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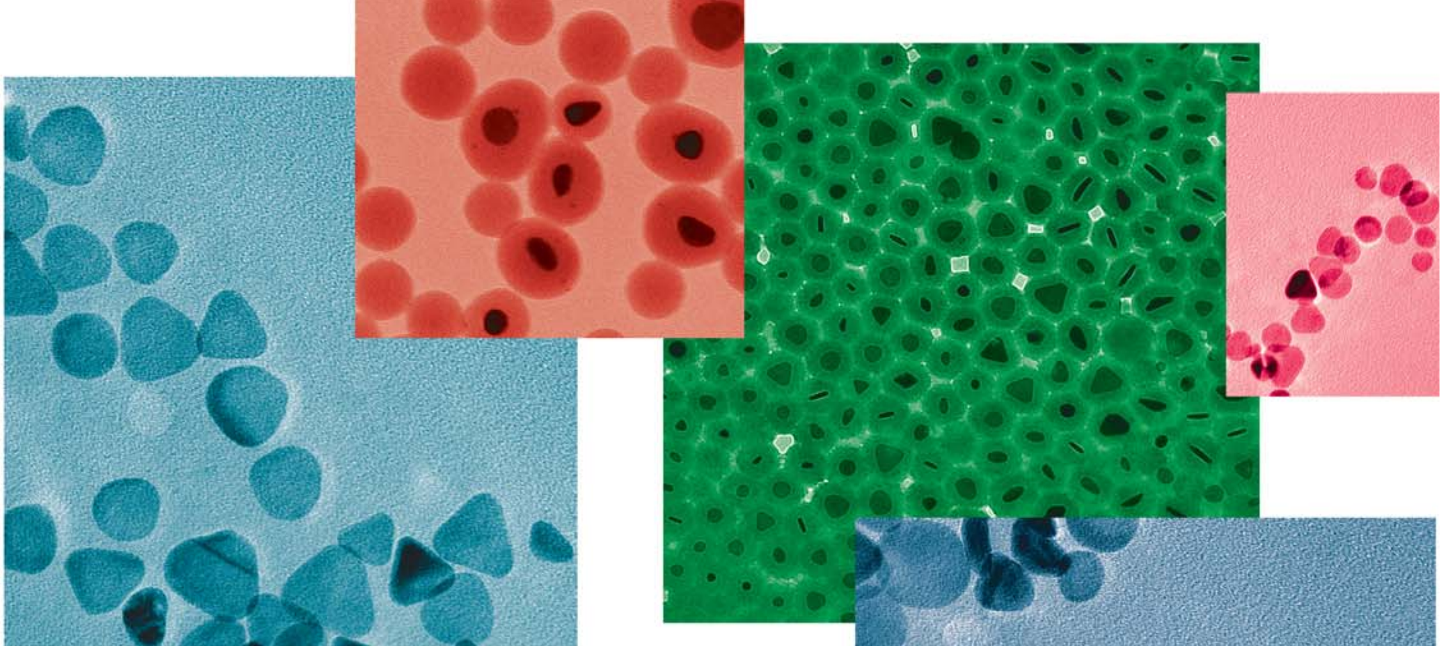

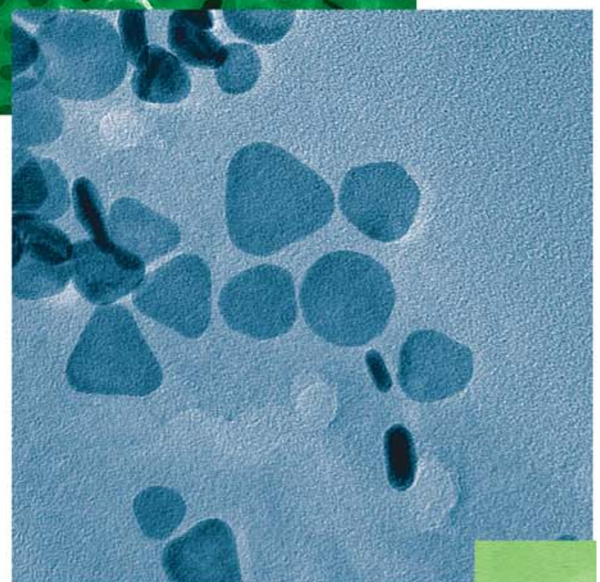

Boosting SOLAR ENERGY CONVERSION with NANOFLUIDS

Suspensions of metallic nanoparticles can harvest valuable heat from sunlight that would otherwise go to waste in a photovoltaic cell.

Natasha E. Hjerrild
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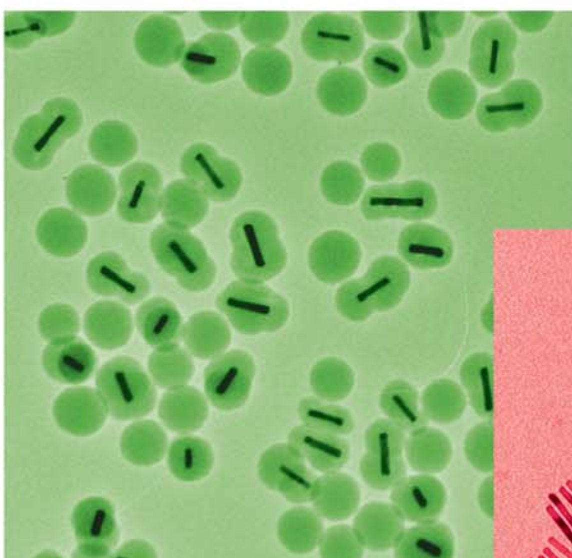

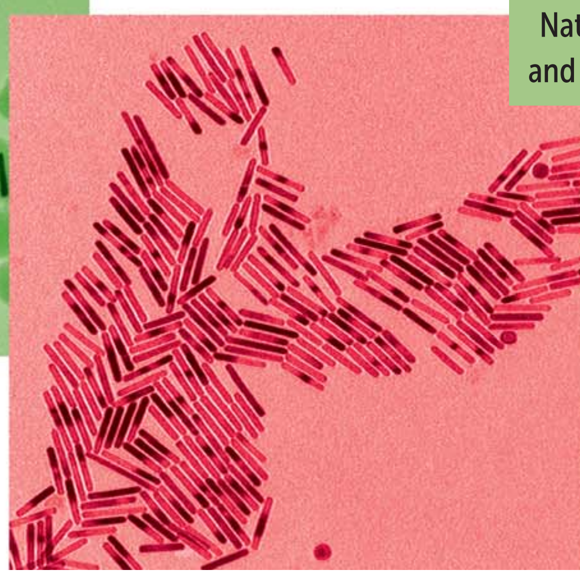

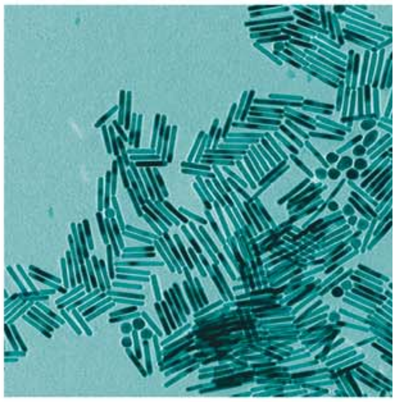

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The market trends are unequivocal: Solar energy is the world's fastest-growing energy technology. The global market for photovoltaic (PV) cells has increased by 4200% over the past 10 years, and the market for solar thermal collectors, which convert sunlight into useful heat, has grown by 500% over the same period.[1] As the costs of PV cells and thermal collectors fall below those of the peripheral system components (mounting, wiring, conduits, electronics, and so forth), the solar industry needs to improve conversion efficiencies to sustain the rapid market growth.

One promising approach is to combine PV and thermal-collection technologies into hybrid photovoltaic–thermal (PVT) collectors that generate electricity and usable heat simultaneously. Typical PV cells operate efficiently only in a narrow band of the solar spectrum, so current PV modules convert only a fifth of the energy from the Sun into electricity. A thermal collector operating in tandem with the cell could harvest much of the remainder as heat. Not only would hybrid PVT collectors be significantly cheaper to mount than individual PV and thermal collectors, they would potentially take up 40% less rooftop area.[2] As an added bonus, the thermal collector would help keep the PV cell cool and thus boost the cell's efficiency.

The concept of hybrid PVT solar energy collection isn't new. It was first investigated in the mid 1970s as a simple way to heat air or water while keeping solar cells cool. During the late 1990s, a handful of companies began to commercialize the technology;[3] they boasted reduced installation, framing, and lamination costs and combined electric and thermal conversion efficiencies of up to 85%. So, with such big efficiency boosts available, why do hybrid PVT collectors command such a tiny share of the solar energy market?

Part of the answer is that in the traditional hybrid design, in which the PV cell is mounted directly atop the thermal collector, thermal output and electrical efficiency are in tension with one another. The rated efficiency of a PV cell is achieved only when operating at 25 °C. For every 1 °C above that, the relative efficiency diminishes[4] by 0.4–0.5%. To provide water for domestic heating, thermal collectors must operate between 60 °C and 70 °C. To generate steam for industrial use, they must operate above 100 °C. Either the PV component will suffer significant efficiency losses due to overheating or fossil fuels must be used to boost the temperature of the water heated by the thermal collector.

In recent years a low-cost solution to that problem has emerged from an unexpected source: the field of nanotechnology. The new approach provides a way to thermally decouple the PV and thermal components, improve thermal conversion efficiencies, and more effectively cool the PV components. Interestingly, the key ingredient—a unique optical effect of metal nanoparticles—has been exploited by humankind for centuries.

The PV window

PV modules have become a symbol of energy independence for a clean-energy future. Solar panels are now a common sight atop houses, on commercial buildings, and in agricultural fields. In 2017, the world is expected to have more than 350 GW of installed solar capacity.

PV cells convert light to electricity by way of photoexcitation in semiconductors: When an impinging photon excites an electron from the valence band to the conduction band, the resulting electric potential can be captured as current. But only photons with an energy greater than the semiconductor's bandgap can produce an excitation. Silicon, the dominant player in the PV market, has a bandgap energy around 1.1 eV, roughly equivalent to a photon in the near-IR. Solar radiation at energies lower than that does not generate current and effectively goes unused.

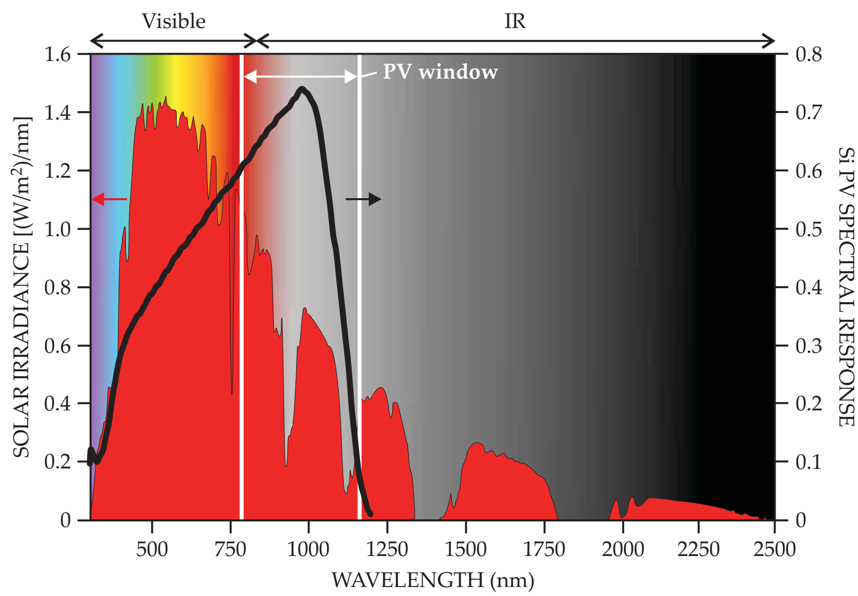

FIGURE 1. THE BULK OF THE SUN'S IRRADIANCE (red filled area) is distributed across wavelengths ranging from the near-UV to the far-IR. But typical silicon photovoltaic (PV) cells can efficiently extract electricity only from red and near-IR wavelengths, as indicated by the silicon PV spectral response (black curve). Nanofluids can be used to harvest energy from the remaining wavelengths as heat. To maximize the combined output of electricity and heat, the nanofluids should absorb only at wavelengths outside the so-called PV window.

Much of the energy potential of higher-energy solar radiation also goes untapped in conventional PV cells. If an impinging photon's energy is much greater than the bandgap—say, in the blue or UV—it excites electrons far above the floor of the conduction band, and the excess energy is dissipated as heat. Not only is electric potential wasted, but the added heat can warm the cell above its optimal operating temperature and thereby diminish the cell's efficiency.

So although PV cells can in theory generate electricity from a broad spectral range, they do so most efficiently in a narrow waveband just above the bandgap energy. (That stands in stark contrast to the broadband absorbers used in rooftop solar thermal collectors, which have few wavelength constraints.) Silicon, for instance, efficiently converts wavelengths between 700 nm and 1100 nm. Figure 1 contrasts silicon's spectral response, a measure of how efficiently the material converts light to electrical current, with the spectral energy distribution of sunlight. Roughly 40% of the energy carried at wavelengths of 700 nm and shorter—and nearly all the energy carried at wavelengths of 1100 nm and longer—would go unused in a standalone PV cell. The idea behind hybrid PVT technologies is to put that energy to use without diminishing the PV conversion efficiency.

In a conventional PVT design, illustrated in figure 2a, the PV cell's metal backing serves as an absorber plate. It conducts heat away from the PV cell, and it captures radiation at wavelengths too long for PV conversion. A heat-transfer fluid pumped through a channel behind the absorber plate picks up the heat, which can then be used to provide hot water and household heating. Although the scheme is inexpensive, the PV cell and fluid collector are thermally coupled, so one can't obtain high outlet temperatures from the thermal collector without sacrificing the performance of the PV cell.

If the PV and thermal components could be decoupled, one could simultaneously reap the full benefits of both. In theory, that decoupling could be achieved with a spectrally selective mirror, which could transmit sunlight that can be efficiently converted photovoltaically and deflect the remaining spectrum to a separate thermal collector. But such technologies are typically deployed at small scales and are expensive to manufacture; they can cost more than $250 000 per square meter of coverage.[5] A much cheaper way to achieve physical separation is by swapping out the conventional heat-collecting fluid with what's known as an optical nanofluid.

The power of plasmons

Nanofluids are, to put it simply, fluids in which nanoparticles have been suspended. Such particles, roughly 100 nm or smaller, are far too tiny for the human eye to detect. They are so small, in fact, that their Brownian motion—random movement caused by collisions with surrounding fluid molecules—is sufficient to overcome the pull of gravity. Provided the particles don't agglomerate, they remain suspended indefinitely. The nanoparticles can be carefully chosen to enhance the fluid's thermal, electrical, chemical, or optical properties. In the last case, the fluid is known as an optical nanofluid.

Optical nanofluids have been deployed in biological imaging, tumor-destroying hyperthermia treatments, and a host of other applications. They typically comprise metallic nanoparticles and exploit a phenomenon known as plasmon resonance: When a photon encounters a nanoparticle, the oscillating electromagnetic field causes a cloud of free electrons—collectively known as a plasmon—to move back and forth along the nanoparticle's surface. The plasmonic response becomes heightened at a resonant optical frequency that depends on the size and shape of the nanoparticle and on the density of free electrons in the constituent metal. By changing the nanoparticles' makeup and geometry, one can tailor the plasmons to resonate in specific, well-defined bands, which can range from the UV to the IR. In fact, plasmons in metallic nanoparticles have been used for centuries to give stained glass windows their vibrant hues. (For more on nanoplasmonics, see the article by Mark Stockman, PHYSICS TODAY, February 2011, page 39.)

Deployed in a PVT solar collector, plasmon-based optical nanofluids essentially combine the absorber and thermal fluid into one, as illustrated in figure 2b. The nanoparticles absorb resonant sunlight and, due to their large surface-to-volume ratios, rapidly dissipate the heat to the surrounding fluid. Unlike in a conventional absorber-plate design, the sunlight penetrates the fluid and heat is dispensed uniformly throughout the fluid's volume. That so-called volumetric absorption eliminates tem-

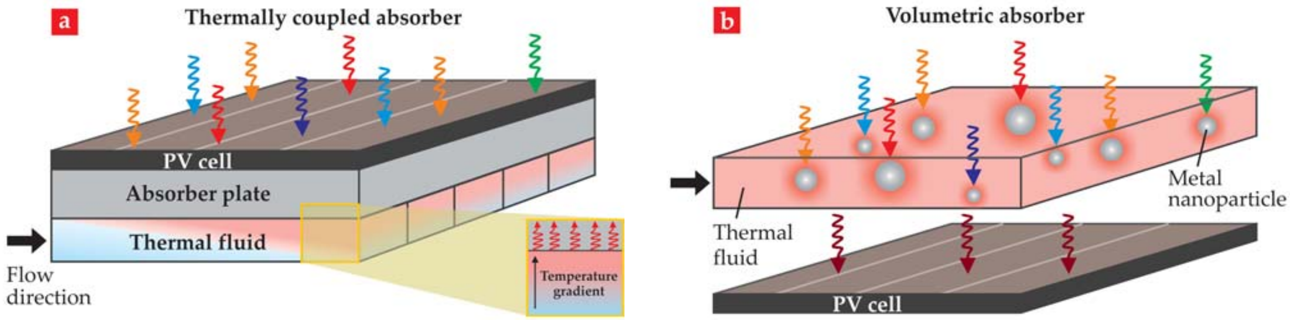

FIGURE 2. HYBRID PHOTOVOLTAIC–THERMAL (PVT) SOLAR MODULES harvest, as heat, sunlight that can't be efficiently converted to electricity. **(a)** In the conventional, thermally coupled design, the metal backing of the PV cell serves as an absorber plate: It conducts heat away from the cell, and that energy is then transferred to a thermal fluid, which can be used for household heating. In the fluid, pink regions indicate warmer temperatures; the inset illustrates radiative heat losses from the thermal fluid to its surroundings. **(b)** In the volumetric-absorber design, the thermal fluid contains metal nanoparticles and is positioned above the PV cell. The nanoparticles absorb wavelengths of light that can't be efficiently converted by the PV cell and transmit those that can. Because the thermal fluid and PV cell don't touch, the fluid can attain temperatures hot enough to generate steam without degrading the PV cell's performance.

perature gradients, reduces radiative heat loss, and can increase the thermal efficiency of the collector.

Because the optical nanofluid can be tailored to absorb only wavelengths that aren't efficiently converted photovoltaically, it can be positioned in front of and physically separate from the PV cell, where it can capture IR, visible, and energy-dense UV radiation directly. Because the PV and thermal components don't touch, the thermal collector can operate at high temperatures without degrading the PV cell. Paired with concentrating mirrors, nanofluid thermal collectors can achieve outflow temperatures of 100 °C or more—hot enough to generate steam for industrial applications ranging from food and beverage sterilization to chemical and manufacturing processes.

Using a nanofluid PVT collector, a business could potentially operate solely on renewable energy, impervious to swings in gas and electricity prices. And only a tiny nanoparticle concentration—less than 0.1% of the total nanofluid volume—is needed to maximize the fluid's absorption. For most metals, that volume fraction works out to a materials cost of about a dollar per liter, which pales in comparison to the cost of the rest of the system.

Custom nanofluids

The nanofluid in a PVT collector must be carefully designed to absorb only at wavelengths outside the PV's high-efficiency range, lest it filter away light that could be used to generate valuable electricity. (Although prices vary significantly by region, a general rule is that electricity is worth about three times as much as heat.) The precise spectral bounds will vary depending on local energy costs, but for silicon, the ideal optical nanofluid should absorb only outside the 700–1100 nm range, which can be defined as silicon's PV window. That means an ideal nanofluid should act as a bandpass filter, able to absorb both in the visible and in the IR.

Of the various metallic nanoparticles that absorb visible light, none absorb more strongly than silver. That is because silver has the highest free-electron density of any metal. It also has a broad plasmonic response range; silver nanoparticles can absorb wavelengths ranging from 300 nm to more than 1200 nm. Gold and copper also have high free-electron densities and strong plasmonic responses, but those materials are most effective in the IR.

Ultimately, to achieve wavelength-specific absorption, one must precisely control the nanoparticle's size and shape. To date, nanoparticles have been synthesized in almost every shape imaginable, including spheres, disks, triangles, hexagons, rods, stars, cubes, tetrahedrons, and octahedrons. (See, for example, the electron microscopy images on this article's opening page.) Small, round particles tend to absorb intensely at short wavelengths, whereas large particles with sharp corners absorb more moderately over a larger range of wavelengths.

The geometry dependence is due to the role of dipole moments in the plasmon resonance. When a photon encounters a plasmonic nanoparticle, it induces an alternating electric field, which generates an oscillating dipole moment as the free electrons shift. The strength of the dipole depends on the number of oscillating electrons and their degree of separation in the particle. For instance, in a disk-shaped nanoparticle, where electron mobility is more confined in one dimension, the dipole is stronger—and the plasmonic response more intense—than in a sphere. A nanodisk absorbs about twice as strongly as would a sphere of the same radius. But size also matters. Larger particles permit greater charge separation, which supports longer-wavelength resonances.

If the nanoparticles become too large, however, they will not only absorb light but significantly scatter it. That renders the fluid opaque and reduces the efficiencies of both the thermal collector and the underlying PV cell. Scattering can be minimized by limiting the particles' diameters to no more than about 50 nm and by limiting their volume fraction to 0.1% or less.[6]

In 2016 we and our colleagues fabricated several batches of silver nanodisks—each batch with a different mean particle diameter tailored to absorb different wavelengths of visible light.[7] When the nanodisks were suspended in fluid, the effect of just a 10 nm difference in diameter could be seen with the naked eye; as diameter decreased, the fluid absorbed shorter wavelengths, and the color of the fluid changed from aqua to orange, as shown in figure 3. By suspending disks of various diameters in the same fluid, we could create a cocktail that absorbed the entire spectrum of visible light.

In the IR portion of the solar spectrum, nanorods are ideal absorbers. Long and slender, they permit large charge-separation distances and can therefore absorb strongly at long wavelengths. Researchers at the University of Tulsa in Oklahoma showed that by doubling the aspect ratio of gold nanorods, they could engineer plasmon resonances[8] ranging from 600 nm to 1200 nm. Much like the nanodisks, nanorods of different lengths can be concocted into a fluid that absorbs a broad near-IR spectrum.[9]

Stability, selectivity, and scale-up

As it turns out, a key advantage of optical nanofluids may also be their biggest vulnerability: The nanoparticles' high surface-to-volume ratio facilitates rapid heat transfer, but it also makes them susceptible to damage by heat and UV light. Reduced to the nanoscale, a metal melts at temperatures far below its bulk melting point.[10] That is particularly problematic for nanofluids intended to operate at high temperatures in industrial thermal collectors. When nanoparticles melt and lose their shape, they also lose their desirable optical properties, and they may begin absorbing or scattering light that is intended for the underlying PV cell. Additionally, melted nanoparticles tend to aggregate with other suspended particles and settle at the bottom of the channel, which undermines the ability of the nanofluid to operate as a volumetric absorber.

Various strategies can be used to circumvent the melting problem. For example, a thin oxide shell can be applied to the nanoparticle to function as a solid casing. For oxides such as silica, titanium dioxide, and zinc oxide, the energy required to melt the casing is approximately 10 times as large as that required to melt the metal nanoparticle it encloses. So even if the metal melts, the particle will retain its shape.

Additionally, silica shells protect the particles from chemical degradation.[11] High temperatures and intense UV irradiation can trigger chemical side reactions in the PVT collector that change the pH of the nanofluid, and metals are highly sensitive to pH variation. (Consider the discoloration of jewelry exposed to bleach and metal statues exposed to years of acid rain.)

Crucially, the oxide shell must be miscible with the thermal liquid. Silica, for example, is highly hydrophilic—it readily suspends in water-based nanofluids but not in oil-based ones. To stably suspend the particles in oils and glycols commonly used in industrial-strength thermal collectors, one must modify their surfaces.

The absorption spectrum of an optical nanofluid isn't wholly determined by the optical properties of its constituent nanoparticles. The surrounding liquid, or base fluid, is also important. All fluids have an intrinsic absorption spectrum, which must be considered when designing an optical nanofluid. For example, water absorbs all IR wavelengths longer than 1350 nm, which eliminates the need for nanoparticle absorbers in that range. But water also has a sharp absorption peak corresponding to an O–H vibrational mode at 975 nm, well inside the PV window. That peak produces parasitic absorption that ultimately diminishes the electrical output of the PV cell.

Unlike nanoparticles, the base fluid's intrinsic absorption peaks cannot be manipulated. Nevertheless, weak to moderate parasitic absorption can be limited by reducing the depth of the fluid channel. The parasitic absorption cannot be eliminated entirely, however, and the nanoparticle concentration must be increased to compensate for the reduced fluid volume.

Nanoparticles can also give rise to parasitic absorption. Large-scale synthesis techniques that produce liter quantities of nanoparticles inevitably introduce some variance in the particle-size distribution. And a mere 10–20 nm difference in diameter can shift a particle's absorption peak by hundreds of nanometers. That presents a difficult choice: One can use labor-intensive small-scale techniques to fabricate nanoparticles with very precise size distributions or use cheaper, large-scale techniques that are bound to produce some parasitically absorbing nanoparticles. Chemists, materials scientists, and other researchers are currently investigating techniques to produce high yields of quality nanoparticles. However, further work is necessary before the particles can be synthesized on scales large enough for commercial use in nanofluid PVT collectors.

Making it to market

Several combinations of nanoparticles and base fluids have been tested as potential nanofluids for PVT systems: polypyrrole in water; Cu_9S_6 in oleylamine;[12] indium tin oxide in heat transfer oil;[8] silica-encased silver in water;[7,13] and antimony tin oxide in water.[14] The systems have demonstrated combined absolute conversion efficiencies up to 20% larger than those of stand-alone PV cells and have been designed to generate outlet temperatures of 100 °C. One prototype system, pictured in figure 4, used 0.6 L of nanofluid in a 1.2-cm-deep channel and produced 60 W of combined heat and electricity.[13] Assuming, conservatively, that the same ratio of energy to fluid volume holds for larger systems, a 100 kW system for a commercial building would require about 1000 L of working fluid, or roughly $1000 worth of metal nanoparticles. Residential nanofluid PVT collectors would require much smaller volumes.

Although nanofluid PVT collectors show promise, they have struggled to penetrate the risk-averse, competitive energy market. Because PVT collectors

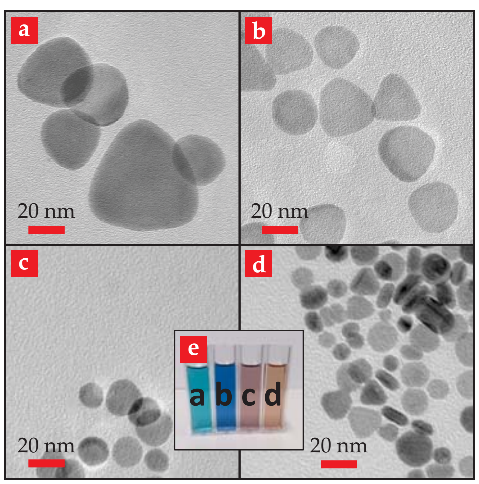

FIGURE 3. THE SILVER NANODISKS in these electron microscopy images have mean diameters of **(a)** 40 nm, **(b)** 30 nm, **(c)** 20 nm, and **(d)** 10 nm and produce absorption peaks at 644 nm, 590 nm, 495 nm, and 447 nm, respectively. **(e)** Suspended in water, the batches of nanodisks from panels a–d exhibit hues ranging from aqua to orange.

produce two commodities—electricity and heat—they are appealing to investors only if the prices of both are high. In the US, the hydraulic fracturing boom has suppressed the price of natural gas, the leading energy source for heating, but not all countries have easy access to cheap and abundant natural gas.

Another potential reason behind PVT collectors' slow growth is that their value is tricky to assess. The efficiency of a PVT system depends on a host of factors, including the flow rate, inlet and outlet temperatures, and heat capacity of the thermal fluid. For example, a thermal collector operates most efficiently when its outflow is only slightly warmer than ambient temperature so that minimal heat is lost to the surrounding environment, but practical PVT collectors operate at much higher temperatures.

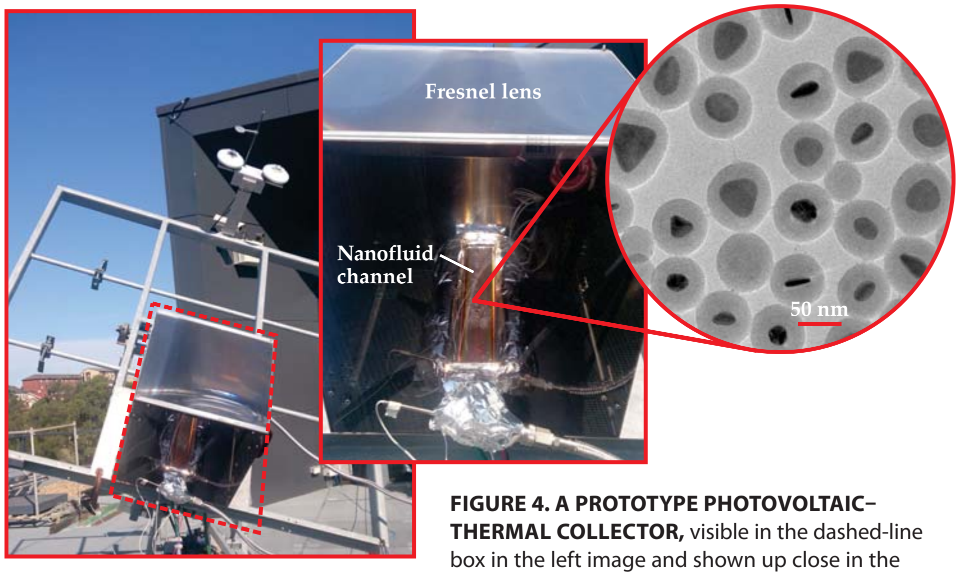

FIGURE 4. A PROTOTYPE PHOTOVOLTAIC–THERMAL COLLECTOR, visible in the dashed-line box in the left image and shown up close in the middle image, exploits plasmonic resonances in silica-coated silver nanodisks, right, to extract heat from sunlight. The nanodisks convert green and blue light to heat and transmit red and IR wavelengths to an underlying photovoltaic cell. A Fresnel lens focuses the sunlight to boost energy conversion.

So how do nanofluid PVT collectors stack up to conventional sources of electricity and heat? It largely depends on local energy prices. Based on 2016 gas and electricity prices in the European Union, a 4 kW Ag–SiO_2 nanofluid PVT system would reduce residential annual energy costs by more than 20% compared with a stand-alone PV. On average, the hybrid system would pay for itself in about 20 years, although estimated payback periods vary according to regional solar availability and local energy prices.[13,15,16] In the US, the cost-effectiveness of PVT technology varies from state to state. In, say, South Dakota or Colorado, where natural gas is inexpensive, nanofluid PVT collectors are not yet economically viable. But in Hawaii, where residents pay 260% more than the national average for natural gas, a household nanofluid PVT system could pay for itself in just 10 years.[17] (Compare that with the 22-year payback period for a conventional, thermally coupled PVT in the same state, as estimated by a 2015 National Renewable Energy Laboratory study.[15]) Deployed widely, nanofluid PVT systems could bolster Hawaii's efforts toward energy independence. In countries such as Australia and Japan, where natural gas costs more than four times the average US price, nanofluid PVT technology is especially promising.

The energy market is notoriously slow moving. Although the first solar cell was demonstrated at Bell Labs in 1954, only in the past decade have investors started pouring money into the PV industry. Optical nanofluids have only just come onto the renewable energy research scene in the past 5 to 10 years. To appeal to investors, they will need to prove chemically robust and economically viable for years of use.

According to Bloomberg's New Energy Outlook report for 2016, investments in domestic and industrial solar energy will balloon to an estimated \$3.4 trillion between 2016 and 2040. Even if PVT technology accounts for just 1% of that growth, that would translate to \$34 billion in investment over the next two decades. As renewable energy technologies and manufacturing processes continue to mature, nanomaterials researchers and market forces will ultimately determine the role nanofluids will play in the energy economy. However, if the nanofluids prove stable and producible at industrial scales, the low-cost technology will be hard for investors to ignore.

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