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Carbon nanotube conducting arrays by consecutive amidation reactions†

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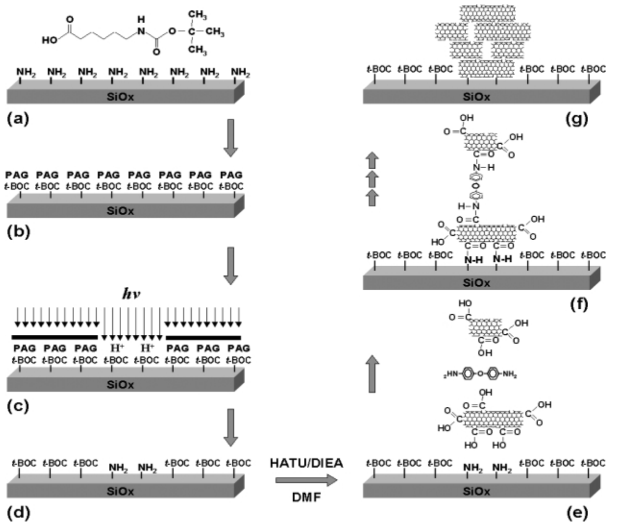
Carbon nanotube conducting arrays were constructed *via* consecutive amidation reactions with the aid of a linker molecule and a condensation agent on a patterned amine-terminated glass substrate. The electrical resistivity of the nanotube films was sensitive to the degree of coverage for the substrate, making it possible to tailor nanotube multilayers suitable for use in micro- or nanoscale electronic devices and circuits.

Metallic or semiconducting properties of single-walled carbon nanotubes (SWNTs), which depend on their helicity, make SWNTs suitable for use as nano-wires in IC circuits and chemical sensors.[1] In most of the applications reported to date, nanotubes have been used as individual SWNTs, although ensembles of SWNTs are very important for practical applications at the micro- or nanoscale. However, in applications requiring the transmission of an electrical signal from one location to another, it is crucial to employ a high density of nanotubes that are selectively immobilized on a patterned substrate, ranging from macroscopic to nano-scale dimensions.[2]

Here, we report a novel fabrication method for forming patterned SWNT conducting arrays with high-density multilayers (Scheme 1). To prepare the prepatterned substrate, amine-modified slide glass was treated with 6-(BOC-amino) caproic acid containing the BOC protecting group. Then the precursor of the photogenerated acid (PGA) was used to remove the protecting group from the amino acid.[3] The substrate was covered with a photolithographic mask of the desired pattern, and finally treated with UV light causing the generation of PGA that removed the protecting group from the amino acids. The SWNTs terminated with carboxylic acid groups (cut in acid[4]) were immobilized to the aminated surface, and then multiple layers of SWNTs were created by successive condensation reactions between carboxyl groups on the SWNTs and the amino groups on a linker molecule (oxydianiline (ODA)) with the aid of a condensation agent.[5] Repeated treatments of the reaction cycle led to the formation of high-density SWNT multilayer film. This approach enables the formation of micro-patterned SWNT conducting arrays on solid substrates. To the best of our knowledge, the fabrication of nanotube arrays by this route has not been investigated.



Scheme 1 Overview illustrating the SWNTs multilayer film patterned: **(a)** formation of *t*-BOC protected group, **(b)** PGA treatment for acid generation, **(c)** UV exposure using photomask, **(d)** developing process, **(e)** chemical attachment of SWNTs onto slide glass modified with amino groups with the aid of a condensation agent (HATU/DIEA), **(f)** chemical bonding of SWNT layers *via* oxydianiline (ODA) linkers between the layers, and **(g)** SWNT multilayer film formation through repeated condensation reactions. HATU = *O*-(7-azabenzotriazol-1-yl)tetramethyluronium hexafluorophosphate; DIEA = *N*,*N*-diisopropylethylamine.

To observe if the amount of SWNTs linked per reaction cycle was uniform, the stacked SWNT films were monitored by UV–vis–NIR. The spectra show the increase in absorbance for various cycles after each SWNT treatment on amine-modified slide glass (Fig. 1(a)). Since the linker molecule and the condensation agent don't absorb in the spectral region monitored, the measured absorbance is only due to the SWNTs. The spectra of the absorbed SWNT films contained strong adsorption peaks at about 300 nm, broad electronic transitions at about 700 nm, and broad transitions at about 1020 nm. A set of peaks near 700 nm is assigned to the first van Hove transition of metallic SWNTs.[6] Also, a set of peaks

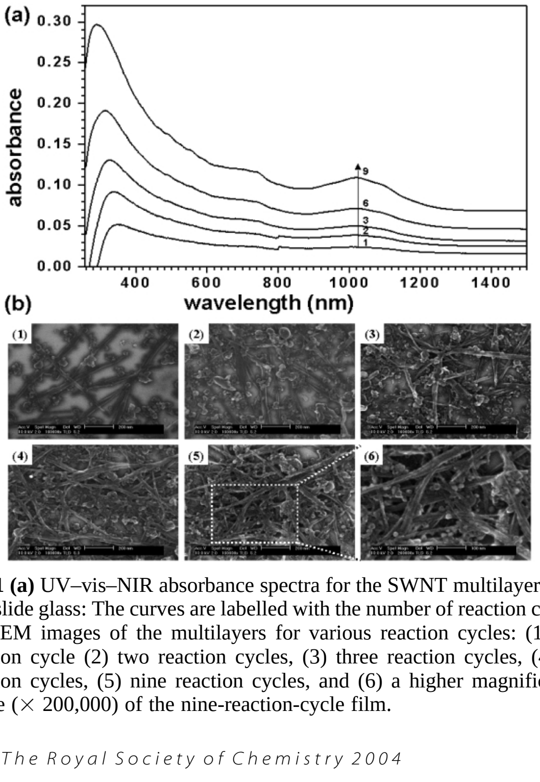


Fig. 1 (a) UV–vis–NIR absorbance spectra for the SWNT multilayer films on a slide glass: The curves are labelled with the number of reaction cycles. **(b)** SEM images of the multilayers for various reaction cycles: (1) one reaction cycle (2) two reaction cycles, (3) three reaction cycles, (4) six reaction cycles, (5) nine reaction cycles, and (6) a higher magnification image (× 200,000) of the nine-reaction-cycle film.

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† Electronic Supplementary Information (ESI) available: fabrication method and characterization data for micropatterned SWNT conducting arrays. See http://www.rsc.org/suppdata/cc/b3/b315348g/

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corresponding to the second van Hove singularity is seen near at 1020 nm. They were positions that agree with reported literature spectra for purified SWNTs.[7] To investigate the degree of the SWNT surface-density, the absorbance was analyzed at 1020 nm. The surface-density of SWNTs on glass with amino group was confirmed by the linear increase as a function of the number of reaction cycles. On glass without amino groups, however, surface-density remained constant at absorbance near zero (see ESI†). These results indicate that the SWNT films were formed though covalent bonding between functional groups, which increased linearly for the surface-density (not thickness) during subsequent reaction cycles.

Fig. 1(b) shows SEM images taken after one, two, three, six, and nine successive reaction cycles. The accumulation of SWNT layers allows surface density to increase on the glass substrate. The SEM image of the sample after one reaction cycle shows that the substrate is sparsely covered with randomly oriented SWNT ropes of 400–600 nm in length (Fig. 1(b)-1). Compared to the sparsely covered surfaces after the initial one or two reaction cycles, the SWNT multilayers formed after three or more reaction cycles (Fig. 1(b)-3–5) exhibit uniform and complete surface coverage over large areas. Close inspection of the multilayer formed after nine reaction cycles (Fig. 1(b)-6) reveals that the SWNT ropes have been piled up to a height of 5–7 layers. The overlapping morphology of the multilayers is consistent with SWNT accumulation occurring *via* an alternating reaction in which SWNTs react with ODA–SWNT ropes already on the amine-modified surface and then these SWNTs, after reaction with ODA, form a new layer for the next reaction cycle. The SEM images confirm that the proposed fabrication technique based on ODA linkers produces films with superb uniformity and high surface density over large areas.

To enable nanotube-based electronic devices, we fabricated the pattern with groups of parallel lines of various widths on the glass slide prepatterned by photolithography. After chemically attaching the SWNTs to the prepatterned regions, a regular array of lines corresponding to the photo mask was clearly observed by SEM (Fig. 2, taken after six reaction cycles). Fig. 2(a) shows the SEM image of the patterned three groupings of parallel lines of different widths: 1.25 μm, 2.5 μm, and 3.75 μm respectively. Fig. 2(b) shows a slightly magnified SEM micrograph for the 1.25 μm line group. Close inspection of the SEM image (Fig. 2(c), ×100000) reveals that the fabricated micro-patterned SWNT films are uniform and of high surface-density, that the SWNT ropes have been piled up with a number of layers. The SEM image clearly showed an obvious boundary between the SWNT film region (light gray) and the area of clean substrate (dark gray). SWNT ropes were hardly observed in the region with the BOC protecting group, indicating that the shielding by the BOC protecting groups prevented the amino groups of the substrate from reacting with the carboxyl groups of the SWNTs.

To investigate the electrical properties of the SWNT multilayers, the electrical resistivities (ρ) and thicknesses of the SWNT multilayers were measured as a function of the number of reaction cycles.‡ As shown in Fig. 3, the electrical resistivity decreased with increasing number of reaction cycles. A sharp increase in the thickness and conductivity ($k = 1/\rho$) was observed during the initial three reaction cycles, and these quantities grew steadily during subsequent reaction cycles. These observations indicate that the films become fairly uniform after the third reaction cycle, which is consistent with the SEM results. The resistivity of the films is particularly sensitive to their uniformity, with the high resistivity values of the films after one and two reaction cycles being attributed to poor SWNT coverage on the substrate. After the third reaction cycle, the electrical resistivities were in the range of 0.5 to 1.0 μΩ m. The resistivities of ensembles of SWNT multilayer films prepared by our fabrication method are of the same order of magnitude as those reported previously.[8]

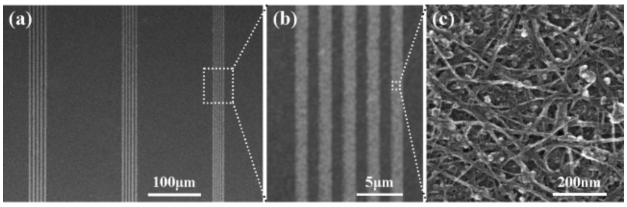

Fig. 2 (a) SEM image of the line patterned SWNT multilayer film on an amine-modified glass substrate; the bright lines correspond to the regions covered with SWNTs. The widths of the line are 3.75 μm, 2.5 μm, 1.25 μm, respectively (b) Magnified SEM image of the 1.25 μm lines. A higher magnification image of (c) an inside region of a line (× 100,000).

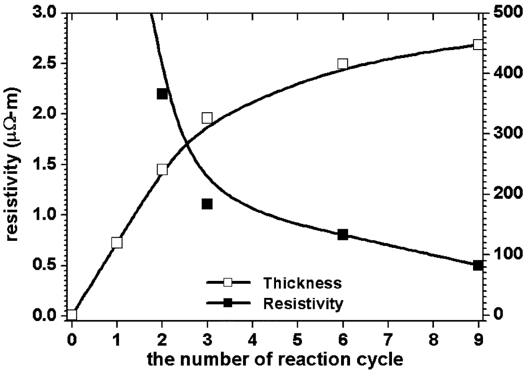

Fig. 3 Variation of the resistivities (■) and thicknesses (□) of SWNT multilayers as a function of the number of reaction cycles.

In summary, we developed a novel fabrication method for patterned SWNT arrays using consecutive condensation reactions and photolithography. The high-density SWNT multilayer film showed complete and uniform coverage of the substrate and good electrical conductivity for electronic device application. Further studies are in progress to estimate the minimum feature size that might be achieved using this method.

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Notes and references

‡ The resistivity was calculated using the equation $\rho = (\pi t/\ln 2)(V/I)$, where ρ is the sheet resistivity, t is the thickness of SWNTs film, V is the voltage, and I is the current. The current remained constant at 1.0 nA, and all measurements carried out at room temperature.

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