J. of Supercritical Fluids 101 (2015) 110–116

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Noble metals supported on carbon nanotubes using supercritical fluids for the preparation of composite materials: A look at the interface

Elsa Garrido[a,b], Cyril Aymonier[a,b,*], Lucian Roiban[c,e,**], Ovidiu Ersen[c], Christine Labrugère[a,b], Patrice Gaillard[d], Mélanie Lamirand-Majimel[a,b]

[a] CNRS, ICMCB, UPR 9048, F-33600 Pessac, France
[b] Univ Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
[c] Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS – Université de Strasbourg, 23 rue du Loess, 67037 Strasbourg Cedex 02, France
[d] Arkema, Groupement de Recherches de Lacq, BP 34, 64170 Lacq, France
[e] Université de Lyon, Insa-Lyon, MATEIS, 7 Avenue Jean-Capelle, 69621 Villeurbanne Cedex, France

ARTICLE INFO

Article history:
Received 11 December 2014
Received in revised form 19 March 2015
Accepted 19 March 2015
Available online 27 March 2015

Keywords:
Carbon nanotubes
Supercritical fluids
Metallic nanoparticles
Deposition

ABSTRACT

Carbon nanotubes (CNTs) have attracted great interest from scientific and industrial communities thanks to their remarkable properties. However, even if their mass production is nowadays well-known, the methods commonly used lead to bundles made of hundreds of single nanotubes with inert surface. Through the description of a simple, rapid and green procedure to uniformly decorate CNTs with metal nanoparticles (Ag, Pd), this paper presents a look at the CNTs-metal interface as a function of the functionalization technique.

Three types of CNTs are considered for deposition: raw CNTs, CNTs functionalized with the reference HNO_3/H_2SO_4 method and CNTs functionalized with our approach using $CO_2/EtOH/H_2O/H_2O_2$ under temperature and pressure. For functionalized CNTs the Pd atoms and CNTs are linked by oxygen atoms and the coating is made of metallic palladium nanoparticles while palladium oxide nanoparticles are formed on raw CNTs, the functionalization having an influence on the nucleation and growth phenomenon. Furthermore the surface treatment of CNTs in acidic solution has a major drawback with CNTs contamination that is why a functionalization with $CO_2/EtOH/H_2O/H_2O_2$ under temperature and pressure is preferred. In addition, electron tomography has shown that the use of supercritical fluids leads to a uniform deposition of metal inside the bundles of CNTs. The orientation relationship between palladium nanoparticles and CNTs has also been determined; the {1 1 1} planes of palladium nanoparticles are parallel to the CNTs graphite planes. The supercritical fluids chemical deposition method appears as an interesting alternative process for the uniform decoration of CNTs with strong interfaces for the preparation of composite materials.

1. Introduction

Since their discovery, carbon nanotubes (CNTs) have attracted much interest from scientific and industrial communities. Thanks to their remarkable physical, mechanical, electrical and chemical properties, carbon nanotubes could find a place in many applications and emerge as potentially attractive materials as reinforcing elements in composites. CNTs-based composites and particularly CNTs-inorganic matrix composites could be used for a wide range of applications (electronics, aeronautics, automotive...) [1–4]. The processing of such materials involves the homogeneous introduction of an inorganic phase at the surface of the CNTs. CNTs have also been considered as new supports for metal catalysts because of their small size, high chemical stability and large surface area [5–8].

Three main techniques are used to synthesize carbon nanotubes: arc discharge, laser ablation and chemical vapour deposition (CVD). Arc discharge technique has been used to synthesize

* Corresponding author at: CNRS, ICMCB, UPR 9048, F-33600 Pessac, France. Tel.: +33 540002672.
** Corresponding author at: Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS – Université de Strasbourg, 23 rue du Loess, 67037 Strasbourg Cedex 02, France. Tel.: +33 472436131.
E-mail addresses: aymonier@icmcb-bordeaux.cnrs.fr (C. Aymonier), lucian.roiban@insa-lyon.fr (L. Roiban).

http://dx.doi.org/10.1016/j.supflu.2015.03.009
0896-8446/

fullerenes for the first time and has been historically used by Ijima [9]. The drawbacks of arc discharge and laser ablation techniques are (1) the low quantities of CNTs obtained because of the size limitations of the carbon source [10] and (2) the formation of byproducts requiring a purification step. With the chemical vapor deposition technique it becomes possible to have an industrial production of CNTs [11].

However, even if mass production of CNTs is nowadays well-known, the method commonly used leads to bundles made of hundreds of tangled single nanotubes with rather inert surface [12]. This implies: (1) a lack of dispersibility of CNTs in the inorganic matrix and (2) weak interactions between metal and CNTs. To solve this problem, functionalization techniques have attracted a huge interest during the last decade [13]. Moreover the interface between CNTs and metallic or inorganic materials is important. For example, defects may decrease the composite properties. Organic and inorganic CNTs functionalization appears to be a good mean for overcoming the lack of dispersibility and optimizing interfaces.

The functionalization techniques are useful to deagglomerate CNTs but also to remove the metallic particles used as catalysts for the synthesis of CNTs [14–22]. A treatment with a mixture of HNO_3 and H_2SO_4 at 80 °C seems to be the most efficient method, but it requires further purification and drying steps of CNTs because of the treatment occurs in solution [15]. Our team has recently developed another efficient technique which allows avoiding this step. A mixture of CO_2/EtOH/H_2O/H_2O_2 is used at high pressure and high temperature [23,24].

The inorganic functionalization of CNTs opens new applications by employing them as supports of catalysts, as for instance, precious metals as Ru, Rh, Pd, Ag, Au, Pt [5–8,25,26]. The metallic precursors can be first added to the carbon source used for the carbon growth, but this route implies harsh conditions [27–29]. Another way is the deposition of metallic nanoparticles on the walls of the CNTs. This can be carried out in solution but the yield of the reaction is low and an important amount of waste is generated [7,30–33]. Alternative approaches with supercritical carbon dioxide and water have been used as green media for the synthesis of new materials and especially CNTs-metal composite materials [25,34–40]. A supercritical fluid is a fluid at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It possesses both liquid- and gas-like nature combining their viscosity, diffusivity and surface tension properties. Consequently it can effuse through solids like a gas and dissolve materials like a liquid. These unique properties make supercritical CO_2 and water an attractive media for chemical treatment or material deposition on complicated and poorly wettable surfaces. As compared to chemical vapour deposition (CVD), which is the most widely used and cost effective process for depositing high-quality thin films on conventional substrates, supercritical fluid chemical deposition (SFCD) presents undeniable advantages for the deposition of nanoparticles and thin films over various substrates.

According to the nature of the deposited metal, the homogeneity and the size of the coating can vary. Thus Ti, Ni and Pd form continuous and quasi-continuous coating while Au, Al and Fe form only discrete particles on CNTs surface [41,42]. To understand these behaviors, studies at the interface level are necessary. Only few characterizations of this CNTs-metal interface have been reported from chemical and crystallographic point of views [43–45]. Some calculations have been realized and allow explaining the experimental data [46–50]. One can however wonder if the CNTs-metal interface depends on the functionalization method and/or deposition process. The aim of this paper is to report a simple, rapid and green procedure to homogeneously decorate CNTs with metal nanoparticles (Ag, Pd) and to fully characterize the deposition and the CNTs-metal interface as a function of the functionalization technique.

2. Experimental procedure

The experimental setup is shown in Fig. 1. The experiments were performed using a 50 cm^3 stirred stainless steel vessel reactor operating up to 400 °C and 40 MPa. The used mixture is 95/5 M CO_2/EtOH mixture (T_c = 55 °C, p_c = 9.5 MPa). CNTs were dispersed in ethanol containing the palladium precursor (hexafluoroacetylacetonate of palladium) or the silver precursor ((1,5-cyclooctadiene) hexafluoroacetylacetonate of silver); this solution was added into the high pressure and high temperature reactor. The reactor was closed, filled with hydrogen and then carbon dioxide and reaches the operating conditions. After 1 h reaction time, pure supercritical CO_2 flows through the reactor to remove ethanol and organic residues from metallic precursor. The dried CNTs were then recovered without any additional filtering step.

Carbon nanotubes used in this study were multiwalls Graphistrength C100 carbon nanotubes provided by Arkema. Three types of CNTs were considered: (1) raw CNTs, (2) CNTs functionalized with HNO_3/H_2SO_4 [15] and (3) CNTs functionalized using CO_2/EtOH/H_2O/H_2O_2 (0.49/0.10/0.09/0.32, molar composition) mixture at 200 °C and 20 MPa [23,24]. Deposition of palladium and silver was performed at 80 °C and 15 MPa from palladium hexafluoroacetonate and silver (1,5-cyclooctadiene) hexafluoroacetylacetonate in the supercritical CO_2/EtOH mixture. This composition was chosen to have a critical point as low as possible and a quantity of ethanol high enough to solubilize the metallic precursors.

Surface chemical characterization was carried out by XPS. A VG ESCALAB 220-iXL apparatus equipped with a monochromatic Alα XR source (1486.6 eV) was used. Spectra analysis was realized with AVANTAGE software from ThermoFischer Scientific. Experimental conditions for the survey were Ep = 150 eV and 1 eV step and for the high resolution spectra Ep = 20 eV and 0.2 eV step.

The amount of deposited metal was measured by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) using a Variant 720ED apparatus. Complete dissolution of metallic particles was performed with HNO_3/H_2O_2/H_2O mixture at high temperature and was microwave assisted. The obtained solution was finally filtered to remove nonsoluble CNTs.

Samples for transmission electron microscopy (TEM) were prepared by suspending the CNTs powder in alcohol by ultrasonication and depositing a drop of the suspension on a copper grid covered with a carbon film. The grid was finally air-dried for 15 min. TEM and high-resolution TEM (HRTEM) observations as well as Energy Dispersive Spectroscopy (EDX) analyses were performed using a Jeol 2200FS equipped with a field emission gun operating at 200 kV and with a point resolution of 0.23 nm. High-resolution TEM micrographs were acquired with a Gatan Ultrascan CCD 2k*2k and digital

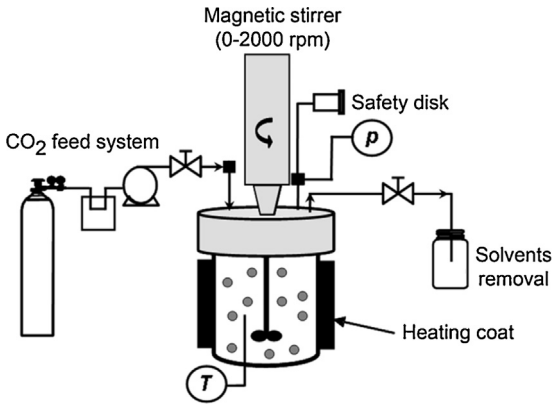

Fig. 1. Experimental setup for supercritical deposition.