

quickly elucidated. Although the study by Klatt *et al.* simply grouped participants into *Lactobacillus*-dominant (i.e., eubiotic) and non-*Lactobacillus*-dominant (i.e., dysbiotic) groups, emerging data now hint that the complexities of these conditions are considerably more nuanced, perhaps an important lesson for the broader field of microbiota research. Molecular techniques that enable species-level classification of *Lactobacilli* suggest that not all *Lactobacilli* are created equal with respect to their ability to protect the female reproductive tract. For example, vaginal microbiota dominated by *L. iners* have been associated with increased acquisition of sexually transmitted infections (11) and preterm birth (12). There is emerging evidence that within the same species, different strains of *L. iners* may be more or less beneficial (13). Similarly, strain-specific differences in the anaerobe *Gardnerella* have been documented (14).

Precision medicine, defined by the U.S. National Institutes of Health as “an emerging approach for disease treatment and prevention that takes into account individual variability in genes, environment, and lifestyle for each person,” must also account for the variability of the individual’s microbiota. This raises a critical question: Can a woman’s vaginal microbiota be altered? Unfortunately, dysbiosis is difficult to treat: Although in the short-term, antibiotic therapy substantially alters the structure and composition of the vaginal microbiota in women with bacterial vaginosis, nearly 60% will have a recurrence within a year following therapy (15). Thus, effective antibiotic-sparing pre- and probiotics are actively being sought.

To date, variability in study designs, outcomes (prevention versus treatment of dys-

biosis as well as methods of measurement of the vaginal microbiota), and strains limit the ability to draw definitive conclusions on probiotic efficacy. The study by Klatt *et al.* is a reminder that without a deeper understanding of the structure, function, and dynamics of the vaginal microbiome, successful interventions to optimize it and improve women’s health will remain elusive. ■

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APPLIED PHYSICS

Applying plasmonics to a sustainable future

Plasmonic technologies may form components of a future clean and sustainable society

By Alberto Naldoni,^{1,2} Vladimir M. Shalaev,¹ Mark L. Brongersma³

Chemistry is fundamental for powering our society. A flurry of very promising experiments demonstrate that plasmonics may have a transformative impact on the way we will drive, manipulate, enhance, and monitor chemical processes in the future. Plasmonics offers the ultimate spatial and temporal control over light and photochemistry, with the help of metallic nanostructures capable of concentrating electromagnetic energy into nanoscale volumes. Surface plasmons (SPs) are charge-density oscillations at the surface of a conducting material and decay by reemission of a photon or through the creation of highly energetic (“hot”) electrons and holes. The subsequent equilibration of hot carriers with lattice phonons can lead to appreciable local heating.

All these physical phenomena can be leveraged to efficiently produce fuels and chemicals. One example is the use of resonant nanostructures combined with semiconductor photocatalysts to increase the rate of interband transitions or to extend light harvesting to sub-bandgap photons (1, 2). Plasmonic or high-index dielectric nanostructures could be used to engineer ultrathin semiconductor layers, which, through field-enhancement or light-trapping effects, reach broadband near-unity absorption with an accompanying reduction in materials and device cost. In contrast to semiconductor photocatalysis, hot-carrier-driven transformations on metal surfaces offer the opportunity to explore new

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The microbicide tenofovir prevents retroviral replication. As a vaginal gel, it offers a feasible method for preventing HIV infection.

types of chemistry that are typically only possible at high temperatures and pressures (1).

Hot electrons can be injected into empty molecular orbitals of adsorbates, forming a transient negative-ion state, which thereby facilitates the rate-limiting step of a specific chemical reaction. A remarkable case in point is hot-electron-driven ethylene epoxidation (3). In this system, O₂ dissociation controls the reaction rate, and a fourfold rate enhancement in ethylene epoxidation was demonstrated for the hot-electron-driven process in comparison to the thermal case (3). Similarly, hot-electron-driven H₂ dissociation on AlPd nanoparticles (4) enabled an increased selectivity of ethylene and ethane production by acetylene hydrogenation.

However, an intrinsic limitation of this mechanism is that, after excitation of SPs, the concentration of hot carriers is highest close to the Fermi level, and therefore hot-electron-driven chemical transformations preferentially proceed through the adsorbate orbitals closest to the Fermi level.

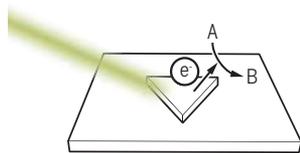
Recently discovered alternative charge transfer pathways (5, 6) allow for the instantaneous decay of SPs and subsequent scattering of hot electrons into a specific unoccupied adsorbate orbital, leaving behind an energetic hole in the plasmonic nanoparticle (see the figure). By engineering the plasmonic catalyst-molecule (semiconductor) interface, a surface electronic state with a desired energy can be created at will; this ability offers a tremendous opportunity to selectively enhance favorable chemical pathways, while suppressing undesired ones.

Further potential for using SPs in chemistry is the sudden and intense temperature increase generated by the coupling of the electron density wave to lattice vibrations. This heating can be localized in space and time, offering the opportunity for running out-of-equilibrium chemistry with enhanced energy efficiency and without the need of macroscopic heat sources for heating supporting materials or for vaporizing chemical species. Early demonstrations included thermally stimulated catalysis (7) and plasmon-enhanced chemical vapor deposition for the growth of nanostructures (8). More recently, new applications have emerged in which the use of local heating holds promise, including water purification, separation of chemicals, and solar distillation (see the figure).

Saltwater desalination is a notable case. The world is facing a freshwater crisis, and

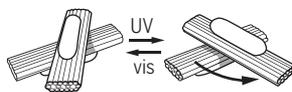
Ways to use plasmonics as energy input

Plasmonic materials concentrate light into nanoscale volumes, thus producing intense electric fields, highly energetic electrons, and local heating that can be used to drive, enhance, and manipulate chemical processes.



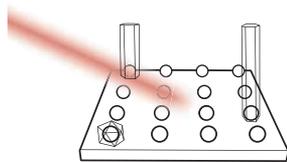
Catalysis

Reactions such as splitting of water into oxygen and hydrogen, or reducing CO₂ into methanol and water



Plasmonic machines

Providing energy to rotate molecules on a surface



Materials synthesis

Nanoscale heat sources to grow materials with tight spatial control



Molecular purification

Local heating for the distillation of high-value chemicals

cheap, efficient production of fresh water from salt water would mean an end to this global challenge. Plasmonic nanoparticles can be self-assembled inside the nanochannels of an anodic alumina membrane that can float naturally on a water surface (9). Upon irradiation, the plasmonic device absorbs more than 96% of the solar spectrum and focuses the absorbed energy in nanoscale

“Plasmonics offers the ultimate spatial and temporal control over light and photochemistry...”

water volumes, enabling steam generation and efficient (~90%) desalination.

Moreover, it would be possible to exploit local heating for separation of molecular mixtures generated from photocatalytic CO₂ reduction or H₂ production from sustainable bioalcohols. Neumann *et al.* (10) have shown that Au-SiO₂ nanoshells can produce light-induced water-ethanol distillation, generating a vapor phase more rich in ethanol (and more efficiently) than that obtained by conventional thermal distillation. If the mixture is composed of 1-pro-

panol/water, a liquid-liquid phase separation is also observed.

Another exciting and novel application of plasmonics could be in the use of reconfigurable metamaterials for chemistry (11). In particular, by combining plasmonic nanoparticles and DNA nanotechnology, three-dimensional metamolecules can be created on demand (12). DNA serves as both a structural material to self-organize plasmonic nanoparticles and as fuel for driving conformational changes. At the same time, the light-driven plasmonic nanosystem transduces the molecular motions into a detectable optical signal. Such plasmonic machines could be implemented for carrying out smart operations such as transport of molecules and information processing (see the figure).

Taking inspiration from the 2016 Nobel Prize in Chemistry, awarded for work on molecular machines, we could imagine the use of molecular devices that pump, move, and assemble molecules to plasmonic nanostructures, or even to topological defects with optical singularities, to create light-driven plasmonic molecular robots.

High-performance plasmonic materials will be central to the development of ultrathin and efficient portable devices, which would have a strong impact on the decentralized production of fuels and chemicals. Scaling plasmonic chemistry to the industrial level would require the development of new alternative plasmonic materials, the use of metasurfaces, and flexible nanophotonic platforms. The transition to a clean and sustainable society is already taking place. Plasmonics can help accelerate this changeover by enabling, manipulating, enhancing, and monitoring chemical processes with atomic-scale precision and control. ■

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