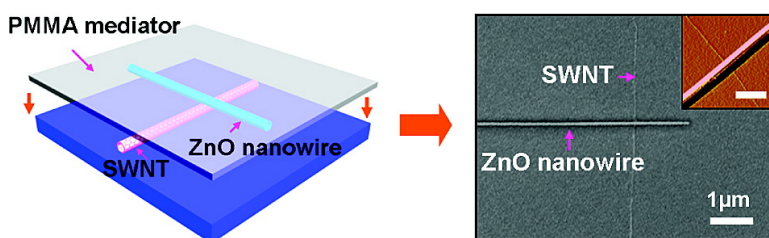## Communication

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Creation of Nanostructures with Poly(methyl methacrylate)-Mediated Nanotransfer Printing

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Integration of nanoscale building blocks into functional structures represents a key challenge for the production of nanodevices. Great efforts have been made to date on generating organized structures of nanoscale building blocks by flow-directed assembly,[1,2] Langmuir−Blodgett technique,[3−5] chemical template assembly,[6,7] and transfer printing.[8−13] Different from the wet assembly technique, transfer printing is a dry process that utilizes a poly(dimethylsiloxane) (PDMS) stamp as a mediator to transfer nanomaterials from one substrate to another. The difference in van der Waals interactions between stamp−nanomaterials and substrate−nanomaterials enables an efficient transfer process. However, this approach has limitations in creating complex nanostructures via a multiple transfer operation. In a sequential transfer process, a PDMS stamp will pick up pretransferred nanomaterials when separating from target substrates without a protecting layer. Here we present a poly(methyl methacrylate) (PMMA)-mediated nanotransfer printing technique, which aims at creating arbitrary purpose-directed nanostructures with various nanoscale building blocks.

Our strategy is based on the utilization of PMMA film as a macroscopic mediator for handling tiny nanoscale building blocks. The transfer process involves four basic steps (Figure 1a), including loading nanomaterials onto a PMMA mediator, peeling off the mediator from the source substrate, attaching the mediator to the target substrate, and releasing the loaded nanomaterials to the target. To load nanomaterials onto the mediator, a PMMA solution (M_w = 950K, 4 wt%, AR-P 679.04, Allresist) was spin-coated onto the source substrate and then baked to obtain a thin film embedding nanomaterials. The typical thickness of the PMMA mediator was ca. 200−300 nm. The peeling-off of the PMMA film is the key step of this transfer approach. Hydrolyzation of PMMA in basic solution (1 M KOH aqueous solution, 80 °C) was utilized to separate the PMMA−nanomaterials film from the source substrate. To make the peeled-off film adhere firmly to the target substrate, the film was annealed at 50 °C for 5 min after being attached onto the target substrate. To release the nanomaterials to the target substrate, PMMA was dissolved in acetone vapor, which is a commonly used solvent for removing PMMA in the lift-off process without perturbing the underlying nanomaterials. In the case of patterned target substrates, PMMA was removed by thermally decomposing at 300 °C under the protection of an Ar flow to avoid capillary force introduced in the liquid process (see Supporting Information (SI) for details of transfer process). Figure 1b−d show the SEM images of the single-walled carbon nanotube (SWNT) array on the source substrate, in transit, and transferred to target substrate, respectively. By comparing the SEM images, we concluded that these SWNTs were faithfully transferred with the aid of the PMMA mediator.

The choice of PMMA as a mediator is vital for reliably transferring nanoscale building blocks and sequentially building
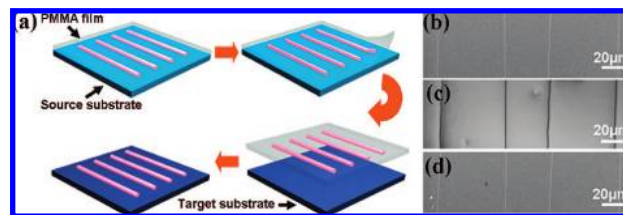

Figure 1. (a) Illustration of the procedures of PMMA-mediated nanotransfer printing technique. Spin-coating a PMMA film on source substrate, peeling off the film from substrate, attaching the film to target substrate, and finally removing the mediator. SEM images of SWNT array (b) on SiO₂/Si substrate before transfer, (c) embedded in PMMA film, and (d) transferred to another SiO₂/Si substrate.

nanostructures on designed surfaces. Compared with the PDMS stamp, PMMA has a number of prominent features. First, relatively low viscosity (43.4 mPas at 25 °C) and good wetting capability make the PMMA solution we used conform well to nanoscale topography on source substrates.[14] Therefore, the baked PMMA film can embed all the nanomaterials on source surfaces (see SI, Figure S1). This physical encapsulation in addition to van der Waals interactions ensured 100% loading efficiency and faithful transfer (see Figure S2 for comparison of SEM images of SWNTs before and after transferring). Second, PMMA is easily soluble in several organic solvents and decomposable above ca. 250 °C. So the transferred nanomaterials can be totally released from the mediator to the target substrate by removing PMMA (see SI, Figure S3a and b). This release process ensures that the sequential transfer operations will not disturb pretransferred structures (see SI, Figure S3c). As a result, complex structures can be created via multiple transfers of homo- or heterogeneous nanoscale building blocks. Besides, no reactant is introduced to remove PMMA, and therefore the mild removal treatment maintains the pristine properties of nanomaterials and substrates (see Raman spectroscopy and electrical characterization of transferred SWNTs in the SI, Figures S4 and S5). Third, the flexible PMMA film is easily shaped into various configurations, providing the possibility of shaping the loaded building blocks by manipulating the PMMA film at the macroscale.[15] Moreover, this PMMA-mediated approach also holds advantages similar to those the PDMS-mediated approach, such as universality, simplicity, and controllability.[10] Arrays and random CVD-grown SWNTs were successfully transferred from Si, SiO₂/ Si, Si₃N₄/Si, quartz, and sapphire surfaces onto flat, patterned, curved, and flexible substrates (see SI, Figure S6).

These features of the PMMA-mediated nanotransfer printing technique enabled the generation of complex nanostructures with various nanoscale building blocks. Figure 2 demonstrates some typical structures created with our technique. Shown in Figure 2a is an example of an ultralong SWNT array transferred onto a
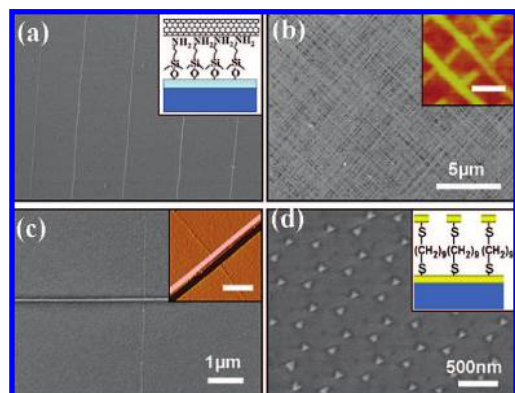
Figure 2. SEM images of typical structures created with PMMA-mediated nanotransfer printing technique. (a) Ultralong SWNT array transferred onto the APTS monolayer-modified Si surface. Inset, schematic cross-sectional view. (b) High-density crossbar array of SWNTs. Inset, AFM image of the cross-junction. Scale bar, 50 nm. (c) Heterogeneous cross-junction of ZnO nanowire and a semiconducting SWNT. Inset, AFM amplitude image of the junction. Scale bar, 200 nm. (d) Triangular gold nanosheets−SAM−gold film sandwich structures. Inset, schematic cross-sectional view.

3-(aminopropyl) triethoxysilane (APTS) monolayer-modified silicon surface from a source SiO_2/Si substrate. As evidenced by X-ray photoelectron spectra (XPS) data (see SI, Figure S7), the structure of the self-assembled monolayer (SAM) was not disturbed in the transfer process. Such a nanotube-on-SAM structure offered opportunities of investigating and modulating fluorescent[16] and other properties of SWNTs. High-density crossbar arrays of SWNTs were fabricated by crosswise transferring aligned SWNTs grown on the sapphire substrate to the SiO_2/Si surface. As shown in Figure 2b, the intertube spacing is <50 nm, giving a junction density of >10^{10}/ cm^2. A hybrid n-ZnO nanowire/p-SWNT cross-junction was obtained by consecutively transferring an SWNT (diameter ∼1.5 nm) and a ZnO nanowire (diameter ∼100 nm) (Figure 2c). Besides one-dimensional (1D) nanotubes and nanowires, our technique is also compatible with two-dimensional (2D) nanostructures. Figure 2d exhibits a metal−SAM−metal sandwich structure fabricated by transferring a gold nanosheet (diameter ∼116nm) array onto a 1,9-nonanediol SAM-modified gold surface. This approach offered a controllable way for fabricating top electrodes of molecular electronic devices to eliminate unexpected penetration of metal atoms into the organic monolayer, which often occurs in a conventional vacuum evaporation process.[17]

Novel structures of nanoscale building blocks can be generated by manipulating the flexible PMMA mediator. For instance, ultralong SWNT arrays were shaped into a zigzag array by folding the PMMA film twice (see SI, Figure S8). By reversing the gold nanostructures deposited on the well-ordered array of polystyrene (PS) nanospheres (Figure 3a) with the aid of the PMMA mediator, we obtained a 2D array of gold nanobowls (Figure 3b; see SI for details, Figure S9). These small bowls with an inner diameter of 450 nm can serve as nanocontainers.[18] The macroscopic manipulation of a flexible PMMA mediator adds new freedom for building functional structures.

To demonstrate the potential application of this approach in fabricating electronic devices, we built a metallic-semiconducting SWNTs crossbar circuit as shown in Figure S10. This crossbar circuit was created by selectively placing individual semiconducting
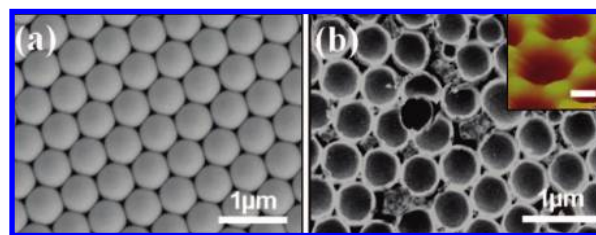

Figure 3. SEM images of (a) gold coated PS nanosphere array and (b) gold nanobowl array. Inset, 3D AFM image. Scale bar, 200 nm.

and metallic SWNTs onto predefined electrodes with a two-step transfer operation (see SI for details, Figure S11). The $I−V$ curve of the obtained circuit showed obvious rectifying characteristics.

In summary, we present a universal PMMA-mediated nanotransfer printing approach for reliably transferring nanoscale building blocks and sequentially creating complex nanostructures. Various nanostructures were generated by integrating or manipulating carbon nanotubes, nanowires, SAMs, and metallic nanostructures with this approach. This nanoscale bricklaying technique paves the way to generate purpose-directed nanostructures with homo- or heterogeneous building blocks, which facilitates exploring their fundamental properties and building novel devices.

Supporting Information Available: Experimental details and supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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