Applied Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Silylesterification of oxidized multi-wall carbon nanotubes by catalyzed dehydrogenative cross-coupling between carboxylic and hydrosilane functions

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A R T I C L E I N F O

Article history:
Received 10 January 2014
Received in revised form 26 February 2014
Accepted 9 March 2014
Available online xxx

Keywords:
Hydrosilane
Dehydrogenative cross-coupling
Oxidized carbon nanotubes
Solubility tests

A B S T R A C T

Surface modification of oxidized carbon nanotubes (O-CNTs) with silicon based anchoring groups (R-SiR$'_3$) is a relatively uncommon approach of the CNTs functionalization. Hydrosilane derivatives constitute an attractive subclass of compounds for silanization reactions on the CNTs surface.

In this work, we report on the $ZnCl_2$ catalytically controlled reaction (hydrosilane dehydrogenative cross-coupling, DHCC) of fluorinated hydrosilane probes with the carboxylic functions present on the surface of oxidized multi-wall carbon nanotubes. Carbon nanotubes functionalized with essentially alcohol groups are also used to compare the selectivity of zinc chloride toward carboxylic groups.

To assess the efficiency of functionalization, X-ray Photoelectron Spectroscopy is used to determine the qualitative and quantitative composition of the different samples. Solubility tests on the oxidized and silanized MWNTs are also carried out in the framework of the Hansen Solubility Parameters (HSP) theory to apprehend at another scale the effect of DHCC.

1. Introduction

Since their discovery in 1991 by Ijima [1] carbon nanotubes (CNTs) have attracted a great deal of attention. The numerous studies carried out on single-wall (SWNTs) and multi-wall (MWNTs) carbon nanotubes have evidenced unique electrical, mechanical and thermal properties [2,3] that are particularly attractive for a wide range of applications in many fields [4,5]. Presently, one of their major applications is as advanced fillers in polymer composites [6]. However, the difficulty in dispersing CNTs in most aqueous and organic solvents as well as in polymer matrices requires proper surface modifications of the CNTs to achieve their compatibility and dispersion in the polymer host matrices [7]. A major approach to deal with this problem is to covalently functionalize the CNTs. In that respect, oxidation of CNTs (O-CNTs) is probably the most convenient method to modify the CNTs in the laboratory [8–10] as well as at the industrial scale (Nanocyl^{TM} NC3101, MKN-MWCNT-COOH3050, for example). Oxidation creates on the CNTs surface chemical functions (–OH, –COOH, etc.) of direct interest for applications [11,12] or which can be further exploited in a quite large variety of chemical reactions whereby new functions and properties can be imparted to the CNTs surface [13,14].

Surface modification of oxidized carbon nanotubes (O-CNTs) with silicon based anchoring groups (R-SiR$'_3$) is quite significant considering the number of molecules, existing or to create, that could be used in that type of chemistry [15]. The first report is on the reaction of trimethoxysilane (R′ = –OMe) on the carboxylic groups of oxidized carbon nanotubes [16]. More recently, alcohol functions of CNTs have been reacted with triethoxysilane and trimethoxysilane [17,18]. In that spirit, our group has been interested in reacting –OH groups of the MWNTs with chlorosilane derivatives [19,20]. However, if the reaction between –OH functions and chlorosilanes is quite effective and fast, it has two major drawbacks: the formation of hydrochloric acid as byproduct and the fast hydrolysis of the Si—Cl bond which imposes fairly restrictive experimental conditions.

Hydrosilane derivatives constitute an attractive subclass of compounds for silanization reactions on the CNTs surface. They are not only easier to store and handle than their chlorosilane analogs, but also more suitable for chemical reactions under less stringent experimental conditions. In 2006, Hemraj-Benny and Wong have reported the photochemical silylation of raw SWNTs with trimethoxysilane and hexaphenyldisilane [21]. To the best of our knowledge, reacting oxidized CNTs with hydrosilane derivatives

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http://dx.doi.org/10.1016/j.apsusc.2014.03.066

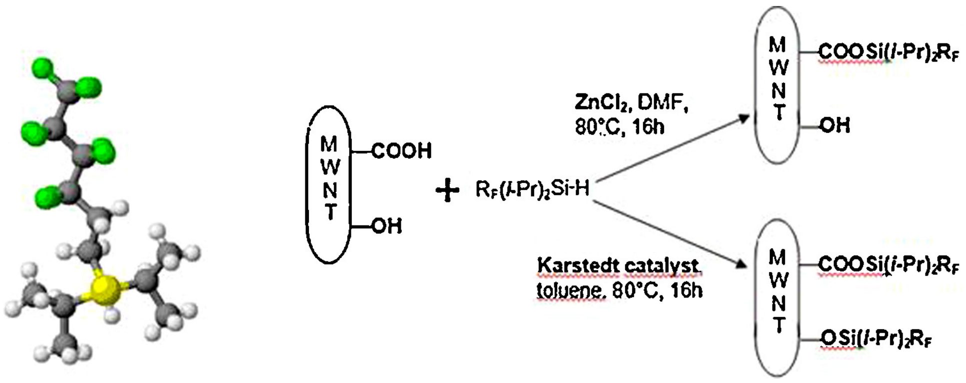

Fig. 1. Molecular structure of the diisopropyl(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silane ($R_F(i\text{-}Pr)_2Si\text{-}H$) and scheme of the reactions considered in this work.

has not been reported while it is a promising alternative to the functionalization of CNTs.

The catalytic coupling of hydrosilanes and oxygenated groups is well known in organic chemistry. Depending on the catalysts, hydrosilanes can react with –OH and –COOH functions simultaneously or selectively. For example, the coupling between –OH groups and hydrosilane can be catalyzed by tris(pentafluorophenyl)borane [22], ruthenium complexes like $[RuCl_2(p\text{-cymene})]_2$ [23] and $Ru_3(CO)_{12}$ [24], etc. The formation of silylesters by reaction between hydrosilane and carboxylic acids is catalyzed by tris(pentafluorophenyl) borane [25], $Pd(OAc)_2$ [26] or zinc chloride [27]. The last reaction, developed by Liu et al., is a selective modification of carboxylic acids using a quite simple and low cost catalyst. Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum (0) complex; hereafter Karstedt catalyst) is essentially used for the hydrosilylation of vinyl compounds [28] even if this catalyst has been reported to form silylethers with alcohols [29].

In this work, we report on the $ZnCl_2$ catalytically controlled reaction of the hydrosilane (–Si—H) function with the –COOH groups present on the surface of oxidized multi-wall carbon nanotubes (O-MWNTs). The probe molecule used is the commercially available monofunctional diisopropyl(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silane ($H(C_3H_7)_2Si(CH_2)_2(CF_2)_4F$) referred to as $R_F(i\text{-}Pr)_2Si\text{-}H$ in the sequel (Fig. 1). This molecule, sterically hindered at the level of the –SiH functional group, is chosen to prevent the formation of networks around the carbon nanotubes which usually form when polyfunctional silanes are involved in silanization reactions [19,20,30] and would slant the results. The fluorinated part serves as XPS marker of the reaction outcome.

The MWNTs used in this work have been synthesized and purified in the laboratory to control the purification step and keep to a minimum the residual amount of catalyst and catalyst support that could interfere with the silanization [31]. $R_F(i\text{-}Pr)_2Si\text{-}H$ is reacted with weakly (O_w-MWNTs), strongly (O_s-MWNTs) oxidized and "reduced" (R_{ed}-MWNTs) MWNTs in presence of the $ZnCl_2$ catalyst. The Karstedt catalyst is also used for comparative purposes.

2. Materials and methods

2.1. Chemicals

Nitric acid (Acros Organics, extra pure, 62% in water), sulfuric acid (Sigma–Aldrich, 95–98 %), diisobutylaluminium hydride (DIBAL-H) (Sigma–Aldrich, 25 wt% in toluene), absolute ethanol (VWR), toluene (VWR), dimethylformamide (DMF) (VWR), diisopropyl(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silane (≥95%, Sigma–Aldrich), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene (Pt ~2%, Sigma–Aldrich) (Karstedt catalyst), zinc chloride (Fluka) were used without further purification. Thin multi-walled carbon nanotubes were synthesized in the laboratory as described below.

2.2. Characterizations

X-ray Photoelectron Spectroscopy (XPS) is used to assess, qualitatively and quantitatively, the composition of the different samples. For the XPS analyses, carbon nanotubes are placed on a special conductive Scotch tape (AGG3939, Agar Scientific). Spectra are collected on a Surface Science SSX-100 spectrometer. The photoelectrons are excited using Al Kα radiation (1486.6 eV), collected at 35° from the surface normal and detected with a hemispherical analyzer. The spot size of the XPS source on the sample is 600 μm and the analyser is operated with a pass energy of 20 eV. During data acquisition pressure is kept below (10^{-9} Torr). The binding energies of the peaks are referenced to the C1s line set at 285.0 eV and the spectra are fitted using a 80%/20% linear combination of Gaussian and Lorentzian profiles. Peak positions obtained after analysis are found essentially constant (±0.3 eV) and typical of those reported in the literature for similar atomic environments [32].

Transmission electron microscopy (TEM) measurements are performed with a Tecnai 10 Philips microscope. Prior to the analyses, the samples are dispersed in ethanol and a drop of the suspension is deposited on a holey carbon-coated copper grid.

Solubility tests on the oxidized and silanized MWNTs are carried out in the framework of the Hansen Solubility Parameters (HSP) theory [33–35] to assess the effect of the various silanization reactions.

2.3. MWNTs synthesis, purification, oxidation, reduction and characterization

Thin multi-walled nanotubes (MWNTs) are synthesized by CCVD reacting ethylene on a Co/Fe catalyst supported on alumina [36]. The synthesis setup is a tubular 5 l quartz reactor (diameter: 72 mm, length: 1240 mm). The gas flows are 2 l/min for N_2 and 4 l/min for ethylene. In a typical experiment, 10 g of catalyst are spread on a quartz nacelle placed in the quartz tube and a purge of 5 min under N_2 is carried out at room temperature. The quartz tube is then introduced into the preheated furnace (700 °C) and the N_2 flow is maintained for 10 min. The catalytic reaction is kept running during 20 min and, at the end, the tube is cooled down to room temperature under nitrogen. After synthesis, 30 g of product are obtained. They contain a mixture of MWNTs, catalyst and support.

The purification step is needed because catalytic residues (alumina and iron or cobalt oxides) can be exposed by the oxidation of the amorphous carbon and the hydrosilanes are known to graft

Please cite this article in press as: J.-F. Seffer, et al., Silylesterification of oxidized multi-wall carbon nanotubes by catalyzed dehydrogenative cross-coupling between carboxylic and hydrosilane functions, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.03.066