Bio Focus

Bacterial biofilm demonstrates nonwetting behavior

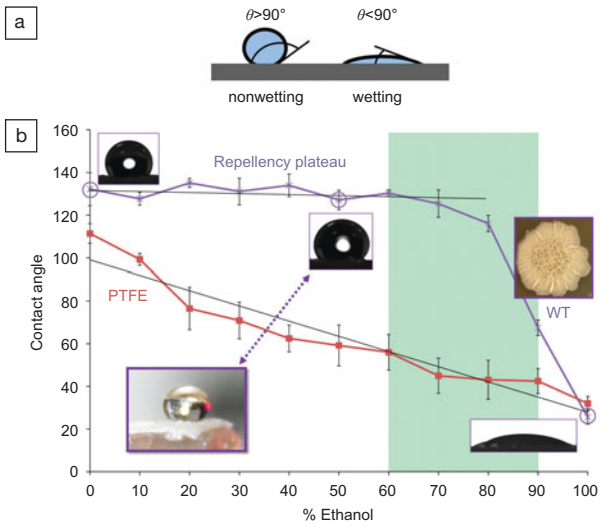
The performance of heat exchangers, ventilation systems, ship hulls, and medical implants are often compromised by biofilms. Biofilms are communities of microorganisms that form on solid or fluid interfaces and are designed to protect the individual cells, such as bacteria, from the environment. Protection largely comes from the extracellular matrix (ECM) that is secreted by the cells. The ECM hinders diffusion of molecules through the biofilm, which limits the effectiveness of antimicrobials and can lead to drug resistance. The resulting pernicious nature of biofilms is commonly associated with the complex chemistry of the ECM. However, researchers at Harvard University have recently demonstrated that the chemistry and topography of biofilms of the bacteria *Bacillus subtilis* exhibit nonwetting behavior, which provides an additional defense mechanism.

As reported in the January 18th issue of the *Proceedings of the National Academy of Sciences* (DOI: 10.1073/pnas.1011033108; p. 995), A.K. Epstein, B. Pokroy, A. Seminara, and J. Aizenberg measured the contact angle of a series of water/ethanol solutions on biofilms of *B. subtilis*. Surprisingly, the biofilm maintained a constant contact angle (~135°) up to a concentration of 80% ethanol. Hydrophobic materials such as Teflon® exhibit a linear decrease in contact angle with ethanol concentration and even 20% ethanol solution wets its surface. This is significant because it demonstrates that liquid does not reach the bulk of the biofilm and no chemical change occurs in the biofilm exposed to 60–70% ethanol—a range commonly thought to be disinfectant.

To further describe the fluid-repellent nature of the biofilm, the researchers examined the influence of topography. These biofilms naturally have an undulating surface at the 10s–100s μm scale. Confocal microscopy showed that drops containing a fluorescent dye stained only on the top layer of the biofilm and did not penetrate into the grooves of the surface. This demonstrates that the biofilm exhibited Cassie–Baxter wetting, a state which traps gas within the topography and is common for many superhydrophobic surfaces. However, epoxy replicates of the surface did not reproduce the contact angle behavior of the biofilm. This shows that a combination of the topography and a dynamic chemistry of the ECM are responsible for liquid repellency.

The researchers demonstrated that water repellency on the macroscopic scale may provide bacteria an additional defense mechanism to antimicrobial agents. The researchers are careful to note that this strain of bacteria is commonly found in soil, so biofilms that are constantly submerged in water will likely exhibit different behavior. Yet this research demonstrates that some sterilization techniques, such as soaking in disinfectant, may not be effective for certain types of bacteria.

Scott Cooper



(a) Schematic of contact angles on nonwetting (θ > 90°) and wetting (θ < 90°) surfaces. (b) Contact angle of the wild-type (WT) biofilm of *B. subtilis* for a series of water/ethanol solutions. The contact angle remains relatively constant at ~135° up to a concentration of 80% ethanol. Polytetrafluoroethylene (PTFE) demonstrates an incremental decrease in contact angle with the concentration of ethanol (surface tension of the liquid). The green region denoting 60–90% ethanol is commonly regarded as antimicrobial for free-swimming bacteria. *Source: PNAS* **108** (3)(2011) DOI: 10.1073/pnas.1011033108; p. 995.

Mid-infrared Fe:ZnSe laser achieves output energy scaling at room temperature

The development of a compact mid-infrared (mid-IR) laser operating over a 2–10 μm spectral range has been a challenge for several decades. This range contains the atmospheric transparency window that allows for easy passage of radiation to the earth's surface. Many important atmospheric constituents have absorption lines in the 2–10 μm "molecular fingerprint" region. Mid-IR lasers are thus suitable candidates for applications in space optical communications, as well as in remote sensing, trace gas analysis, laser surgery, and medical diagnosis. Lasers based on II–VI compounds doped with transition metals (such as Fe-doped binary and ternary chalcogenides) with a gain bandwidth of up to 50% of the central wavelength constitute a viable route for broadly tunable mid-IR coherent sources. They can provide very high power levels with good beam quality, but realizing these in practice has been a challenge. While some sources have been developed, the output energy levels have been unacceptably low. N.-S. Myoung, S.B. Mirov, and colleagues from the University of Alabama at Birmingham have now achieved energy scaling in a 4.3 μm Fe:ZnSe mid-IR laser at room temperature by optimizing the fabrica-

https://doi.org/10.1557/mrs.2011.48 Published online by Cambridge University Press

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tion technique based on post-growth thermal diffusion of Fe in polycrystalline ZnSe.

As reported in the January 1st issue of *Optics Letters* (DOI:10.1364/OL.36.000094; p. 94), the researchers investigated Er:Cr:YSGG laser-pumped Fe:ZnSe lasing in a Fabry–Perot cavity in the temperature range of 236–300 K. Thermal diffusion of Fe was carried out in sealed quartz ampoules at 10^{-5} Torr for 14 days at 1000°C, which resulted in a highly concentrated (Fe concentration 2×10^{19} cm^{-3}) gain element. High gain in the developed active medium ensured reduced oscillation build-up time, improved temporal overlap of the pump pulse (20 ns) and output oscillation (15 ns), and effective absorption of the pump pulse, leading to increased output energy. A fourfold increase in the output energy of the gain-switched Fe:ZnSe laser was obtained. The maximum laser output energy was 4.7 mJ at 4.3 μm and 236 K, and 3.6 mJ at 4.37 μm and 300 K (limited by available pump energy) with maximum obtained power of 0.3 MW at 4.3 μm. The researchers said that additional improvements can be achieved by further optimization of the laser cavity and also by using a pump with higher energy.

Mousumi Mani Biswas

Energy Focus

ZnO nanoforest delivers high-efficiency solar cell

Inspired by the network of branches that trees use to gather sunlight, an innovative team of researchers recently grew a "nanoforest" of light-absorbing nanowires to ramp up productivity in dye-sensitized solar cells (DSSC). As detailed in the January 5th online edition of *Nano Letters* (DOI: 10.1021/nl1037962), S.H. Ko and co-workers at the Korea Advanced Institute of Science and Technology and University of California, Berkeley developed a multi-stage seeded growth process to grow intricately branched structures of ZnO nanowires that resemble a tightly packed forest of pine trees. The team then fabricated the nanoforests into a DSSC and demonstrated a significant jump in the solar cell's efficiency.

In a DSSC, a wide-bandgap semiconductor works in conjunction with a sensitizing dye to absorb incident sunlight and convert it to electrical energy. ZnO is an effective semiconductor for this purpose and is appealing due to the ease with which it can be grown, but the resulting solar cells suffer from low efficiencies. However, this nanoforest approach could be the crucial step to making ZnO a viable DSSC component.

To achieve the forest-like structure, the researchers first grow nanowires by a hydrothermal growth process, depositing seed particles (ZnO quantum dots) on a substrate and immersing it in a solution containing zinc nitrate hydrate and the polymers hexamethylenetetramine (HMTA) and polyethylenimine (PEI). Then they wash off the polymer, bake the sample, and deposit a new layer of seed particles over the pillar-like nanowires. Next they repeat the hydrothermal growth step, which now causes nanowires to form along the length of the original wires, like branches on a tree. They perform additional cycles to create higher orders of branching, leading to a dense network of hierarchically branched nanowires.

The team demonstrated that both the "trunk" and the "branches" of ZnO are crystalline and grow along the wurtzite *c*-axis. The trunks are 40–50 μm long with an aspect ratio greater than 100, while the branches are 2–10 μm in length.

To test the usefulness of these novel structures, the researchers fabricated DSSCs by sandwiching a dye-sensitized ZnO nanoforest between electrodes. The measured current–voltage characteristics show a light-induced current that increases with trunk length and the degree of branching. Ko and the research team report efficiencies of 2.6% for their devices, which is an increase of 350–500% over devices made with regular, non-branched ZnO nanowires. The team cites the increased surface area as the primary cause for improvement, as it allows for greater dye-loading and photon absorption. They also said that the complex network of overlapping branches allows for better electron transport to the collection electrodes.

Alison Hatt

Nano Focus

Functionalization of graphene leads to enhanced hydrogen adsorption

The on-board, high-capacity, facile, and reversible storage of hydrogen fuel is one of several significant challenges for hydrogen-fueled vehicles. While gas-adsorbant metal-organic framework structures display high H_2 uptake, the volume of H_2 they can hold is insufficient due to the material's low density. The densities of carbon materials are sufficiently high but their capacity for H_2 adsorption is low. Strategies for increasing the H_2-uptake capacity of carbon materials include surface modification with heteroatoms or functional groups in order to polarize the H_2 molecules. Pillared graphene's potential for H_2 storage has been demonstrated with theoretical calculations. In addition, recent experiments show that H_2 uptake by thermally exfoliated graphene (TEG) increases linearly with surface area. Recently, C. Kittrell and J.M. Tour of Rice University, K.J. O'Neill of the National Renewable Energy Laboratory (NREL), and co-researchers hypothesized that H_2 uptake in TEG could be improved by engineering nanospaces; carbon scaffolds could be created by insertion of molecular spacers between graphene sheets.

As reported in the February 22nd issue of *Chemistry of Materials* (DOI: 10.1021/

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