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Nanoelectrodes for Molecular Devices: A Controllable Fabrication

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The miniaturization of components for the construction of useful devices is an essential feature of modern technology. Their miniaturization permits the assembly of ultra-densely integrated circuits and faster processors. However, along with the developing of silicon-based electronics, it is becoming apparent that intrinsic limitations will prevent their miniaturization down to the nanoscale. To solve these problems, an alternative and promising strategy, called the bottom-up approach, was suggested by an eminent physicist and visionary, Richard Feynman, in 1959. In the bottom-up approach, one can build nanodevices starting from atom or molecules. Via this strategy, a series of significant advances have been achieved in recent years. However many problems still exist, hampering its further development.

This said, the researchers were faced with a puzzling problem—How can nanoelectrodes with a controllable gap size be fabricated? This is particularly important because the fundamental basis of molecular electronics requires the electrodes to be fabricated with a gap size commensurate to the size of molecules of interest. Despite reports on successful attempts such as break junction, electrochemical method, and nanowire lithography, the precise control of the gap size still need be resolved. For instance, it is a problem to provide a real time characterization during the fabrication of the nanoelectrodes; thus, the exact gap size is usually undetectable, leaving the precise control of the gap size unfeasible and inefficient. Moreover, the existing methods often are far routine, low yielding and difficult to implement.

To solve these problems, Chinese scientists have demonstrated a new method based on the electron-beam-induced deposition (EBID) process to realize a real time and in situ characterization in nanoelectrode fabrication. This technique has thus far been successful in easily and precisely controlling the gap size of the nanoelectrodes.

"The research of molecular electronics was launched in 1974, when Ari Aviram and Mark A. Ratner proposed an electrical rectifier by a single molecule with suitable electronic asymmetry. From that time, the fabrication of nanoelectrodes with a molecular gap size remains a puzzle for the researchers. This is also the first obstacle we encountered." Prof. Yunqi Liu explains, "We tried many methods; however, the present methods are too fastidious for us to implement. Most important, we need a real time and in situ characterization in the fabrication for controlling the gap size of nanoelectrodes; however, the present methods could not afford."

"EBID is a maskless process using a high-intensity electron beam to deposit nanoscale structures on a scanned surface, and it has been widely used in nanofabrication." Says Prof. Liu "In the scanning electron microscopy (SEM) test of carbon nanotubes (CNTs), we found that the CNTs became broader after electron beam irradiation, and this should originate from EBID. Based on this finding, we developed a new method to produce nanoelectrodes."

Yunqi Liu, the Professor of Institute of Chemistry at the Chinese Academy of Sciences in Beijing, P. R. China, developed the method along with graduate student Dacheng Wei. This work has been published in the May 23, 2008 online edition in Nano Letters ("Real time and in situ control of the gap size of nanoelectrodes for molecular devices).

"We place a CNT between Au/Ti electrodes on a SiO_2/Si wafer, and then cut it at the middle to form a wide original gap in the range of 10–60 nm. The electrode is exposed to organic vapor to absorb organic molecules on the CNT." Prof. Liu describes the process, "if we place the

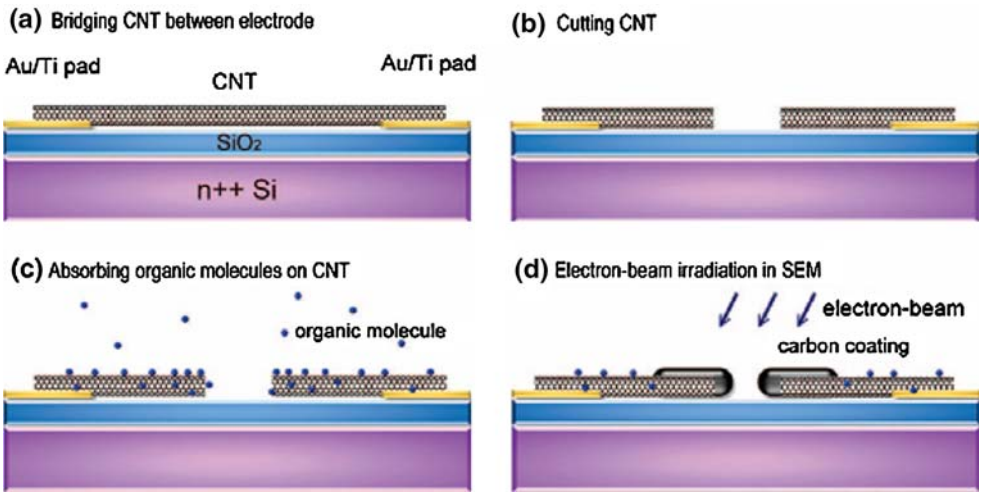

Fig. 1 Schematic diagram of the process of the fabrication of a CNT electrode with a controlled nanogap. (**a**) Bridging a CNT between Au/Ti electrodes. (**b**) Cutting the CNT by current breakdown method. (**c**) Adsorbing organic molecules on or in the CNT. (**d**) Irradiating the gap of the CNT by electron beam with in situ observation in SEM. (Reprinted with permission from American Chemical Society)

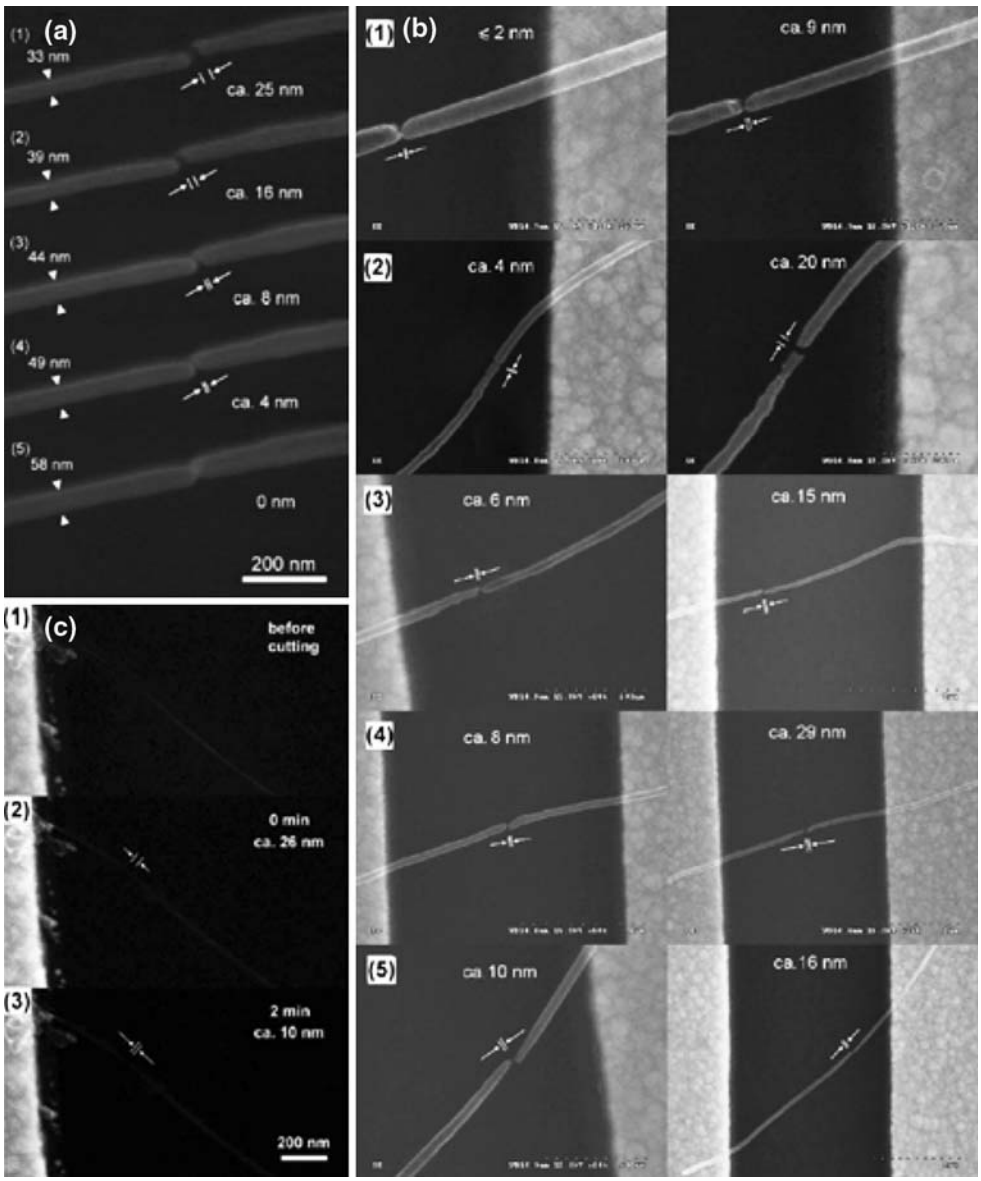

Fig. 2 SEM images of the CNT nanoelectrodes. (**a**) SEM images of a CNT electrode in the EBID process: (1) just after current breakdown; (2–5) after an EBID process of 2, 4, 6, and 10 min, respectively. (**b**) CNT electrodes with a series of gap sizes fabricated by the EBID method: (1–5). The left images are SEM images measured after the EBID process, the gap sizes are ca. 2, 4, 6, 8, and 10 nm, respectively, and the right images are SEM images measured before the EBID process. (**c**) SEM images of a nanoelectrode which is made of single-walled CNTs (1) before current breakdown, (2) before the EBID process, and (3) after about 2 min in the EBID process. (Reprinted with permission from American Chemical Society)

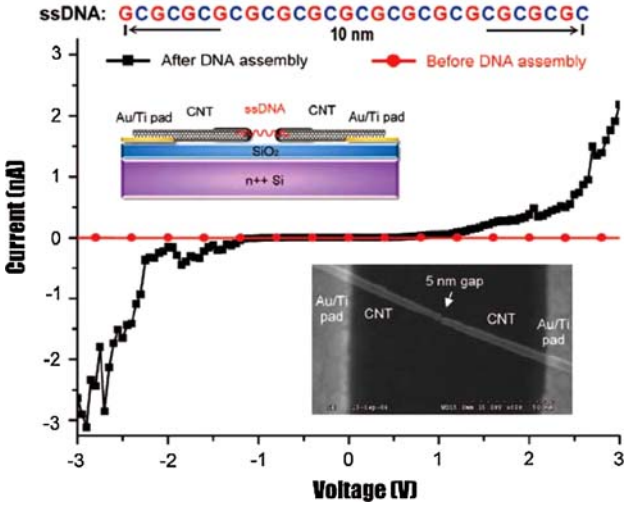

Fig. 3 The electrical properties of a DNA device fabricated by using the CNT electrodes. The I–V curves are measured before (red) and after (black) the assembly of DNA on the nanoelectrode. The upper inset shows a scheme of the device, and the lower inset is the SEM image of a CNT nanoelectrode used in the device. (Reprinted with permission from American Chemical Society)

electrode in SEM and focus a high-density electron beam on the area of the gap of the electrode, the irradiated part of the CNT will gradually become broader, and as a result the gap becomes narrower. Because this process is observed in real time and in situ by SEM, we can stop the process at any time, and then an electrode with the gap size corresponding to our need is obtained" (Fig. 1).

Juxtapose to existing methods, the method proposed by Prof. Liu's group is very simple and controllable. "What we need is a SEM. In previous research, the SEM serves primarily as a tool to precisely characterize the gap size of the nanoelectrodes. In our method, the SEM plays two roles. First, the SEM provides an in situ and real time characterization of the gap size. Second, the electron beam of SEM induces broadening of CNTs and narrowing of the gap. Now it is very simple for us to fabricate nanoelectrodes with certain gap size. We can fabricate nanoelectrodes with a series of gap sizes." Prof. Liu says, "moreover, It is a clean process without introducing impure atoms and a nondestructive process for CNT electrodes" (Fig. 2).

The nanoelectrodes produced by this method have a π-conjugated surface. Prof. Liu et al. tested the nanoelectrodes after EBID by Raman, and the Raman spectra showed that the deposit was sp^2-rich amorphous carbon, which offered the nanoelectrodes a π-conjugated surface. By using these nanoelectrodes, Prof. Liu's group produced molecular devices by using DNA molecules.

"Since the DNA has a strong π–π interaction with π-conjugated surface, the DNA molecules will assemble between the nanoelectrodes. And after assembly, typical I–V curves of DNA molecules are observed, which means that these nanoelectrodes are available for the use in molecular devices." Prof. Liu says, "in previous research, DNA molecules have been connected in circuit by Au nanoelectrodes or scanning probe microscope tips, and the current flows through the electrode/DNA interface by tunneling barriers or chemical bonds. However, in our case, the current through the interface by the π–π stacking between the nanoelectrodes with π-conjugated surfaces and the DNA molecules, thus the π–π stacking can also provide a well contact" (Fig. 3).

Prof. Liu's group has contributed to the current state of molecular electronics by providing a simple and efficient method to fabricate nanoelectrodes with controlled gap size with a real time and in situ characterization. It will be most valuable for the current efforts to investigate or realize molecular electronics and nanoelectronics.

Kimberly Sablon