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# Characterization of the chemical interaction between single-walled carbon nanotubes and titanium dioxide nanoparticles by thermogravimetric analyses and resonance Raman spectroscopy

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ABSTRACT

Raman spectroscopy is a powerful technique that is used to characterize or observe alterations in the structure or properties of carbon nanotubes and its composites. This method can provide information about electronic changes or quantify them. We used Raman spectroscopy to study the chemical and electronic changes in a composite formed by titanium dioxide nanoparticles and single-walled carbon nanotubes. This composite was characterized by scanning electron microscopy to investigate the morphology and by thermogravimetric analyses to assess the thermal stability of the isolated carbon nanotubes as compared with the nanotubes by titanium dioxide nanoparticles. The Raman results showed that the modification of the nanotubes with the $TiO_2$ nanoparticles generates a new material with different structure of the nanotubes, resulting in a decrease in defects. The charge transfer from the $TiO_2$ nanoparticles to the nanotubes alters the electronic properties of both moieties in the hybrid material. The interaction between the nanotubes and nanoparticles decreases the C—C bound order of the nanotubes and decreases their thermal stability.



## 1. Introduction

Carbon allotropes such as carbon nanotubes, graphene or fullerene have been used to enhance the properties of catalysts and photocatalysts. The high surface area of these carbon compounds and their lipophilicity makes them material excellent adsorbents for removing organic compounds such as polyphenols, hormones, and aliphatic hydrocarbons. These characteristics significantly increase the concentration of these molecules on the surface of the catalyst. The presence of defects in the structure of the nanotubes also generates traps for electrons, which is a vital characteristic in photocatalysts for generating holes to degrade organic compounds [1–7].

Single-walled carbon nanotubes (SWNTs) are one of most interesting allotropes of carbon and are generally found within bundles with diameters of 2–10 nm and lengths of several micrometers. However, their conductive properties draw more attention. SWNTs can be classified as semiconducting or metallic, which are generally associated with the differences of the diameters or with the chiralities of a specific nanotube. These differences in the electronic properties confer a vast number of applications, such as molecular electronics and doping in catalysts [8–11].

Raman spectroscopy has been one of the most important techniques for characterizing carbon nanotubes and catalysts. With this technique, it has been possible to observe the oxidative process on the carbon structure or inclusion of defects, to characterize the number of layers in the structure, and to spectroscopically "separate" nanotubes with metallic or semiconducting nature, since they can be resonantly excited with distinct laser wavelengths [8,12,13].

Recently, we demonstrated that the interaction between multi-walled carbon nanotubes and nanostructured titanium dioxide or SWNTs and polypyrrole could be quantitatively investigated based on the ratio of D/G Raman bands and the Raman shift of the D or G bands. These alterations are related to a charge dislocating in the structure of the composite [14,15].

This work demonstrates how the chemical interaction between SWNTs and $TiO_2$ nanoparticles can affect the stability and the

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electronic properties of both materials. For this purpose, a composite of SWNTs and $TiO_2$ nanoparticles was prepared and analyzed by scanning electron microscopy, thermogravimetric analyses, and resonance Raman spectroscopy.

## 2. Experimental section

### 2.1. Materials

Deionized water with resistivity of 18 MΩ was obtained from a Direct-Q 3UV purification system from MilliUni. Nitric acid (65% w:w), ethanol (>99%), and sodium hydroxide (>98%) were purchased from Sigma-Aldrich. The SWNTs produced by the arc discharge method were purchased from Carbon Solutions Inc. (2–10 nm in bundle diameter and >95% purity). Titanium dioxide nanoparticles (P25) were purchased from Degussa.

### 2.2. Equipment

The morphology of the samples was characterized by scanning electron microscopy using field emission gun scanning electron microscopy (FEG-SEM, Jeol JSM-7401F). Thermogravimetric analyses were carried out in a thermobalance (model sTA i 1500 from ISI Instrument Specialists Incorporated) in synthetic air atmosphere. The samples were ramped from 40 to 950 °C at a rate of 10 °C per minute. The Raman spectra were acquired using two different Raman spectrometer models from Renishaw. An inVia equipped with a CCD detector and coupled to a Leica microscope allowed rapid accumulation of Raman spectra with a spatial resolution of approximately 1–2 μm (micro-Raman technique). The laser beam was focused on the sample with a 20× objective (Numeric Aperture = 0.40), and the samples were irradiated at 632.8 nm with a He–Ne laser or 785 nm with a diode laser.

The second equipment was a System 3000 equipped with a CCD detector and coupled to an Olympus microscope (BTH2) with a 20× objective (Numeric Aperture = 0.40) and a spatial resolution of approximately 1 μm (micro-Raman technique). The samples were irradiated at 514.5 nm using an $Ar^+$ laser. The laser power was around 0.25 mW when analyzing the samples, and the spectra were obtained by one accumulation with exposure time of 60 s at 10 different points on the sample. The experiments were performed in ambient conditions using backscattering geometry.

### 2.3. Procedures

The SWNTs were oxidized with a modification of the procedure by Zhang [16]. A 125-mL reaction flask was equipped with a reflux condenser, magnetic stirrer, and thermometer in an oil bath. In this flask, 100 mg of SWNTs was refluxed in 15 mL of 3 mol $L^{-1}$ nitric acid at 120 °C for 24 h. The SWNTs oxidized (o-SWNTs), dispersed in acid, were centrifuged, and washed with deionized water until the aqueous solution reached pH 7. The o-SWNTs were filtered through a 0.45-μm Millipore membrane and dried at 60 °C for 24 h.

The synthetic procedure used to obtain the composites of $TiO_2$ and o-SWNTs was based in an impregnation method [10], with 10% o-SWNTs (w:w). In this method, 100 mL of ethanol, 10 mg of o-SWNT, and 90 mg of $TiO_2$ were added to a 250-mL Erlenmeyer flask. The mixture was stirred for 1 h, and the suspension was centrifuged for 15 min at 7000 rpm. The precipitate was isolated and dried at 60 °C for 24 h.

## 3. Results and discussion

### 3.1. Characterization of composites

The titanium nanoparticles were obtained from Degussa as a mixture of two crystalline forms of titania (anatase and rutile forms). The percentage of these forms can vary, but they are estimated to be 75% anatase and 25% rutile. The anatase nanoparticles are typically spherical, while rutile has an elongated form [17].

The SWNT obtained commercially, which are in bundles with diameters between 2 and 10 nm, were initially oxidized by nitric acid, as described in literature, generating this oxidized form (o-SWNT) [16]. The procedure of generating o-SWNTs inserts hydroxyl, carbonyl, and carboxylic groups in the structure of the nanotubes. These oxygen groups are able to bind to the surface of metallic oxides materials (like aluminum oxide, silicon dioxide, or titanium dioxide) [18–21], the absence of these groups makes the interaction between carbon nanotubes and titanium dioxide weaker.

The strong interaction of oxygen groups and metallic oxides allows the generation of composite between o-SWNTs and $TiO_2$ nanoparticles by the simple methodology of impregnation. Fig. 1 shows the SEM images of the composite $TiO_2$/o-SWNTs at different magnifications.

SEM shows that the size of the $TiO_2$ nanoparticles is in the range of 20–60 nm. It can be observed that they modified the o-SWNTs in a non-homogenous way with regions of high density of particles and others with no nanoparticles, even with a higher concentration of $TiO_2$. The thermal stability of this composite was investigated by thermogravimetric analysis. Thermogravimetric analysis is an important tool to characterize modifications in materials as well as quantify these modifications. In the case of carbon nanotubes or

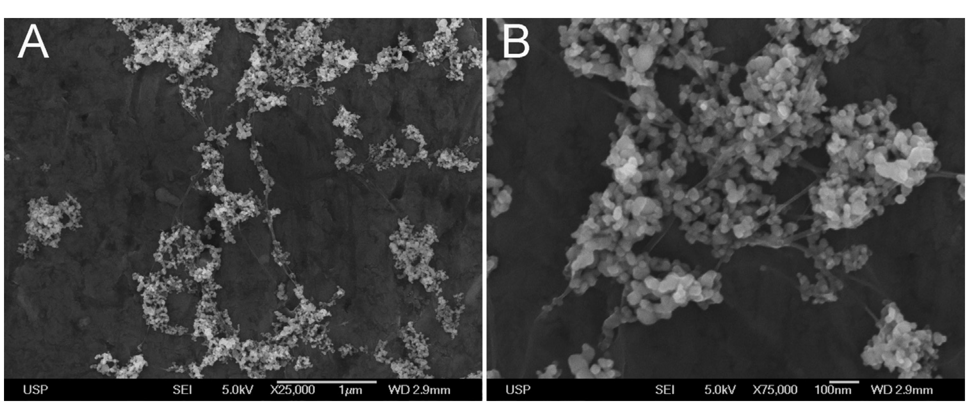


**Fig. 1.** SEM images of the $TiO_2$ nanoparticles modifying o-SWNT obtained with two different magnifications (A) 25000× and (B) 75000×.