Carbon 105 (2016) 607–614

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Covalently grafted TEMPO on graphene oxide: A composite material for selective oxidations of alcohols

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ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form
28 April 2016
Accepted 2 May 2016
Available online 3 May 2016

ABSTRACT

4-Amino-TEMPO, a stable nitroxide free radical, was covalently grafted onto graphene oxides through an amide bond and the new composite solid materials thus obtained were characterized using scanning electron microscopy, thermal and elemental analysis, infrared, Raman and electron spin resonance spectroscopy. It was found that these materials can be successfully used as easily recoverable solid catalysts for selective oxidation of alcohols, using NO_x as co-catalyst and oxygen as final oxidant, under very mild conditions.

1. Introduction

Carbon is a naturally occurring element found in large quantities on the Earth and having a tremendous importance for human society, due to its major role as a fuel. Allotropes of carbon (graphite, diamond) also have significant technical applications; more unusual forms of carbon (fullerenes, nanotubes, graphene) have recently found astonishing use in the state-of-the-art technologies [1–3].

Carbon-based materials are cheap and available in large quantities, and can be used in electronics and energy conversion and storage [4]; in addition, they can be easily functionalized to be employed in more specific applications. Chemically modified carbon-based materials have the potential to be used on an industrial scale [5,6].

Graphite (G), although inexpensive and readily available, as a natural or artificial material, does not easily exfoliate to monolayer graphene sheets; in contrast, graphite oxide, simply obtained through oxidation of graphite (and therefore containing abundant oxygen-based groups) can be exfoliated to graphene oxide (GO) nanosheets using different means, including ultrasonic devices [7]. Although interest in studying GO started in 1859 with B. C. Brodie [8], the Hummers method [9] published in 1958 can be considered as a milestone in obtaining GO and is one of the most used today. The improved method reported recently by J. M. Tour [10] has a simpler protocol, other major advantages being the higher yield and the absence of any toxic gas evolution during synthesis.

GO is the practical precursor of graphene (reduced GO, rGO); both of them are known as functional materials with many possible applications. GO is in fact highly oxidized graphite which is exfoliated into sheets containing functionalities such as hydroxy, epoxide, carbonyl and carboxyl groups; these hydrophilic groups make GO dispersible in highly polar solvents (water, DMF). Moreover, these oxygen-containing groups facilitate exfoliation, and more importantly, ensure the possibility of covalent functionalization with organic molecules. Because the graphene layer can be regarded also as a polyaromatic composition, a large number of physical interactions with organic molecules, such as π–π stacking, are possible.

There are many reproducible methods to functionalize GO, and these can be mainly divided into covalent and non-covalent functionalization. Covalent functionalization takes advantages of the carbon surface chemistry; for example, carboxyl and hydroxyl groups can be easily derivatized using standard chemistry (i.e. with porphyrins [11], ferrocene [12], and polymers [13]). In addition, another route is the use of aryl diazonium salts, which can also be tailored by organic chemistry [14,15]. Non-covalent functionalization is based, as mentioned before, on π–π stacking, ionic, cation-π or van der Waals interactions [16].

Such functionalized GO has new properties (which can be

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http://dx.doi.org/10.1016/j.carbon.2016.05.006
0008-6223/

chemically tuned) and has therefore found new and interesting applications, from electrochemical energy conversion and storage to robust and highly selective carbocatalysts [17].

One of the most important organic chemistry reactions is the selective oxidation of alcohols to aldehydes or ketones. Such a process usually requires a difficult management of the reaction conditions, as transition metal species are involved in at least equimolecular quantities and the resulting toxic waste is hard to process. Novel systems involve more gentle (air, oxygen, hydrogen peroxide, etc.) or non-conventional (carbon-based materials, stable free radicals, etc.) oxidants, with certain and large advantages: clean reactions, mild working conditions, recovery and re-use of the catalyst, less or no toxic by-products, and so on [18–24].

Many catalytic processes involve metals or metal ions with high toxicity, therefore the finding of a new benign catalyst represents itself as an important goal. Organic stable free radicals of nitroxide type (or their functionalized materials) are nowadays a good practical choice for reliable, green and clean synthesis of carbonylic compounds obtained *via* oxidation of alcohols [20,25,26].

The stable free organic radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) can be involved in redox processes as it can be readily oxidized to the oxoammonium salt or reduced to the corresponding hydroxylamine. TEMPO can be grafted onto inert materials in order to exploit its redox properties in catalytic processes. In the literature, there are a very few papers describing GO functionalized with TEMPO moieties: *i*) coupling the HO group from 4-hydroxy-TEMPO with the activated COOH group of GO [27], *ii*) using a malonyl derivative of 4-hydroxy-TEMPO (following the Bingel–Hirsch reaction) [28] or *iii*) using the oxoammonium salt of TEMPO [29] (which in fact is not a free radical). None of those have been used in the catalytic selective oxidation of alcohols.

In this work, we covalently bound 4-amino-TEMPO to GO, using standard amide bond formation in two steps. The first step refers to the activation of COOH groups from GO by transforming them into the corresponding acid chloride COCl. The second step is represented by the reaction of COCl with 4-amino-TEMPO (Fig. 1). The choice of this method is justified by the highest yield of coupling, as is also shown in the literature [27] and by the higher stability of the amide group. Amides are much more stable than esters (which can easily hydrolyze under basic conditions); moreover, epoxide groups from GO can also react with 4-amino-TEMPO, resulting in a highly functionalized GO.

All of the materials thus obtained were first characterized by elemental analysis, infrared (IR), electron spin resonance (ESR) and Raman spectroscopy, thermo-gravimetric analysis (TGA) and scanning electron microscopy (SEM), and further tested as heterogeneous catalysts in selective oxidation of alcohols.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were purchased from Sigma–Aldrich or Chimopar and used as received. Synthetic graphite powder (size less than 20 μm) has been used as starting material. IR spectra were recorded on a Jasco FTIR 4100 apparatus (KBr discs). ESR spectra were recorded on a Jeol JES FA100 apparatus using the following typical settings: frequency 8.99 GHz, field 3330 G, sweep width 100–200 G, sweep time 60–120 s, time constant 30 ms, gain 50–500, modulation frequency 100 kHz, modulation width 1 G, using 1 mm inner diameter plain glass tubes). Raman spectra were measured in a Horiba Jobin-Yvon LabRam spectrometer. Measurements were carried out in the backscattering geometry, at room temperature, with a 50× microscope objective, in the range from 50 to 2000 cm^{-1}, with acquisition times of 60 s; using as excitation source the green line ($\lambda = 514.5$ nm) of an Ar^+ laser, with a power of ~20 mW, the laser spot size was ~1–2 μm. Thermal measurements were performed on a Netzsch STA 449 F1 Jupiter Simultaneous Thermal Analyzer apparatus in dynamic argon atmosphere, with a heating rate of 5 °C min^{-1}. NMR spectra were recorded on a Bruker Fourier apparatus at 300 MHz using $CDCl_3$ as solvent (isotopic purity 99.9%) and TMS as internal standard. Specific surface areas were measured by N_2 adsorption–desorption at −196 °C using an automatic adsorption system (Micromeritics ASAP 2020). The surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on adsorption data in the partial pressure (P/Po) range of 0.05–0.3. Before analysis, the samples were degassed for 12 h at 100 °C under vacuum. Microstructural studies were carried out by Field Emission (FE) Scanning Electron Microscopy (SEM) in a Dual Beam 3D FEG FEI. Secondary electron images were recorded at accelerating voltages between 1.2 and 2 kV. Elemental analysis measurements by Energy Dispersive X-ray (EDX) spectroscopy were carried out in the same apparatus, operating at an accelerating voltage of 20 kV. Elemental analysis was performed on a CHN Perkin Elmer 2400 apparatus.

2.2. Synthesis of GO/iGO

Two methods for obtaining graphene oxides were followed [9,10], with slight modifications, as follows: *i*) Hummers methods (GO): to a mixture formed by 1 g of graphite and 0.5 g of sodium nitrate was slowly added under stirring 25 mL of cold concentrated sulfuric acid, using also an external cooling of the reaction mixture with ice, then 3 g of potassium permanganate was added in portions and the resulting mixture stirred for about half an hour, then

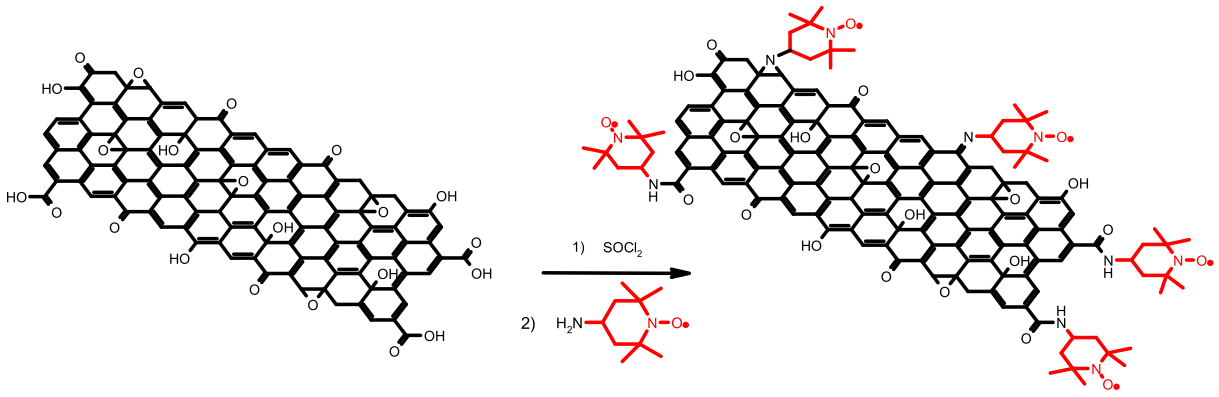

Fig. 1. Representation of TEMPO functionalization of GO. (A colour version of this figure can be viewed online.)