New hybrid functional materials based on carbon: synthesis, characterization and study of properties
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2016

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 1

Introduction

“It doesn’t matter how beautiful your theory is, it doesn’t matter how smart you are. If it doesn’t agree with experiment, it’s wrong”

Richard P. Feynman, American physicist

1.1 Motivation

This thesis constitutes a part of my research project which has been focused on the synthesis of novel hybrid systems based on carbon (including graphene, carbon nanodiscs and fullerene derivatives), the characterization of these systems and in some cases the proof-of-principle experiments to validate their potential for certain bioapplications (drug delivery, cytotoxic agents, enzyme supports).

1.2 Carbon allotropes

Until 1985, six crystalline allotropes of carbon structures were known: the alpha and beta graphite, diamond, a rare hexagonal structure of the diamond, chaoite and carbon (IV).[1] Diamond is composed of carbon atoms with sp³ hybridization, creating equivalent rigid and durable bonds. Diamond is stable up to 1800 °C but if heated to higher temperature it converts because the sp² bonded state is energetically favorable.[1] It is the hardest of all known materials and has excellent photoelasticity. Diamond cannot be melted and converts into carbon dioxide when it burns. The graphite consists of sp²-bonded carbon atoms. The bonds between the atoms in the planes are strong and rigid, causing the material to remain solid state up to 3300 °C.[1] It cannot be affected
by the acids and is a good conductor of heat and electricity.\textsuperscript{[2]} Chaoite or white carbon is a mineral whose existence was questioned. Discovered in Bavaria, it is slightly harder than graphite.\textsuperscript{[3]}

In 1985, during the laser ablation of graphite, under certain conditions, a new allotropic carbon structure was created, called fullerene. A fullerene molecule is composed of a network of pentagons and hexagons forming a spherical or rugbyball-like molecule.\textsuperscript{[4]} In 1991, in the course of investigations of fullerenes, the carbon nanotubes were discovered. The carbon nanotubes are sheets of carbon arranged in a honeycomb lattice, rolled-up to form single (single-walled carbon nanotubes) or concentric tubes (multiwalled carbon nanotubes), which are closed at the edges by half a fullerene.\textsuperscript{[5]}

Graphene is a two-dimensional hexagonal arrangement of carbon atoms, the same structure which forms the wall of the carbon nanotube. In 2004, Konstantin Novoselov and Andre Geim, accomplished to isolate both few-layer and monolayer graphene using the “Scotch tape” technique (micromechanical cleavage of graphite). The structure of the layer consists of two equivalent sublattices of carbon atoms, which form hexagonal rings. In few layer graphene, the stacking of graphitic layers takes place in such a way that half the carbon atoms are above the centres of the hexagons of the underlying ones, just as in the pyrolytic graphite.\textsuperscript{[6]} All these allotropes of carbon are shown in Figure 1.

\textbf{Figure 1}: a) Diamond, b) Graphite, c) Chaoite or White Carbon, d) Fullerene, e) Carbon Nanotubes (single- and multi-walled), f) Graphene.
1.3 Fullerenes

Let us consider more in detail the 3rd allotropic form of carbon for the discovery of which the Nobel Prize of Chemistry was awarded in 1996.[1, 7] The most stable fullerene is C$_{60}$ in which 60 carbon atoms are arranged in the form of a football as shown in Figure 2. Its name pays homage the architect Buckminster Fuller who planned domes with similar structure. In 1990 Krätschmer and Huffmann in Germany developed a technique for producing macroscopic quantities of fullerenes. This technique will be described below.[8]

Fullerenes are created in flames and discharges but their late discovery is due to the fact that they are unstable in the presence of air and light because the photoexcited state of fullerenes very easily reacts with oxygen. The creation of fullerenes is not limited to the earth; in 1969, in Mexico, samples were taken from the meteorite Allende and their analysis proved that they had structure of fullerenes.[9]

Like all fullerenes, C$_{60}$ contains an even number of carbon atoms (arranged in 20 hexagons and 12 pentagons). The structure of C$_{60}$ presents two types of bonds: (i) bonds between carbons which are part of a pentagon and the adjacent hexagon (5,6); (ii) bonds which are common to two adjacent hexagons, which have one shorter length and can be regarded as double bonds (6,6). In fullerenes carbon presents sp$^2$ hybridization with a slight mixing with sp$^3$ hybrid orbitals to induce curvature.[10]

C$_{60}$ and C$_{70}$ present similar electrochemical behaviour and their oxidation is irreversible. Generally, being electrophilic molecules, fullerenes create salts with general form [D]$^+$ [C$_{60}$]$^-$.[11] Fullerides are created by the reaction of C$_{60}$ with metallic ions; several of these compounds have excellent superconductive properties.[12] The fullerenes can participate in addition reactions as well behave more as alkenes due to the existence of the double bonds in the molecule (30 double bonds). Finally, great interest present the reactions of fullerenes with free radicals [C$_{60}$R]'[13]
From their discovery until today fullerenes and their derivatives have been extensively studied concerning their chemical reactivity. Due to their great electronegativity they show a high reactivity towards organic radicals. During the chemical functionalization of fullerenes with electron-releasing groups, the electronegativity of the derivatives is significantly reduced. This decrease is due to reduction of the chemical response as a result of the radicals’ adding. Fullerenes can not only be functionalized by grafting groups to their outer surface, they can also be filled with one or more atoms or even small groups – these compounds are called endohedral fullerenes; carbon atoms of the cage structure can be replaced, for example by nitrogen, giving rise to heterofullerenes, and open-cage structures can be formed. However exohedral fullerenes constitute the greatest category of fullerene derivatives.[14]

In this thesis the fullerenes were functionalized through various chemical reactions (oxidation, bromination, hydroxylation and neutralization) in order to create derivatives with excellent conductive properties.

### 1.3.1 Addition reactions of fullerenes

C$_{60}$ fullerenes can be easily functionalized due to their high reactivity; a scheme of the various possibilities is presented in Figure 2. The exohedral addition reactions constitute the most important methods in order to chemical transform the fullerene cage. There are many different types of reactions that have been investigated up to now, such as reduction, nucleophilic and radical addition, hydrogenation, transition metal complex formation, cycloadditions, oxidation and reaction with electrophiles, namely oxygenation, osmylation, halogenation and reactions with strong oxidizing reagents and acids.

Particularly important is the case of halogenation. Using various procedures polyhalogenated derivatives of fullerenes, denoted as C$_{60}$X$_n$ (X: F, Cl, Br), can be produced. There are two different methods to synthesize fluorinated derivatives of C$_{60}$, either by the treatment of dichloromethane solutions with
XeF$_2$ or allowing Fluorine gas at low pressure. The chlorination procedure of C$_{60}$, which results in the decoration of the cage with different numbers of chlorine atoms, can be achieved by the treatment of solid C$_{60}$ with liquid chlorine at -35 °C or by allowing a slow gas stream of chlorine gas to react with C$_{60}$ in a hot glass tube at temperatures between 250-400 °C. Until today, three brominated derivatives of fullerenes have been reported extensively, C$_{60}$Br$_n$ (n: 24, 8, 6). The functionalization with 24 bromine atoms takes place between the C$_{60}$ and liquid bromine whereas the C$_{60}$Br$_8$ and C$_{60}$Br$_6$ occur by the treatment in CS$_2$ and benzene or CCl$_4$ respectively.[15]

**Figure 2:** Schematic representation of fullerene chemical reactions. [Review: Journal of Nanomaterials 2015(4), August 2015, DOI: 10.1155/2015/567073]
1.3.2 Bromofullerenes and fullerols

Bromofullerenes or poly-brominated fullerenes (C\(_{60}\)Br\(_n\)) constitute a category of halogenated derivatives of fullerenes, which are produced via the mechanism of addition nucleophilic reactions. The bromination of fullerenes can be achieved either by dissolving in organic solvent or by treatment with neat bromide. In literature three fullerenes bromides with different bromine atoms, C\(_{60}\)Br\(_6\), C\(_{60}\)Br\(_8\) and C\(_{60}\)Br\(_{24}\), whose structure has been determined by diffraction methods, are widely reported. Djordjevic et al.\(^{[16]}\) synthesized C\(_{60}\)Br\(_{24}\) through the reaction between C\(_{60}\) and elementary bromine in the presence of the catalytic quantities of FeBr\(_3\). Birkett et al.\(^{[17]}\) used tetrachloride or benzene in order to obtain C\(_{60}\)Br\(_6\). In the case of C\(_{60}\)Br\(_8\), during the synthetic procedure carbon disulfide or chloroform was applied as reaction medium. On the contrary, Scharff and co-workers\(^{[18]}\) synthesized C\(_{60}\)Br\(_6\) using carbon disulfide and prepared C\(_{60}\)Br\(_8\) in tetrachloride solution.

The fullerols are poly-hydroxylated derivatives of fullerenes; namely each C\(_{60}\) molecule displays multiple hydroxyl groups (-OH) are attached on its surface, as shown in Figure 3. The chemical formula of fullerols is C\(_{60}\)(OH)\(_n\). The “n” represents the number of oxidized or hydroxylated carbon atoms in the fullerol molecule. There are numerous techniques for the synthesis of hydroxylated fullerenes and each one of them can produce a molecule with unique properties. Some of the most common procedures for fullerol production are described below:

- Oxidation under strong oxidation conditions\(^{[19]}\)
- Oxidation under strong alkaline or basic conditions\(^{[20]}\)
- Reaction of C\(_{60}\)^{\(n\)} lithium salt with the acidified methanol/water solution in the presence of oxygen\(^{[21]}\)
- Substitution of bromine atoms with hydroxyl groups in alkaline environment (pH = 13)\(^{[22]}\)

Figure 3: Structure representations of poly-hydroxylated fullerenes, with chemical formula $C_{60}(OH)_n$. The “n” represents the number of hydroxylated carbon atoms: (a) $C_{60}(OH)_2$, (b) $C_{60}(OH)_{12}$, (c) $C_{60}(OH)_{24}$, (d) $C_{60}(OH)_{36}$.

(http://prmarcoux.free.fr/Fullerols_3D.htm)

1.4 Graphite oxide

Graphite oxide (also known in the last decade as graphene oxide) is a layered material, which is produced by the oxidation of graphite[23] and contains a significant quantity of oxygen in the form of functional groups on the surface of the sheets. Functional groups like OH, COOH and C-O-C impart hydrophilicity to graphite oxide, rendering it dispersible in water and other polar organic solvents.[24] Graphite appears with various morphologies but the most common for the enhanced oxidation is that of «graphite flake», which contains a large number of defects that assist the oxidation process. The oxidation of graphite was described in 1840 by C. Schathaeutl[25], who was
studying the behaviour of different metals, mainly iron and cast iron. In his philosophical study he indicates that graphite in contact with strong sulfuric acid changes colour and becomes brown.

The graphite oxide was synthesized for the first time at 1859 by B.C. Brodie\cite{23b}, who studied the structure of graphite. He reported a mass increase of the initial material after oxidation with fuming acid \( \text{(HNO}_3 \text{)} \) and potassium chlorate \( \text{(KClO}_3 \text{)} \); the reaction time was 3-4 days at 60 °C. After four successive chemical treatments the ratio \( \text{C:H:O} \) was determined to be equal to 61.04:1.85:37.11, which corresponds to an atomic ratio of \( \text{C:O} \) of \( \sim 2.1 \). This material with chemical formula \( \text{C}_{2.19}\text{H}_{0.80}\text{O}_{1.00} \) could be dispersed in water or basic solution but not in acid media. After thermal treatment at 220 °C, the ratio \( \text{C:H:O} \) altered to 80.13:0.58 :19.29 with the following chemical formula \( \text{C}_{5.51}\text{H}_{0.48}\text{O}_{1.00} \). Forty years later, in 1899, L. Staudermaier\cite{23c}, improved the Brodie method, using a mixture of sulfuric and nitric acid \( \text{(H}_2\text{SO}_4 / \text{HNO}_3) \) in a ratio of ratio 2:1 v/v, achieving the oxidation in a single step while maintaining the atomic ratio of \( \text{C:O} \sim 2.1 \). In 1858, Hummers and Offeman\cite{23a} developed an alternative oxidation procedure of graphite using potassium permanganate \( \text{(KMnO}_4 \text{)} \), sodium nitrate \( \text{(NaNO}_3 \text{)} \) and concentrated sulfuric acid \( \text{(H}_2\text{SO}_4) \). This procedure required less than 2 hours and low temperatures (> 45°C).

For many years, the exact chemical structure of graphite oxide was the subject of studies. Until now there is not an undeniable structural mode, for example due to the complexity and non-stoichiometric composition of the samples. Nevertheless, there have been significant studies with great success.

Hofmann and Hols\cite{26} were the first who suggested a structural model of graphite oxide which presents epoxy groups onto the graphite sheets. A variation of this model was proposed in 1946 by Ruess\cite{27}, in which hydroxyl groups are placed along the graphite oxide sheets. Using this model, the percentage of hydrogen can be successfully confirmed, according to the elemental analysis. Comparing the two models it is observed that the Ruess model includes sp\(^3\) hybridized carbon while the previous model is constituted
by only sp² carbon atoms. In 1969, Scholz and Boehm \cite{28} suggested a model with ketone- and hydroxyl-groups, inducing changes to the graphitic lattice. Once more model was presented in 1994 by Nakajima and Matsuo \cite{29}. Lerf and Klinowski \cite{30} have published papers about the structure of graphite oxide using the Nuclear Magnetic Resonance Spectroscopy (NMR). In this model there are hydroxyl-, epoxy- and carboxyl- groups onto and at the edges of the sheet, as well as defects which are occurred by the oxidation process. These researchers proposed a slightly variant model, which is the most prevalent, in which the epoxy- and hydroxyl- groups are located along each sheet and the carboxyl-groups are created only at the edges of the material sheet. In conclusion, the graphite oxide is a derivative of the graphite, containing oxygen groups (hydroxy, epoxy and carboxyl groups) which are covalently attached onto the surface, while the material retaining the laminate structure with a larger interlamellar space than the initial graphite due to the presence of water molecules between the sheets.

Figure 4: Schematic representation of certain models that has been proposed for the structure of Graphite oxide.
In this thesis, graphite and carbon nanodics were functionalized via chemical oxidation reactions in order to obtain graphite oxide and oxidized carbon nanodiscs. The further modification of graphite oxide led to the creation of two new graphite oxide derivatives, sulfonated and carboxylated graphite oxide.

1.5 Outline of the thesis

This thesis is organized in six chapters. The chapters are presented in more detail below.

Chapter 2 describes all the techniques, which were used for the characterization of the initial and the hybrid functional materials. Moreover, the synthesis and the functionalization procedures of each nanomaterial are detailed.

Chapter 3 presents our mini-review article entitled “Non-covalent Interactions of Graphene with Polycyclic Aromatic Hydrocarbons” which gives an overview of the interactions of PAHs with graphene and graphene-based materials. We describe the methods to prepare these materials and their potential for applications (electrical, biomedical, polymer reinforcement applications). Finally, we discuss environmental remediation issues specifically the use of graphene to remove the polycyclic aromatic compounds.

Chapter 4 concerns a novel, facile, versatile and reproducible approach, based on Staudenmaier method, for the chemical oxidation of fullerenes. This method leads to the creation of functional oxygen groups on the surface of fullerenes rendering them dispersible in polar solvents (e.g. water). Due to the presence of epoxy groups, the oxidized fullerenes can be further functionalized via nucleophilic substitution reactions in order to generate new fullerene derivatives, which are ideal to be applied in many applications in medicine, biology and as composite materials.
In Chapter 5 we describe the chemical oxidation of carbon nanodiscs via a simple, versatile and reproducible approach, which is based on the well-known Staudenmaier method. As a result of this oxidation procedure the carbon nanodiscs become hydrophilic due to the creation of various oxygen functional groups on their surface. The obtained material can be applied in many fields including bioapplications.

Chapter 6 focuses on graphite oxide and its derivatives as efficient drug delivery system. In the last years drug delivery systems based on nanomaterials present great interest in the field of biomedical applications. Especially graphite oxide is considered especially promising in this context due to its properties. In this PhD project we studied the release of Ibuprofen, an anti-inflammatory drug, in simulated gastric and intestinal fluid (Sigma-Aldrich), using three materials as carriers, graphite oxide and two of its derivatives, namely sulfonated and carboxylated graphene oxide.

Chapter 7 is devoted to our four published articles entitled “Hopping Conductivity and Polarization Effects in a Fullerene Derivative Salt”, “Ultraslow Dynamics of Water in Organic Molecular Solids”, “Variable-range electron hopping, conductivity cross-over and space-charge relaxation in C_{60}Br_6” and “Water-Triggered Conduction Mediated by Proton Exchange in a Hygroscopic Fulleride and Its Hydrate”. Using different reactions the following fullerene derivatives were synthesized: fullerols [C_{60}(OH)_{24}], polybrominated fullerenes (C_{60}Br_6) and sodium oxofulleride [C_{60}(ONa)_{24}] and their conductivity properties were studied extensively.
References


