

Resolution limits of polymer nanoimprint lithography

Reliable patterning at the 2-nm scale that uses polymer nanoimprint lithography has been demonstrated by lead investigator John Rogers at the Univ. of Illinois at Urbana-Champaign and colleagues at Dow Corning Corp., Midland, Mich. By accurately replicating features with nanometer dimensions, this method could play future roles in fabricating structures in fields as diverse as microelectronics, nanofluidics, and biotechnology.

This approach generates molds with true nanoscale relief structures that are defined by the geometry of the SWNTs (single-walled carbon nanotubes). Its success relies on two key factors:

- Van der Waals adhesion forces, which bind the SWNTs to the substrate with enough strength to prevent their removal when the cured polymer mold is peeled away.

- Complete absence of polymeric residue on large regions of the SWNT masters after the fabrication process.

To obtain features with 2-nm resolutions, the average distance between polymer cross-links (~1 nm) and the lengths of individual chemical bonds (~0.2 nm) become key in the molding process. In addition, there is a countable number of polymer bond lengths that are available to replicate the relief structure—

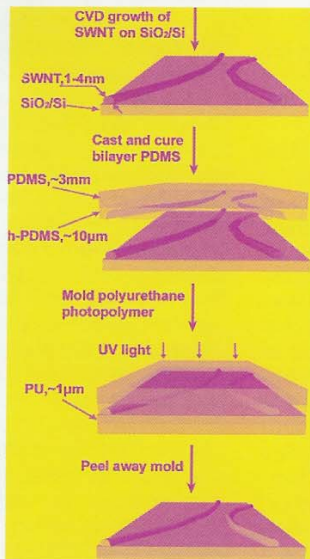


Fig. 1. Steps for polymer imprint lithography with nanometer resolution. Source: John Rogers, Univ. of Illinois at Urbana-Champaign.

this method has the ability to accurately replicate the nanoscale features of the SWNTs (Fig. 1)

In the process, high-quality submonolayers of small diameter SWNTs are grown on a Si wafer. Then, a mold of the nanotubes is prepared by pouring a thermal-setting polymer over the wafer. After curing the mold, it is gently pressed against a thin layer of PU (photocurable polyurethane). Passing light through the transparent mold causes the material to cross-link and harden. An AFM is used to measure the heights of the resulting relief structures and a TEM is used to determine their widths.

The ultimate resolution is correlated to the ability of the prepolymer to conform to the surface and the ability of the cross-linked polymer to retain the molded shape. Additionally, optimized materials enable reliable, repetitive patterning.

This imprinting procedure offers reliable replication capability for features with horizontal and vertical dimensions >2 nm, partial capability for features between 1-2 nm, and little to no capability for features <1 nm.

The work is described in the December 2004 issue of *Nanotechnology*.

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Nanotechnology

New chemistry benefits nanotechnology

Clusters of Al (aluminum) atoms that have chemical properties similar to single atoms of metallic and nonmetallic elements when they react with I₂ (iodine) clusters have been reported by lead investigators A. Welford Castleman at Pennsylvania State Univ., University Park, and Shiv N. Khanna at Virginia Commonwealth Univ., Richmond. These stable clusters provide a route to an adaptive chemistry that introduces the Al-cluster species into nanoscale materials, tailoring them to create desirable properties.

Depending on the number of Al atoms in the cluster, the superatoms show properties of either halogens or alkaline earth metals.

A cluster of Al₁₃ atoms behaves like a single I₂ atom, while a cluster of Al₁₄ atoms behaves like an alkaline earth atom. To make the superatoms, I₂ atoms are replaced with Al clusters in naturally occurring networks of I₂ atoms and polyiodides. When the I₂ atom is substituted with the Al cluster (Al₁₃), the chemistry of the compound changes, causing the other I₂ molecules to break apart and bind individually to the cluster. When 12 I₂ atoms are bound to a single Al₁₃ cluster, it forms a completely new class of polyiodides.

The enhanced stability of these superatoms is associated with a balance in the superatom's atomic and electronic states. While the clusters resemble atoms of other elements in their interactions, their chemistry is unique, creating stable compounds with bonds that are not identical to those of single atoms. The work is described in the Jan. 14, 2005 issue of the journal *Science*.

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Biotechnology

Molecular surgery on a buckyball

A method that uses C₆₀ fullerenes, which are modified to have a large opening and then are closed via molecular surgery, has been demonstrated by lead investigator Koichi Komatsu at Kyoto Univ., Japan. This four-step organic reaction method completely closes a 13-membered ring orifice of an open-cage fullerene. Earlier work centered on preparing a C₆₀ derivative containing a 13-membered-ring orifice that is filled with H₂ (hydrogen). In the current work, the hole is synthetically sewn to make a nanocontainer. In the process (Fig. 1), it is crucial that the presence of a sulfur atom on the rim of the orifice be present. Once H₂ is trapped within the fullerene, the sulfide group is oxidized to create a sulfoxide. Then, the sulfoxide is excised photochemically, shrinking the hole by one atom. Titanium-mediated coupling of carbonyl groups tightens the opening to an eight-membered ring. The application of heat to this last step does not cause serious loss of H₂ since the orifice is reduced sufficiently to prevent loss. The fullerene derivative rearranges via thermal allowed electrocyclicization, restoring the C₆₀ cage and eliminating 2-cyanopyridine and diphenylacetylene in the process.

Potential applications are in molecular electronics, magnetic resonance imaging, and nuclear magnetic resonance analysis. The work is described in the Jan. 14, 2005 issue of the journal *Science*.

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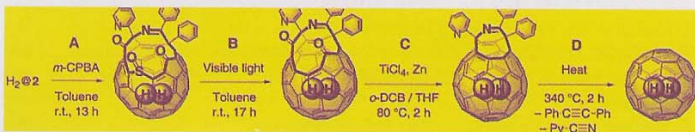


Fig. 1. Size reduction/closure of orifice of open-cage fullerene encapsulating H₂ in four-step process. Source: Koichi Komatsu, Kyoto Univ., Japan.