Nanometer-Scale Printing

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If global NPP is fixed by planetary constraints, then no substantial increase in plant growth may be possible. Hence, the obvious policy question must be whether the biosphere can support the 40% increase in global population projected for 2050 and beyond.

To determine if humanity can co-opt a higher fraction of global NPP, the previously defined planetary boundaries become relevant, starting with land use. According to the most recent estimates from global satellite data sets, humans currently appropriate 38% of global NPP, which would appear to leave 62%, or about 33 Pg, available for future consumption (see the figure) (*9*). However, the authors also estimate that 53% of global NPP is not harvestable. This nonharvestable part includes plant growth in root systems, preserved land (for example, in national parks that are critical for ecosystem services and biodiversity), and wilderness areas where no transportation exists for harvesting. If one subtracts this unavailable NPP, only about 5 Pg, or 10% of total global NPP, theoretically remains for additional future use by humans.

Agriculture now consumes 38% of the global land surface, with major new expansion only available in underdeveloped parts of South America and Africa (*10*). Land put in to agriculture often has lower production than the natural ecosystem replaced, but growth is concentrated in the components that humans value. Crop production exceeds the natural ecosystem when augmented with irrigation and fertilizer applications. Cropland under irrigation has roughly doubled in the last 50 years, and fertilizer use has increased by 500% (*10*).

Many analyses now conclude that freshwater use for irrigation has already reached a planetary boundary. As some rivers are completely drained for agriculture and groundwater withdrawal limits are reached in some regions, irrigated crop area could decrease in coming decades (*11*). Likewise, Rockström *et al*. (*3*) concluded that the nitrogen and phosphorus cycles may have already exceeded planetary boundaries, as evidenced by massive river pollution and ocean anaerobic dead zones. If anything, future increases in NPP must be achieved with less, not more, irrigation and fertilizer use.

Possibly the biggest unknown in this global analysis is the future of bioenergy. If every chloroplast of the remaining 5 Pg of NPP were used for bioenergy, only 40% of current global primary energy consumption would be satisfied (*9*). There will be very real policy dilemmas if land previously allocated to food production is transformed to bioenergy production, raising food prices for the people who can least afford it (*12*).

Any analysis of global biospheric limits includes many assumptions and considerable uncertainties. Yet, global monitoring will document every parcel of land that is converted from a natural ecosystem to cities, agriculture, or bioenergy. Every such conversion increases the fraction of NPP consumed by humanity. The question is thus not whether humans will reach the global NPP boundary but when we will do so. The projected 40% increase in human population by 2050 CE, combined with goals to substantially improve standards of living for the poorest 5 billion people on Earth, implies at least a doubling of future resource demand by 2050. As suggested 40 years ago (*1*), the limits to growth as measured by human consumption of NPP may well be reached in the next few decades.

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MATERIALS SCIENCE

Nanometer-Scale Printing

A method using rubber stamps and molecular-scale fracture can produce patterns with feature sizes in the nanometer range.

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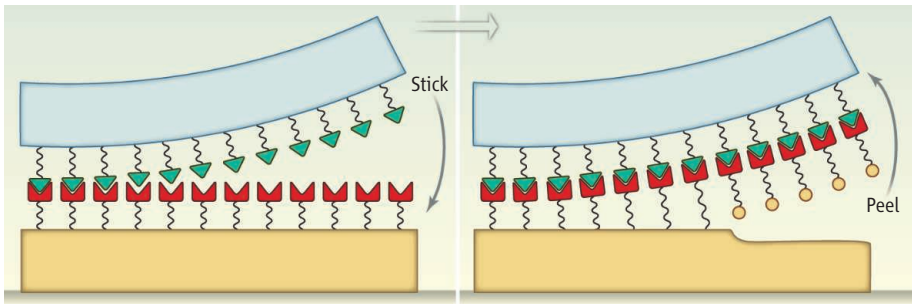
Progress in nanotechnology relies on the ability to fabricate structures with precisely defined, nanoscale dimensions. Historically, this task has been accomplished with energetic beams of electrons, ions, or photons, using sophisticated tools whose origins lie in the semiconductor industry (*1*). Although well suited for manufacturing of integrated circuits and related devices, such techniques are often not the best choices for exploratory research because they require expensive equipment and specialized facilities. They also tend to work well only with narrow classes of materials, and they can be prohibitively slow for use over large areas. On page 1517 of this issue, Liao *et al*. (*2*) introduce a scheme that bypasses these limitations, in which rubber stamps affect nanoscale pattern transfer via molecular-scale fracture. Their technique represents a conceptual advance on a class of "soft lithographic" methods in which elastomers with fine features of relief on their surfaces deliver molecules (*3*, *4*) or materials (*5*, *6*) onto substrates of interest, in a process of contact printing. By providing advanced nanofabrication capabilities to researchers with limited access to complex apparatus, these simple methods have played a central role in the emergence of nanotechnology as a broad, vibrant field of study.

The work of Liao *et al*. is important in this context because it enhances the resolution of one of the most widely used soft lithographic techniques, in which stamps made of poly(dimethylsiloxane) (PDMS) print molecules onto substrate surfaces with which they covalently react to form densely packed, monolayer films, referred to as self-assembled monolayers (SAMs) (*3*). This process, even when carried out by hand in an ordinary laboratory environment, can yield patterns of SAMs with features as small as a fraction of a micrometer. Two aspects, however, frustrate operation in regimes of resolution that are relevant to the frontiers of modern nanotechnology (*7*–*9*). First, the molecules that form the SAMs diffuse slightly along the surface during and after printing, thereby blurring the edges of the patterns. Second, gas-phase transport can carry molecules from the recessed, noncontacting regions of the stamp to the substrate, yielding partial monolayers



Stick it and rip it. In a new, high-resolution method for nanofabrication, Liao *et al*. show that rubber stamps (top; blue) with siloxyl groups (green) on their surfaces react covalently with hydroxyl-terminated (red) self-assembled monolayers (SAMs) on gold (bottom; gold) at points of physical contact. Peeling the stamp away initiates fracture near the surface layer of the gold, yielding SAMs with precisely patterned geometries.

in the unprinted areas. Past attempts to minimize these effects achieved some limited success through the use of molecular inks with large molecular weights (*9*). Liao *et al*. take a completely different approach, with even better results. Instead of using stamps to print molecules onto bare surfaces in the usual way, they exploit chemically functionalized stamps to remove molecules from preformed, unpatterned SAMs. Here, upon physical contact, covalent bonds form between the stamp and reactive groups exposed on the surface of the SAM. Peeling the stamp away "mechanically desorbs" molecules from the SAM in regions defined by contact with the stamp. SAMs patterned in this way can then serve as molecular templates for etching the underlying substrate or for guiding the deposition of other materials (*2*–*4*). The most important practical aspect of this technique, termed chemical lift-off lithography, is that its resolution in patterning SAMs exceeds that of previous soft lithographic techniques.

Optimized surface chemistries are critical to the successful operation of the process. Liao *et al*. find that Si-OH groups on PDMS and hydroxyl-terminated SAMs on gold rapidly and covalently react to form strong Si-O-SAM linkages that remain intact as the stamp is removed. Here, mechanical fracture occurs within a near-surface region of the gold, such that both the SAM and, roughly, a monolayer of gold atoms peel off of the substrate (see the figure). These steps of contact-induced chemistry followed by nanoscale fracture can occur in minutes, over areas limited only by the sizes of the stamp and substrate, and with efficiencies of SAM removal that approach ~80%. Furthermore, the edges of the patterns can be extremely sharp and well defined, with roughness at the level of only a few nanometers. As a result, patterns with dimensions in the nanometer regime are possible. Liao *et al*. demonstrate 40-nm features, apparently limited only by the sizes of the relief features on the stamps.

The capabilities demonstrated by Liao *et al*., especially with such an extremely simple printing method, offer powerful modes of use in research, particularly when overlay registration is not required. Further development of the technique to eliminate such constraints will require engineering innovation. Fundamental extension of the resolution will demand improved understanding of the underlying mechanisms and, in particular, the relative roles of the molecular chemistry of the SAMs, the materials science of the substrate and stamp, and the physics of nanoscale fracture. Such topics represent appealing opportunities for interdisciplinary work, with strong potential for impact in nanoscience and nanotechnology alike.

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STRUCTURAL BIOLOGY

Versatility from Protein Disorder

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Synergy between disordered regions and structured domains increases the functional versatility of proteins and their interaction networks.

Many protein functions can be attributed to segments (domains) that fold independently and adopt specific three-dimensional structures (*1*). Intrinsically disordered regions (*2*, *3*) are unstructured segments whose amino acid compositions prevent autonomous folding. Some eukaryotic proteins are either fully disordered (intrinsically disordered proteins) or structured, but most have both types of regions (see the figure). The notion that disordered regions are largely passive is being actively challenged by the idea that they perform diverse functions, and that synergy between structured and disordered regions expands the functional repertoires of proteins.

Understanding how disordered regions mediate function requires accurate physical descriptors of sequence-disorder relationships. Recent studies based on a combination of polymer theory, computer simulations, and biophysical experiments have revealed some coarse-grain conformational properties of disordered regions. Sequences enriched in polar amino acids and deficient in hydrophobic residues form compact, globular conformations (*4*, *5*). As the net charge per residue within disordered regions increases, they undergo continuous transitions to loosely packed ellipsoidal random coils (*6*, *7*).

The growing list of features attributed to disordered regions suggests that they act as molecular rheostats to support a continuum of conformational states and transitions. These features enable disordered regions to mediate highly specific interactions with multiple binding partners (*2*, *3*). Conformational fluctuations of these regions can control the exposure of short linear motifs (*8*) that interact with protein domains, thereby regulating protein interactions. Posttranslational modifications within or near these linear motifs may modulate conformation and affinities, thus increasing the functional capabilities of disordered regions. Examples include the tails

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