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All that glitters need not be gold

Refractory plasmonic ceramics provide durable nanophotonic solutions

By **Alexandra Boltasseva**[1,2] *and* **Vladimir M. Shalaev**[1,2]

Recent years have seen dramatic growth in the field of nanoscale optics. The advantages of nanophotonics—wide bandwidth, no cross-talk, high speed, and compactness—are key factors enabling optical technologies that have an impact on many areas of society, including information and communications, imaging and sensing, health care, energy, manufacturing, and national security. Gold nanostructures have long been seen as building blocks for subwavelength optical and hybrid electronic-photonic systems providing functional solutions for the above-mentioned applications (*1*). By making use of the resonant properties of metal nanostructures, particularly the subwavelength coupled oscillations known as surface plasmons, the fields of plasmonics and optical metamaterials have brought forth numerous nanoscale device concepts (*1*, *2*).

Nanophotonics technologies offering extreme durability would be of great use in defense and intelligence, information technology, and the aerospace, energy, chemical, and oil and gas industries. However, most of the optical systems commercially available or in development today fall short of meeting the challenges that such applications would require, particularly where wide temperature ranges, high pressure,

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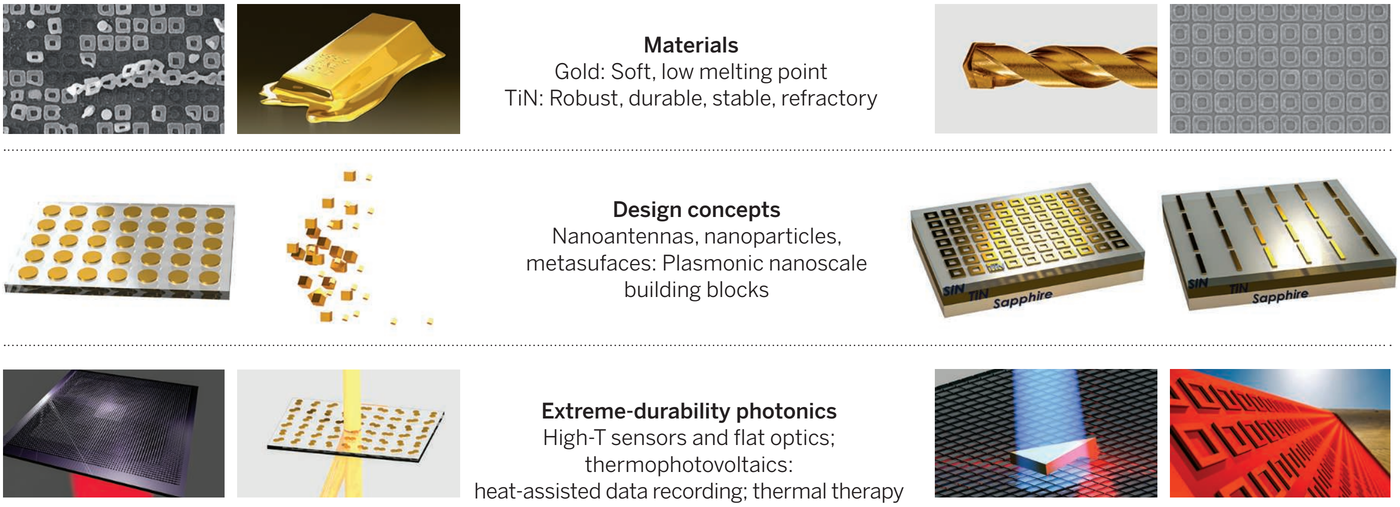
Optoelectronics in harsh environments



Golden titanium nitride. TiN, used nowadays to coat domes of Russian churches, is also seen as a replacement for gold in device concepts that make use of nanoscale plasmonic resonances enabling unparalleled optical functionalities. Because of their softness and low melting point, noble metals are not suitable for applications in extreme operational conditions such as high temperature and harsh chemicals. Plasmonic ceramic materials such as TiN serve as refractory (high temperature–stable) building blocks that could enable ultradurable photonic technologies for use in information technology, oil and gas production, and other industrial processes. (**Top**) Au (left) and TiN (right) nanostructures after exposure to heat; melting point ot TiN is 2930°C. (**Middle**) Schematics of a TiN-based plasmonic nanoparticle array and colloidal plasmonic particles (left) and light absorber designs (right). (**Bottom**) Plasmonic device applications.

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harsh chemical environments, and strong vibrations are present. Despite many device demonstrations for on-chip optics, data recording, sensing, imaging, and solar energy harvesting, the proposed gold-based devices fail to meet the application-specific requirements that real devices face in extreme operational conditions. Because of the softness of noble metals and their low melting points, conventional plasmonic structures cannot provide chemically, mechanically, and thermally stable solutions for the realization of rugged optical equipment.

The discovery of plasmonic ceramic materials as alternative "metals" marks the beginning of a technology-driven era for the fields of plasmonics and nanophotonics (*3*, *4*). Transition metal nitrides such as titanium nitride (TiN) and zirconium nitride (ZrN) have recently been proposed as refractory—that is, capable of sustaining high-temperature plasmonic materials (*4*) that exhibit good optical properties while also offering biocompatibility, compatibility with CMOS (complementary metal-oxide semiconductor) devices, chemical stability, corrosion resistance, and mechanical strength and durability (see the figure). The attractiveness of TiN for practical devices is illustrated by its extensive use in semiconductor manufacturing, microelectronics, and biotechnology.

Plasmonic ceramics can provide a unique platform for an emerging energy conversion concept, namely solar thermophotovoltaics (STPV), which promises efficiencies up to 85% (*5*). The high operational temperatures (well above 800°C) and the low melting points of noble metals have hindered progress in the STPV field. By contrast, TiN absorbers have been shown to provide high optical absorption (about 95%) over a broad range while enduring strong light illumination (*6*). TiN also holds great promise to enable efficient, TPV-based waste heat recovery. Heat energy harvesting could have a transformative effect on many industries, including metal casting, aerospace, and gas and oil, by providing fossil fuel–based power generation, fuel-fired cells, and portable power generators. TiN's properties are also well suited for solar thermoelectric generators (*7*), plasmon-mediated photocatalysis (*8*), and plasmon-assisted chemical vapor deposition (*9*).

Another heat-generating application of plasmonic nanoparticles is in health care. Because metallic nanoparticles can concentrate light and efficiently heat a confined nanoscale volume around the plasmonic structure (*10*), they can be used in thermal therapy, in which nanoparticles delivered to a tumor region can be heated via laser illumination and induce the death of cancerous cells. Gold nanoparticles are now being investigated for uses in cancer therapy as drug carriers, photothermal agents, contrast agents, and radiosensitizers. However, gold nanoparticles resonate at specific light wavelengths that lie outside the biological transparency window, thus requiring larger dimensions and complex geometries such as nanoshells (*10*); in turn, larger sizes affect nanoparticles' pharmacokinetics, biodistribution, and in vivo toxicity. TiN nanofabricated particles have been shown to exhibit plasmonic resonance in the biological transparency window and higher heating efficiencies than gold (*6*). Moreover, TiN obviates the need for complex geometries and provides a simple, small-size particle solution that is critical in optimizing cellular uptake and clearance from the body. Because TiN is a contamination-safe material already widely used in surgical tools, implants, and food-contact applications, TiN particles could become a solution for tumor-selective photothermal therapy and medical imaging.

Refractory plasmonic materials are also candidates for applications that make use of nanometer-scale field enhancement and local heating. An example of such application is an emerging, higher-density data recording approach, namely heat-assisted magnetic recording (HAMR) (*11*). In contrast to noble metals that are prone to deformations such as melting and creep, any degradation

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of refractory plasmonic materials can be avoided with the proper material integration (*6*). TiN antennae have recently been shown to satisfy the stringent requirements for an optically efficient, durable HAMR near-field transducer, thereby paving the way to the next-generation data recording systems (*6*).

The durability and refractory properties of TiN and ZrN could also make them the material building blocks for high-temperature, harsh-environment optical sensors and flat photonic components such as ultrathin lenses, as well as for spatial light modulators using the concepts of the emerging field of metasurfaces (*12*). Refractory flat optical components would last longer in harsh environments, provide more reliable data, and offer ultracompactness combined with a planar fabrication process. In the oil and gas industry, for example, ultracompact, extremely durable plasmonic sensors could replace electrical sensors and enable new measurement concepts for pressure, flow, drill bit temperature, and breakage detection.

The stability of TiN, along with its high conductivity and corrosion resistance, makes it an ideal material for nanofabrication. TiN can be used for making durable imprint stamps with unparalleled hardness and resistance to wet chemistry processes. When combined with emerging plasmonic nanolithography schemes, TiN films can be used to create multiple-use master molds and fabrication concepts for large-scale patterning at resolutions below 10 nm.

Having an excellent combination of performance properties, durability and contamination safety, plasmonic ceramics hold promise for enabling highly robust, ultracompact, CMOS-compatible optical devices capable of addressing numerous application-specific challenges and operating in harsh environments containing high temperatures, shock, and contaminants. ■

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MATERIALS SCIENCE

Building supermicelles from simple polymers

Precise control of the polymer building blocks enables synthesis of a range of micrometer-scale structures

By **In-Hwan Lee**, **Suyong Shin**, **Tae-Lim Choi**

Toy blocks such as Lego allow complex structures to be built from the simple blocks. Similarly, synthetic chemists are attempting to make large and complex molecules from simple reagents (*1*). On page 1329 of this issue, Qiu *et al.* (*2*) report an elegant strategy for making well-defined micrometer-scale superstructures by using a series of polymerization techniques and selective self-assembly processes.

A classic strategy for making large molecules is polymerization, which yields macromolecules as large as 10 nm. However, as the sizes increase, it becomes much harder to control their shapes and molecular weights. Also, conventional polymerizations produce macromolecules with a range of molecular weights. Living polymerization overcomes some of these problems, producing macromolecules with controlled molecular weight and narrow dispersity (*3*). This approach has allowed the synthesis of block copolymers that consist of at least two distinct polymer segments connected together.

To obtain even larger molecules (with diameters of several hundred nanometers), chemists have developed supramolecules, which consist of molecules connected by noncovalent interactions. For example, amphiphilic block copolymers produced by living polymerization can self-assemble into various micelles (*4*), such as spheres, cylinders, vesicles (*5*), toroidal rings (*6*), caterpillars (*7–9*), and stars (*10*), when placed in a selective solvent in which one segment is soluble and the other is not. Again, controlling the sizes and shapes of the micelles is extremely challenging. Recently, Manners, Winnik, and co-workers reported crystallization-driven self-assembly (CDSA), a living supramolecular micellization strategy that yields polymeric nanostructures with very narrow dispersity (*11–13*).

Qiu *et al.* now build on this strategy to create much larger, but well-defined, micrometer-scale supermicelles from amphiphilic cylindrical triblock comicelles (which consist of three connected micelle segments). The lengths and widths of each segment are precisely controlled through the living CDSA method. The first step for the supermicellization is to prepare narrow-disperse block copolymers (see the figure, panels A and B) by living anionic polymerization. These polymers, which contain crystalline poly(ferrocenyldimethylsilane) (PFS), self-assemble in selective solvents to yield short seeds after sonication. From these exposed crystalline PFS seeds, cylindrical micelles can grow epitaxially upon adding unimeric block copolymers, because these unimers selectively crystallize on the seeds. This self-assembly process is exactly the same as a living polymerization, allowing the length and width of each segment to be controlled.

In the second step, the authors prepare amphiphilic triblock comicelles. Because both ends of cylindrical micelles are growing in the living polymerization manner, addition of different unimers with a block of PFS produces triblock comicelles with precisely controlled lengths and widths (see the figure, panels C and D).

> *“Controlling the complexity of large molecules is one of the central themes in synthetic chemistry.”*

Finally, Qiu *et al.* induce supermicellization in selective solvents. For instance, the terminal P segments of P-H-P triblock comicelles are soluble in polar isopropanol, and these comicelles therefore undergo supermicellization in *i*-PrOH to shield the insoluble H segment. Previously, comicelles with thick P segments yielded only simple supermicelles such as spheres (see the figure, panel E) and tilted-elongated micelles (panel F) (*14*). However, switching to thinner P segments leads to micrometer-scale train-track–like or cylindrical brushlike supermicelles, because side-by-side stacking of the H block is now favored (see the figure, panel G).

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