High-resolution nanotransfer printing applicable to diverse surfaces via interface-targeted adhesion switching

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1. Introduction

1.1 Nanotransfer printing (nTP)

• nTP is replicating or printing technology of nanostructured materials using mold like stamps.

• Low-cost and high-throughput fabrication method of highly functional nanostructures

• Essential for development of nanoscale devices such as transistors, sensors, nanomemories and nanowire photovoltatics etc.

• Applicable to flexible and non-planar surface unlike conventional patterning technologies

1.2 Previous Work

Conventional nTP methods use elastomeric molds (ex. Polydimethylsiloxane[1,2] (PDMS)) to replicate structures and following transfer materials onto receiver substrates.

Problems:

• Limitation of resolution (~ 50 nm)[3]

• Low fabrication yield and quality of transferred nanostructure due to low moduli of elastomeric molds

• Limited receiver substrates due to requirement of heat/oxidation treatment[4,5] or SAM deposition[2] to transfer materials

1.3 This Work

• High-resolution sub-20 nm transfer printing method using two polymeric materials

• Large applicability of receiver substrates using dynamic adhesion control with solvent molecules

2. Results and Discussion

2.1 Solvent-assisted transfer printing of sub-20 nm nanowires

• The procedure of solvent-assisted nTP is composed of two sequential steps.

• Step1: Pattern replication and deposition of nanowires on thin film replica

• Step2: Transfer printing on arbitrary substrates using PDMS gel pad

• Poly(4-vinyl pyridine) (P4VP) provides ultra-high replication resolution (sub-10 nm).

• Polystyrene (PS) can easily be detached from adhesive film by penetration of toluene.

• PDMS gel pad acts as solvent-emitting transfer medium to weaken adhesion between PS and adhesive film and also provides facile release of materials onto various receiver surface.

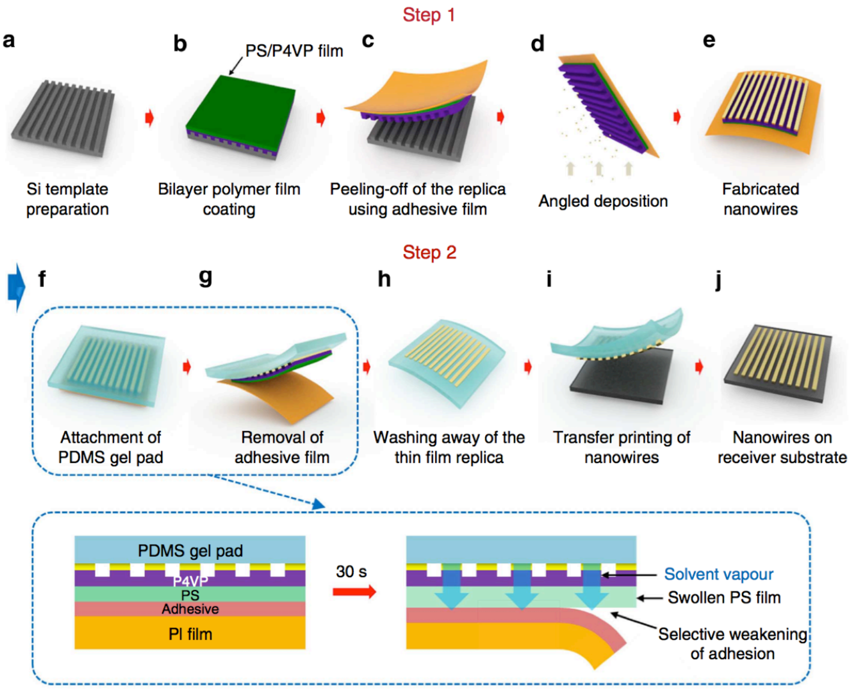

Figure 1. Procedure of solvent-assisted nanotransfer printing Step 1 is composed of (**a**) master mold fabrication by photolithography or block copolymer self-assembly, (**b**) replication using a bilayer polymer thin film (PS/P4VP), (**c**) peeling-off of the replica using a polyimide (PI) adhesive film, and (**d**,**e**) nanostructure formation on the replica via the angled deposition of functional materials. Step 2 is composed of (**f**) contact of solvent-swollen PDMS gel pad on the nanostructures to be transferred, (**g**) removal of adhesive film by weakening the PS/PI film adhesion through the incorporation of solvent molecules from the gel pad, (**h**) elimination of polymer replica by solvent-washing and (**i-j**) transfer-printing of the functional nanostructure on various substrates by making contacts.

• Polymer thin film can replicate the high-resolution patterns of master mold substrate successfully with 15 nm and 8 nm scale. (Figure 2)

• In addition to gold (Figure 3a-f), aluminum, copper, silver and cobalt nanowires (Figure 3g-k) were fabricated using this method.

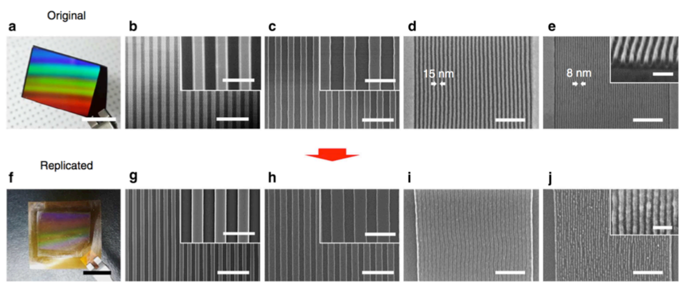

Figure 2. Preparation of polymer thin film replica (**a**) photograph of original master substrate with periodic surface patterns. (**b-e**) SEM images of surface grating patterns of master substrates. (**f**) Optical image of the polymer replica prepared via step 1. (**g-j**) Corresponding SEM images of grating patterns of the replica. Scale bars are 1 cm (**a**,**f**), 15μm (**b**,**g**), 5μm (insets in **b**,**g**), 1μm (**c**,**h**), 500 nm (insets in **c**,**h**), 200 nm (**d**,**e**,**i**,**j**), and 50 nm (insets in e,j)

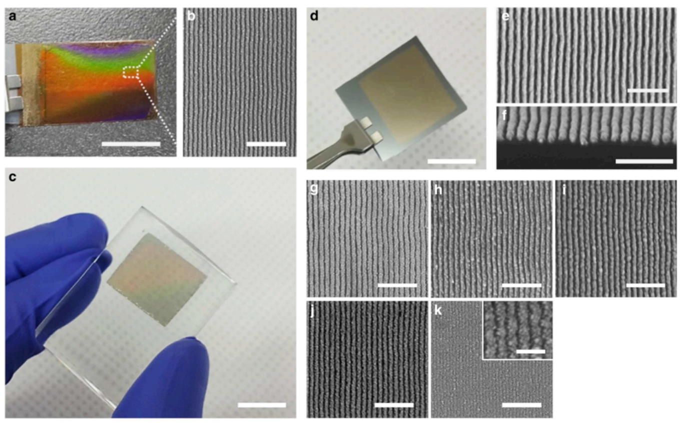

Figure 3. Transfer-printed nanostructure (**a**) Optical image showing the Au nanowires on replica/PI film (**b**) SEM image of Au nanowires on replica substrate (**c**) Photograph of transferred Au nanowires onto PDMS pad (**d**) Optical image showing Au nanowires on Si wafer (**e**) Top-down and (**f**) cross-section SEM images of printed Au nanowires (**g-j**) 20-nm-wide (**g**) Al (**h**) Cu (**i**) Ag and (**j**) Co-nanowires printed on Si wafer (**k**) 9-nm-wide Cr nanowires

2.2 Mechanism of solvent-assisted adhesion control

• In the delamination of an adhesive from a substrate, the interfacial friction has a critical role.

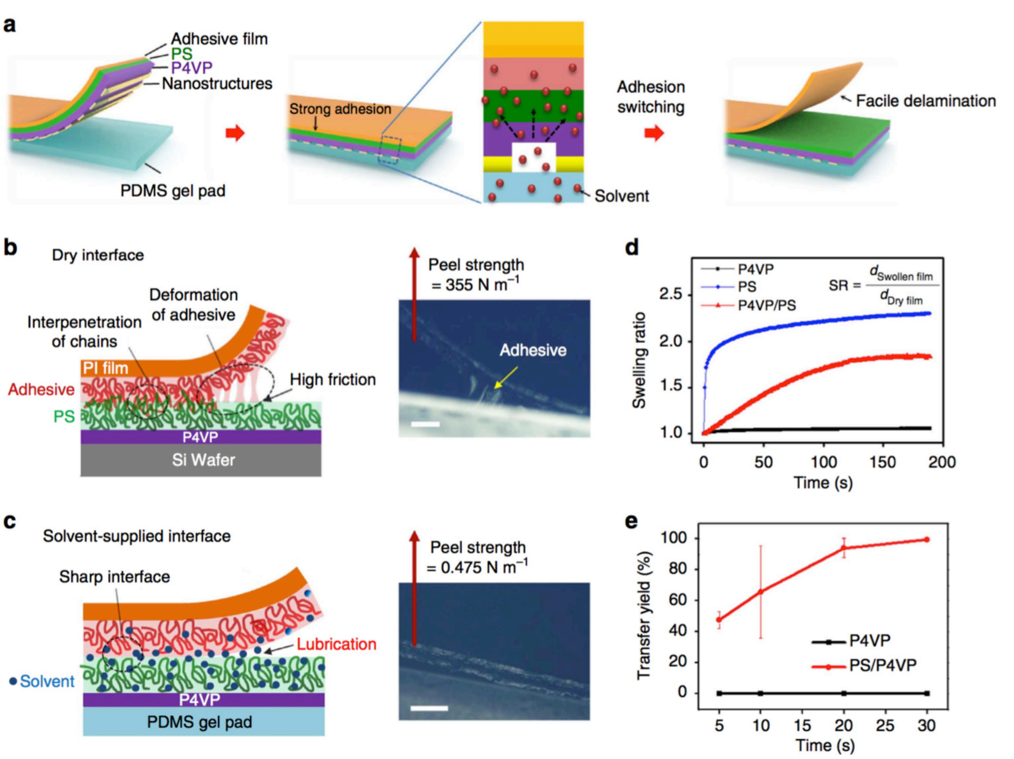

Figure 4. The mechanism of solvent-assisted adhesion control (**a**) Procedure of solvent assisted adhesion control. The out-diffused solvent molecules enable facile delamination of adhesive film from the polymer replica. (**b**,**c**) Schematic illustration describing adhesion mechanisms and the cross-section photographs for (**b**) dry and (**c**) solvent-supplied interface between the adhesive film and PS layer. (**d**) In-situ measured swelling ratio (SR = thickness of swollen film/thickness of dry film) of polymer films. (**e**) transfer yield of the nanostructures from the adhesive film to the PDMS gel pad depending on the supply time of toluene. Scale bar of (**b**,**c**) is 100 μm.

• In a dry state, the friction coefficient at the adhesive and PS is high due to strong van der Waals interactions resulting from interpenetration of polymer chains.

• In the presence of a good solvent, the interpenetration between extended chains is suppressed due to large entropic penalty.

• The solvent molecules present between the films cause hydrodynamic lubrication and the resistance of friction was reduced.

• The solvent also reduced adhesion between materials and PDMS gel pad and contributed to facile and reliable transfer printing.

2.3 Demonstration 1: Nanotransfer printing onto diverse surfaces

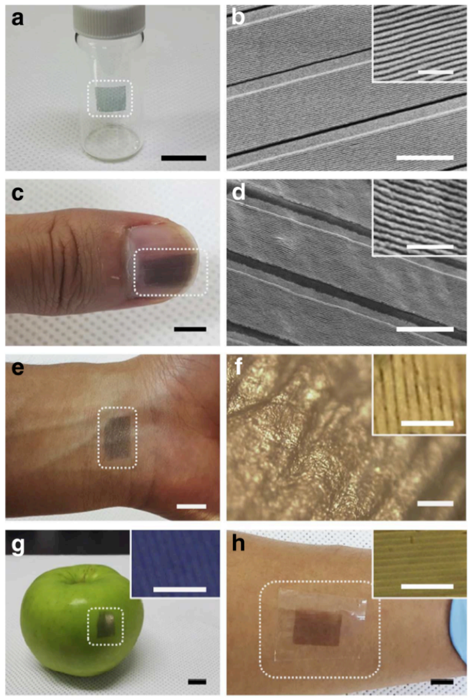

Figure 5. Metallic nanowires onto various surfaces via solvent-assisted nanotransfer printing (**a**,**b**) Nonplanar glass vial, (**c**,**d**) human finger nail, (**e**,**f**) wrist skin (**g**) surface of an apple, (**h**) flexible substrate attached on skin. Scale bar is 1 cm (**a**,**c**,**e**,**g**,**h**), 100 μm (**f**), 5 μm (insets in **f**,**g**,**h**), 1 μm (**b**,**d**) and 200 nm (insets in **b**,**d**)

- This printing method is applicable to various surface even human skin or fruit peels.
- Printed Ag nanowire on various surfaces were used for surface-enhanced Raman spectroscopy (SERS) and it made possible to detect molecules at an extremely low concentration. (ex. Ag nanowires attached apples can be applicable to detection of pesticide residues (1μg/cm^2) on its surface.)

2.4 Demonstration 2: Flexible and printable hydrogen sensor

- Combination of this nanotransfer printing method for fabrication of nanomaterials and conventional shadow mask technique for deposition of electrode enable to make real device such as hydrogen sensor as demonstrated in Figure 6.

3. Conclusion

- Practical nano-transfer printing approach was developed in sub-20 nm regime.
- Facile adhesion switching with solvent molecules enabled release of functional nanostructures on diverse substrates.
- Using this method, the application of SERS measurement and fabrication of flexible hydrogen sensor were demonstrated.

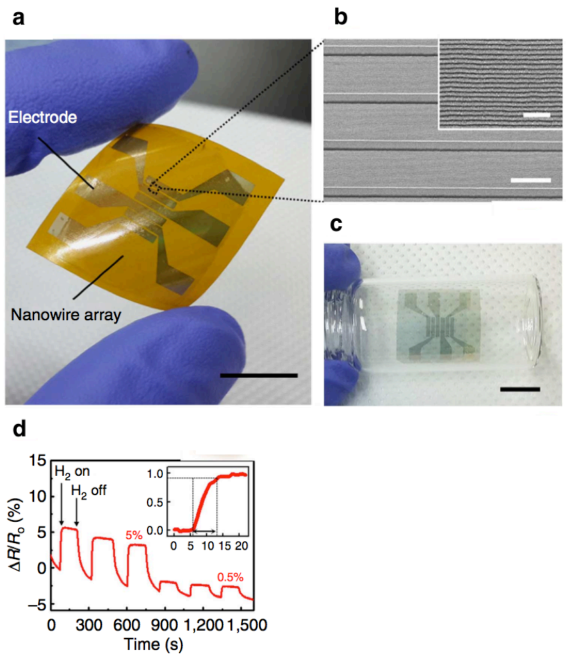

Figure 6. Demonstration of flexible and printable hydrogen sensor (**a**,**c**) A photograph of the fabricated flexible hydrogen sensor on a plastic substrate (**a**) and curved surface of glass vial (**c**). (**b**) SEM image showing Pd nanowires between electrodes. (**d**) Performance of the hydrogen sensor device

4. Reference

1. Zaumseil, J. et al. *Nano Lett*. **2003**, 3, 1223-1227
2. Rogers, J. A. et al. *J. Am. Chem. Soc*. **2002**, 124, 7654-7655
3. Hwang, J. K. et al. *Nat. Nanotech*. **2010**, 5, 742-748
4. Lee, Y. C. et al. *J. Micromech. Microeng*. **2010**, 20, 025034
5. Rogers, J. A. et al. *Appl. Phys. Lett*. **2002**, 81, 562-564