Multilevel, Multicomponent Microarchitectures of Vertically-Aligned Carbon Nanotubes for Diverse Applications

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ABSTRACT A simple multiple contact transfer technique has been developed for controllable fabrication of multilevel, multicomponent microarchitectures of vertically aligned carbon nanotubes (VA-CNTs). Three dimensional (3-D) multicomponent micropatterns of aligned single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) have been fabricated, which can be used to develop a newly designed touch sensor with reversible electrical responses for potential applications in electronic devices, as demonstrated in this study. The demonstrated dependence of light diffraction on structural transfiguration of the resultant CNT micropattern also indicates their potential for optical devices. Further introduction of various components with specific properties (*e.g.*, ZnO nanorods) into the CNT micropatterns enabled us to tailor such surface characteristics as wettability and light response. Owing to the highly generic nature of the multiple contact transfer strategy, the methodology developed here could provide a general approach for interposing a large variety of multicomponent elements (*e.g.*, nanotubes, nanorods/wires, photonic crystals, *etc.*) onto a single chip for multifunctional device applications.

KEYWORDS: carbon nanotube · contact transfer · multilevel · multicomponent · multifunctionality

Multilevel and multicomponent hybrid nanostructures arranged in a controllable fashion (*e.g.*, micropattern and heterojunction) have attracted much attention owing to synergistic properties arising from these spatially well-defined different components.[1−3] Compared with a simple single component system, complex multicomponent nanostructures can attain novel function not available in their single-component counterparts, and realize multifunctionality through integration of different functional components into designed complex structure. The physical and chemical properties of individual components can also be tailored by the rational interactions between those components.

Carbon nanotubes (CNTs), including multiwalled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs), especially in an aligned and micropatterned array form, have been extensively studied for various applications, ranging from nanoscale sensors to electronic circuits.[4−7] Although many micropatterning methods, including photolithography,[8−10] soft lithography,[11,12] block copolymer lithography,[13,14] and electron or laser beam lithography,[15,16] have been devised for producing single component vertically aligned (VA-) CNT micropatterns for some years, the effort in making multicomponent vertically aligned VA-CNT micropatterns is very recent. In this regard, we have reported previously the preparation of multicomponent micropatterns of VA-MWNTs interposed with nanoparticles,[17] nonaligned CNTs,[18] or VA-SWNTs[3] by chemical absorption, self-assembly, or direct chemical vapor deposition. Apart from the aforementioned multicomponent patterning of VA-CNTs, it is also highly desirable to achieve the multilevel and multicomponent micropatterns by using a prepatterned substrate for formation of complex, hierarchical microarchitectures through multiple contact transfer. However, as far as we are aware, there is still no discussion in literature on the fabrication of multilevel multicomponent microarchitectures of aligned CNTs by a multiple contact transfer approach.

Contact transfer strategy[18−20] has been demonstrated in our previous studies to be a powerful approach for producing 2-D and 3-D VA-CNT micropatterns with a controllable region-specific property for diverse applications. Recently, we have exploited the contact transfer method to sequentially extract CNTs from their vertically aligned arrays on growth substrates, which enabled us to fabricate the CNT nanoelectrode

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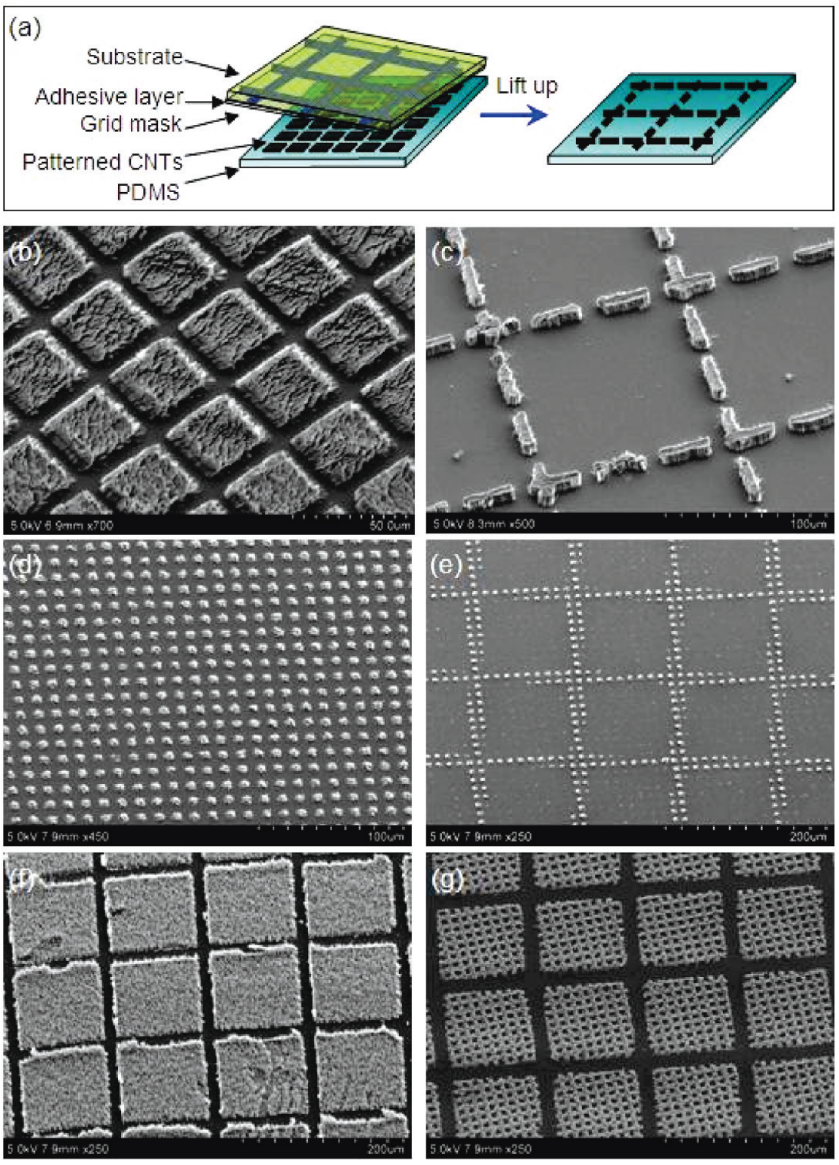

Figure 1. (a) A schematic illustration of the preparation of line multilevel pattern of VA-MWNTs by applying second contact transfer onto the primarily formed patterns on PDMS. (b, d, and f) SEM images of the primary patterned VA-MWNT patterns on PDMS by first contact transfer (Supporting Information, Figure S1), and (c, e, and g) the corresponding multilevel patterns formed after second contact transfer process, respectively.

arrays with tailor-made surface morphologies and properties for electroanalysis.[21] There is an interesting recent report about using graphene as the transferable substrate along with retaining the Ohmic electrical contact.[22] However, the fabrication process for the transferable samples is very complicated, and the graphene layer is relatively fragile. In this study, we present a simple multiple contact transfer method for fabricating multilevel, multicomponent microarchitectures of VA-CNTs on flexible substrates such as polydimethylsiloxane (PDMS) film and transparent tape (3M, polypropylene-film-supported acrylic adhesive). A variety of nanocomponents with different chemical or physical properties can be arranged into the patterned structures of VA-CNTs. For instance, aligned SWNTs, ZnO nanorods, and SiO_2 microspheres have been interposed into the patterned structures of VA-MWNTs to demonstrate the versatility and feasibility of the newly developed multiple contact transfer strategy for tailoring the properties of resultant multicomponent micropatterns for potential applications in micro/nanophotoelectronic devices.

RESULTS AND DISCUSSION

The multiple contact transfer technique uses primary contact transferred structures with predesigned patterns of aligned CNTs on a flexible substrate, such as PDMS film and transparent tape (Supporting Information, Figure S1), for the subsequent contact transfer of various nanocomponents. Figure 1 shows the formation of multilevel micropatterns of VA-MWNTs. A prearranged pattern of VA-MWNTs was formed on PDMS

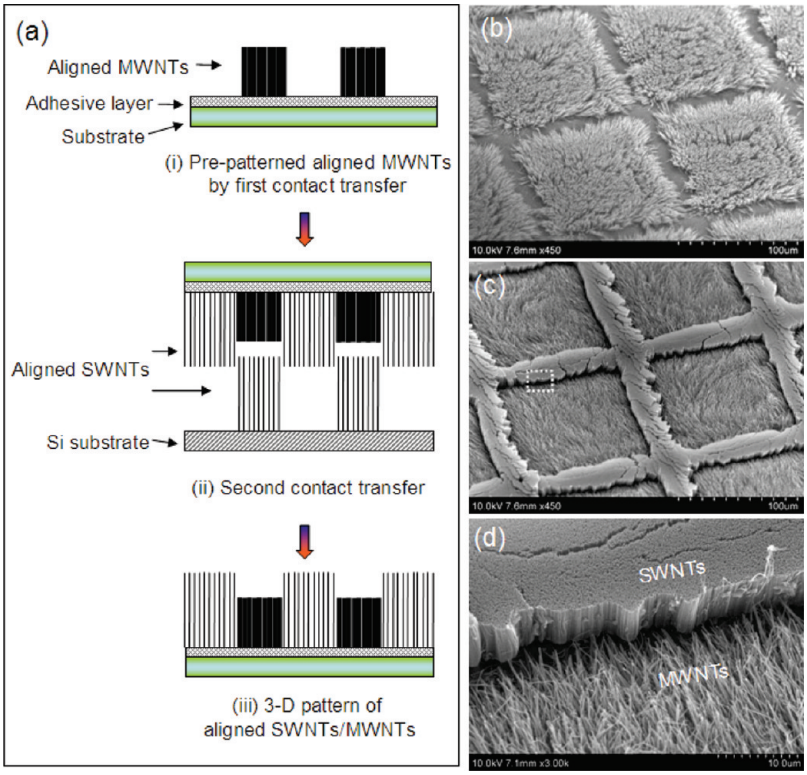

Figure 2. (a) A schematic illustration of the multiple contact transfer for multicomponent micropatterns of VA-SWNTs/VA-MWNTs. (b) SEM image of aligned MWNTs transferred onto the transparent tape after the first contact transfer (Supporting Information, Figure S1). (c) Aligned SWNT/MWNT micropattern on transparent tape after the second contact transfer. (d) An enlarged view of the selected region in panel c.

through first contact transfer (Supporting Information, Figures S1 and S2).[18] After the formation of primary micropatterns of VA-MWNTs on PDMS, the second contact transfer is applied to selectively remove the aligned MWNTs by a grid mask covered adhesive substrate (*e.g.*, transparent tape). The adhesives within the uncovered regions on the transparent tape will pull out the nanotubes underneath, and the aligned MWNTs under the shadow of the grid frame will remain on the PDMS surface to form subpatterns along the line direction (Figure 1a–c). This multiple contact transfer process for multilevel micropatterns provides room to tune the final hierarchical structures by prefabrication of the primary pattern and an applied second patterning process. For example, following the procedure in Figure 1a, we can obtain interlaced dot line structures (Figure 1e) by using uniformly distributed MWNT bundles (*ca.* 5 μm in size) as the primary pattern (Figure 1d). The preformed microsquares of aligned MWNTs on PDMS (Figure 1f) can also be further reformatted by applying a second contact transfer (Figure 1a) with a fine grid mask. As shown in Figure 1g, the network pattern of aligned MWNTs is formed within the prepatterned microsquare regions in Figure 1f. The formation of multilevel micropatterns on PDMS will facilitate the further contact transfer to other substrates for various optoelectronic applications.[23,24]

Apart from the multilevel micropatterns, the developed multiple contact transfer process will also allow us to assemble various components into micropatterns. Here, we take the VA-SWNT/VA-MWNT micropatterns as one of the examples to illuminate the detailed procedure for the formation of controlled multicomponent micropatterns. Figure 2a shows a schematic representation of the procedures for fabricating 3-D VA-SWNT/VA-MWNT multicomponent micropatterns. First, we adhered a TEM grid consisting of square windows (*ca.* 100-μm wide) onto a commercially available transparent tape as a physical mask (Supporting Information, Figure S1) for the first contact transfer of VA-MWNT micropatterns from the as-synthesized nonpatterned VA-MWNT film.[17,20] After careful removal of the TEM grid, a VA-MWNT micropattern replicated the TEM grid structure formed on the transparent tape (Figures 2a(i),b and Supporting Information, Figure S2), which was then used as a stamp to directly contact with the as-synthesized nonpatterned VA-SWNT array with a different length from that of the VA-MWNT array for the second contact transfer (Figure 2a(ii)). Finally, a 3-D multicomponent micropattern with VA-SWNTs interposed into the VA-MWNT patterned structure was obtained on the transparent tape (Figure 2a(iii),c). The SEM images under higher magnifications (Figure 2d and Supporting Information, Figure S3) reveal that both the VA-MWNTs and VA-SWNTs almost remain perpendicularly aligned in full lengths even after performing the contact

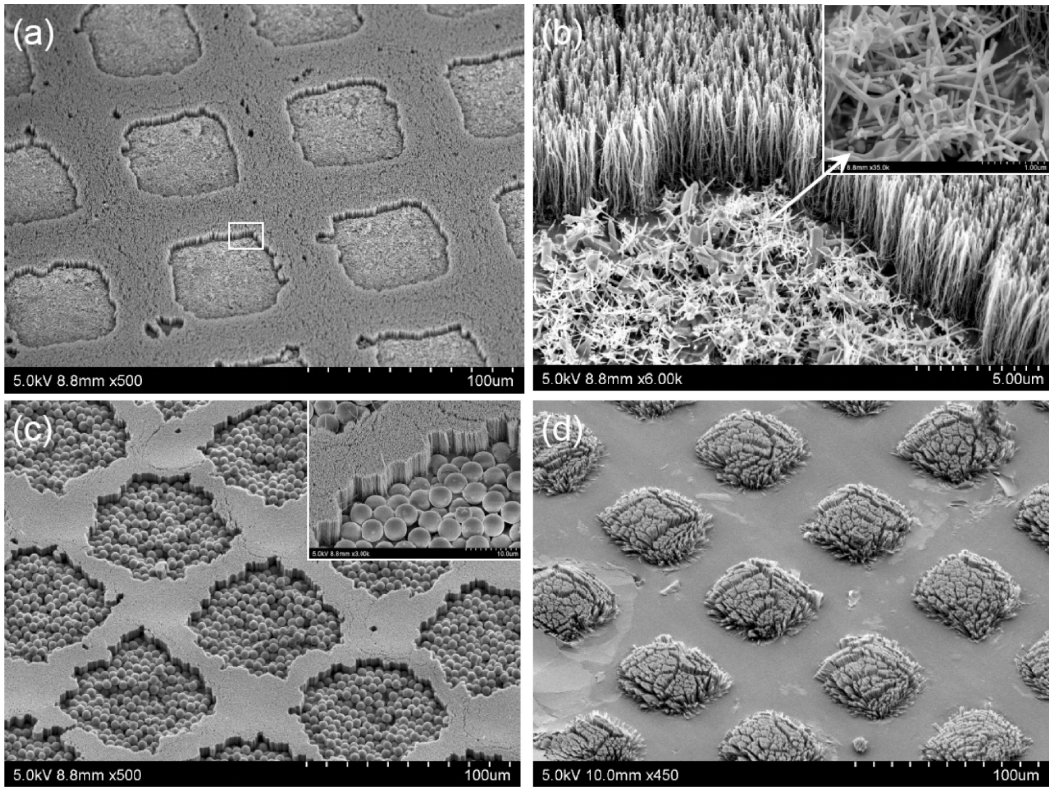

Figure 3. (a) SEM image of ZnO nanorods/VA-MWNTs pattern; (b) An enlarged view of the marked area in panel a; (c) SEM image of SiO_2 microspheres/VA-MWNTs pattern; (d) SEM image of the VA-MWNTs pattern embedded into a TiO_2 thin film.

transfer two times, due to the demonstrated excellent mechanical flexibility of aligned CNTs.[25−27] Therefore, the dry contact transfer did not cause any obvious detrimental effect on their alignment.[17,20]

The multiple contact transfer approach developed here is quite versatile and is able to assemble various components with specific properties into ordered multicomponent microarchitectures. For example, nanostructures of inorganic semiconductors such as ZnO nanorods and nanowires have unique properties for applications in electronics, optoelectronics, sensors, and electromechanical coupled devices.[28,29] In this study, we have fabricated multicomponent micropatterns of ZnO nanorods and VA-MWNTs by the multiple contact transfer method. As shown in Figure 3 panels a and b, the ZnO nanorods (Supporting Information, Figure S4) were interposed into the windows of VA-MWNT patterns. Similar to the VA-MWNTs and VA-SWNTs transfer process, the randomly oriented ZnO nanorods and VA-MWNTs retain their initial structures in the final pattern (Figure 3b). Similarly, we have also assembled other nano/microstructures like SiO_2 microspheres into the VA-MWNT patterns with good region-specific confinement (Figure 3c). The ordered arrangement of spherical particles will benefit the potential applications to the assembly of photonic crystals,[30,31] nanosphere lithography,[32] and colloidal stamps.[33] By further using the multiple contact transfer, the VA-MWNT micropatterns can also been interposed into the TiO_2 thin film (Figure 3d).

As we have seen above, the multiple contact transfer technique developed in this study provides a powerful tool to build different multilevel or multicomponent microarchitectures. In fact, the combined 3-D multilevel multicomponent micropatterns can also be fabricated in a controllable fashion. As an example shown in Figure 4, VA-MWNT square-type and grid-type micropatterns with different size were assembled on PDMS (Figure 4a) and transparent tape (Figure 4b) by first contact transfer (Supporting Information, Figure S1). Subsequent contact transfer of the formed micropatterns in Figure 4a onto Figure 4b will produce a new multilevel pattern (Figure 4c). As VA-SWNTs with different lengths are exploited as the next contact transfer target, 3-D multilevel multicomponent micropatterns will form on transparent tape surface (Figure 4d). The enlarged view of Figure 4d shown in Figure 4 panels e and f clearly reveals the 3-D structures. It is notable that the shape, size, and composition of final micropatterns are determined by the predesigned mask and selected nanocomponents beyond those demonstrated here. An alternative contact transfer method for 3-D multilevel multicomponent micropatterns has also been included in the Supporting Information (Figure S5).

Unlike the 3-D single-component VA-MWNT micropatterns,[20] the 3-D multicomponent micropattern with VA-SWNTs region-selectively interposed into the VA-MWNT patterned structure showed interesting

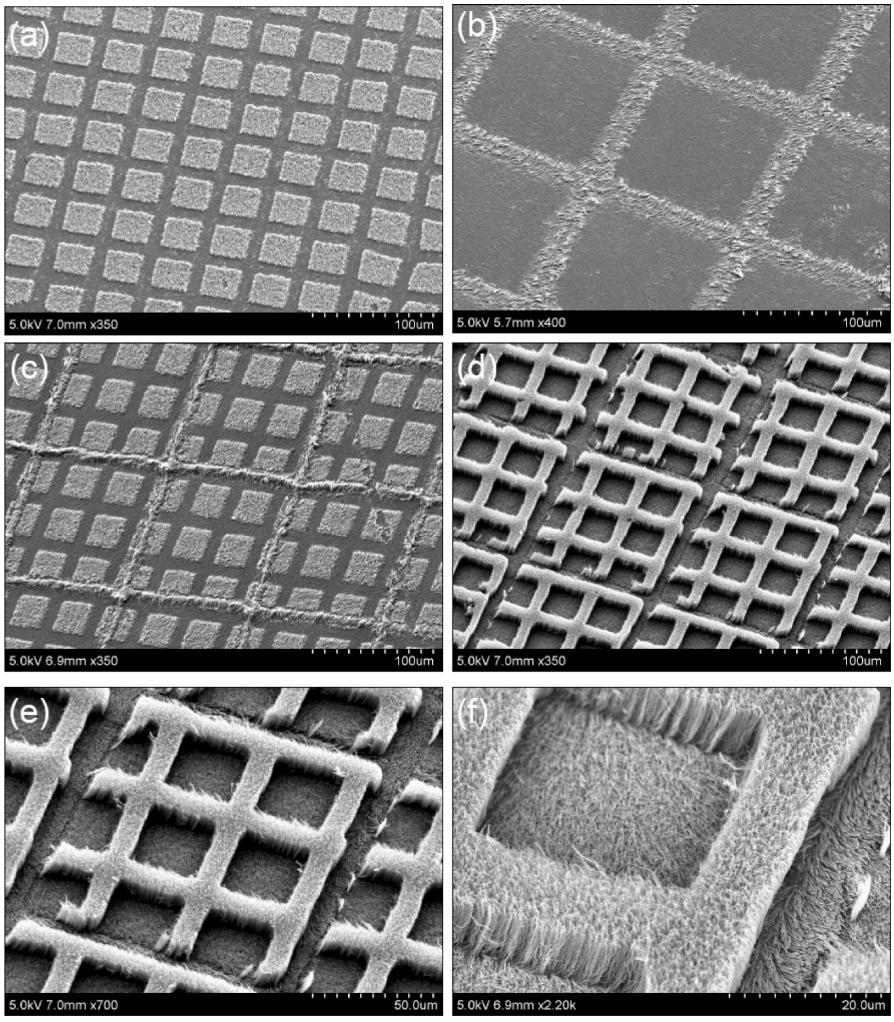

Figure 4. (a,b) SEM images of VA-MWNT patterns on PDMS (a) and transparent tape (b) by the first contact transfer. (c) SEM image of transparent tape after contact transfer of VA-MWNT patterns from panels a to b. (d) SEM image of panel c after contact transfer of VA-SWNTs. (e, and f) SEM images of enlarged view of panel d.

region-specific electronic properties characteristic of the micropatterned semiconducting SWNTs and metallic MWNTs, respectively.[3] Therefore, these 3-D VA-MWNT/VA-SWNT micropatterns should be useful for the development of various novel electronic devices for a wide range of potential applications. To demonstrate the potential of the newly prepared 3-D VA-MWNT/VA-SWNT multicomponent micropatterns, we replaced the transparent tape with a conductive adhesive tape (*e.g.,* copper conducting adhesive tape, 3M) for the double contact transfer (Figure 2) and placed a conducting ITO glass plate on the top surface of the resultant 3-D nanotube patterns to form the top electrode (Figure 5a). As the VA-SWNTs used in this study are longer than the interposed VA-MWNTs, a current (I)−voltage (V) curve characteristic of the semiconducting VA-SWNTs was observed initially (curve i in Figure 5c). Upon compression by pressing down the ITO glass (*ca.* 100 g loading, Figure 5b), an effective contact between the VA-MWNTs and ITO glass was made while the VA-SWNTs were mechanically compressed.[25] As a result, an Ohmic $I-V$ behavior was obtained (curve ii in Figure 5c) as the metallic VA-MWNTs contributed the major current flow between the two electrodes in the compression state. Owing to the reversible mechanical compressibility of the VA-SWNTs,[25−27] we found that $I-V$ characteristics of the 3-D multicomponent micropattern with the shorter VA-MWNTs interposed into the longer VA-SWNTs could be reversibly switched between the metallic and semiconducting states during the compression−decompression cycles. Under a constant voltage of 5 V, a strong current response (by a factor of 2) to compression−decompression cycles was observed (Figure 5d), which is apparently fast with a good repeatability (>90% recovery based on average response current). Inset of Figure 5d shows an enlarged view for a small portion of the current response curve. The peak current intensity and response time can be tuned by developing the 3-D VA-MWNT/VA-SWNT multicomponent micropatterns with various patterned geometries and/or nanotube length differences. These newly developed 3-D multicomponent

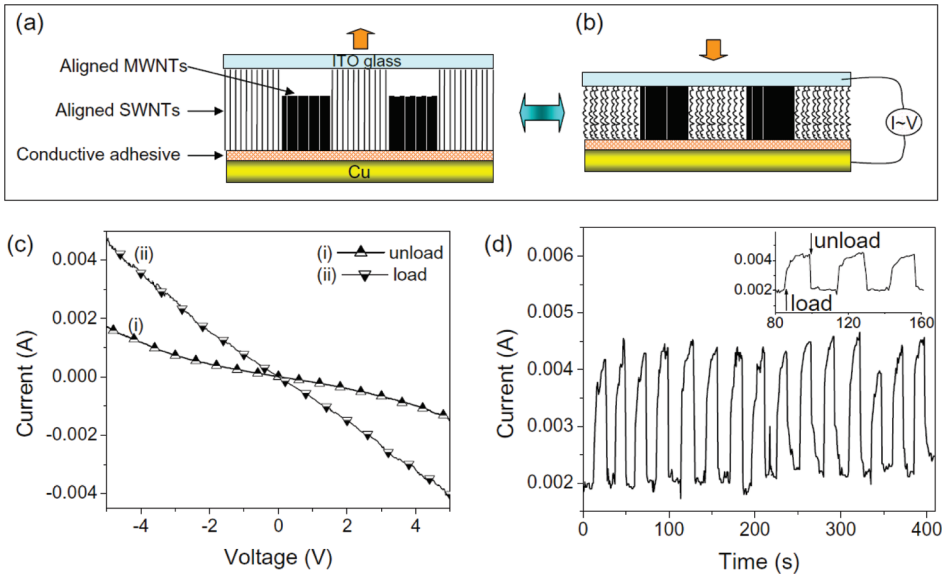

Figure 5. (a,b) Schematic illustrations of the 3-D VA-MWNT/VA-SWNT multicomponent micropatterns at the decompression and compression states, respectively. (c) Current−voltage responses (i) and (ii) corresponding to sketches a and b, respectively. (d) Current response to the compression−decompression cycles at a voltage of 5 V. Tested pattern area: 1 mm^2.

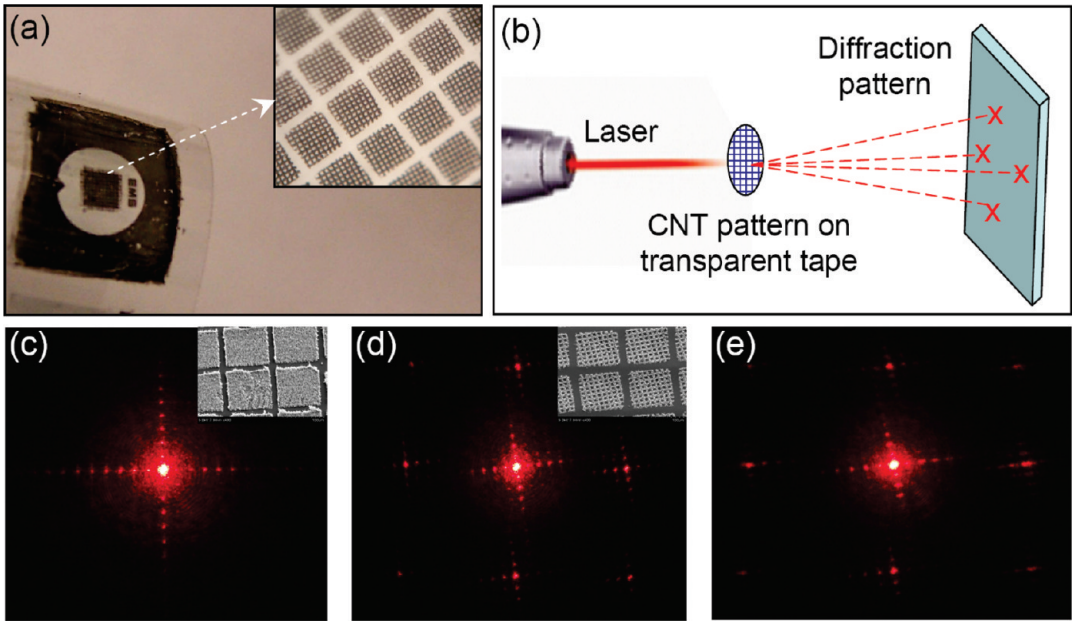

Figure 6. (a) Photo of VA-MWNT pattern on transparent tape (inset: microscopic view). (b) Schematic diagram of light diffraction through patterned CNTs on tape. (c) Light diffraction from microsquare pattern of VA-MWNTs on transparent tape (corresponding to Figure 1f. Inset shows SEM image, square length = 100 μm). (d) Light diffraction from multilevel microsquare pattern of VA-MWNTs on transparent tape (corresponding to Figure 1g. Inset shows SEM image, square length = 100 μm). (e) Light diffraction as in panel d from incurved transparent tape (*cf.* Figure 6a).

VA-MWNT/VA-SWNT micropatterns with reversibly switchable electronic properties can be potentially useful for many device applications, including touch sensors, memory storages, and electronic switches.

Because of the flexibility and transparency of the transfer substrates used, such as PDMS and transparent tape, the formed micropatterns of aligned CNTs can be applied in flexible electronics and optical devices. Figure 6a shows a photo of multilevel micropatterns of VA-MWNTs on transparent tape with a forced mechanical distortion. The microscopic view inserted in Figure 6a reveals the integrity of the micropatterns. Figure 6b schematically illustrated the setup for optical investigation of the VA-MWNT patterns on transparent tape. A laser pen is used as light source, and VA-MWNT patterns on transparent tape plays the role of optical grid. As we can see in Figure 6c, the microsquare patterns of VA-MWNTs (Figure 6c inset and Figure 1f) present a cross of linear light spots. However, the multilevel micropatterns, the patterned microsquare

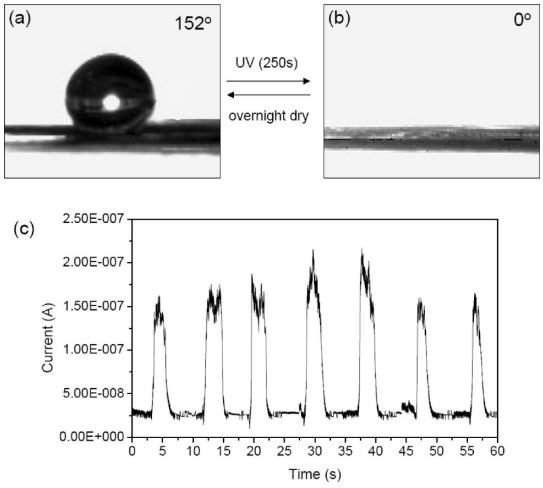

Figure 7. (a and b) Photos of a water droplet on a ZnO nanorod/VA-MWNT micropattern (Figure 3a,b) without or under UV irradiation, respectively. (c) Light response at 2.5 V bias voltage of TiO_2 infiltrated aligned MWNT pattern film (Figure 3d).

regions (100 μm) in Figure 6d (inset) and Figure 1g, show a corresponding multilevel light diffraction. The center main diffraction is surrounded with six well-proportioned sublight diffractions, and each diffraction is consistent with that in Figure 6c and is composed with a cross of linear light spots. Apart from the efficient regulation of light diffraction through the CNT micropatterns, the light diffraction behavior can also be tuned by deformation of flexible VA-MWNT patterns on transparent tape. We find that the initial square shape (Figure 6d) of the diffraction pattern transforms to a rectangle (Figure 6e) due to the curvature of the transparent tape. The observed dependence of light diffraction on the transfiguration of the CNT pattern indicates the potential for optical devices.

In addition to many possible electrical and optical applications exemplified by the aforementioned aligned CNT micropatterns, the surface physical and chemical properties of single component aligned-CNT micropatterns can also be tailored by the introduction of new components with specific functionality. For example, the VA-MWNT arrays or patterned films have intrinsically superhydrophobic surface properties.[34,35] However, in combination with ZnO nanorods within the VA-MWNT patterns (Figures 3a and b), the wettability of aligned MWNT patterned films can be controlled reversibly between superhydrophobicity and superhydrophilicity. As can be seen in Figure 7a,b, the superhydrophobic aligned CNT patterns interposed with ZnO nanorods (water contact angle of 152°, Figure 7a) show a superhydrophilic surface property (0°, Figure 7b) under ultraviolet (UV) irradiation (100 W) due to the change of surface chemistry of ZnO nanorods.[36] Similarly, the TiO_2 film infiltrated aligned CNT patterns (Figure 3d) show reversible photocurrent generation in response to the light characteristic of TiO_2 (Figure 7c).[37] It is notable that, during the transfer process, the CNTs within the resultant patterns still have a density similar to those initial ones. We have not observed an obvious change in alignment and bundling of VA-MWNTs and VA-SWNTs during the transfer process, which, otherwise, may have a possible effect on the mechanical, electrical, and optical properties of the final patterned microarchitectures.

CONCLUSIONS

We have developed a multiple contact transfer technique for controllable fabrication of multilevel, multicomponent microarchitectures of aligned CNTs. The resultant 3-D VA-MWNT/VA-SWMT multicomponent micropatterns with region-specific nanotube lengths have been demonstrated to have a fast and reversible pulsed current response to compression−decompression cycles at a constant voltage associated with the intrinsic semiconducting and metallic state characteristic of the VA-SWNTs and VA-MWNTs, respectively. The multilevel micropatterns of VA-MWNTs on transparent tape have also presented the potential for optical devices due to the micropattern-dependent light diffraction and its change with mechanical deformation. Other materials with specific properties such as ZnO nanorods, SiO_2 microspheres, and TiO_2 thin film have also been interposed into the patterned structures of aligned CNTs. The surface physical and chemical properties of these multicomponent aligned-CNT micropatterns have been demonstrated to be dependent on the nature of the constituent components and their spatial distributions, leading to various responsive smart surfaces. The newly developed multiple contact transfer strategy should be applicable for interposing a large variety of multicomponent elements beyond those demonstrated in this study for diverse multifunctional device applications.

METHODS

The nonpatterned VA-MWNT films with a homogeneous tube length of ~5 μm on a quartz glass plate were synthesized by pyrolysis of iron phthalocyanine (FePc) in Ar/H_2 atmosphere at 1100 °C as we previously reported,[19] while nonpatterned VA-SWNT films with a uniform length of about 10−15 μm were synthesized by plasma enhanced chemical vapor deposition according to our published procedure.[25] The CNT samples used in this study have a density of *ca.* 10^9−10^{11} nanotubes per centimeter square for VA-MWNTs, and *ca.* 10^{10}−10^{12} nanotubes per centimeter square for VA-SWNTs.[25] ZnO nanorods with branch structures were synthesized by thermal evaporation of Zn on Si wafer.[38] Breifly, Zn powders were put into an alumina cylindrical crucible with one end open and then kept in a quartz tube (diameter of 1 in and 4 ft long) placed inside of a resistively heated furnace. The synthesis temperature and duration time were maintained between 600−700 °C and 10 min, respectively.

Si(100) substrate was kept face inverted on the crucible. The furnace has open ends on both sides. ZnO nanostructures as a white film were collected on the Si surface (Supporting Information, Figure S4). TiO_2 thin films with a thickness of approximate 2 μm were prepared by electrophoresis on a Si wafer.[37] Photocurrent measurement of TiO_2/aligned MWNT patterns was carried out at 2.5 V bias voltage. It was shown that the multicomponent TiO_2/VA-MWNT micropatterned film has a good photoresponse to a pulsed light beam (λ = 254 nm, 4 W). SiO_2 microspheres with a size of about 5 μm were purchased from Polyscience, Inc. and used as received. SiO_2 microspheres dispersed in water were cast on a glass slide to form a uniform film for contact transfer process. Scanning electron microscopic (SEM) images were recorded on a Hitachi S-4800 high-resolution SEM unit. Current−voltage measurements on the aligned carbon nanotubes were performed using an EG&G potentiostat (model 263A).

The primary contact transfer process is similar to that reported previously.[18] As shown in Supporting Information, Figure S1, we first put a physical mask (*e.g.*, TEM grid in this study) on PDMS (or transparent tape) and then put it in contact with the aligned CNTs. Because of the adhesion interaction between CNTs and PDMS or transparent tape, the CNTs will be transferred onto an area of the PDMS or transparent tape corresponding to the region not covered by the mask. After removal of the physical mask, a pattern of vertical aligned CNTs will form on the PDMS or transparent tape. Depending on the applied physical mask with predesigned pattern structure, different micropatterns of aligned CNTs will be obtained. Supporting Information, Figure S2 shows one example of microsquare patterns formed on PDMS (Figure S2,b) and of a microgrid of aligned MWNTs left on the Si substrate (Figure S2,a). The micropatterns on the Si substrate can also be further transferred onto PDMS or transparent tape by one more contact transfer.

For the formation of multicomponent micropatterns, the pretransferred aligned CNT patterns on PDMS or transparent tape are put in contact with other components such as ZnO nanorods, SiO_2 microspheres, and even TiO_2 thin film. They will be transferred into the exposed regions surrounded by aligned CNT patterns.

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Supporting Information Available: Experimental details and Figures S1−S5. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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