Etude a l'échelle nanométrique de molécules uniques sur une surface : propriétés physico-chimiques de nanotubes de carbone modifiés

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Résumé :
Les nanotubes de carbone mono-paroi consistent en une feuille de graphène roulée sur elle-même, et possèdent des propriétés uniques pour des applications extrêmement prometteuses pour des composants électroniques, mécaniques ou chimiques. En fonction de leur diamètre et chiralité, les nanotubes peuvent représenter des fils unidimensionnels de type métallique ou semi-conducteur. Ainsi, un grand nombre de dispositifs électroniques ont pu être réalisés expérimentalement, comme des transistors mono-électroniques ou à effet de champ. De tels systèmes peuvent aussi servir comme bases pour d'autres applications telles que des capteurs chimiques ou des dispositifs électromécaniques. Les défauts structurels de la maille de carbone, tels que dislocations, lacunes, fonctionnalisation chimique ou molécules adsorbées, peuvent modifier substantiellement les propriétés électroniques des nanotubes de carbone. Une compréhension poussée des liens entre ces modifications et leurs effets sur les propriétés des nanotubes permettra de contrôler effectivement ces dernières.
Le microscope à effet tunnel (en anglais STM) est l'un des instruments les plus performants pour étudier la structure à l'échelle atomique ainsi que les propriétés électroniques de systèmes constitués de molécules uniques sur des surfaces. Il permet de plus d'agir directement sur des processus chimiques élémentaires, soit par action mécanique avec la pointe (manipulation), soit par l'effet du champ électrique créé dans la jonction et l'énergie libérée par les électrons tunnels.
Nous présentons un nouveau projet de recherche par microscopie à effet tunnel utilisant des nanotubes de carbone comme substrat et/ou réactant pour des réactions avec des molécules organiques.

Abstract :
Single-walled carbon nanotubes (SWCNT), which consist in graphene sheets rolled-up into cylinders, have proven to possess unique properties for promising applications in electronic, mechanical and chemical devices. Depending on their diameter and chirality, SWCNT can be either one-dimensional metals or semiconductors, and a variety of electronic devices based on SWCNT, such as single-electron and field-effect transistors, have been realized experimentally. These systems can serve as well as a basis for other related applications such as chemical sensors and electromechanical devices. Structural defects in the carbon lattice of SWCNT, such as topological defects, vacancies, chemical functionalization, and molecule adsorption can substantially modify the electronic properties of SCWNT. A good control and understanding of such modifications is required for allowing a fine tuning of their properties.
Scanning tunneling microscopy (STM) is one of the most efficient tools for determining the atomic-scale structure and investigating electronic properties of individual molecules at surfaces. It allows furthermore to directly act on individual chemical processes, either by mechanical action with the tip (manipulation), or through the electric field in the junction and the energy delivered by the tunneling electrons.
We present a new project of single-molecule chemistry by Scanning Tunneling Microscopy utilizing carbon nanotubes as a substrate and/or reactant for chemical reaction with organic molecules.

Introduction :

Nanoscale studies on molecules at well-defined surfaces have proven to be particularly promising, for the fundamental interest of understanding chemistry at the single-molecule level as well as with regard to the extensive versatility of such systems, whose functionality, structure and properties can be extensively tuned. Scanning tunneling microscopy (STM) is one of the most efficient tools for determining the atomic-scale structure and investigating electronic properties of individual molecules at surfaces.[1] It allows furthermore to directly act on individual chemical processes, either by mechanical action with the tip (manipulation), or through the electric field in the junction and the energy delivered by the tunneling electrons. It has been demonstrated that the latter can induce electronic and/or vibrational excitations of the adsorbates that cause various surface phenomena. STM studies can reveal the pathway to how the energy stored with such excitation is transferred to the chemical reaction of the molecules. In addition, they shed light on the electronic and/or vibrational structure itself, giving supplemental information to the spectroscopic data. Locally resolved inelastic tunneling spectroscopy (IETS) in a STM is a candidate for the ultimate chemical analysis.

We present a new project of single-molecule chemistry utilizing carbon nanotubes as a substrate and/or reactant for chemical reaction with organic molecules.

Single-walled carbon nanotubes (SWCNTs), which consist in graphene sheets rolled-up into cylinders, have been discovered by Iijima in 1991. Since then, legions of studies have revealed their unique properties and their promising applications in electronic, mechanical and chemical devices. Depending on their diameter and chirality, SWCNTs can be either one-dimensional metals or semiconductors, and a variety of electronic devices based on SWCNTs, such as single-electron transistors and field-effect transistors, have been realized experimentally.[2] These systems can serve as well as a basis for other related applications such as chemical sensors and electromechanical devices. Most of experimental and theoretical investigations have focused on defect-free SWCNTs with perfect honeycomb carbon arrangements. Recent studies have shown, however, that structural defects in the underlying carbon lattice, such as topological defects, vacancies, chemical modifications, and molecule adsorption can substantially modify the electronic properties of SWCNTs.[3] For example, functionalization of nanotube walls by atomic hydrogen can be very useful for transistor and memory application, where a semi-conducting character is required. The hydrogenated SWCNT has been predicted to reveal the band gap opening due to a local rehybridization from sp^2 to sp^3 of the carbon network. It has been reported that hydrogen functionalization of SWCNTs can transform the electronic structure systematically from metallic to semi-conducting and from narrow-gap semi-conducting to large-gap semi-conducting. By dedicating the powerful atomic-scale capabilities of STM to such novel materials we intend to attain new insights for tuning the functionality of SWCNTs by modifying their surface with molecular species, and therefore be able to create systems with tailored structure and properties.

In conclusion, we are using low-temperature scanning tunneling microscopy (LT-STM) to perform fine measurements on molecular systems at surfaces. The well-established atomic scale imaging capabilities of this technique will be enlarged by the recent developments which demonstrate very high sensitivity to the electronic and magnetic states at the local scale. The investigations planned should deliver a deeper understanding of the basic properties of matter at the nanometer scale, and open new opportunities for the development of novel functional materials.

References

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