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Short communication

Synthesis of sheathed carbon nanotube tips by the sol–gel technique

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Abstract

We describe the first elaboration of carbon nanotube tips (CN-tips) by the sol–gel technique. The CN-tips consist of single carbon nanotubes (CNs) or bundles sheathed by a nanometric layer of TiO_2 fixed to the apex of a W base tip and oriented along its major axis. The straight-forward method potentially permits low cost batch fabrication. Structural analysis has been realized by transmission electron microscopy (TEM). These CN-tips are interesting for applications in applied surface science such as field emission (FE) sources and near field microscopy probes. A first field emission study has also been carried out showing that the TiO_2 layer does not block FE. Relatively stable emission at voltages usual to FE from CNs at up to 0.8 μA current were obtained.

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Keywords: Carbon nanotubes; TiO_2 thin films; Field emission; Sol–gel

1. Introduction

Carbon nanotubes (CNs) are characterized by their nanometric dimensions, high aspect ratio, chemical stability, high Young modulus [1] and interesting electrical properties [2,3]. These properties open up a wide spectrum of applications in applied surface science, nanoscience and vacuum microelectronics particularly for individual nanotubes. For instance CNs have been recently shown to have excellent characteristics as probe tips in scanning tunneling and atomic force microscopies (STM and AFM). They have been used for imaging biological materials [4,5] and CNs themselves by AFM with very high resolution, superb stability and with no damages to either the sample or the CN probe itself. Another important application of CNs are as field emission (FE) electron sources studied for applications in electron microscopy and vacuum microelectronics [6–8]. Several recent experiments [9–11] have shown that FE experiments on CN-tips can also be used to determine intrinsic parameters of the CNs themselves such as resistance [9] and the Young's modulus [11]. In the case of FE applications, emission stability is of prime importance especially in the presence of background oxygen which reacts strongly with carbon.

A necessary step is the development of methods of mounting individual nanotubes at the apex of larger

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support tips to form a carbon nanotube tip (CN-tip) permitting easy manipulation. Several techniques have been used to realize these CN-tips : (1) bonding mechanically the CN to a tip apex using an acrylic (conductive) adhesive [12–15], (2) growing it on a tip apex with chemical vapor deposition (CVD) [16,17] and (3) attaching it to a tip apex using dc voltage in an electron microscope [18–20]. Nevertheless, these techniques are rather cumbersome, time consuming and demand a rather specialized knowledge with an infrastructure not readily available. In this article, we present a new method for fabricating CN-tips which should lead itself to easier batch processing. The CN-tips are produced by dipping and then pulling W base tips from a sol–gel solution in which nanotubes had been previously dispersed. We obtain individual CN-tips sheathed with a thin TiO_2 inorganic layer with a rather good orientation of the CN with the major axis of the base tip. The sol–gel method is known for its easy use for elaboration of very thin layers of different thicknesses ranging from 1 to 1000 nm [21]. The thin TiO_2 layer serves to bind the CN strongly to the base tip and as well may allow for better FE stability in the presence of O_2 since it is a stable oxide layer itself.

In the first part of the article, the CN-tip elaboration is described in details. The practical aspects of the method and its reproducibility are emphasized. In a second part, structural analysis by transmission electron microscopy (TEM) are presented to show the general shape of the CN-tip. The results of a preliminary FE study using the CN-tip as an electron source are presented in the third part. Finally, a summary of the important points and a brief discussion of the potential of this new method of CN-tip fabrication are presented in the conclusion.

2. CN-tips elaboration

Two types of CNs were used in the CN-tip synthesis. Multiwall nanotubes (MWNT) were produced by catalytic decomposition (CVD) of acetylene on cobalt supported on a NaY zeolite prepared by porous impregnation. The MWNTs had average inner and outer diameters of, respectively, 5 and 15 nm. The CNs have then been treated to obtain a well graphitized and pure powder of CNs. Purified singlewall nanotubes (SWNT) in the form of bundles were obtained from Nanoledge and were also used to make CN-tips. Most studies were performed with the MWNTs.

The sol–gel solution of TiO_2 was prepared following a procedure already described [22]. The viscosity of the sol was adjusted by addition of methanol in the preliminary solution. This step is used to control the thickness (from 1 to 1000 nm) of the sol–gel deposition, i.e. in our case the thickness of the TiO_2 layer covering the tungsten tip and the apex CNs. The introduction of CNs into the SG solution is realized by the addition of a preliminary solution of CN diluted in methanol to the SG solution during its preparation in order to obtain better dispersion of the CNs in the sol [23,24].

Once the mixed solution of CNs and TiO_2 is made, we proceed to CN deposition from this solution on the tungsten tip by the dip-coating method. The schematic procedure of the realization of this CN-tip is presented in Fig. 1. The CN-tips used an etched tungsten base tip dipped in the solution which was withdrawn at a precise low speed of 2 cm/min. During the dip-coating process, a voltage of ~200 V was applied between the W tip and a anode placed near the solution containing the nanotubes. This voltage was gradually reduced to zero after the W tip has been removed from the sol to avoid arc formation. After the dip-coating process, the CN-tips were annealed at 350°C under an infra red lamp for 15 min. This heat treatment allows not only

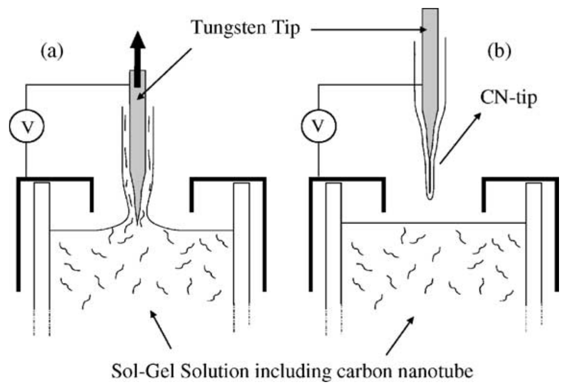

Fig. 1. Schematic procedure for obtaining CN-tips by the sol–gel method. (a) The etched tungsten tips are dipped in the sol–gel solution containing carbon nanotubes. A dc voltage is applied between the tip and a counter-electrode localized near the solution surface. The tips are then pulled from the solution at constant speed. (b) When the tungsten tip is extracted from the solution, the voltage is gradually reduced as the pulling continues. The CN-tips are then ready for the annealing treatment and observations.

the densification of the sol–gel layer deposited on the tip, but also the removal of the SG carbon residues [23]. Furthermore, the annealing is not sufficient to crystallize the sol–gel layer, thus avoiding mechanical constraints in layer that could damage the CN and cause its oxidation.

After a first optimization of the different parameters mentioned above, the best yield obtained with this CN elaboration method is approximatively 40% for having one or several CNs radiating from the tungsten tip apex. Preferential orientation in the dipping direction is evident.

The same process was performed without applying the voltage. In this case, the yield was greatly reduced, showing the necessity of electrical field during the dip-coating process for CN-tip elaboration.

3. Structural analysis

Structural analysis by electron microscopy of the fabricated MWNT CN-tips was performed using a TOPCON EM002B working at 200 kV to obtain their general shape and to check the internal structure of the CN covered by the sol–gel film. We could investigate both the SG thin film structure deposited around the CN and measure its thickness. In Fig. 2, we show observations realized in the conventional microscopy mode on samples of as-elaborated CN-tips, where the CN is arranged along the tungsten tip axis. The contact point of the CN and the tip is shown more precisely in the insert of the Fig. 2a. The free standing CN lengths are 950 nm for radii measured at 9.2 nm. In Fig. 2b, we show another sample with two CNs in contact with the tungsten apex. We can see clearly that each CN wall follows exactly the tungsten tip shape showing that the dip-coating method by the sol–gel solution flow containing CN influenced the precise CN deposit on the W apex. Moreover, this image shows breakage of CNs near the apex tip and modification of the well-defined wall of each CN. This is due to the application of voltage during the dip-coating process which caused a sudden increase of current implying arc formation on the CN apex.

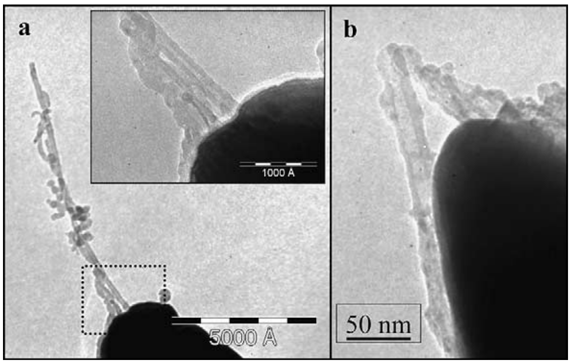

Fig. 2. Transmission electron microscopy observations of the produced MWNT CN-tips. (a) CN-tip with a 950 nm long free standing nanotube. This CN is aligned along the tip axis. *Inset*: Magnified image of the CN–W base tip junction. (b) CN-tip after an electric arc formation during the dip-coating deposition. The CNs were broken near the apex of the tungsten tip and the graphitic layers were destroyed.

In order to check the high quality of CN used and the SG thin film structure, classical and High Resolution TEM observations were made on another sample and are presented on the Fig. 3. The well-defined graphitic structure of CN is shown. For the heat treatment realized on those CN-tips, the TiO_2 layer on the CN surface is amorphous, as has been already observed [23], in the case of CN embedded in TiO_2 matrix realized by the same method. For this reason, SG thin film thickness is difficult to distinguish from the carbon amorphous around the graphitic planes of CN. The TiO_2 thickness can be estimated around 1 nm.

The MWNTs used to fabricate the MWNTs CN-tips were neither extremely pure or long as can be seen by the extraneous particles also attached to the tip. The method was also applied to purified arc electric SWNTs. The SWNTs are arranged in bundles containing many nanotubes. Otherwise the procedure was exactly the same. An example of SWNT CN-tip is shown in the scanning electron microscope image presented in Fig. 4 which shows that ideal forms can be obtained by this procedure [25].

4. FE study

A preliminary FE study was carried out in an all metal UHV vacuum chamber with ultimate pressure of 1×10^{-10} Torr. For this first FE study, the system was not baked and the pressure was in the range of 10^{-8} to 10^{-9} Torr. A CN-tip was spot-welded onto a W wire loop in the classic method of FE tip preparation which

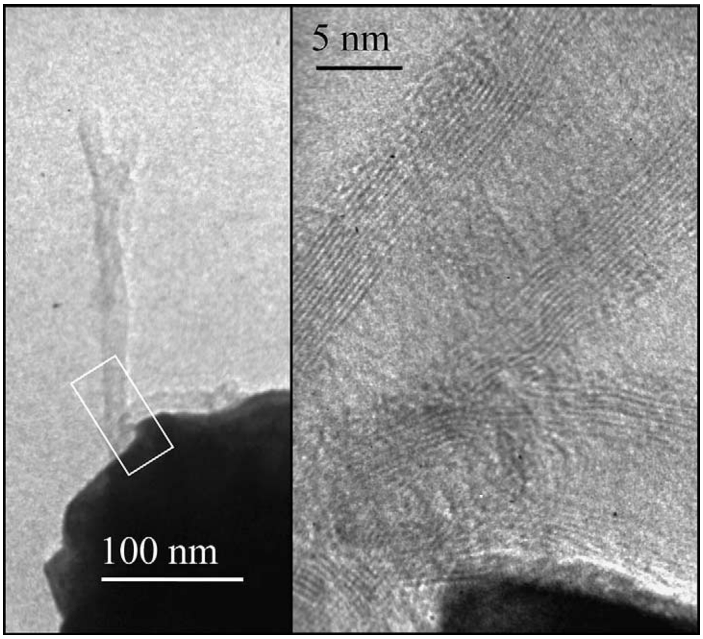

Fig. 3. On the left, conventional TEM image of a CN-tip where the CN is oriented along W base tip axis. On the right, HRTEM observation of the white box in the left image showing the well-defined graphitic structure of the CN.

permitted controlled heating experiments. It had a single CN at the apex. The temperature of the tip was monitored by micropyrometry for temperatures above 650 °C. The FE patterns were observed on a fluorescent screen placed in front of the CN-tip.

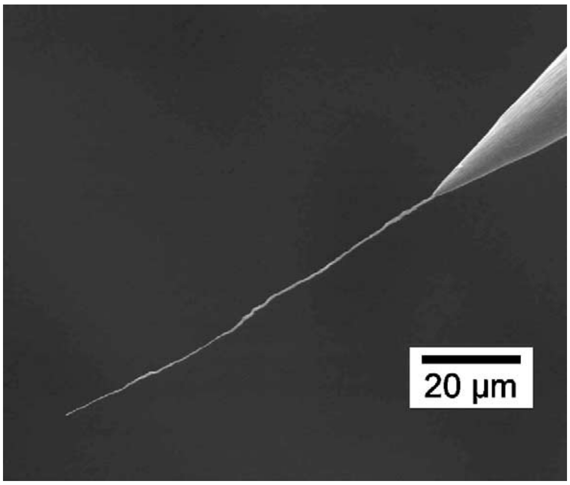

Fig. 4. SEM observation of a CN-tip fabricated by the sol–gel method using a solution in which bundles of SWNTs have been dispersed. The CN at the tip apex likely consist of many aligned bundles [25].

Emission currents were measured by the current leaving the tip and/or from a stainless steel shutter which could be rotated in front of the emitting CN-tip.

Upon applying the first voltage ramp to the CN-tip, unstable FE appeared in the nA range at 1200 V. The voltage then had to be dropped quickly to prevent current runaway until a relatively stable emission occurred in the nA range at 500 V. This voltage drop is common to any FE tip just introduced to the vacuum. Two possible mechanisms are the partial field desorption of a lightly physi-adsorbed overlayer which partially blocks FE and the formation of nanometric protrusions on the CN apex surface by field driving and local FE induced heating [26,27]. The FE pattern then consisted of a single spot emitting off-axis characteristic of FE from a single nanometric scale zone. The I/V characteristics were measured and are shown in Fig. 5. They follow rather well the Fowler–Nordheim law. From the slope of the FN-plot $m \simeq 0.5\,\phi^{3/2}/\beta$ and assuming a work function $\phi = 5$ eV, we can estimate the field enhancement factor β defined by $F = \beta V$. F is the field in V/Åand V is the applied voltage. We get a rough estimate for the apex radius from $r_{apex} \approx 1/\beta\kappa \approx 30$ nm. $\kappa \cong 5$ is a correction factor due to the point-screen geometry. r_{apex} is in the order of magnitude of that expected for the CN-tip from the SEM measurements. The maximum current tested for this first study have been 0.8 μA with good stability during one hour.

A good mechanical contact between the CN and the tip is required in numerous applications. To test this bonding, the tip was raised numerous times to 700 °C for about ten seconds and the *I*/*V* and current stability measurements were repeated. The FE pattern was still the same single area though its opening angle was became somewhat larger. Thus, the mechanical fixation of the CN-tip easily withstands the 700 °C treatment. Also note that the field applied during FE also exerts a considerable force on the CN which however did not move in position.

Finally, after the FE study, SEM observations of the CN-tip showed no degradation of the carbon nanotube confirming that FE process and the heat treatments were not destructive for the emitting CN.

5. Discussion

Different practical aspects of this preliminary study are worth emphasizing. First, the method of nanotube deposition on the base tip should be easily achievable in a batch process. Once made the sol–gel solution may be used for a production of large numbers of CN-tips which may also be dipped simultaneously. For example, in our experiment the dipping process was realized simultaneously on five W tips giving in the best case four interesting tips. Numerous parameters, such as sol–gel viscosity and nanotube density, can be varied to optimise the technique and adapt it to different applications. The CNs introduced in the sol–gel solution can be SWNTs or MWNTs of specific shape and length. CNs produced by arc-discharge and with very few defects can be used for obtaining straight CN-tips. The sol–gel layer can be precisely defined and its thickness chosen. The possibility to remove partially the sol–gel layer after dip-coating can be studied. Other aspects such as the nature of the oxide used and the form of the tip geometry may also be varied.

Different parameters have still to be optimized to enhance the yield. Firstly, the solution viscosity is expected to modify the meniscus shape during the dip-coating process and then influence the NT deposition on the apex of the tip. It has been noticed that the dispersion of CNs in the SG solution also influences this viscosity. Secondly, different experiments showed that the tip geometry and more precisely its surface state, is an important parameter regarding both the deposition of the CN and the diameter of the CN expected to be deposited. Finally, concerning the dip-coating process, we have shown that a faster tip retraction speed will reduce drastically the yield. Another important parameter is the voltage applied during the dip-coating process and the electrodes shape and localization.

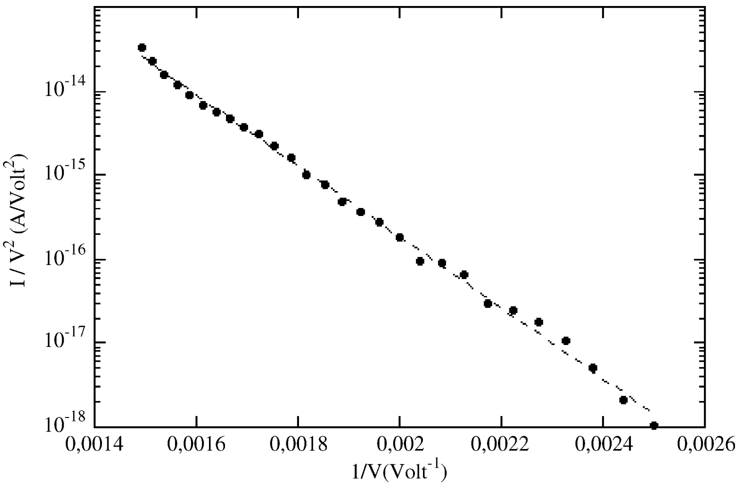

Fig. 5. Fowler–Nordheim plot obtained with an as-produced CN-tip before any treatment. The slope of the curve gives an estimation of the apex radius of ~30 nm coherent with the scanning electron microscopy observations. The emission characteristics show that the TiO_2 layer does not block the field emission process and proves that there is good electrical contact between the CN and the metallic tip.

The goals of this first FE study were to answer several basic questions about the FE from this TiO_2-covered CN. Firstly, does the CN-tip emit electrons at reasonable voltages and does the current follow the FN law of $I \sim V^2 \exp(a/V)$ in the presence of the TiO_2 overlayer. Though obvious for a metallic tip of the same sharp apex of the CN, it is possible that the nominally insulating TiO_2 may block or greatly inhibit the electron emission either at the surface of the apex or because of poor electrical contact between the CN and the W base tip. From Fig. 5, we see that the FN-plot is linear before heat treatment. Furthermore, from the FN-plot of the untreated tip, we estimated the value of r_{apex} to be in the range expected for this CN-tip. Therefore, we can conclude that the TiO_2 layer that covers the CN and its interface with the base tip does not impede FE in an appreciable way.

A second important question was whether the TiO_2 bonding of the CN can withstand appreciable temperatures that are useful for cleaning the CN-tip with the view of stabilizing the FE current. Because the voltages remained in the same range after the heat treatment and the emission pattern position did not vary the CN did not move at all on the base tip apex. Many more heating cycles were carried out at $\approx$700°C and the CN never moved. Therefore the TiO_2 provides excellent bonding of the CN.

In summary, although further investigations are necessary, this clearly proves that these CN-tips can be used for FE sources.

6. Conclusion

A new, simple and cheap method has been developed for placing aligned CNs on support tips. It provides an effective bonding of the CN to the base tip that can withstand temperatures to at least 700 °C and does not inhibit FE. Optimization of the method is being pursued with the future goal of batch fabrication. It will be interesting to use straighter and more structurally perfect CNs and to apply it as a local probe in near field microscopy for high lateral resolution.

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