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An insight into the functionalisation of carbon nanotubes by diazonium chemistry: Towards a controlled decoration

Patrizio Salice [a], *Enrica Fabris* [b], *Camillo Sartorio* [c], *Davide Fenaroli* [a], *Viviana Figà* [c], *Maria Pia Casaletto* [d], *Sebastiano Cataldo* [c], *Bruno Pignataro* [c,*], *Enzo Menna* [a,b,*]

[a] *Università di Padova, Dipartimento di Scienze Chimiche, via Marzolo, 1, 35131 Padova, Italy*
[b] *Istituto CNR per la Tecnologia delle Membrane (ITM), UOS Padova, Italy*
[c] *Università di Palermo, Dipartimento di Fisica e Chimica, V.le delle Scienze, Parco d'Orleans II, 90128 Palermo, Italy*
[d] *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Consiglio Nazionale delle Ricerche (CNR), via Ugo La Malfa, 153, 90146 Palermo, Italy*

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ABSTRACT

The derivatisation of materials including iron, gold, and carbon by addition of diazonium salts is a reliable process to tune their interfacial interaction with the surrounding media. In this regard, the functionalisation of carbon nanostructures by diazonium chemistry is a versatile strategy to obtain soluble nanomaterials with degrees of functionalisation among the highest ever reported. Starting from these premises we have studied the functionalisation of multi-walled carbon nanotubes by addition of the aryl diazonium salts generated in situ by treatment of 4-methoxyaniline with isopentylnitrite. Following a thorough purification and characterisation protocol (UV–vis, TGA, ATR-IR, cyclic voltammetry, AFM and other surface analytical techniques), we have investigated the key parameters to obtain both functionalised multi-walled carbon nanotubes, where the amount of functional groups anchored to the carbon surface is less than a monolayer, and superfunctionalised carbon nanotubes, with a carbon nanotube core and a multilayered aryl coating. The results outlined provide the basis for the design and controlled processing of novel decorated carbon nanostructures that would be useful for a number of technological applications.

1. Introduction

Aryl radicals obtained from the mono-electronic reduction of diazonium salts can react with the surface of metals, semiconductors and carbon allotropes [1–3], allowing the grafting of molecules or chains with high surface coverage. This reaction is therefore particularly effective to alter the interaction between the functionalised material and the surrounding medium. For example, the diazonium salt of 4-aminodiphenylamine has been grafted on the surface of a carbon electrode through electrochemical reduction, to provide an interface layer that acts as a coupling agent for the electropolymerisation of aniline [4].

* *Corresponding authors*. Address: Università di Padova, Dipartimento di Scienze Chimiche, via Marzolo, 1, 35131 Padova, Italy (E. Menna); Università di Palermo, Dipartimento di Fisica e Chimica, V.le delle Scienze, Parco d'Orleans II, 90128 Palermo, Italy (B. Pignataro).
E-mail addresses: bruno.pignataro@unipa.it (B. Pignataro), enzo.menna@unipd.it (E. Menn).
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Moreover, it has been shown that a large excess of diazonium salt precursors often leads to the growth of aryl layers through aromatic homolytic substitution (or biaryl coupling) on top of the first monolayer [5]. Among other applications, the use of the diazonium functionalisation has been also exploited to enhance the processability of insoluble nanomaterials in liquid media. Carbon nanotubes (CNTs) have in particular benefited from the pioneering work by Tour and coworkers, who largely contributed to the development of simple, affordable, and rapid processes to obtain highly functionalised and soluble nanotubes [6,7]. Indeed, they demonstrated that single-walled carbon nanotubes (SWCNTs) are functionalised by diazonium salts generated in situ upon treatment of different anilines with isopentylnitrite [8], nitrous acid [6,7], and by electrochemical reduction [6].

As reported in Fig. 1, it is accepted that the first step of the addition of diazonium salts to CNTs involves the reductive dissociation of the diazonium salt with loss of N_2 and formation of an aryl radical [9]. This in turn may react with carbon–carbon double bonds along the nanotube walls according to the so called Meerwein arylation [10].

This process yields functionalised CNTs with degree of functionalisation, density of defects and solubility amongst the highest reported in the literature due to the high reactivity of the radical species involved. For example, treatment of SWCNTs dispersed in aqueous SDS solutions with diazonium fluoroborates affords nanotubes with up to one ninth of their carbon atoms linked to an aryl group [11]. As a consequence, the electronic properties of these functionalised nanotubes are severely affected, as witnessed by the disappearance of the Van Hove transitions from UV–vis-NIR absorption spectrum and by a drastic enhancement of the disorder-induced band (D band) in Raman spectrum, compared to the G band (higher D/G ratio). Interestingly, the mechanism of addition starts with the reduction of the diazonium salt by one electron from the valence band of the CNTs, thus the functionalisation occurs preferentially on metallic nanotubes which have a higher density of states around the Fermi level [9]. This notion has provided an interesting tool to selectively alter the properties of metallic tubes and also to separate metallic from semiconducting CNTs [12]. More recently, the chemistry of diazonium salts has been proved to be applicable to different carbon allotropes, including the selective functionalisation of the outer shell of double-walled carbon nanotubes by Martel and coworkers [13] and the chemical modification of graphene nanoribbons [14].

Although a number of works have methodically explored a wide range of applications for this reaction in the field of CNT functionalisation, including CdS quantum dots/CNT hybrids for photovoltaic applications [15], carbon allotropes coated with free radicals [16] and carbon nanostructures covalently functionalized with ethynyl groups [17], much is left to be explored. Since our recent observations that the covalent functionalization of SWCNTs by addition of diazonium salts may lead to products with very different characteristics [18], we have been investigating those chemical parameters that control the decoration of the nanotube surface. In particular, our investigation has explored the possibility to control the transition from functionalised multi-walled carbon nanotubes (f-MWCNTs), where the amount of functional groups anchored to the carbon surface is less than a monolayer, to nanostructured materials with a CNT core and a multilayered aryl coating, hereafter referred to as superfunctionalised carbon nanotubes (sf-CNTs).

2. Experimental

2.1. Materials

All the reagents and solvents were purchased from Sigma–Aldrich and were used as received if not otherwise specified. VCTP membranes with 0.1 μm porosity were bought from Millipore. MWCNTs produced by Arkema were purchased from Sigma–Aldrich (#677248) and were purified according to the following procedure. 304 mg of MWCNTs were weighted on a quartz ampule and annealed under air at 320 °C for 2 h in a quartz furnace. The sample was then dispersed in 250 mL of aqueous HCl (37%) and heated under reflux overnight. The MWCNTs were recovered by filtration on a Millipore membrane (VCTP 0.1 μm), washed with 500 mL of milliQ water and dried under an IR lamp for 2 h obtaining 237 mg of carbon nanotubes (78% yield). After that the sample was annealed under air at 420 °C for 90 min in a quartz furnace. The sample was then dispersed in 250 mL of aqueous HCl (37%) and sonicated in a bath sonicator for 1 h. The MWCNTs were recovered by filtration on a Millipore membrane (VCTP 0.1 μm), washed with 500 mL of milliQ water and dried under an IR lamp for 2 h obtaining 212 mg of carbon nanotubes (89% yield). TGA analysis indicated that the final product contains 0.18% of metal impurities. 4-methoxyaniline was crystallized from aqueous ethanol.

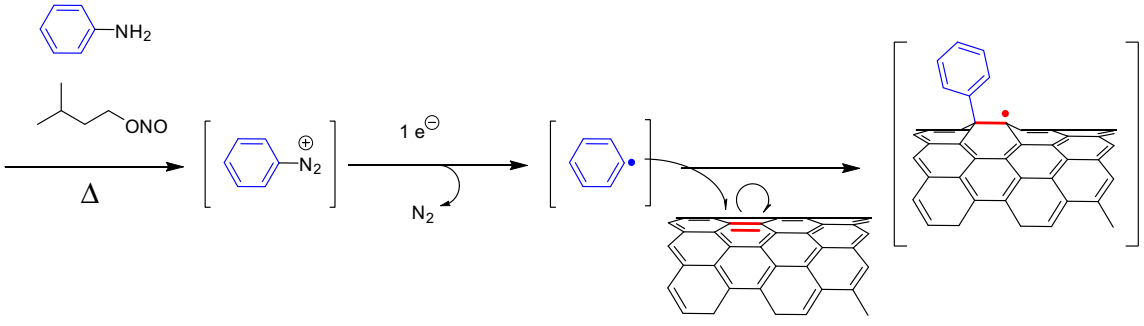

Fig. 1 – First step in the mechanism of functionalisation of CNTs by addition of diazonium salts. (A colour version of this figure can be viewed online.)

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