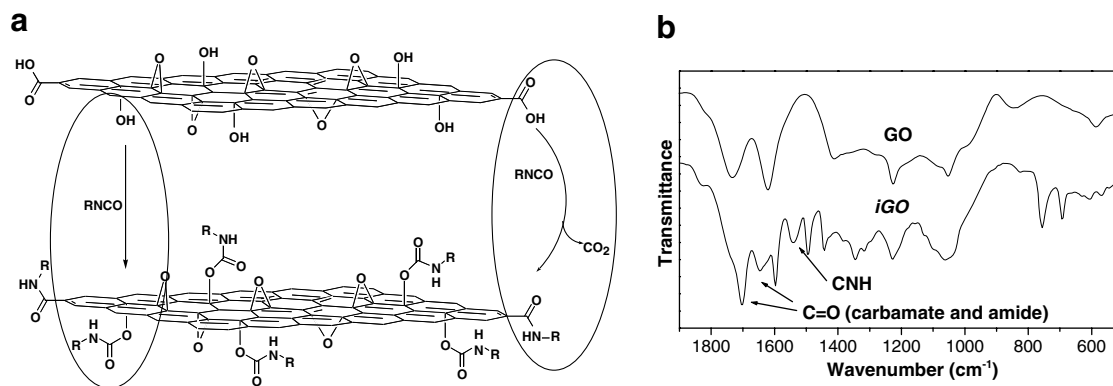


Fig. 2. (a) Proposed reactions during the isocyanate treatment of GO where organic isocyanates react with the hydroxyl (left oval) and carboxyl groups (right oval) of graphene oxide sheets to form carbamate and amide functionalities, respectively. (b) FT-IR spectra of GO and phenyl isocyanate-treated GO.

unit for every 7.6 graphene carbons (Table 1, entry 6). Under the same conditions, exposure to phenyl isocyanate affords a graphene carbon/carbamate ratio of 15.7. However, prolonged treatment can lead to further functionalization with one carbamate unit incorporated for every 8.7 graphene carbons. This chemistry is quite general for a variety of isocyanates, including those containing reactive functionalities (Table 1, entries 5–7). Hence, isocyanate treatment can be used to engender a plethora of functional groups on GO nanoplatelets, not only for tailoring surface properties, but also for further chemical modifications. As such, *i*GOs that have been functionalized with carbonyl, cyano, and azidosulfonyl groups (Table 1, entries 5–7) can be used for the covalent linking of GO nanoplatelets to a variety of materials containing complementary reactive functional groups to afford new nanostructures.

In the case of phenyl isocyanates possessing a second reactive functional group that can also react with the surface hydroxyls, crosslinking of the adjacent GO layers occurs and the corresponding *i*GO derivatives do not exfoliate well. For instance, GO treated with phenyl isocyanates bearing *p*-chloromethyl or *p*-chlorosulfonyl functional groups did not exfoliate at all. In addition, the exfoliated *i*GO obtained by using 4-isocyanatophenyl isothiocyanate would gradually, over several weeks, precipitate. An isolated sample of 4-isocyanatophenyl isothiocyanate-treated GO would eventually lose its ability to be re-dispersed in DMF. Although isothiocyanates react with hydroxyl groups much slower than isocyanates [21], interlayer crosslinking occurs over time, even in the solid state and re-dispersion is prevented.

As the functionalization degree of GO can be controlled via either the reactivity of the isocyanate or the reaction time, it should be possible to prepare graphene oxide nanoplatelets with partial isocyanate functionalization and then subject them to a second chemical treatment to functionalize the remaining hydroxyls. In this way, graphene oxide nanoplatelets with two or more different surface functionalities can be readily accessed. For instance, reaction of GO that has been partially functionalized with phenyl isocyanate (1 carbamate unit/15.7 graphene carbons) with an

excess of 4-cyanophenyl isothiocyanate for 24 h results in further functionalization of the remaining hydroxyls and incorporation of the nitrile functionalities on the surface of the nanoplatelets as was evident by FT-IR (see ESI). Based on elemental analysis, one cyanide-functionalized carbamate unit was incorporated for every 23.3 graphene carbons, bringing the overall functionalization degree to 9.4.

The level of exfoliation of *i*GO in DMF, chosen for its lowest boiling point among the polar aprotic solvents that form a stable dispersion with *i*GO (*vide supra*), was evaluated using AFM in a non-contact mode. In all cases, the corresponding AFM images show that *i*GO samples underwent complete exfoliation in DMF and that the dispersions contain platelets that are ~ 1 -nm thick almost exclusively (Fig. 3 shows the example of phenyl isocyanate-treated GO; several other *i*GO specimens were also analyzed by AFM, exhibiting platelets that are uniformly ~ 1 -nm thick). This observed thickness of exfoliated *i*GO platelets in DMF is essentially the same as the thickness observed by us for GO platelets exfoliated in water [14], suggesting that while the isocyanate treatment of GO leads to chemical functionalization of the surface of the platelets (*vide supra*), it results in no increase in their thickness detectable by AFM. This is consistent with the incomplete functionalization of the graphene carbon sites (for the *p*-acetylphenyl isocyanate-functionalized platelets, which has the highest degree of functionalization (Table 1, entry 6), there is one amide or carbamate moiety per every four graphene rings). Such isolated subnanometer features on the platelet surface are unlikely to be detected in a routine AFM experiment, especially since the GO platelets can also contain adsorbed solvent molecules on their surface. While the pristine graphene sheet is flat with a well-known van der Waals thickness of ~ 0.34 nm, the graphene oxide sheets are expected to be thicker due to the presence of covalently bound oxygen and the displacement of the sp^3 -hybridized carbon atoms slightly above and below the original graphene plane. From XRD experiments, the intersheet distance for graphite oxide varies with the amount of adsorbed water, with values such as 0.63 nm [19] and 0.61 nm [20]

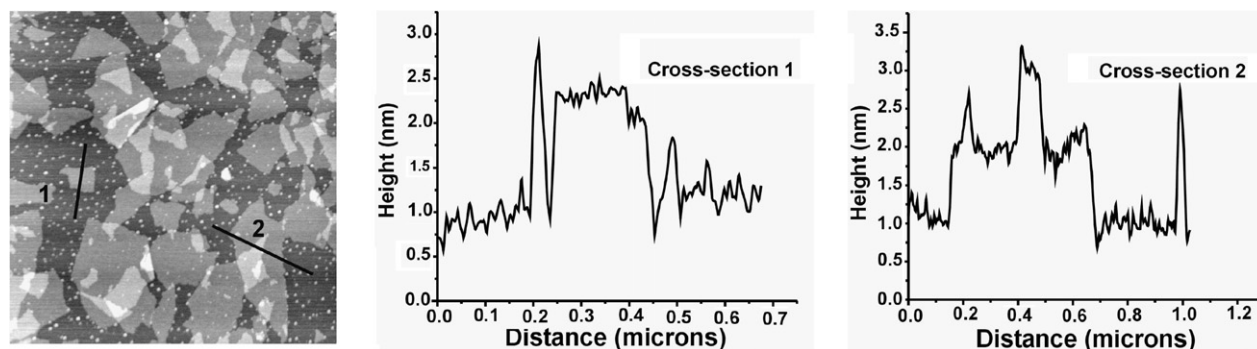


Fig. 3. A non-contact AFM image of nanoplatelets deposited on a mica surface from a dispersion of phenyl isocyanate-treated GO in DMF (left) with height profiles (middle and right). The small dot-like structures on the surface of the mica substrate are attributed to particles of inorganic salts that are leftovers from the preparation of GO.

reported for “dry” GO samples (complete drying of GO is probably impossible [5]) to 1.2 nm for hydrated GO [20]. If these values represent the “thickness” of an individual GO layer, given that all platelets in our *i*GO materials observed by AFM are of the same thickness (~ 1 nm) and that either thicker or thinner platelets are never detected, we believe that these represent fully exfoliated, chemically functionalized graphene oxide sheets. The slightly larger 1-nm thickness value that we observe by AFM compared to the [0.6–1.2 nm] range of thicknesses from published XRD experiments could perhaps arise from physisorption of species (such as water and solvent molecules) onto the platelet surface, as noted above. Based on our AFM data, our nanoplatelets appear to be highly varied in both shapes and sizes.

We also employed dynamic light scattering (DLS) to obtain a rough measure of the lateral size distributions in the exfoliated samples of phenyl isocyanate-treated GO (*pi*GO, Fig. 4). As this analysis assumes spherical shapes and our *pi*GO platelets are more accurately described as 2-D objects, the average platelet diameter that we report from DLS (560 ± 60 nm with a polydispersity index of 0.80 ± 0.14) is not their average dimension but rather the effective hydrodynamic diameter of an equivalent sphere described by the tumbling of the platelets [26]. Additionally, even though our *pi*GO platelets appear rigid when deposited on an atomically flat surface (for the AFM experiment), in reality they are highly pliant sheets that easily conform to any features on that surface. As such, their exact morphology in solution is not known. Nevertheless, one can still infer that the size distribution of our *pi*GO platelets as being highly polydisperse, consistent with the AFM data.

The formation of carbamate esters upon treatment of GO with isocyanates removes the ability of the surface hydroxyls and edge carboxyl groups to engage in hydrogen

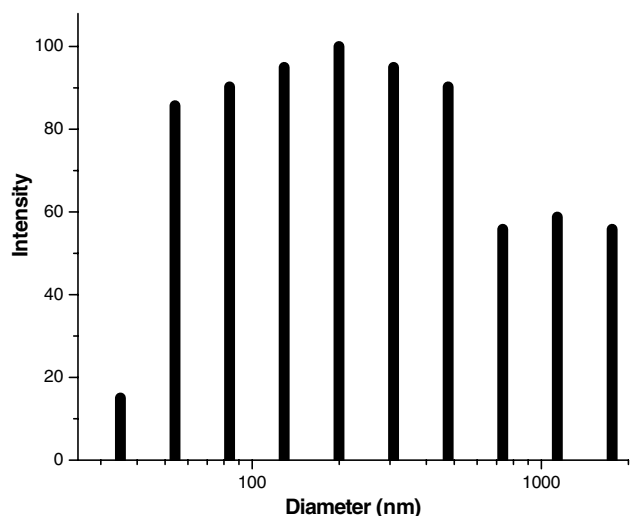


Fig. 4. CONTIN analysis showing the intensity-weighted hydrodynamic diameter distribution of phenyl isocyanate-treated GO nanoplatelets exfoliated in DMF.

bonding, thus rendering graphene oxide sheets less hydrophilic and hence more compatible with the polar aprotic solvents than with water. Noteworthy is the fact that exfoliation of *i*GO in polar aprotic solvents does not require complete derivatization of all the surface hydroxyls in GO. Even *i*GOs with a lower degree of functionalization (such as the *tert*-butyl isocyanate-treated GO) exfoliate easily in polar aprotic solvents. In addition to a decrease in the density of surface hydroxyl groups, the addition of hydrocarbon substituents via isocyanate treatment weakens the hydrogen bonding between adjacent layers in GO, thus allowing for their exfoliation in polar aprotic solvents. As expected, the functionalization of GO with hydrocarbon-containing isocyanate leads to an increased surface hydrophobicity in the resulting *i*GOs, reduces the hydration of the remaining hydroxyl groups, and prevents the exfoliation of the *i*GO sheets in water.

4. Conclusion

In conclusion, we have demonstrated that treatment of GO with organic isocyanates results in a new class of *i*GO materials possessing reduced hydrophilic properties which can be exfoliated in polar aprotic solvents to yield derivatized graphene oxide nanoplatelets. To the best of our knowledge this is the first demonstrated example of complete exfoliation of chemically derivatized graphite oxide in organic solvents. In addition, the use of isocyanates containing orthogonal functionalities such as cyano, keto, and azidosulfonyl allows for further modification of the surface properties and chemistry of *i*GO.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.carbon.2006.06.004](https://doi.org/10.1016/j.carbon.2006.06.004).

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