Solar steam nanobubbles

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Abstract

Silica-gold core-shell nanoparticles that are immersed in water act as efficient nanoscale generators of steam when illuminated with sunlight. In their recent paper in ACS Nano, Halas, Nordlander and coworkers demonstrate this intriguing phenomenon that results from the nucleation of steam at the surface of individual nanoparticles that are heated by the sun. The same effect is also used to demonstrate distillation of ethanol. The solar steam nanobubble generation phenomenon results from the complex interplay of many different phenomena that occur at the nanoscale, and can find a broad range of applications.

In the past ten years the science and technology of materials at the nanoscale have lead to a wealth of new fundamental insights and applications. The "elemental particle" of this research field is the nanoparticle, a cluster of closely packed atoms that arrange themselves into an often spherical assembly with a diameter of typically 5-100 nm. In optics, such nanoparticles are of great interest because they pack a large density of polarizable units, the atomic and molecular bonds, in a small volume. Such highly polarizable nanoparticles interact strongly with light, with the strength of this interaction dependent on the frequency of the light. Gold nanoparticles, for example, strongly absorb blue/green light, due to a resonance in the polarizability for light at a frequency corresponding to these colors. For noble metal nanoparticles, these optical resonances are related to the high density of unbound electrons in the metal, called the electron plasma, and the optical excitations in these particles are called plasmons.

Several years ago, Naomi Halas and her research group at Rice University (TX, USA) have added a new degree of freedom to the design of metal nanoparticles.[1] They designed core/shell nanoparticles, in which a dielectric core is surrounded by a metal shell. As it turned out, the optical resonances of these core-shell nanoparticles are highly tunable by varying the core diameter and metal shell thickness.[2,3,4] And importantly, these particles can be reproducibly fabricated at large volumes using chemical synthesis. Now, in a recent paper in ACS Nano, Halas, Nordlander, and co-workers demonstrate an entirely new application of these new geometries that may have a very large impact.[5]

They found that if nanoparticles made of a silica core and a gold shell are immersed in water, and the solution is irradiated by sunlight, small bubbles of steam emerge from the solution. In this steam formation process, individual nanoparticles act as efficient absorbers of light, heat up, and transfer energy to the surrounding water. While intuitively one would think this would lead to a gradual increase of the water temperature, Halas *et al*. found that steam is generated from the solution right when the illumination starts.

The microscopic mechanism of this nanoparticle-catalyzed steam formation is very intriguing. As the nanoparticles are heated by the incident light, they rapidly transfer heat to the water in its immediate surrounding. Because the nanoparticles are strong absorbers of light a thin shell of water that is in direct contact with the nanoparticle rapidly heats above its boiling point and transforms into steam. Then, because steam is a poor thermal conductor, heat transfer from the heated particle to the water is strongly inhibited. As the nanoparticle is further heated by the sunlight the thickness of the steam shell gradually grows further. Once the steam shell a reaches a thickness of several hundred nanometers, the weight of the steam/nanoparticle assembly becomes less than that of an equivalent volume of water and as a consequence it will buoy towards the surface. Finally, the steam bubble annihilates at the surface and steam escapes from the water. In this way steam is generated without heating the entire water volume to the boiling point. The overall conversion efficiency of incident energy from the sun to steam generation as claimed by the authors is 24%.

The steam generated in such a relatively simple and compact solar steam reactor can find many applications. For example, in developing countries the generation of high-temperature steam can be used for the desalination and purification of drinking water. Also, steam can be used for the sterilization of medical instruments, replacing conventional chemical methods. Indeed, the temperature of steam generated in the experiments by Halas *et al.* is as high as 140 °C, high enough for sterilization purposes. The generated steam may also be used to directly drive a turbine for electricity generation. Using solar irradiation of the metal-nanoparticle solutions steam can be generated instantaneously when it is needed, with no power source needed other than the sun. Furthermore, the nano-heating process can be used as for distillation. Halas *et al*. demonstrate this too in their experiments, collecting over 99% rich ethanol from a water-ethanol mixture, much higher than the 95% achieved using conventional processes.

Previously, the formation of steam by the irradiation of metal nanoparticles has only been marginally investigated. The formation of nanobubbles and catalytic reactions by gold nanoparticles were studied in microfluidic circuits, where the behavior of individual nanoparticles could be investigated.[6,7,8,9] Steam formation was also observed from a nanostructured Cu surface under laser irradiation.[10] Other plasmon-induced (pulsed) laser heating experiments in solution were performed as well.[11,12,13] More generally, laser- excited plasmons in metal nanoparticles have served to catalyze many different chemical reactions, such as *e.g.* the growth of semiconductor nanowires.[14] The nucleation of steam was also observed during pulsed-laser melting of silicon under water.[15] Under pulsed laser irradiation, heat flow into the substrate is much slower than the heating rate by the laser, so that water can transform to steam even in geometries that would not generate steam under continuous-wave irradiation. All of these prior studies relied on the use of lasers. The strength of Halas' new work is that it demonstrates the formation of large volumes of steam in a quantitative way using just the sun as the energy source. In addition, the direct demonstration of distillation using sunlight is an important novel finding. The optical system that guides light from the sun into the nano-steam reactor is very simple, involving only a planar Fresnel lens to focus the light.

The steam formation around solar-heated metal nanoparticles is a highly nonequilibrium process. As described in the paper, a simple thermal heat flow model does not predict the formation of steam nanobubbles, but rather a gradual increase in temperature of the water bath. Indeed, at the nanoscale, the interface between two dissimilar materials acts as a barriers to heat flow. A first-order model described in the paper predicts the formation of a several-micrometer-thick steam shell within a few microseconds. A more detailed study of the transfer of heat at the metal-nanoparticle/water/steam interface would be interesting, but is quite complex (see Fig. 1). It must include studies of the (time and spatially-varying) molecular vibration energies in water molecules that mediate the energy transfer in (high-pressure) steam at the interface. The intermolecular coupling between these excited states and the coupling of these vibrational excitations to the metal shell are key elements. In addition, the metal surface may play a catalytic role in the nucleation and growth of the steam from liquid water, possibly assisted by hot electrons generated by the light-induced plasmons. Effects induced by the strong optical near field must also be taken into account as well as temperature gradients inside the nanoparticle. Furthermore, sputtering at gas-solid and gas-liquid interfaces may occur and thermal desorption at the metal-water interface may affect the heat transfer as well. Formation of the steam shell will affect the plasmon resonance energy as well as the plasmon damping. Simple model systems are required to provide the first insights in each of these processes. Once these processes are better understood, the nano-thermal steam generation process could be further optimized.

An intriguing fact described in the paper by Halas *et al.* is that the metal nanoparticles remain in solution and are not removed from it along with the escaping steam bubbles. More research is necessary to investigate this further, in particular for the distillation experiments, where it is essential that the distillates are not contaminated with nanoparticles. It should be noted that the overall volume density of nanoparticle required to achieve boiling is relatively small. Due to their high polarizability the effective absorption cross section of core-shell nanoparticles is much larger than their geometrical size. As a result, a single monolayer of closely spaced core-shell particles has an optical density high enough to fully absorb incident light.[16] In the experiments Au/SiO_2 colloids with a plasmon resonance peaking at 800 nm were used, overlapping well with a major portion of solar spectrum. In a further optimized geometry, colloids with different dimensions and thus different resonance wavelengths can be embedded in the solution to cover the entire solar spectrum from 400-2500 nm.

While it is clear that many challenging studies on the fundamental aspects of nanoscale steam are ahead, a key imminent challenge is to develop the various applications of this new process. Demonstrator devices have already been made, as reported in the paper, and the next step is to develop practical steam generators for water desalination and purification as well as sterilization. It seems that this technical development can be done in a relatively short period of time. If that is successful, steam nanobubble generation would be a unique example of fundamental research in the lab leading to practical applications in a short period of time.

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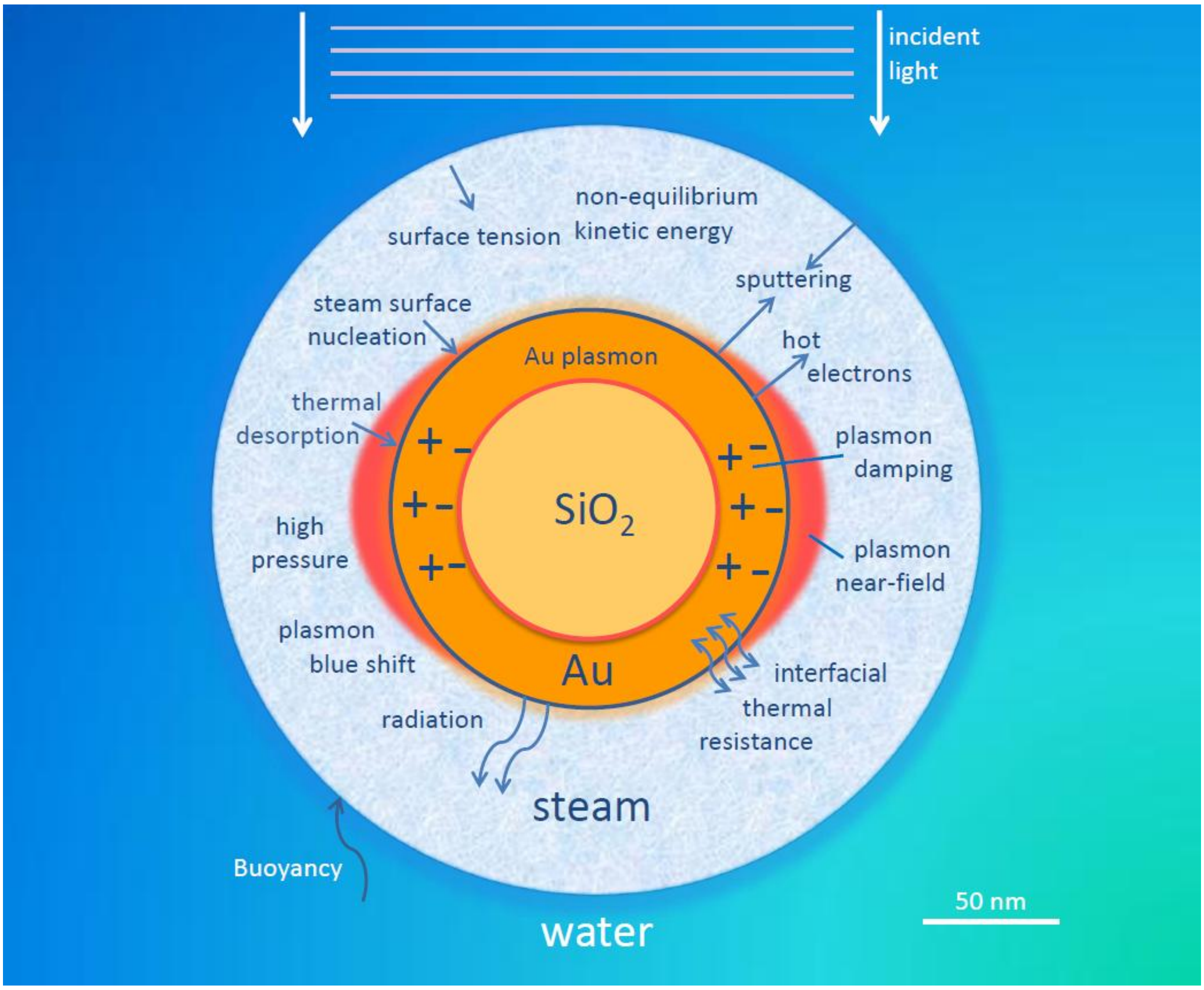

Figure 1. **Known unknowns**. Schematic of various interacting processes that play a role in solar steam nanobubble formation.