

# Selective Positioning and Integration of Individual Single-Walled Carbon Nanotubes

Liying Jiao, Xiaojun Xian, Zhongyun Wu, Jin Zhang, and Zhongfan Liu\*

*Centre for Nanoscale Science and Technology, Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China*

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## ABSTRACT

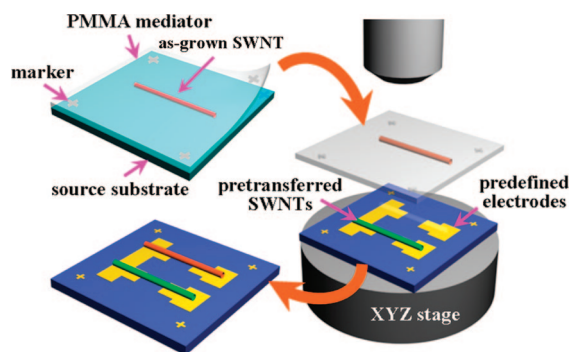
We present a general selective positioning and integration technique for fabricating single-walled carbon nanotube (SWNT) circuits with preselected individual SWNTs as building blocks by utilizing poly(methyl methacrylate) (PMMA) thin film as a macroscopically handleable mediator. The transparency and marker-replicating capability of PMMA mediator allow the selective placement of chirality-specific nanotubes onto predesigned patterned surfaces with a resolution of ca. 1  $\mu\text{m}$ . This technique is compatible with multiple operations and p–n conversion by chemical doping, which enables the construction of complex and logic circuits. As demonstrations of building SWNTs circuits, we fabricated a field effect inverter, a  $2 \times 2$  all-SWNT crossbar field effect transistor (FET), and flexible FETs on plastic with this technique. This selective positioning approach can also be extended to construct purpose-directed architecture with various nanoscale building blocks.

A breakthrough on integrating one-dimensional (1D) nanoscale building blocks into circuits is vital to their practical application in nanoelectronics. The technological difficulties of fabricating practical scalable circuits with nanowires or single-walled carbon nanotubes (SWNTs) mainly arise from organizing these nanoscale building blocks into designed hierarchical structures. A series of techniques have been developed to assemble nanowires, including electric field assembly,<sup>1</sup> fluidic flow assembly,<sup>2,3</sup> Langmuir–Blodgett technique,<sup>4</sup> patterned chemical assembly,<sup>5</sup> contact printing,<sup>6,7</sup> and other methods.<sup>8</sup> The obtained integrated architectures of nanowires have been demonstrated to work as transistors,<sup>1</sup> complex logic gates and computational circuits,<sup>9</sup> nanosensors,<sup>10</sup> nanophotonic devices,<sup>1,11</sup> three-dimensional (3D) multifunctional devices,<sup>6,7</sup> and so on. Different from nanowires, the electronic properties of SWNTs are dependent on both tube diameters and chiralities. The coexistence of semiconducting and metallic SWNTs introduces greater challenge for integrating them into devices. Although most of the assembly techniques mentioned above can also be applied to align collections of SWNTs,<sup>12–16</sup> they lack the ability to control and assemble individual SWNTs with specific chirality into functional structures. Recently, placement of individual SWNTs with specific chirality was realized by directly transferring as-grown suspending SWNTs

from substrates with slit<sup>17</sup> or pillars<sup>18</sup> to target substrates. Obviously, the utilization of special structured substrates introduced restrictions to geometry and length of the SWNTs of interest. The necessary mechanical contact of two solid surfaces in this case may also disturb and even damage the transferred SWNTs. Despite these efforts, to date, no effective method has been developed to selectively handle individual SWNTs in a well-controlled fashion for fabricating purpose-directed electrical circuits. Here we demonstrate a general approach for precisely positioning chirality-specific SWNTs on solid surfaces by using poly(methyl methacrylate) (PMMA) as a macroscopically handleable mediator, which enabled fabrication of various SWNT electronic devices by the selective positioning of metallic, p- and n-type semiconducting tubes to predefined electrode patterns.

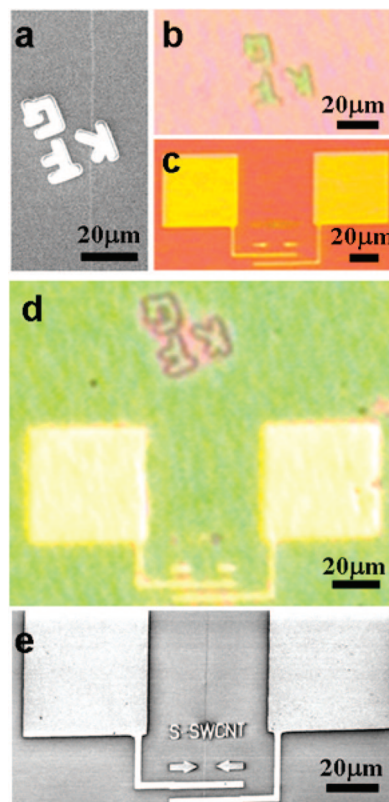
The present approach is based on the manipulation of individual SWNTs by handling the PMMA mediator at macroscale. Briefly, SWNTs with desired properties on a source substrate are first loaded onto PMMA mediator. Then the mediator is driven to contact with target substrate at the desired location with an aligning system. Finally, the PMMA film is removed to release the SWNTs onto the target surface. Such a macroscopic manipulation process of nanoscale building blocks is schematically shown in Figure 1, which takes the fabrication of a SWNT inverter as an example. Arbitrary architectures and devices with specific SWNTs can be constructed by repeating the above operation. In this work,

\* To whom correspondence should be addressed: tel and fax, 86-10-6275-7157; e-mail, zfliu@pku.edu.cn.



**Figure 1.** Schematic of controlled positioning of individual SWNTs on the target surface at the desired location, taking the fabrication of inverter as an example.

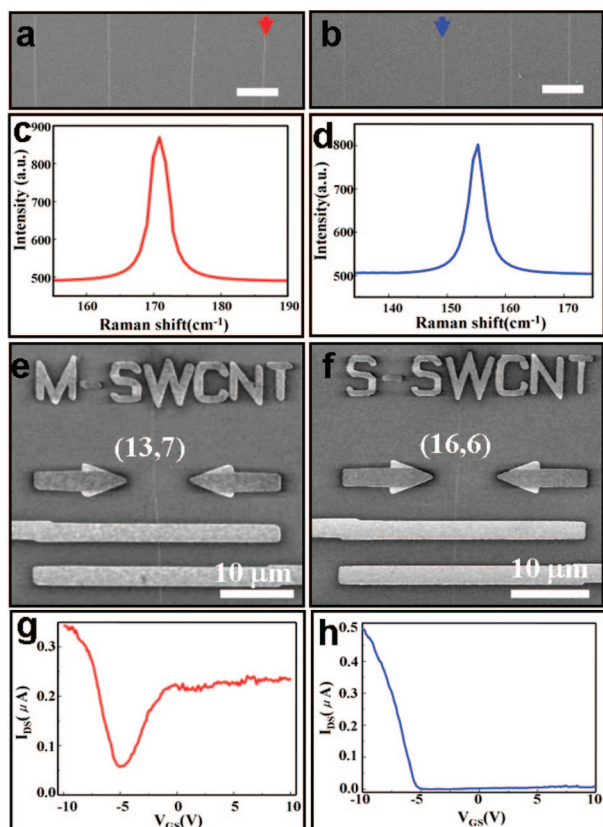
ultralong SWNT arrays were synthesized by flow-directed chemical vapor deposition (CVD)<sup>19</sup> on SiO<sub>2</sub>/Si substrate with a pre-designed marker array. The as-grown SWNTs were characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The possible chirality of SWNTs could be deduced from the radial breathing mode (RBM) frequency at 632.8 nm excitation.<sup>20</sup> Therefore we could recognize and select tubes with specific chirality from the SWNTs array. The relative positions of desired SWNTs to nearby markers were recorded in SEM images. To load the SWNTs of interest onto PMMA mediator, we utilized the nanotransfer printing technique we developed recently.<sup>21,22</sup> By spin-coating PMMA solution ( $M_w = 950$  K, 4 wt %, AR-P 679.04, Allresist) at 3000 rpm for 1 min on source substrate, followed by baking at 170 °C for 2 h, the SWNTs were encapsulated in the PMMA mediator. After that, the PMMA–SWNT film was peeled off from the source substrate by controlled hydrolyzation of PMMA in basic solution (1 M KOH aqueous solution, 80 °C). The transparency of peeled-off PMMA–SWNTs film offered the possibility of positioning SWNTs to exact location on target surface with the aid of a marker aligner which was composed of an optical microscope, a fixed top stage, and a XYZ movable bottom stage. To facilitate the aligning process, there are two key points to address. First, it is essential to fabricate markers on PMMA film for positioning the desired SWNTs. Second, a rigid holder is necessary for supporting and handling the flexible mediator film. We simply obtained markers on PMMA in a spin-coating process by replicating the pre-etched marker array fabricated with photolithography and reactive ion etching (RIE) of SiO<sub>2</sub> on source substrate prior to growing SWNTs. The replicated markers array made it possible to locate the SWNTs of interest on PMMA mediator very easily. To support the PMMA film, we designed a holder which was composed of a silicon chip with a centered round hole and a ferrous clip. The peeled-off PMMA mediator film was rinsed in ultrapure water before being attached to the silicon chip, and it adhered well to the chip after drying in air. After that, the silicon chip was clamped to the ferrous clip and then fixed to a magnet on the top stage of the aligner. No glue was introduced to fix the PMMA film, which allowed a clean-transfer printing process. The aligning operation was accomplished by driving the XYZ stage into contact with the PMMA–SWNT film with the assistance of



**Figure 2.** (a) SEM image of an as-grown SWNT with a marker on SiO<sub>2</sub>/Si substrate. (b and c) Optical images of the PMMA–SWNT film and target electrodes before aligning, respectively. (d) Optical image of the PMMA–SWNT film adhered to the target electrodes after aligning and releasing. (e) SEM image of the SWNT shown in (a) positioned at the center of the electrodes shown in (c).

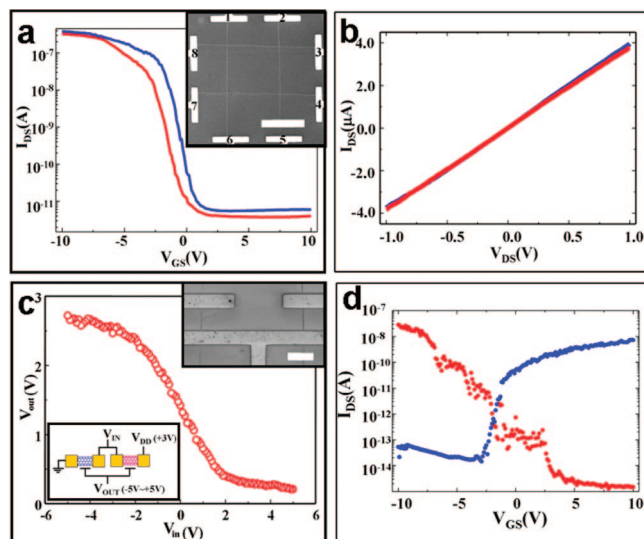
replicated markers on the PMMA and the markers pre-designed on the target surface, both of which were visible under optical microscopy. The PMMA–SWNT film was released from the silicon chip supporter to target substrate by injecting one drop of ultrapure water through the round hole followed by drying with high-purity nitrogen flow (see Supporting Information for details, Figure S1). The target substrate was then retracted with the bottom stage. Finally, the PMMA mediator was removed by dissolving in acetone vapor, leaving the SWNTs of interest anchored on the target surface at a desired location. Figure 2 shows the positioning process starting from an as-grown SWNT with a marker on the SiO<sub>2</sub>/Si substrate (Figure 2a). Panels b and c of Figure 2 exhibit the optical images of the peeled-off PMMA–SWNT film and the predefined electrode pattern fixed on the top and bottom stages of the aligner, respectively. In Figure 2d is given the optical image of the PMMA–SWNT film attached on the target electrode after aligning. After the PMMA mediator was dissolved, the SWNT of interest was successfully placed at the center of the electrode pattern (see Figure 2e). These results demonstrated the controlled positioning capability of this PMMA-mediated approach.

A serious challenge for creating SWNTs electronic devices is the chirality controlled growth and chiral separation.<sup>23</sup> The as-grown SWNT samples are always a mixture of nanotubes having different chiralities, which makes it difficult to create a chirality-specific SWNT device. Figure 3 demonstrates the



**Figure 3.** Controlled positioning of selected SWNTs with specific chirality onto the predefined electrodes. (a and b) SEM images of as-grown arrays of parallel SWNTs, where the arrows indicate the selected tubes. Scale bar, 20  $\mu\text{m}$ . (c and d) Raman spectra of the selected tubes shown in (a) and (b), respectively. The possible assignment of two tubes is (13, 7) and (16, 6), indicating they are metallic and semiconducting SWNTs, respectively. (e) SEM image of the metallic SWNT placed onto gold electrodes marked with “M-SWCNT”. (f) SEM image of the semiconducting tube placed onto electrodes marked with “S-SWCNT”. The spacing between two opposite arrows is 8  $\mu\text{m}$ . (g and h)  $I_{\text{DS}}-V_{\text{GS}}$  curves (at  $V_{\text{DS}} = 0.1$  V) of the transferred tubes measured with the electrodes shown in (e) and (f), respectively.

possibility of solving this problem using our PMMA-mediated selective positioning approach. A selection of nanotubes with specific chirality from SWNTs array was done by Raman spectral mapping. As shown in Figure 3a–d, two specific nanotubes with RBM frequencies of 171.0 and 155.1  $\text{cm}^{-1}$  were chosen in this case, corresponding to a possible chirality of (13, 7) and (16, 6),<sup>20</sup> respectively. Using a PMMA-mediated positioning approach, the metallic (13, 7) tube and semiconducting (16, 6) tube were placed onto the predefined electrodes marked with “M-SWCNT” (Figure 3e) and “S-SWCNT” (Figure 3f), respectively. A spatial resolution of ca. 1  $\mu\text{m}$  for tube positioning has been achieved, which is determined by the optical microscope and XYZ stage used and can be further improved by employing a piezo device. As demonstrated in panels g and h of Figure 3, the transferred tubes exhibit typical characteristics of metallic and semiconducting SWNTs, respectively. The on-state resistance of this 4  $\mu\text{m}$  semiconducting SWNT was ca. 200 k $\Omega$  and the on–off current ratio was ca.  $10^5$ , which proved that good SWNT–electrode contacts can be generated with



**Figure 4.** (a) Inset shows the SEM image of a  $2 \times 2$  SWNTs crossbar circuit. Scale bar, 50  $\mu\text{m}$ . The red curve represents  $I_{\text{DS}}-V_{\text{GS}}$  characteristic (at  $V_{\text{DS}} = 0.1$  V) of two vertical semiconducting SWNTs measured with 3 and 4 as contacts and the blue one with 7 and 8 as contacts. (b) Current–voltage characteristics (at  $V_{\text{GS}} = -10$  V) of the vertical semiconducting tubes shown in (a) measured with two pairs of different terminals of metallic tubes (red, 3 and 4; blue, 7 and 8). (c) Transfer characteristics of the inverter shown in the upper inset. The right tube is n-type while the left one is p-type. Scale bar, 10  $\mu\text{m}$ . The lower inset displays the schematic device configuration. (d)  $I_{\text{DS}}-V_{\text{GS}}$  curves of the right tube shown in (c) before (red curve) and after (blue curve) doping with PEI.

this technique. This selective positioning approach allows the construction of a SWNT-based circuit with desired metallic and semiconducting SWNTs.

One of the prominent features of this PMMA-mediated approach is its compatibility with multiple positioning operations, which enables the construction of complex architectures. As an example, we created a  $2 \times 2$  crossbar circuit consisting of two vertical semiconducting tubes and two horizontal metallic tubes connected to eight individual microelectrodes as shown in the inset of Figure 4a. Four consecutive positioning operations were involved in locating these chirality-specific nanotubes onto the electrode patterns. Obviously, the sequential positioning operation did not perturb the pre-existing architectures. With the semiconducting tubes as conduction channels, the metallic tubes as interconnects, and the underlying silicon as bottom gate, the circuit operated as an all-SWNTs FET device. It exhibited a p-FET characteristic with an on–off current ratio of ca.  $10^5$  by measuring two pairs of different terminals (see  $I_{\text{DS}}-V_{\text{GS}}$  curves shown in Figure 4a). The linear  $I_{\text{DS}}-V_{\text{DS}}$  curves (Figure 4b) indicate good electrical contact between metallic and semiconducting tubes. This is a direct experimental demonstration of individual metallic SWNTs working as effective interconnects. Such kinds of crossbar structures have been successfully generated with layer-by-layer assembly of as-grown heterogeneous nanowires.<sup>2,9</sup> But the strategy cannot be extended to SWNTs because it lacks the capability of selecting semiconducting SWNTs from metallic mixtures. The SWNTs circuit we obtained with the selective

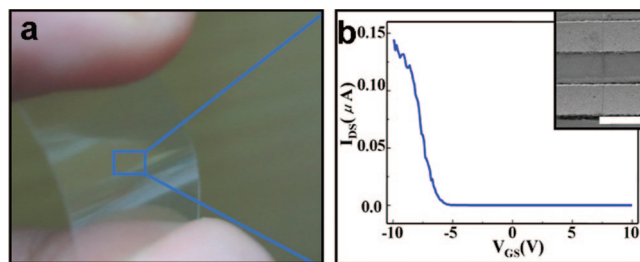


positioning technique is expected to be the starting point of constructing complex all-SWNTs circuits.

Obtaining and integrating both p- and n-type FETs is also a key challenge for building SWNTs-based integrated devices. The as-synthesized SWNTs are generally p-type in air due to the doping effect of oxygen.<sup>24</sup> Current approaches focused on generating p- and n-FET along individual SWNTs by doping<sup>25,26</sup> or using metal contacts with different work functions.<sup>27</sup> There is still lack of efficient ways to integrate p- and n-type SWNTs in an arbitrary manner. To demonstrate that our PMMA-mediated approach is capable of integrating p- and n-type SWNTs, we built a SWNTs field-effect inverter (Figure 4c). To fabricate the inverter, we first transferred a p-type semiconducting SWNT onto a predefined electrodes pattern and converted it into n-type by doping with poly(ethylenimine) (PEI).<sup>28</sup> The obtained  $I_{DS}-V_{GS}$  curves (Figure 4d) exhibiting the p–n conversion of the doped tube. Then we positioned another p-type tube in a parallel fashion with one end being interconnected with the n-type tube as the  $V_{in}$  terminal. From the  $I_{DS}-V_{GS}$  curves of the n- and p-type tubes after the second transfer (see Supporting Information, Figure S2), we concluded that the p–n conversion by chemical doping was compatible with our selective positioning process. Figure 4c gives the transfer characteristics of the inverter with operating voltage  $V_{dd} = +3$  V using the underlying silicon as bottom gate. This simple PMMA-mediated approach paves the way to build logic circuits by integrating p- and n-type tubes in a well-controlled fashion.

SWNTs combine strength, flexibility, and high mobility,<sup>29</sup> which opens up a great opportunity for fabricating high-performance flexible electronic devices. The low-temperature process, in addition to the selective positioning capability of our approach, allows the fabrication of SWNT-based electronic devices on flexible plastics. As a demonstration, we fabricated a p-type SWNT FET on poly(ethylene terephthalate) (PET). Indium tin oxide (ITO) film (50 nm thick) was deposited on PET as a bottom gate. Lift-off resist (LOR, 1A, MicroChem), a commonly used bottom resist in bilayer EBL,<sup>30</sup> was spin-coated at 3000 rpm for 1 min on an ITO/PET sheet and then baked at 130 °C for 1 h to serve as dielectric layer. We chose LOR as dielectric material with the following considerations. First, it was insoluble in acetone, which made it compatible with the removal step of PMMA mediator. Second, it was tolerant with the fabrication of electrode pattern by EBL. After placing an individual semiconducting SWNT on prefabricated electrodes on a LOR/ITO/PET sheet, we obtained a flexible SWNT-FET. Figure 5 displays the optical image of thus-created plastic FET (Figure 5a) and its transfer characteristics (Figure 5b, the inset is the SEM image of the FET). It shows unipolar p-channel behavior with an on/off current ratio of ca.  $10^5$ , better than those made on  $\text{SiO}_2/\text{Si}$  substrates (see Supporting Information, Figure S3 for comparison of  $I_{DS}-V_{GS}$  curves of the same SWNTs on  $\text{SiO}_2/\text{Si}$  and plastics). Obviously, multiple positioning of SWNTs could generate complex functional devices on plastics.

In summary, we demonstrated a general selective positioning and integration technique of individual single-walled



**Figure 5.** (a) Optical image of the transparent and flexible PET sheet with SWNT-FET. (b)  $I_{DS}-V_{GS}$  curve (at  $V_{DS} = 0.1$  V) of the obtained SWNT-FET (inset) on PET sheet using ITO and LOR as gate electrode and dielectric, respectively. Scale bar, 5  $\mu\text{m}$ .

carbon nanotubes for fabricating chirality-specific SWNTs circuits. The utilization of PMMA thin film as mediator is the key to success for positioning SWNTs with desired properties on structured surfaces. This approach is compatible with multiple operations, which has been proved by locating different nanotubes step-by-step on patterned electrodes for creating SWNTs circuits. Moreover, this technique is tolerant with p–n conversion by chemical doping, which allows for the construction of logic circuits. As a starting point of building complex SWNTs architectures, we demonstrated the fabrication of  $2 \times 2$  all-SWNTs crossbar transistor, field effect inverter, and flexible FET on plastics by integrating metallic, p- and n-type semiconducting SWNTs. In addition to these advantages, this approach holds the unique feature of handling individual SWNTs with specific chirality compared with other reported techniques. Nevertheless, the sequential process may limit the efficiency of operation. And the resolution of integration was low compared with high-density structures generated with assembly and contact printing techniques. This approach can certainly be extended to other building blocks, making it possible to construct purpose-directed architectures with micro/nanoscale wires, tubes, dots, and 2D sheets. It provides a powerful means for device-related fundamental studies though there still is a great challenge for practical device fabrication.

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**Supporting Information Available:** Figures illustrating the process for releasing PMMA film from holder to target substrate, transfer characteristics of tubes after doping and after transfer, and current–voltage curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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