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Thermal behavior of carbon nanotubes decorated with gold nanoparticles

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Abstract Three different forms of carbon, i.e., multi-walled carbon nanotubes (CNTs), single-walled CNTs, and soot, were decorated with gold nanoparticles by a new method. In this method $C_{10}H_8^-$ ions transfer electrons to the CNTs or soot. These electrons on the carbon surface can then reduce Au^{3+} species to form supported Au nanoparticles with a narrow particle size distribution. Thermogravimetric/differential thermal analyses (TG/DTA), XRD, Raman, and TEM show that naphthalene molecules remain trapped inside the Au nanoparticles and can only be removed by treatment at ca. 300 °C. Remarkable effect of the Au nanoparticles on the oxidation of carbon by O_2 is also observed by TG/DTA, i.e., on-set oxidation temperature and activation energy (E_a). It is shown that as the Au particle size decreases from 25 to 2 nm a linear decrease of the oxidation temperature is observed. Au particles larger than 25 nm do not produce any significant effect on carbon oxidation. These results are discussed in terms of spillover catalytic effect where Au nanoparticles activate O_2 molecules to produce active oxygen species which oxidize the different carbon supports.

Keywords Carbon nanotubes · Soot · Thermal stability · Gold nanoparticles · TG/DTA

Introduction

Carbon nanotubes (CNTs) have been intensely investigated due to their unique chemical, mechanical, and electrical behavior. The inherent properties of CNTs make them versatile supports for metallic nanoparticles and applications in areas related to catalysis and sensoring [1–5]. The interaction of the metallic nanoparticles with the carbon surface and their effect on the thermochemical stability of the nanotubes are important features for the development of potential applications. Although no systematic study has been published, some references show that metal nanoparticles might significantly affect the thermal stability of CNTs [6–8]. It has been observed that metallic particles from the catalyst used during CNT synthesis led to a decrease of the carbon oxidation temperature by O_2 [9, 10]. Guan et al. [11] and Brukh et al. [12] clearly demonstrated that the single-walled carbon nanotubes (SWNTs) oxidation temperature decreased significantly when the metal impurity of the sample increased. Iijima et al. [13] reported that SWNT can be purified by using gold nanoparticles deposited on carbonaceous soot followed by controlled oxidation with O_2. An overall analysis of these reports suggests that the effect of metallic particles on the oxidation of CNTs depends on different factors, such as the nature of the metal, the size, and crystallinity of the metal and the degree of interaction with the CNT surface. An interesting aspect of these dependencies is that the oxidation of carbon by O_2 can be a versatile probe reaction to obtain key information of decorated CNTs.

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We have recently proposed a new method to prepare metallic nanoparticles, e.g., Au and Pd, based on the charge transfer from naphthalene anion to CNTs followed by metal reduction [14]. In this report, this method was used to produce different carbon forms, i.e., SWNTs, multi-walled carbon nanotubes (MWNTs), and soot, decorated with Au nanoparticles with a narrow particle size distribution. Other Au-decorated SWNTs, MWNTs, and soot were also produced in this study by different methods, i.e., UV photochemical reduction [15] and nitric acid treatment [16]. All these Au-decorated carbons with different particle sizes were analyzed by TG/DTA to correlate the effect of particle size with the oxidation of SWNT, MWNT, and soot by oxygen.

Experimental

Synthesis and purification of CNTs and carbon nanoparticles

The SWNTs were synthesized by the DC arc discharge method using a composite rod containing graphite, Y_2O_3 (at 1%), and Ni (at 4.2%) as the anode and a graphite rod as the cathode, under a helium pressure of 300 torr with a current of 100 Å. MWNTs were produced by the chemical vapor deposition method (CVD) using ferrocene as a floating catalysts and ethylene as the carbon source. The purification was done through a repetitive sequence of thermal oxidation at 390 °C and reflux in hydrochloric acid (6 M), to remove catalyst particles and amorphous carbon. Carbon nanoparticles (CNPs) were isolated from the purified SWNTs previously obtained. Typically, 500 mg of purified SWNTs were treated thermally at 550 °C for 2 h in air followed by reflux in hydrochloric acid (6 M).

Synthesis of SWNT/Au, MWNT/Au, and CNP/Au hybrids

The attachment of gold nanoparticles to the carbon materials was performed by a previously described method [14]. In a typical synthesis, 48 mg of purified SWNTs, MWNTs, or CNPs were dispersed in 50 mL of dry tetrahydrofuran (THF). 38.45 mg of naphthalene and 500 mg of wire of sodium were added to the dispersion under inert atmosphere. This mixture was stirred overnight yielding a dark green solution. For decoration of carbon materials, 33.90 mg of $HAuCl_4$ was dissolved in 20 mL of dry THF and added to the reduced CNTs solution. The product was filtered, washed, and dried under vacuum at 90 °C overnight.

Sample characterization

The samples were characterized by X-ray powder diffraction using a Rigaku, Geigerflex 2037 apparatus with graphite monochromated Cu K_α radiation (0.154051 nm). Raman spectra were obtained with the excitation wavelength of 514.5 nm. The morphology of the materials was examined by transmission electron microscopy using a Tecnai-G^2 instrument, fabricated by FEI, operating at 100 kV.

Thermogravimetric analyses (TGA) were performed using a Shimadzu DTG60/60H instrument at a flow rate of 100 mL/min of synthetic air. Approximately 2 mg of the materials was placed in a sintered Al_2O_3 crucible and the studies were carried out at a constant heating rate of 5, 10, and 20 K min^{-1} in the temperature range of 25–800 °C.

Results and discussion

Different forms of carbon, i.e., SWNTs, MWNTs, and carbon soot (CNP) were decorated with gold nanoparticles. The naphthalene anion was used to transfer electrons to the carbon to enable the surface reduction of gold (Eq. 1, 2):

$$n\mathrm{C_{10}H_8^-} + \mathrm{Carbon} \rightarrow \mathrm{Carbon}^{-n} \quad (1)$$

$$\mathrm{Carbon}^{-n} + \mathrm{HAuCl_4} \rightarrow \mathrm{Au/Carbon}. \quad (2)$$

The TEM images show the presence of gold nanoparticles covering the entire surface of the carbonaceous materials. Figure 1a shows an image of MWNT-containing Au nanoparticles with an average diameter of 5.8 nm. In Fig. 1b the presence of bundles of SWNTs covered by gold nanoparticles with average diameter of 4.4 nm can be observed. Figure 1c shows a typical TEM image of CNP of carbon soot decorated with Au nanoparticles with diameter of ca. 3.7 nm.

The carbon materials decorated with gold nanoparticles were also characterized by X-ray diffraction, as shown in Fig. 2. All XRD patterns show the presence of peaks for the face-centered cubic crystalline gold structure (JCPDS 4-784). The diffraction peaks appearing at 26° and around 54° are assigned to the reflections of graphitic planes.

Figure 3 shows the TG/DTA curves performed at 10 K/min at a flow of 100 mL/min for the purified MWNTs and for the Au-decorated MWNTs. The TG/DTA analysis reveals a single well-defined thermal event that can be associated to carbon oxidation (Fig. 3a). It corresponds to a mass loss of 89%, as determined by the TG curve, and to an exothermic DTA peak centered at 607 °C. On the other hand, Au-decorated MWNTs show completely different TG/DTA profiles with two exothermic peaks at lower temperatures, i.e., 298 and 481 °C. Similar results were found for samples of purified and Au-decorated SWNTs and CNPs (Fig. 4).

Pure SWNT sample show a typical profile with two exothermic mass losses, i.e., at 457 and 703 °C, related to

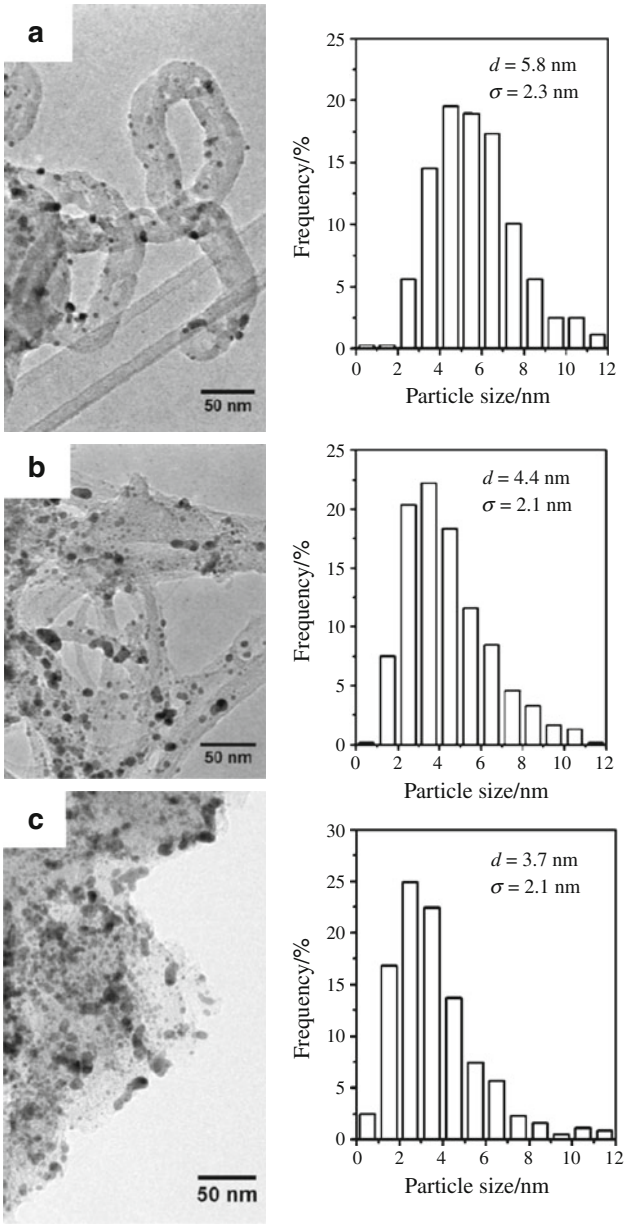

Fig. 1 TEM images and corresponding gold particle size distribution for **a** MWNT/Au, **b** SWNT/Au, and **c** CNP/Au

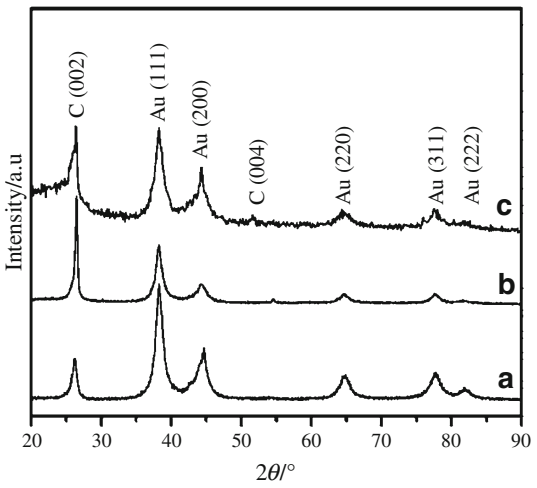

Fig. 2 X-ray diffraction of (*a*) MWNT/Au, (*b*) SWNT/Au, and (*c*) CNP/Au

the oxidation of SWNTs and more stable structures [13, 17]. The presence of Au on the SWNT surface strongly modifies the TG/DTA profile showing three peaks at lower temperatures, i.e., 307, 403, and 602 °C. Also a remarkable change was observed for the oxidation of carbon soot (CNP) which was shifted from 581 to 393 and 301 °C. It is interesting to note that all Au-decorated carbons showed an exothermic peak at ca. 300 °C. The nature of this exothermic process was investigated by interrupting the thermogravimetric analysis of SWNT/Au sample in air at 350 °C and quenching of the sample to room temperature. Raman analysis (Fig. S1 in Electronic Supplementary Information) of the obtained sample shows no significant difference of the G and D bands or RBM modes before and after oxidation at 350 °C. Different TEM images of the SWNT/Au sample (Fig. 5) suggest that the Au nanoparticles became more spherical and regular after thermal treatment at 350 °C. The TEM images also suggest no noticeable change of the carbon structures.

These results suggest that the first exothermic TG peak is not related to the oxidation of carbon. Moreover, TG analysis of MWNT/Au sample (see Electronic Supplementary Information) obtained by a different process based on photochemical reduction do not show any TG event near 300 °C, suggesting that this peak is related to the preparation method using naphthalene.

To further investigate the origin of this peak the SWNT/Au sample was heated under a He flow up to 350 °C with a liquid N_2 trap to condense any released volatile compounds. The condensed material was dissolved in toluene and analyzed by GC/MS. The obtained result shows the presence of naphthalene with the molecular ion at *m*/*z* of 128 (Fig. S3). These experiments indicate that the TG exothermic peak around 300 °C can be related to the oxidation of naphthalene released from the SWNT/Au sample. This naphthalene is likely not adsorbed on the SWNT walls since the SWNT/Au sample was extensively washed with toluene and treated under vacuum overnight. Moreover, control experiments with pure SWNTs impregnated with naphthalene washed with toluene and treated under vacuum did not show any TG weight loss at ca. 307 °C. Therefore, naphthalene molecules should be strongly interacting with Au, for example, trapped inside the Au nanoparticles as schematically represented in Fig. 6. The $C_{10}H_8$ molecules are trapped during the reduction of $HAuCl_4$ on the carbon surface and cannot be removed by washing with toluene and vacuum. Upon thermal treatment

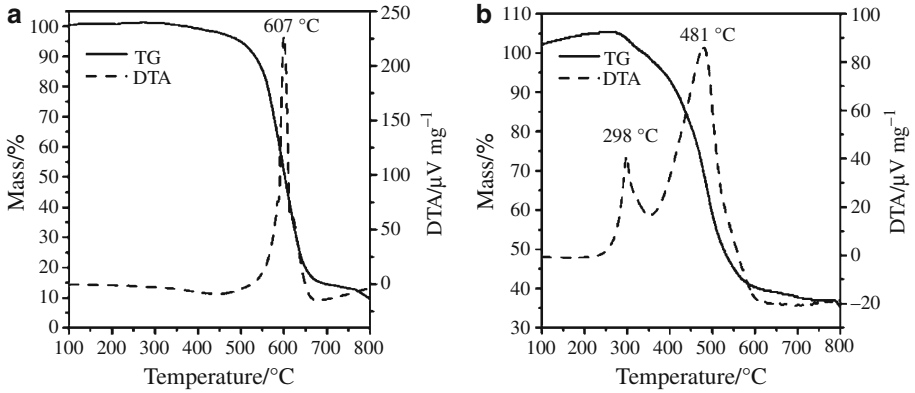

Fig. 3 TG and DTA curves for the **a** purified MWNT and **b** MWNT/Au obtained under air flow at 10 °C min^{-1}

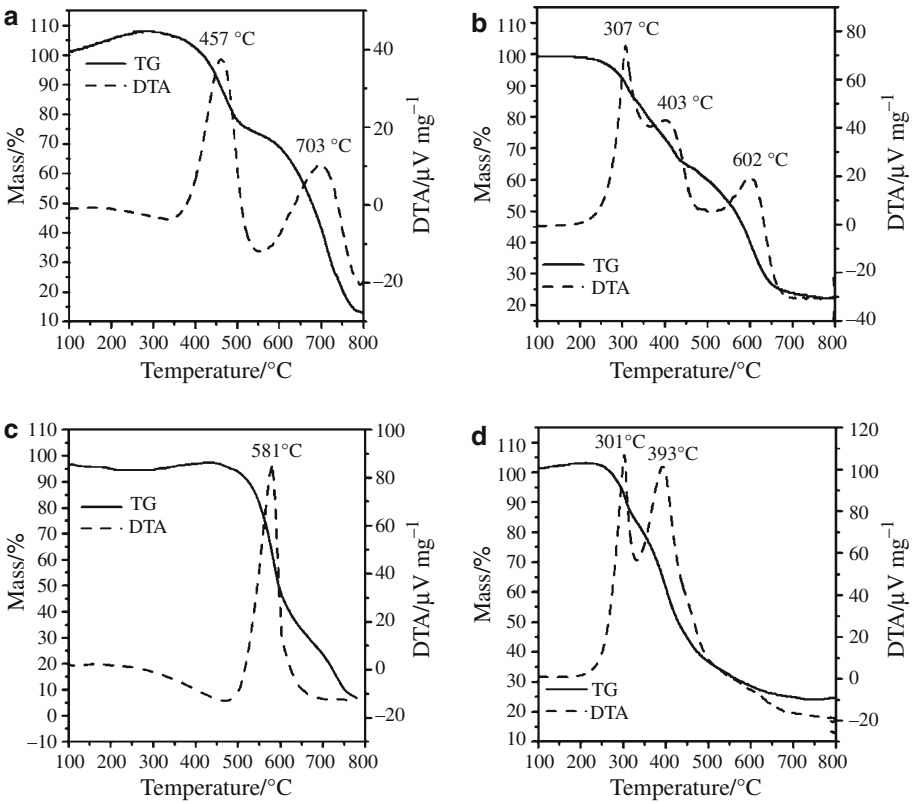

Fig. 4 TG and DTA curves for the **a** purified SWNT, **b** SWNT/Au, **c** purified soot, and **d** CNP/Au obtained under air flow at 10 °C/min

at ca. 300 °C, the naphthalene molecules are released to the gas phase and in the presence of air (TG conditions) are oxidized. As a result of naphthalene elimination, the gold particles become more organized and crystalline as observed by TEM.

The TGs of the MWNT/Au, SWNT/Au, and CNP/Au samples (Figs. 3, 4) also show a remarkable decrease of the carbon oxidation temperatures compared to the non-decorated samples. For example the mass loss observed for MWNT at 607 °C is shifted to 481 °C, whereas for CNP it is decreased from 580 to 393 °C. In the case of SWNT, the two peaks at 703 and 457 °C are associated to the oxidation of different carbonaceous materials. The thermal event at 457 °C is due to the oxidation of SWNTs, while the peak at higher temperature is assigned to the oxidation of more stable carbonaceous impurities that are not removed in the purification process [13, 17]. Upon decoration with Au nanoparticles these peaks are lowered to 402 and 601 °C, respectively, showing clearly that the Au particles are catalyzing the oxidation of the different forms of carbon by O_2. Similar results have been observed before for SWNTs decorated with 20 nm gold nanoparticles [13, 17].

The effect of the average size of Au nanoparticles on the temperature of carbon oxidation was investigated for the different forms of carbon, i.e., MWNT, SWNT, and CNP. Moreover, besides the naphthalene decoration method, two other $HAuCl_4$-based decoration processes were investigated: (i) UV photochemical reduction [15] and (ii) nitric

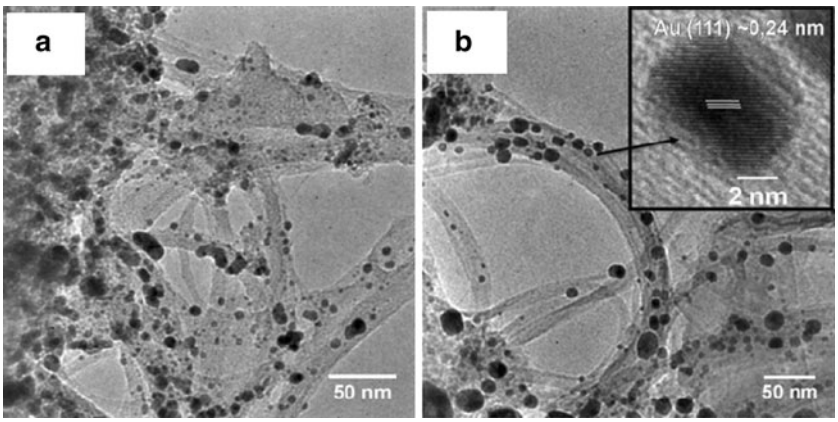

Fig. 5 TEM images of SWNT/Au **a** before and **b** after treatment at 350 °C in air

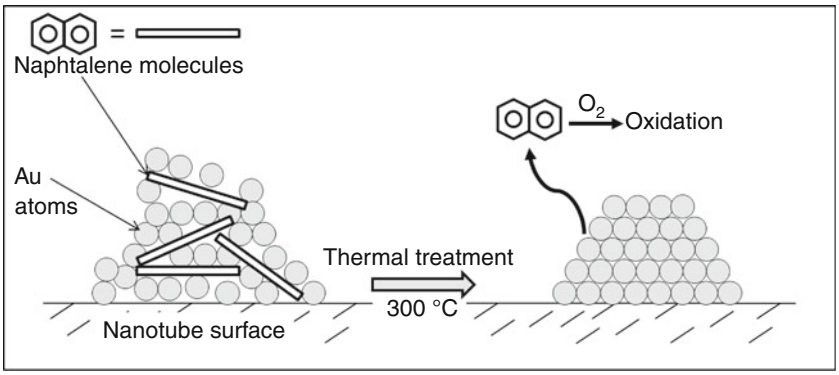

Fig. 6 Schematic representation of Au nanoparticles with naphthalene molecules trapped inside before and after treatment at ca. 300 °C

acid treatment [16]. The characterization of these Au-decorated carbons is presented in the Electronic Supplementary Information (Table S1). The materials having different Au particle size, obtained by these methods, were analyzed by TG/DTA to determine the carbon oxidation temperatures. The correlation between the Au average particle size and TG/DTA oxidation temperatures is presented in Fig. 7.

It can be observed that 3–5 nm Au nanoparticles lead to a decrease of the oxidation temperature to ca. 400 °C. As the Au average particle size increases the oxidation temperature also increases almost linearly to ca. 25 nm. Apparently, Au particles larger than ca. 25 nm do not affect significantly the reaction of carbon with O_2 and the oxidation temperature is very similar to pure carbon materials (without Au).

The activation energy for the oxidation of the carbon materials decorated with Au by the naphthalene method was calculated by a non-isothermal model which relates the heating rate and maximum rate of weight loss with the Arrhenius kinetic parameters, Eq. 3 [12, 18]:

$$\ln\left(T_m^2/m\right) = E_a/(RT_m) + \ln(E_a/A_0), \quad (3)$$

where, T_m is the temperature of the maximum rate of mass loss, obtained by DTG, m the heating rate (K s^{-1}), E_a the activation energy (J mol^{-1}), A_0 the frequency factor, and R the ideal gas constant. The activation energies of the oxidation were calculated by Eq. 3 using heating rates of 5, 10, and 20 K min^{-1}. The obtained Arrhenius plots are shown in Fig. S4 (Supplementary material). The obtained E_a for the different Au-decorated carbon forms are shown in Fig. 8.

The calculated activation energy of 206 kJ mol^{-1} for the purified MWNTs is consistent with previously published data, i.e., 142–269 kJ mol^{-1} [18]. SWNTs presented an E_a of 110 kJ mol^{-1} which is similar to the literature, i.e., 117–180 kJ mol^{-1} [18, 19]. Purified CNP shows an activation energy of 149 kJ mol^{-1}. These results suggest that MWNTs are more stable than the other forms which is related to the lower curvature, giving stability comparable to graphite. It is interesting to note that the presence of Au nanoparticles on the MWNT surface led to a remarkable decrease on the activation energy to 85 kJ mol^{-1}. A significant decrease of the E_a was also observed for Au nanoparticles on the CNP surface to 71 kJ mol^{-1}. These E_a variations clearly indicate that Au nanoparticles have a catalytic effect on the carbon oxidation by O_2. Previous theoretical studies have investigated the O_2 interaction on non-supported Au nanoparticles formed by small clusters of gold [20–22]. The results indicate that the energy barrier of O_2 dissociation on gold surfaces depends strongly on the particle diameter, and that there is critical size for Au nanoparticles to dissociate O_2. Reported E_a for the O_2

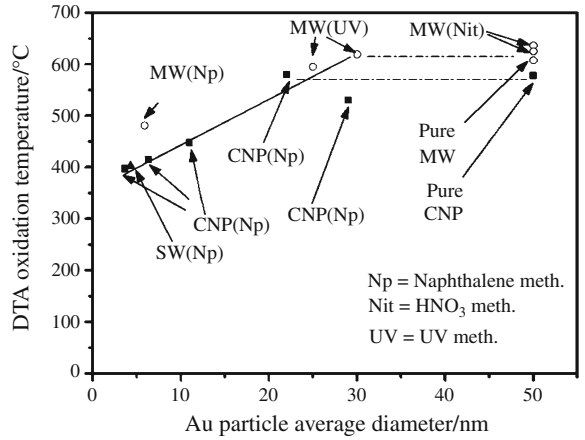

Fig. 7 TG/DTA oxidation temperatures of carbon samples (MWNT, CNP, and SWNT) decorated with Au of different average particle size

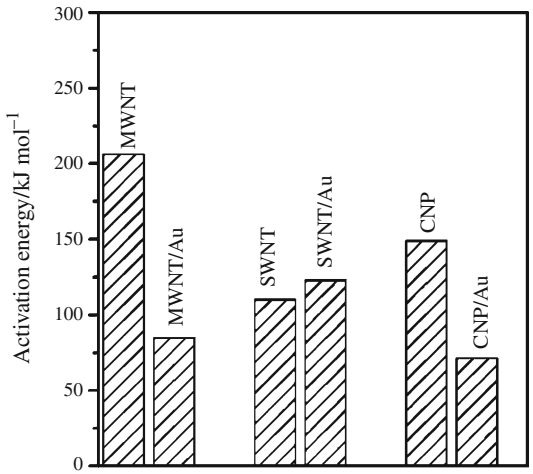

Fig. 8 Activation energies for the oxidation of the different carbon forms decorated with Au nanoparticles prepared by the naphthalene method

dissociation on Au nanoparticles are typically in the range 40–68 kJ mol^{-1} which is in the same range obtained for Au-decorated MWNT and CNP in this study. This data suggests that Au nanoparticles promote the reaction by the catalytic dissociation of O_2 to form active species according to the simplified Eq. 4:

$$0.5O_2 + Au_{surf} \rightarrow Au_{surf} - (O). \quad (4)$$

This reactive (O) surface species are mobile and can move to the carbon support for its oxidation. This catalytic effect is directly dependent on the Au particle size, and is mainly observed for particles smaller than 20–30 nm. This is likely due to effect named spill-over [23, 24] where Au particles activate O_2 molecules from the gas phase by dissociation and transfer them to the carbon support to produce CO_x (Fig. 9).

On the other hand, SWNTs do not show any significant change of the E_a in the absence or presence of Au

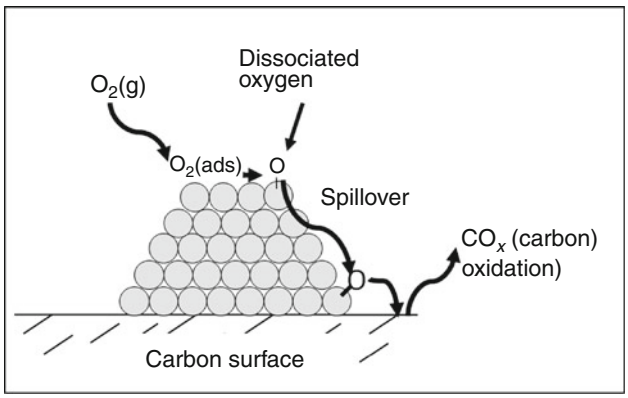

Fig. 9 Schematic representation of the spillover of O_2 from the Au nanoparticles to oxidize the carbon support

nanoparticles, (110 and 123 kJ mol^{-1}, respectively). C–C bonds of the highly curved SWNT surface are very reactive and show typically small activation energy for oxidation. In this case, the Au nanoparticles have no significant effect on the activation of O_2 and a decrease of the E_a is not observed.

Another aspect observed in the Arrhenius plot is the variation on the A_0 pre-exponential factor for the different materials (Fig. S4). The A_0 frequency factor strongly decreases for the MWNT and CNP samples with the addition of gold nanoparticles. The calculated frequency factors for purified MWNT and CNP samples present values in the order of 10^{10} and 10^7, respectively, while in both Au-decorated materials these values are reduced to ca. 10^4. This decrease of the frequency factor is likely related to the catalytic surface availability of Au which is lower compared to the original MWNT and CNP surface. On the other hand, for the SWNT with and without Au similar frequency factors were observed, i.e., 10^6–10^8. This result again suggests that Au does not have any catalytic effect on the carbon oxidation of SWNT.

Conclusions

This study presents the thermal behavior of MWNT, SWNT, and CNP samples decorated with Au nanoparticles, under an air atmosphere. TG/DTA curves for all decorated materials synthesized by the naphthalene method show new exothermic weight losses around 300 °C associated with thermal oxidation of the naphthalene molecules trapped inside the Au nanoparticles. Remarkable decrease on the temperatures of carbon oxidation by O_2 is observed in the presence of surface Au nanoparticles. The effect of Au is directly dependent on the particle size in the range 3–25 nm. Gold particles larger than 25 nm do not produce a significant effect on carbon oxidation. A strong decrease

on the activation energy for carbon oxidation in the presence of Au nanoparticles is also observed, these results are discussed in terms of a catalytic spill-over effect where Au nanoparticles activate O_2 molecules by dissociation and the activated oxygen spill-over to the carbon support.

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