

## Plasmas for Nanomaterials and Nanotechnology

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Macroscopic objects that we can comfortably hold in our hands, such as a coffee cup or teaspoon, consist of an incredibly large number of atoms—roughly a trillion of trillions of atoms. These macroscopic materials can be classified into three categories: metals that conduct electricity, insulators that do not, and semiconductors, such as silicon, that are somewhat conductive and are used to produce the chips that are in our computers, smartphones, TVs and more.

Imagine the possibilities if the physical and chemical properties of materials that we know from the macroscale could be changed or tuned by reducing the number of atoms that they contain. For instance, a single atom of silicon will readily emit light when its electrons are excited, but a bulk piece of silicon will not. But what about a small cluster of maybe a few hundred silicon atoms? Realizing that there may be an unexplored spectrum of materials properties, researchers created the field of “nanotechnology” with the focus on studying the new properties of materials and devices that consist of only a few hundred or thousands of atoms [1]. Because of the small number of atoms in these materials, they are also physically small, often only a few nanometers across (one nanometer is one millionth of a millimeter). For instance, a one nanometer-sized cube of silicon contains 50 atoms, and 50,000 of these cubes lined up in a row would be as long as the thickness of a human hair. Figure 1a shows an electron microscope image of silicon nanocrystals, with the lines in some of the crystals corresponding to planes of atoms. Figure 1b illustrates the size-tunable optical emission of silicon nanocrystals in a solvent when illuminated with UV light, vividly demonstrating how new materials properties are gained at the nanoscale.

How is it possible to make materials this small? One approach is to take a macroscopic piece of material and grind it down. This is indeed possible with a technique called ball milling

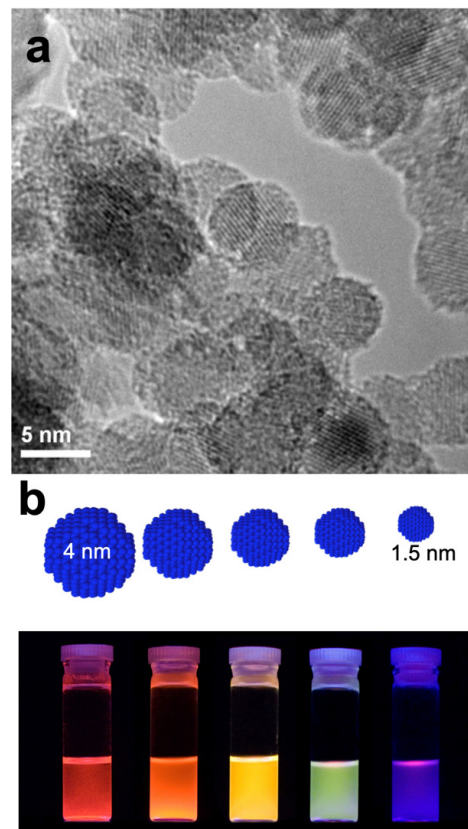


Figure 1: a) Electron microscope image of silicon nanocrystals. The lines seen in some of the crystals are representative of layers of silicon atoms. b) Light emission of silicon nanocrystals of different sizes dispersed in a solvent and illuminated with UV light.

which is practical but time consuming. Exfoliation is another approach to separate atomically thin layers of a material from a bulk piece, as is done with graphene—a single atom thick layer of carbon atoms. Because these techniques start with a large piece of material and through processing end up with a nanomaterial, they are called “top-down” techniques. In contrast, “bottom-up” techniques aim to create nanomaterials by starting from single atoms and assembling them in a controlled manner into larger nanoparticles or nanostructures.

# THE PLASMA CONNECTION

Chemists have developed many effective methods of producing nanoparticles and other nanostructures. Usually, these methods involve dissolving a reactant in a chemical solvent, adding another reactant to initiate the reaction, and using some surfactant molecules that cling to the growing nanomaterials' surfaces to control their growth. These methods have been very effective in creating a wide range of nanomaterials that have shown a spectrum of new and intriguing properties. Moreover, when these nanomaterials are subsequently arranged into macroscale solids, some of their nano-properties persist to produce bulk materials with embedded nano-properties.

However, the range of materials that can be produced with solution chemistries is limited. Solvents and surfactants cannot be exposed to high temperatures that are required for the synthesis of some materials. For instance, it is not possible to create a nanodiamond in solution, or a nanocrystal of titanium nitride or silicon, because the temperatures required are significantly larger than what any organic solvent can survive without thermally decomposing.

Enter plasmas [2]. As partly ionized gases, plasmas are inherently capable of achieving very high temperatures without detrimental degradation of the plasma gas, commonly argon or helium. Plasmas contain free electrons that have been released from some of the plasma gas atoms. These electrons can easily be heated to very high temperatures, think 100,000 °F or 50,000 Kelvin, by applying moderate electrical voltages to the gas. The hot electrons are capable of breaking atomic bonds in molecular chemical reactants that are fed into the plasma. Under carefully chosen conditions, the reactant fragments can start to cluster in the plasma and grow into nanoparticles. A typical nanoparticle synthesis reactor is shown in Figure 2. The plasma gas is flowed through a tubular reactor in which the precursor is dissociated by the hot plasma electrons causing the formation of nanocrystals.

The plasma has a set of unique attributes that enable plasma researchers to achieve a similar level of control as has been achieved in solution chemistry. First, because the hot and very light electrons in the plasma travel with much larger speeds than the heavy positive ions and gas atoms, any nanoparticle immersed in the plasma is likely to become negatively charged by collecting one or more electrons. The negatively charged particles in the plasma repel each other which prevents them from colliding. This leads to very uniform growth and excellent control over the particle sizes, which in the solution synthesis is achieved by the surfactant molecules. Second, very energetic surface reactions can heat the particles to hundreds of Kelvin

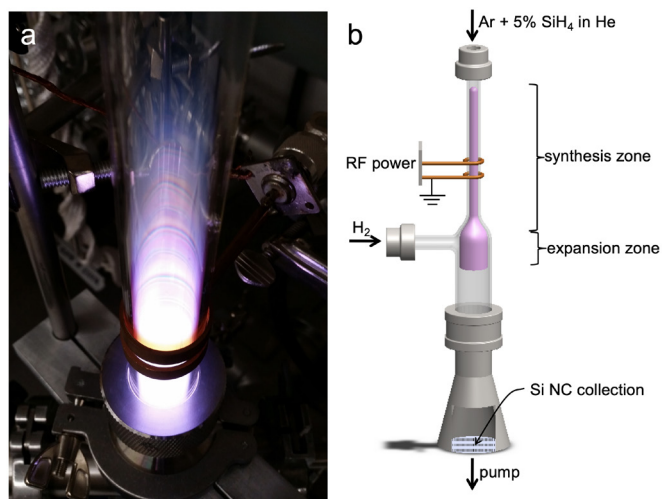


Figure 2: a) Photo of a tubular plasma reactor for the synthesis of nanoparticles. b) Schematic of the reactor. The nanoparticle precursor silane ( $\text{SiH}_4$ ) flows through the reactor typically in a few milliseconds. Dissociation of the precursor and clustering of the fragments leads to the formation of nanocrystals (NC) that are collected at the reactor exit.

beyond the temperature of the surrounding gas, enabling synthesis of crystalline materials that cannot be produced in solution. Hence, plasma synthesis excels at the synthesis of very uniform nanoparticles of materials that require high synthesis temperatures. Being an all-gas-phase technique that avoids the use of chemical solvents and surfactants, plasmas also create less hazardous waste and can be considered as a form of "green chemistry."

But what are plasma-produced nanoparticles good for, if anything? In fact, plasma produced nanomaterials have already demonstrated their potential in a large range of new applications (too numerous for an exhaustive discussion in this article). For example, consider the ability of nanometer-sized silicon crystals (referred to as quantum dots) to efficiently emit light when excited by UV light, different from a bulk piece of silicon that remains dark. These silicon quantum dots have been used in bioimaging applications, due to silicon's biocompatibility, in near-infrared emitting light emitting diodes, and most recently in luminescent solar concentrators. In the latter application, illustrated in Figure 3, silicon quantum dots are coated onto a sheet of glass or are embedded in a transparent plexiglass sheet [3]. They absorb blue light from the sun and reemit it as red light that is guided toward the sheet edges via internal reflections, similar to the working mechanism of optical fibers used in high-speed communication technologies. Very small and cheap solar cells can be placed at the edges of the glass sheet and produce electricity, while the glass is still largely transparent and can be used as a window in buildings or greenhouses.

# THE PLASMA CONNECTION

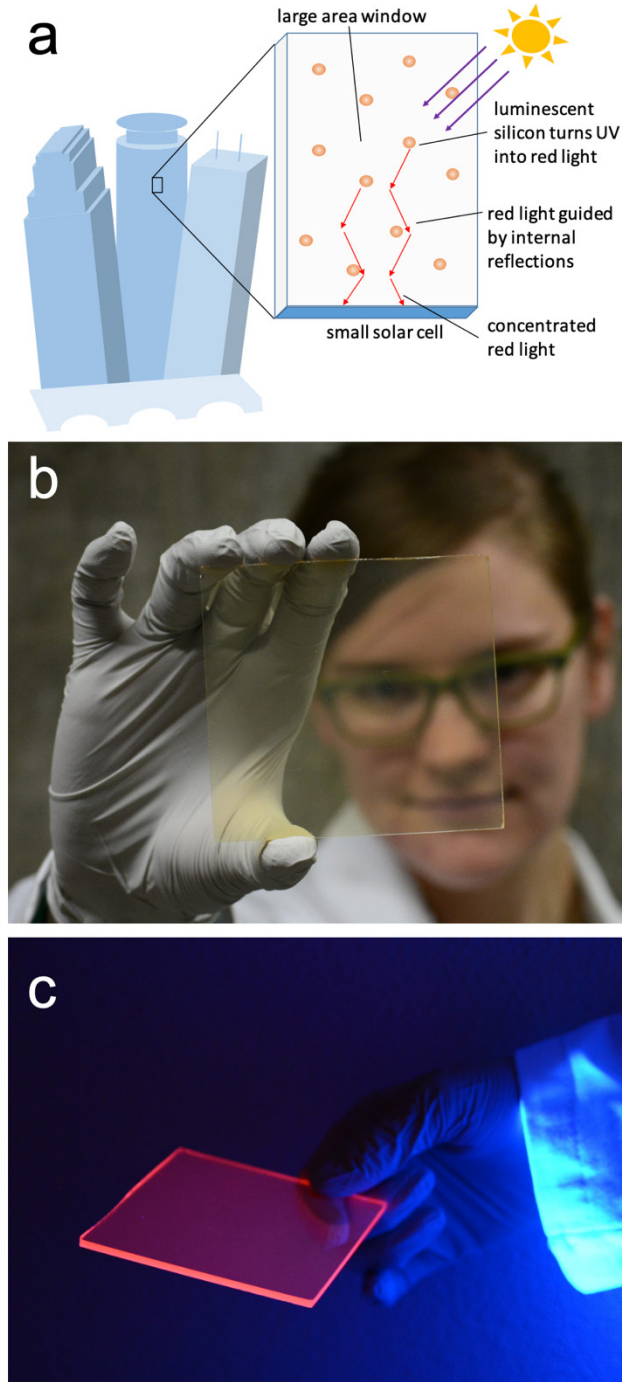


Figure 3: a) Schematic of a luminescent solar concentrator for building integrated photovoltaics. b) Photo of an actual device and c) device under UV illumination. The bright emission at the device edges is the result of light concentration by the device.

Plasma-produced silicon crystals with a size of about 20 nm also have great potential for improving the capacity of lithium ion batteries. Traditional lithium ion batteries use graphitic carbon anodes to store lithium ions when being charged. However, it takes six carbon atoms to store one lithium ion while, theoretically, one silicon atom can bind up to four lithium ions. Hence, silicon's theoretical ion storage capacity per gram of material is almost ten times larger than that of carbon. However, silicon strongly swells during the lithium ion incorporation, often leading to mechanical fracture of silicon particles larger than about 150 nm while smaller silicon particles around 20 nm are stable over hundreds of charge-discharge cycles [4]. Successfully incorporating silicon nanoparticles into lithium ion battery anodes could significantly enhance the battery energy density.

A final example of the unique abilities of plasmas to produce exciting new materials is the synthesis of metal nitride particles such as titanium nitride and zirconium nitride [5]. These materials have excellent plasmonic properties, which means that their optical absorption is resonantly enhanced at certain wavelengths due to the coherent oscillation of electrons in the material when exposed to resonant light. Titanium nitride has a melting point of 5,300 °F and thus cannot be produced with decent quality in solution chemistry. With plasma synthesis, high quality titanium nitride can be produced that can be used for plasmonic heating of tissue for cancer therapy, which to date has been a domain of gold nanoparticles.

Text and images by U. Kortshagen; Edited by M. Laroussi

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## Further Reading:

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- [3] Meinardi F, Ehrenberg S, Dharmo L, Carulli F, Mauri M, Bruni F, Simonutti R, Kortshagen U and Brovelli S 2017 Highly efficient luminescent solar concentrators based on earth-abundant indirect-bandgap silicon quantum dots *Nat. Photonics* **11** 177–85
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Uwe Kortshagen is a Professor of Mechanical Engineering at the University of Minnesota, with graduate faculty appointments in Physics, Chemical Engineering, and Materials Science. He holds the Christenson Chair in Renewable Energy and is a Distinguished McKnight University Professor. His research is in the area of low temperature plasmas science and in the plasma synthesis of nanomaterials and their applications. His work has been published in more than 220 journal articles and he holds 4 US patents. He earned his Dr. rer. Nat. (Ph.D.) in Physics in 1991 and his Habilitation in Experimental Physics in 1995 from the Ruhr University Bochum, Germany. He came to the U.S. in 1995 with a Lynen Fellowship of the Alexander von Humboldt Foundation and spent a year at the University of Wisconsin-Madison. In 1996, he joined the Department of Mechanical Engineering at the University of Minnesota as Assistant Professor, where he was promoted to Associate Professor in 1999, and to Professor in 2003. He served as President of the International Plasma Chemistry Society and as Chair of two Gordon Research Conferences. He is Fellow of the American Physical Society, the American Society of Mechanical Engineers, the Institute of Physics (UK), the International Plasma Chemistry Society, and the Institute on the Environment, and recipient of the 2015 Plasma Prize of the American Vacuum Society.