

This Provisional PDF corresponds to the article as it appeared upon acceptance. Fully formatted PDF and full text (HTML) versions will be made available soon.

## Carbon fibre tips for scanning probe microscopes and molecular electronics experiments

*Nanoscale Research Letters* 2012, **7**:254 doi:10.1186/1556-276X-7-254

Gabino Rubio-Bollinger (gabino.rubio@uam.es)  
Andres Castellanos-Gomez (A.CastellanosGomez@tudelft.nl)  
Stefan Bilan (stefan.bilan@uam.es)  
Linda A Zotti (linda.zotti@uam.es)  
Carlos R Arroyo (carlos.arroyo@uam.es)  
Nicolas Agrait (nicolas.agrait@uam.es)  
Juan Carlos Cuevas (juancarlos.cuevas@uam.es)

**ISSN** 1556-276X

**Article type** Nano Express

**Submission date** 10 January 2012

**Acceptance date** 15 May 2012

**Publication date** 15 May 2012

**Article URL** <http://www.nanoscalereslett.com/content/7/1/254>

This peer-reviewed article was published immediately upon acceptance. It can be downloaded, printed and distributed freely for any purposes (see copyright notice below).

Articles in *Nanoscale Research Letters* are listed in PubMed and archived at PubMed Central.

For information about publishing your research in *Nanoscale Research Letters* go to

<http://www.nanoscalereslett.com/authors/instructions/>

For information about other SpringerOpen publications go to

<http://www.springeropen.com>

© 2012 Rubio-Bollinger *et al.*; licensee Springer.

This is an open access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/2.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

# Carbon-fiber tips for scanning probe microscopes and molecular electronics experiments

Gabino Rubio-Bollinger<sup>1\*</sup>

\* Corresponding address

Email: gabino.rubio@uam.es

Andres Castellanos-Gomez<sup>1\*,2</sup>

\* Corresponding address

Email: a.castellanosgomez@tudelft.nl

Stefan Bilan<sup>3</sup>

Email: stefan.bilan@uam.es

Linda A Zotti<sup>3</sup>

Email: linda.zotti@uam.es

Carlos R Arroyo<sup>1</sup>

Email: carlos.arroyo@uam.es

Nicolás Agrait<sup>1,4</sup>

Email: nicolas.agrait@uam.es

Juan Carlos Cuevas<sup>3</sup>

Email: juancarlos.cuevas@uam.es

<sup>1</sup> Departamento de Física de la Materia Condensada (C–III), Universidad Autónoma de Madrid, Campus de Cantoblanco, Madrid E-28049, Spain

<sup>2</sup> Kavli Institute of Nanoscience, 5046 Delft University of Technology, Delft 2600, GA, Netherlands

<sup>3</sup> Departamento de Física Teórica de la Materia Condensada (C–III), Universidad Autónoma de Madrid, Campus de Cantoblanco, Madrid E-28049, Spain

<sup>4</sup> Instituto Madrileño de Estudios Avanzados en Nanociencia IMDEA-Nanociencia, Madrid E-28049, Spain

## Abstract

We fabricate and characterize carbon-fiber tips for their use in combined scanning tunneling and force microscopy based on piezoelectric quartz tuning fork force sensors. An electrochemical fabrication procedure to etch the tips is used to yield reproducible sub-100-nm apex. We also study electron transport through single-molecule junctions formed by a single octanethiol molecule bonded by the thiol anchoring group to a gold electrode and linked to a carbon tip by the methyl group. We observe the presence of conductance plateaus during the stretching of the molecular bridge, which is the signature of the formation of a molecular junction.

PACS, 07.79.-v, scanning probe microscopes and components, 68.37.Ef, scanning tunneling microscopy (including chemistry induced with STM), 73.63.-b, electronic transport in nanoscale materials and structures, 85.65.+h, molecular electronic devices, 73.40.-c, electronic transport in interface structures

## Keywords

Single-molecule junction, Carbon electrodes, Carbon electronics, STM break junction, Carbon tip, Quartz tuning fork.

## Background

Understanding electron transport through a single molecule is a basic goal in molecular electronics [1]. A primary goal is to find reliable ways to form a stable mechanical and electrical connection between the molecule and macroscopic electrodes. The mechanical and electrical properties of a molecular junction are not only determined by the molecular structure but also by the chemical nature of the electrodes [2].

Here, we have explored the use of carbon-based tips as contact electrodes to form molecular junctions [3]. Using the scanning tunneling microscope (STM) break-junction technique, we have measured the electrical conductance of several hundreds of octanethiol-based single-molecule bridges ( $\text{CH}_3\text{-C}_7\text{H}_{14}\text{-SH}$ ) in which the thiol anchoring group is bound to a gold electrode, and the methyl group is linked to a carbon electrode.

In order to form single-molecule junctions with a carbon electrode, we provide an STM with a carbon-fiber tip [4,5]. The microscopic structure of the tip is composed by graphitic planes aligned parallel to the fiber longitudinal axis, yielding high electrical conductivity  $\sigma = 7.7 \times 10^4$  S/m. Carbon-fiber tips are prepared from freshly cut individual carbon fibers obtained from a commercially available carbon-fiber rope and are mounted in a home-built STM [6].

## Methods

Although the use of mechanically fabricated tips (by simply cutting a metallic wire) is rather common in STM, the atomic force microscope (AFM) resolution strongly depends on the tip sharpness because of long range interactions between the tip and the sample. We have developed an electrochemical procedure to etch carbon-fiber tips that yields sharp carbon-fiber tips.

The setup used to electrochemically etch the carbon fibers [4] is similar to the one used to etch metallic tips [7]. A 5- to 10-mm long fiber is extracted from the fiber rope. One end of the fiber is immersed a few microns into a drop of 4 M KOH solution suspended in a 4-mm diameter gold ring. A voltage bias of 5 V is applied between the fiber end and the gold ring which is grounded. The etching takes place over a period of tens of seconds until the fiber breaks, opening the electrical circuit and stopping the etching. Afterwards, the fiber is rinsed with distilled water. Reproducible tips with sub-100-nm apex radius of curvature can be obtained following this procedure (Figure 1). The tip is then glued with conductive epoxy at the free end of one of the prongs of a miniature quartz tuning fork [8,9]. The fiber is

electrically connected to one of the tuning fork electrodes, which is grounded, in order to be able to simultaneously operate the microscope in STM mode [4].

**Figure 1 Carbon-fiber tip mounted on a tuning fork.** (Left) Optical micrograph of a quartz tuning fork where the carbon-fiber tip is attached at the free end of one of its prongs. (Right) Scanning electron micrograph of an electrochemically etched carbon-fiber tip. The radius of curvature of the tip apex is 50 nm

## Results and discussion

We have studied the interaction force between a carbon-fiber tip and a Au (111) surface when the tip is approached to the surface until reaching the electron tunneling regime. For simultaneous AFM operation, a frequency modulation mode has been used, driving the tuning fork at its resonance frequency using a phase-locked loop circuit [10]. An attractive (repulsive) force gradient acting between tip and sample results in a positive (negative) shift of the resonance frequency. In the limit of a small oscillation amplitude (here 0.2 nm<sub>RMS</sub>), the force gradient can be related to the frequency shift, and the force vs. distance curve (Figure 2a) can be obtained by integration [11]. The time-averaged tunnel current (Figure 2a) is simultaneously measured. We find that tunnel currents of up to 100 pA can be obtained while in the attractive force regime, that is, in the non-contact regime, indicating that the tip is not oxidized or contaminated. The tunnel current vs. tip-sample distance shows an exponential dependence corresponding to a tunnel barrier height of 0.8 eV, which is common for the environmental conditions of the experiment: room temperature in air [12]. We have also measured the change of the quality factor ( $Q$ ) of the tuning fork oscillation during the approach (Figure 2a inset). The  $Q$  factor falls by 40 % before entering the tunnel regime and can be attributed to several sources such as ohmic dissipation or force gradient-induced imbalance of tuning fork prongs [13].

**Figure 2 Carbon-fiber tip and substrate interaction.** (a) Simultaneous measurement of force (black line, left axis) and tunnel current (red line, right axis) during a tip-sample approach. The inset shows the simultaneously measured quality factor of the tuning fork oscillation. (b) Topography image of an octanethiol self-assembled monolayer (SAM) on Au (111) sample obtained in the constant tunnel current STM mode and (c) the simultaneously measured frequency shift of the tuning fork oscillation which enables to unambiguously identify bare gold areas (dark) and SAM-covered regions (bright)

Single-molecule junctions are obtained by repeatedly forming and breaking the contact [2,14,15] between the tip and a gold substrate partially covered with an octanethiol self-assembled monolayer shown in Figure 2b. The molecules were deposited on a gold substrate (commercially available from Arrandee, Werther, Germany) which was initially treated with piranha solution and then flame annealed to prepare a flat reconstructed Au (111) surface. The substrate was incubated for 12 h in a 1-mM solution of octanethiol (Sigma-Aldrich Corporation, MO, USA) in toluene, rinsed and sonicated in pure toluene and subsequently dried in a stream of helium gas. These deposition conditions are well known to yield a densely packed SAM [16]. Molecules are contacted by gentle repeated indentation of the tip into the substrate until the tunnel resistance is 2 M $\Omega$ . The tip is subsequently retracted, and the electrical conductance trace is measured. To overcome junction-to-junction fluctuations, we have performed a statistical analysis [17,18] in which all junction realizations are taken into account to build a conductance histogram (Figure 3) from all the 640 conductance traces

acquired at 20 different spots of the SAM. The hump in the histogram is associated with the presence of conductance plateaus in individual traces and the background with tunnel conduction. We find that the broad hump can be fitted to the sum of two Gaussian peaks in a linear conductance scale whose centers are located at  $G_1 = (5.9 \pm 4.1) \times 10^{-6} G_0$  and  $G_2 = (1.3 \pm 0.5) \times 10^{-5} G_0$ , where  $G_0$  is the conductance quantum ( $2e^2/h$ , with  $e$  the electron electric charge, and  $h$  the Plank's constant). The fact that the value of  $G_2$  is twice that of  $G_1$  suggests that plateaus at conductance  $G_2$  correspond to electron transport through two simultaneously connected molecules, each of which has a conductance  $G_1$ .

**Figure 3 Octanethiol molecule conductance histogram.** Conductance histogram built from 500 traces (dark red) and corrected histogram (light red) after subtracting the tunneling contribution. The corrected histogram shows two conductance peaks. The most probable conductance associated to these peaks is obtained from the fit of the corrected histogram to the sum of two Gaussian curves. The dashed purple and blue curves are the two Gaussians, and the dotted black curve is their sum. The positions of the maximum of the peaks mark the two most probable molecular configurations

## Conclusions

We have fabricated and characterized carbon-fiber tips for their use in combined STM/AFMs based on quartz tuning fork force sensors. We develop an electrochemical procedure to etch carbon-fiber tips which yields sub-100-nm tip apex radius of curvature in a reproducible way, increasing the lateral resolution in AFM measurements. We show that carbon-fiber tips mounted on quartz tuning fork force sensors can be reliably used in force and/or tunnel current vs. distance measurements and simultaneous STM/AFM microscopy.

In addition, we have used carbon fiber tips as electrodes in an STM-break junction configuration to form single-molecule junctions with octanethiol molecules deposited on a gold surface. We find that carbon tips provide a stable mechanical linking to the methyl group allowing to form single-molecule bridges. Therefore, carbon tips can be suitable candidates to contact a variety of organic molecules, and they can also be combined with other substrate materials including carbon itself to form purely organic single-molecule devices.

## Abbreviations

AFM, atomic force microscope; SAM, self-assembled monolayer; STM, scanning tunneling microscope.

## Competing interests

The authors declare that they have no competing interests.

## Authors' contributions

GRB, ACG, CRA and NA participated in the experiment and its interpretation. SB, LAZ and JCC performed Density Functional Theory calculations of the studied molecular junctions. All authors read and approved the final manuscript.

## Acknowledgments

This work was supported by MICINN (Spain) through the programs MAT2008-01735, MAT2011-25046 and CONSOLIDER-INGENIO-2010 ‘Nanociencia Molecular’ CSD-2007-00010; Comunidad de Madrid through program Nanobiomagnet S2009/MAT-1726; and European Union through programs BIMORE (MRTN-CT-2006-035859) and ELFOS (FP7).

## References

1. Reed MA, Zhou C, Muller CJ, Burgin TP, Tour JM: **Conductance of a molecular junction.** *Science* 1997, **278**:252–254.
2. Chen FLX, Hihath JHZ, Tao N: **Effect of anchoring groups on single-molecule conductance: comparative study of thiol-, amine-, and carboxylic-acid-terminated molecules.** *J Am Chem Soc* 2006, **128**:15874–15881.
3. Castellanos-Gomez A, Bilan S, Zotti LA, Arroyo CR, Agraït N, Cuevas JC, Rubio-Bollinger G: **Carbon tips as electrodes for single-molecule junctions.** *Appl Phys Lett* 2011, **99**:123105.
4. Castellanos-Gomez A, Agraït N, Rubio-Bollinger G: **Carbon fibre tips for scanning probe microscopy based on quartz tuning fork force sensors.** *Nanotechnology* 2010, **21**:145702.
5. Sripirom J, Noor S, Kohler U, Schulte A: **Easily made and handled carbon nanocones for scanning tunneling microscopy and electroanalysis.** *Carbon* 2011, **49**:2402–2412.
6. Smit RH, Grande R, Lasanta B, Riquelme JJ, Rubio-Bollinger G, Agraït N: **A low temperature scanning tunneling microscope for electronic and force spectroscopy.** *Rev Sci Instrum* 2007, **78**:113705.
7. Kim P, Kim JH, Jeong MS, Ko D-K, Lee J, Jeong S: **Efficient electrochemical etching method to fabricate sharp metallic tips for scanning probe microscopes.** *Rev Sci Instrum* 2006, **77**:103706–103705.
8. Giessibl FJ: **High-speed force sensor for force microscopy and profilometry utilizing a quartz tuning fork.** *Appl Phys Lett* 1998, **73**:3956–3958.
9. Castellanos-Gomez A, Agraït N, Rubio-Bollinger G: **Dynamics of quartz tuning fork force sensors used in scanning probe microscopy.** *Nanotechnology* 2009, **20(21)**:215502.
10. Edwards H, Taylor L, Duncan W, Melmed A: **Fast, high-resolution atomic force microscopy using a quartz tuning fork as actuator and sensor.** *J Appl Phys* 1997, **82**:980.
11. Giessibl F: **A direct method to calculate tip–sample forces from frequency shifts in frequency-modulation atomic force microscopy.** *Appl Phys Lett* 2001, **78**:123.

12. Hahn J, Hong Y, Kang H: **Electron tunneling across an interfacial water layer inside an STM junction: tunneling distance, barrier height and water polarization effect.** *Appl Phys Mater Sci Process* 1998, **66**:467–472.
13. Castellanos-Gomez A, Agraït N, Rubio-Bollinger G: **Force-gradient-induced mechanical dissipation of quartz tuning fork force sensors used in atomic force microscopy.** *Ultramicroscopy* 2011, **111**:186–190.
14. Xu B, Tao NJ: **Measurement of single-molecule resistance by repeated formation of molecular junctions.** *Science* 2003, **301**:1221.
15. Venkataraman L, Klare JE, Nuckolls C, Hybertsen MS, Steigerwald ML: **Dependence of single-molecule junction conductance on molecular conformation.** *Nature* 2006, **442**:904–907.
16. Poirier GE, Pylant ED: **The self-assembly mechanism of alkanethiols on Au (111).** *Science* 1996, **272**:1145–1145.
17. Gonzalez MT, Wu S, Huber R, van der Molen SJ, Schönenberger C, Calame M: **Electrical conductance of molecular junctions by a robust statistical analysis.** *Nano Lett* 2006, **6**:2238–2242.
18. Xia JL, Diez-Perez I, Tao NJ: **Electron transport in single molecules measured by a distance-modulation assisted break junction method.** *Nano Lett* 2008, **8**:1960–1964.

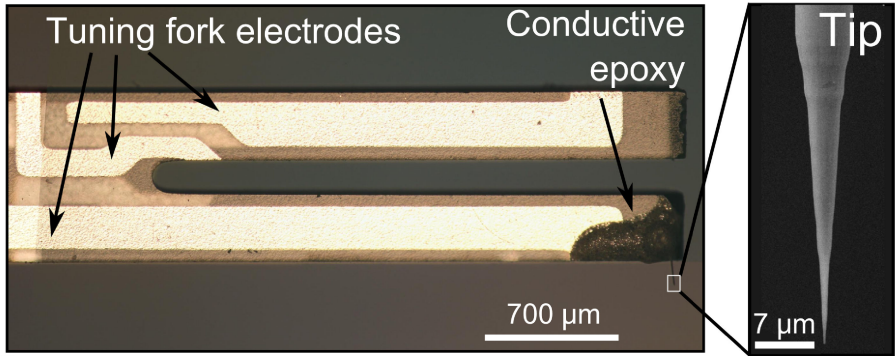
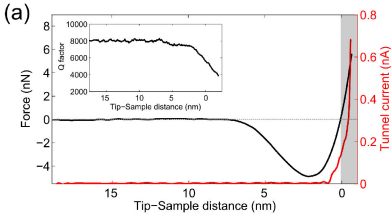


Figure 1





0 nm 1 nm

19 Hz 22 Hz

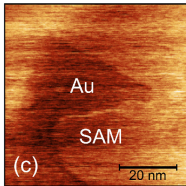
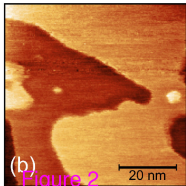


Figure 2

