Plasma Synthesis of Nanoparticles for Nanocomposite Energy Applications

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ABSTRACT
The nanocomposite energy applications for plasma reactor produced nanoparticles are reviewed. Nanoparticles are commonly defined as particles less than 100 nm in diameter. Due to this small size, nanoparticles have a high surface-to-volume ratio. This increases the surface energy compared to the bulk material. The high surface-to-volume ratio and size effects (quantum effects) give nanoparticles distinctive chemical, electronic, optical, magnetic and mechanical properties from those of the bulk material. Nanoparticles synthesis can be grouped into 3 broad approaches. The first one is wet phase synthesis (sol-gel processing), the second is mechanical attrition, and the third is gas-phase synthesis (aerosol). The properties of the final product may differ significantly depending on the fabrication route. Currently, there are no economical large-scale production processes for nanoparticles. This hinders the widespread applications of nanomaterials in products. The Idaho National Laboratory (INL) is engaging in research and development of advanced modular hybrid plasma reactors for low cost production of nanoparticles that is predicted to accelerate application research and enable the formation of technology innovation alliances that will result in the commercial production of nanocomposites for alternative energy production devices such as fuel cells, photovoltaics and electrochemical double layer capacitors.

INTRODUCTION
The emerging field of nanotechnology is leading to exceptional understanding and control over the fundamental building blocks of all materials. At the core of nanotechnology is the ability to work at or near the atomic level in order to create large structures with fundamentally new and advantageous structural organizations. Nanoparticles are commonly defined as particles less than 100 nm in diameter. Due to this small size, nanoparticles have a high surface-to-volume ratio. This increases the surface energy compared to the bulk material. The high surface-to-volume ratio and size effects (quantum effects) give nanoparticles different chemical, electronic, optical, magnetic and mechanical properties from those of the bulk material. Many of the new, highly advantageous behaviors of nanoparticles, and of bulk materials made of nanoparticles, are not easily predicted from those observed at macroscales. The most important changes in behavior are caused not simply by size reduction, but by new properties intrinsic to or becoming predominant at the nanoscale. These phenomena include quantum confinement or size quantization and predominance of interfacial phenomena. Understand the basic control of processing parameters, chemistry, and nucleation processes of nanoparticles should allow generation of tailor-made nanoparticles of tightly controlled chemistry for a wide range of applications. The INL has been exploring ways for large-scale and low-cost production of nanoparticles. The goal is to develop and validate the commercial viability of an extend plasma heating zone reactor with rapid quench capability for production of low-cost, high-performance nanoparticles from inexpensive solid feedstock. The use of solid raw materials and oxidizing, neutral or reducing environments in the plasma reactor could result in a very flexible synthetic method capable of economically producing a wide variety of inorganic nanoparticle compositions, including oxides, mixed oxides, non-oxide ceramics and metals.

BACKGROUND
Many different processes are used to produce nanoparticles, but they generally fall into one of three categories: particle size reduction in the solid phase, liquid phase synthesis, or gas phase synthesis. Size reduction methods can be inexpensive but typically do not give good control of

shape, size and chemistry. Liquid methods can be expensive because of starting materials, multi-step processing, and liquid waste, and generally result in undesirable surface chemistry. Another drawback of liquid synthesis is that, often, entirely new processes must be developed for each new material. Current gas phase processes generally utilize relatively expensive liquid feedstock, do not have the particle size and morphology control afforded by the plasma technology and generally result in undesirable surface chemistry. Both liquid-phase and gas-phase processes generate pollutants (e.g., waste water, carbon dioxide, NOx, chlorine, hydrogen chloride, etc). The high temperature and anhydrous conditions of plasma synthesis allow formation of particles with unique and desirable surface properties and morphology unachievable with other methods. These particle properties are critical to their performance in materials applications.

Aerosol and Gas-Phase Methods
The aerosol methods for production of material particles can be divided into the gas-to-particle and the liquid/solid-to-solid routes. In the liquid/solid-to-solid route, the product particles are formed from droplets of reactant particles via intraparticle reactions. Using this method it is possible to produce single and multicomponent materials of controlled homogeneous compositions. It is a continuous process that can be scaled up. However, this is a complicated technique since many different physical and chemical phenomena (e.g. evaporation of the solvent, chemical reactions) can occur simultaneously. The gas-to-particle route is a common method when nanoparticles are produced through gas-phase processes. In this route, particles nucleate from a supersaturated vapor. Supersaturation can be achieved by physical processes such as cooling of a hot vapor or through chemical reactions of gaseous precursors, which results in the formation of condensable species. Very small particles on the order of nanometers can be produced, and the final products often have high purity. However, the production rates may be low in some processes and multicomponent materials may be difficult to produce. There may also be problems with hazardous reactants and by-products. Varying the process conditions (e.g. the initial concentration of precursor, maximum temperature, residence time, and cooling rate) can control the degree of agglomeration of the synthesized nanoparticles. In the gas-to-particle synthesis there are two routes, physical and chemical, depending on how the vapor supersaturation needed for particle nucleation comes about. However, these processes are identical in terms of the aerosol dynamics that occur once the condensable species have formed. In the physical vapor process, the solid precursor and the final product are the same material. This route is simple since no chemical reactions occur in the gas phase. However, temperatures high enough to vaporize the precursor are needed, and this limits the materials that can be processed. In general the yield in physical vapor condensation of nanoparticles tends to be low. In the chemical vapor route, the production rates can be significant if a precursor with high volatility is available. Therefore, chemicals such as metal chlorides or metalorganic compounds are often used, for example, titania is produced on an industrial scale from $TiCl_4$ using this method. However, in using metal chlorides or metalorganic compounds there is a possible risk of contaminating the final product. Composite particles can be produced using the chemical vapor route. Recently, smaller nanoparticles ranging from 1 to 10 nm with consistent crystal structure, specific surface structures or properties, and a tight particle size distribution have been produced by both gas-phase techniques. The particles produced by these processes have typical size variances of about 20%. However, for measurable enhancement of the quantum effect, the size variances must be reduced to less than 5% [1]. Initial development of new crystalline materials was based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a subatmospheric inert-gas environment [2,3,4]. Various aerosol-processing techniques have been reported to improve the production yield of nanoparticles [5,6]. These include synthesis by combustion flame [7,8,9,10],

plasma [11], laser ablation [12], chemical vapor condensation [13], spray pyrolysis [14], electrospray [15], and plasma spray [16].

Solution Processes

Solution processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment [17]. Size distribution of semiconductor, metal, and metal oxide nanoparticles can be manipulated by either dopant introduction [18] or heat treatment [19]. Better size and stability control of quantum-confined semiconductor nanoparticles can be achieved through the use of inverted micelles [20], polymer matrix architecture based on block copolymers [21] or polymer blends [22], porous glasses [23], and ex-situ particle-capping techniques [24,25]. Additional nanoparticle synthesis techniques include sonochemical processing, cavitation processing, microemulsion processing, and high-energy ball milling. In sonochemistry, an acoustic cavitation process can generate a transient localized hot zone with extremely high temperature gradient and pressure [26]. Such sudden changes in temperature and pressure assist the destruction of the sonochemical precursor (e.g., organometallic solution) and the formation of nanoparticles. The technique can be used to produce a large volume of material for industrial applications. In hydrodynamic cavitation, nanoparticles are generated through creation and release of gas bubbles inside the sol-gel solution [27]. Rapidly pressurizing in a supercritical drying chamber and exposing to cavitational disturbance and high-temperature heating would mix the sol-gel solution. The erupted hydrodynamic bubbles are responsible for nucleation, growth, and quenching of the nanoparticles. Adjusting the pressure and the solution retention time in the cavitation chamber can control particle size. Microemulsions have been used for synthesis of metallic [28], semiconductor [29,30], silica [31], magnetic, and superconductor nanoparticles [32]. By controlling the very low interfacial tension ($\sim 10^{-3}$ mN/m) through the addition of a co-surfactant (e.g., an alcohol of intermediate chain length), these microemulsions are produced spontaneously without the need for significant mechanical agitation. The technique is useful for large-scale production of nanoparticles using relatively simple and inexpensive hardware [33].

Mechanical Attrition

Finally, high-energy ball milling (mechanical attrition), the only top-down approach for nanoparticle synthesis, has been used for the generation of magnetic [34], catalytic [35], and structural nanoparticles [36]. The technique, which is already a commercial technology, has been considered dirty because of contamination problems from ball-milling processes. However, the availability of tungsten carbide components and the use of inert atmosphere and/or high vacuum processes have reduced impurities to acceptable levels for many industrial applications. Common drawbacks include the low surface area, the highly polydisperse size distributions, and the partially amorphous state of the as-prepared powders.

Achieving Monodispersed Nanoparticles

One of the most challenging problems in synthesis is the controlled generation of monodispersed nanoparticles with size variance so small that size selection by centrifugal precipitation or mobility classification is not necessary. Liquid processes have produced the most monodisperse particles, but typically theses processes are high dilution and, hence, not particularly cost effective. Gas-phase synthesis is one of the best techniques for controlled generation with respect to size monodispersity, typically achieved by using a combination of rigorous control of nucleation-condensation growth and avoidance of coagulation by diffusion and turbulence as well as by the effective collection of nanoparticles and their handling afterwards. Plasma gas-phase (chemical and physical) synthesis has the best potential to produce nanoparticles with a narrow and tight size distribution in a very short time. More attention should focus on plasma gas-phase synthesis technology development.

Scale Up

Scale-up production is of great interest for nanoparticle synthesis. High-energy ball milling, already a commercial high-volume process, as mentioned above, has been instrumental in generating nanoparticles for the preparation of magnetic, structural, and catalytic materials. However, the process produces polydispersed amorphous powder, which requires subsequent partial recrystallization before the powder is consolidated into nanostructured materials. For sol-gel processing, the development of continuous processing techniques based on present knowledge of batch processing has yet to be addressed for economical scale-up production of nanoparticles. Other related sol-gel issues concern the cost of precursors, the recycling of solvents, and the disposal of hazardous byproducts. Overall, sol-gel processing may still be attractive for commercial scaleup development. Although gas-phase synthesis is generally a low production rate process in research laboratories, however, higher rates of production process are being developed.

To achieve widespread applications for nanoparticles low-cost and high-rate commercial production processes must be developed. Among all the alternative processes discussed above thermal plasma technology has the best potential for low-cost, large-scale, gas-phase production of nanoparticles. Thermal plasma chemical vapor synthesis of nanoparticles presents no significant technical barriers; however, the cost associated with chemical vapor synthesis would be high, and high vapor pressure reactants are limited. Thermal plasma physical vapor deposition for nanoparticle synthesis should be a much lower-cost production process, but it does have significant technical barrier issues. The technical barriers include short residence time, small high-temperature processing zone, and non-uniform high-temperature field. Technology development must overcome these technical barriers to make thermal plasma physical vapor synthesis a truly viable low-cost commercial nanoparticle production technology.

DEVELOPMENT CONCEPT

Converting feed materials into molecule or atomic scale is the first step of the gas phase process to make nanoparticles. A particle formation process is illustrated in Figure1. Solid feed materials will be vaporized completely in a high-temperature environment. Temperature-time history of the feed particles can determine the degree of vaporization. For example, to vaporize silica the temperature must be above its boiling temperature, and the residence time required depends on the particle size of the feed material. It is estimated that 8 milliseconds (ms) is required for 25 μm particles, and 50 ms is required for 100 μm particles. Particles will be formed through nucleation of the vapor. Particle size, particle morphology, and crystalline form can be controlled through a fast-quenching process using quench gas.
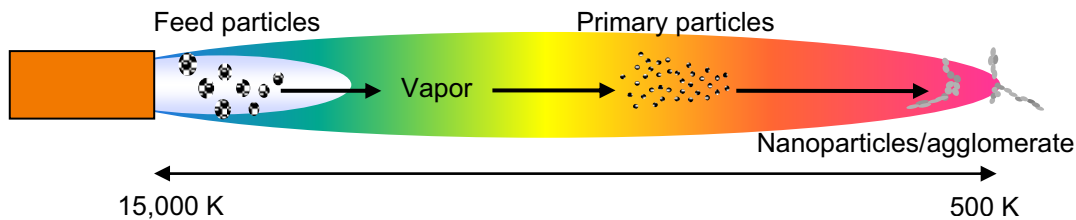

Figure 1. Particle formation processes in a plasma.

INL MODULAR HYBRID PLASMA TECHNOLOGY DEVELOPMENT

The INL has been actively developing advanced plasma technologies for low-cost production of nanoparticles. Early assessment and tests found that processing capabilities of current plasma technologies are severely limited and couldn't satisfy the following critical requirements for low-cost nanoparticle production:

- A very long residence time for full vaporization of low-vapor-pressure materials

- Accept large particle (at least 150 μm) for a continuous, single pass process with the lowest cost feed materials

- Efficient conversion of electricity to thermal energy in a configuration that maintains the temperature of the feed material above its vaporization temperature

The INL developed two advanced hybrid plasma reactor concepts that would produce a large uniform heating zone and a long residence time for the feed materials to achieve full vaporization. The concepts are modular ac/ac hybrid plasma and modular dc/dc hybrid plasma systems. Modular hybrid plasma concept means stacking of plasma torches in sequence to form a long plasma system that produces a large uniform high-temperature heating zone and a very long residence time for feed materials vaporization. The plasma maintains uniform high gas temperatures throughout the length of the processing zone because successive arc discharges are superimposed on the plasma gas in each of the modular torch units. The heat load is successively added to the downstream modular torch unit and raises its overall temperatures. Hybrid means that the "field free" (current free) plasma gas from the upstream torch unit is reheated to a "field active" (current carrying) arc state by superimposing an electric discharge in the downstream units. The modular configuration allows one to manipulate the power settings in each of the modular units to achieve the desired temperature levels. One can add or subtract modular units to achieve the desired residence time for complete vaporization of the feed materials.

The AC/AC Hybrid Plasma Reactor

The first modular concept tested was the ac/ac modular hybrid plasma reactor. In this new reactor concept one has control over the length, size of the processing zone, and the feed material residence time in the plasma by adding or removing modular plasma units in the reactor. In this modular reactor system the residence time of feed material in the high-temperature processing zone can be several factors to orders of magnitude higher than a traditional plasma reactor. There is also a cascading plasma energy loading effect to the downstream modular units thus increasing the available plasma energy content for the last modular unit to complete material processing. Figure 2 shows the axial cutaway view of a three-stage ac/ac modular hybrid plasma reactor concept. The schematic shows the cascading energy loading effect in the plasma reactor, which shows the overall increase in the plasma volume. The net plasma energy content cascading from the modular unit above will increase by superimposition of an arc discharge in the plasma gas and raise the total energy content. This higher net energy loading effect improves plasma ionization in the downstream modular
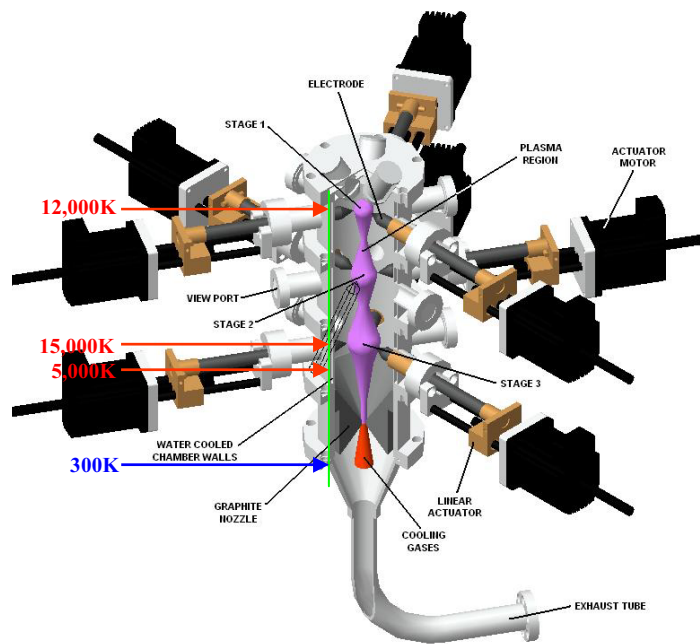

Figure 2. Modular AC/AC Hybrid Plasma Reactor

units and increases the size of the plasma. The approximate temperature profile for this new plasma reactor is also depicted in Figure 2.

Another feature of this new reactor is that the plasma gas flow is very soft compared to traditional plasma jet reactors. A softer plasma flow also enhances the residence time of the feed material in the high-temperature processing zone. A long residence time and a large and uniform high-temperature processing zone allow one to process feed powders up to a couple of hundred microns to produce nanoparticles in a rather small and compact reactor. Figure 3 shows the three-stage hybrid plasma reactor in operation. The reactor operated at a total combined power of about 15 kW and demonstrated its capability to vaporize 180 μm alumina
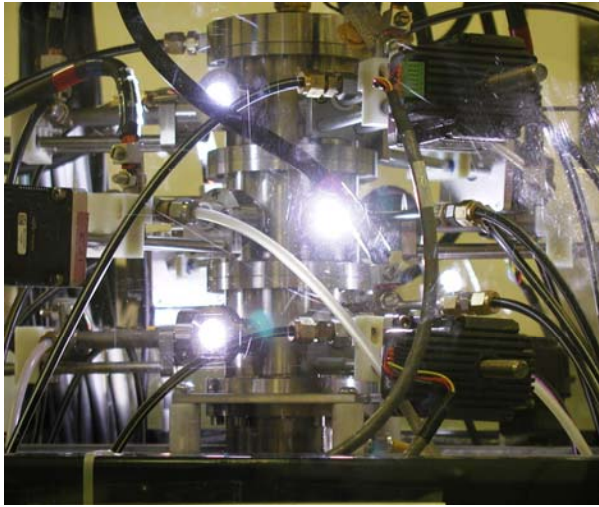
Figure 3. Modular AC/AC hybrid plasma reactor is in operation (US Patent 7232975, June 2007).
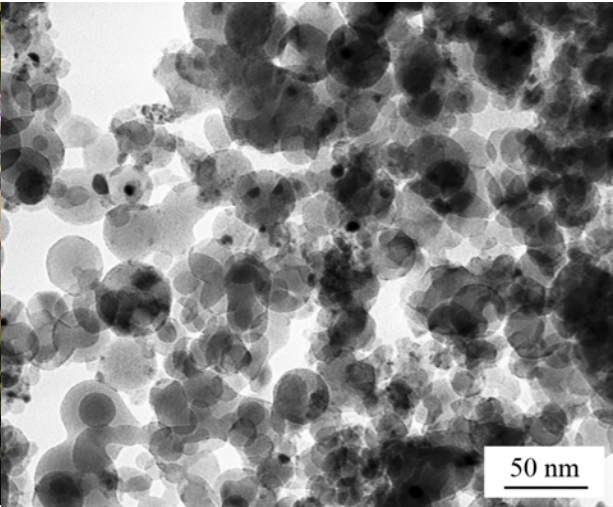

Figure 4. Alumina nanoparticles produced from 150+ micron feed powder using the modular AC/AC hybrid plasma reactor.
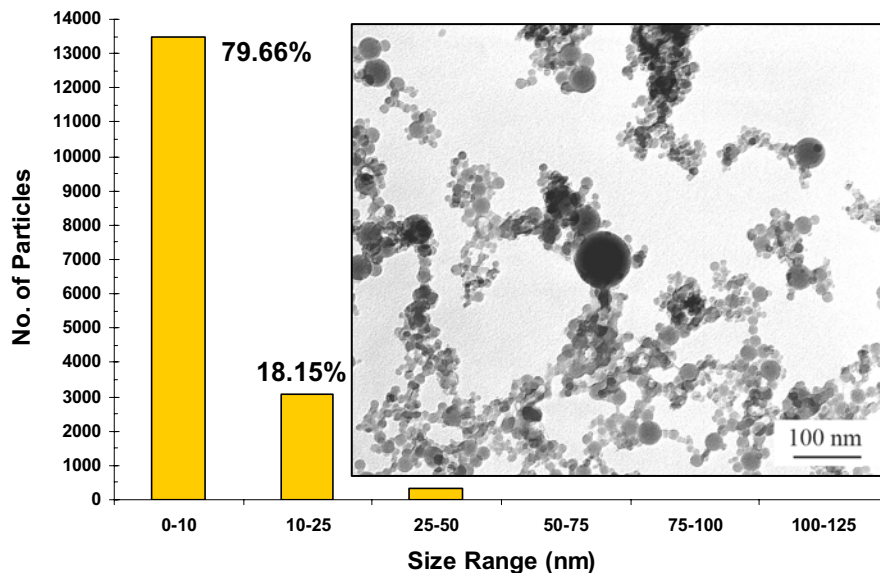

Figure 5. Silica nanoparticle size distribution and TEM morphology

and large silica particles. The morphology of plasma produced alumina nanoparticles is shown in Figure 4 and the particle size distribution is very narrow. Over 90% of the particles produced

are below 25 nm. Figure 5 shows the silica nanoparticles produced have a very tight particle size distribution. Eighty percent of the particles is below 10 nm and about 18% of the nanoparticles lies between 10 and 25 nm. The insert shows the TEM morphology of the produced silica nanoparticles. The particles are spherical and X-ray diffraction showed a completely amorphous material. This system uses tungsten electrodes and it is necessary to use argon plasma gas. The tungsten electrodes were mildly consumed during powder synthesis due to inadequate cooling design.

The DC/DC Hybrid Plasma Reactor

The second concept developed and tested is the dc/dc modular hybrid plasma reactor. In this concept a conventional plasma spray torch is coupled to one or two units of modular plasma torch systems. The plasma spray provides initial and continuous ionization in the modular electrodes to sustain the down stream plasma. The "field free" plasma jet from the upstream spray torch was turned into a "field active" arc in the downstream modular plasma units by applying a discharge. This superimposed heating method creates a very long active arc column, which provides a large and uniform high temperature heating zone with a long residence time for feed materials vaporization. Figure 6 shows the GEN 1 system with a stacking of 2 modular units and an upstream plasma spray torch. In this configuration one has the freedom to manipulate the power input in each of the plasma unit to achieve materials processing goal. GEN 1 was assessed for its capability to vaporize large feed powders. In tests with 180 μm alumina powder, partial vaporization of the feed

Figure 6. GEN 1 hybrid system consists of 2 modular units and an upstream plasma spray torch

was observed. The degree of feed vaporization was a function of the total plasma power, plasma gas enthalpy, arc length, powder residence time, and the powder feed rate. At low powder feed rate more feed powder vaporization was achieved. Figure 7 shows the appearance of the plasma tail flame in the collection chamber when the powder feed rate was set at 0.07 lb/hr. Alumina nanoparticles nucleated into a cloud around the plasma jet. A few of the luminous trails formed by partially vaporized molten alumina powders are visible. Figure 8 shows that at a higher powder feed rate of 0.6 lb/hr the luminous trails are more prominent. The

Figure 7. NanoAl$_2$O$_3$ form a cloud around the plasma. Few luminous trails are visible.
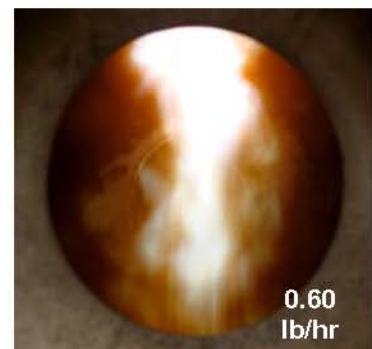
Figure 8. At 0.60 lb/hr powder feed rate more luminous trails observed in the plasma flame

alumina nanoparticle cloud is also very prominent. At high powder feed the plasma intensity appears brighter in the tail flame probably due to higher emissions from a denser particle loading. The alumina nanoparticles produced with the dc/dc modular hybrid plasma system are shown in Figure 9. The majority of the nanoparticles are less than 20 nm and faceted. This is an indication of gas phase nucleation. The system was also tested for silica nanoparticles
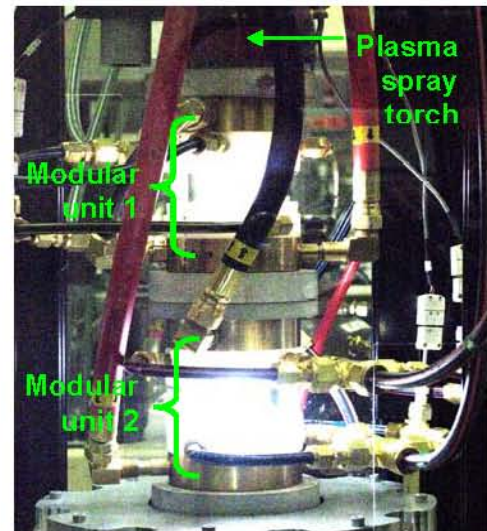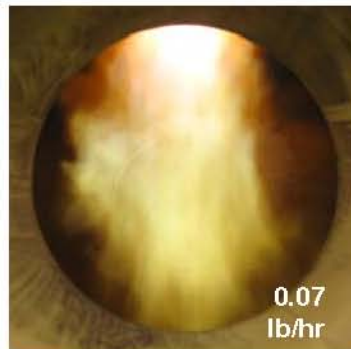
synthesis. Silica has a slightly lower melting temperature than alumina but the boiling temperature is almost identical to alumina. Therefore, vaporization of silica is just as difficult as vaporizing alumina. The tendency of molten silica to foul the reactor components is also high than alumina. Figure 10a shows the TEM picture of the silica nanoparticles and the scale is 20 nm. Figure 10b is a comparison of the feed and processed silica. It shows the volume of the processed powder was twice that of the feed powder. This powder has very high specific surface.
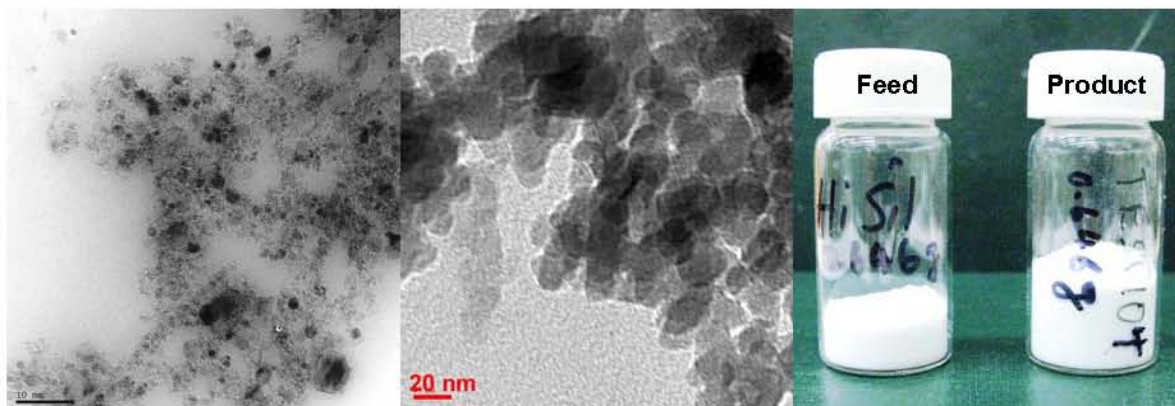

Figure 9. DC/DC hybrid plasma produced nanoAl$_2$O$_3$

Figure 10a. DC/DC hybrid plasma produced nanoSiO$_2$

Figure 10b. Processed and feed SiO$_2$ powders comparison

ENERGY MARKETS AND "PLASMA REACTOR NANOCOMPOSITE" (PRN) APPLICATION DEVELOPMENT

Nanostructured materials and nanocomposites, and the devices engineered and manufactured from them are poised to revolutionize many industries. Nanostructured carbon particles such as fullerenes, nanotubes, nanowires and nanohorns are proving to be very useful in *energy storage* and *energy conversion* devices. On a parallel research and development track, inorganic nanoparticles synthesized as nanoclusters, nanorods, nanowires, nanotubes, and nanodots are also finding the energy market segments very receptive to breakthroughs in technology advancement. The advent of plasma reactor produced nanoparticles is providing additional degrees of freedom to design and produce nanocomposites for a myriad of energy conversion and energy storage systems as well as significantly impacting energy savings in next generation energy efficient solid state lighting. Plasma Reactor Nanocomposites (PRNs) are an emerging new class of functional nanocomposites that hold the promise of facilitating breakthrough innovations in almost all energy market segments. The following is a small sampling of application development opportunities for PRNs.

ENERGY STORAGE MARKETS

Ultracapacitors

Plasma reactor nanoparticle technology platforms are positioned to be part of nanocomposite solutions that provide low resistivity and high surface area for next generation supercapacitors or ultracapacitors. The opportunity exists to develop nanoporous oxides to replace the lower capacitance carbon based electrodes. Ultracapacitors containing PRNs such as "metal ceramic nanocomposites" with enhanced dispersion of plasma nanoparticles are also envisioned to possess superior durability characteristics. Research alliance opportunities exist to couple nanocomposite ultracapacitor innovation with rechargeable battery development to meet the power, energy, voltage and lower-weight modularity needs of the automotive industry.

Batteries

The development of PRNs for higher energy density batteries that also possess higher power-to-weight ratios and can be charged and discharged faster is predicted to grow as plasma reactor nanoparticle production costs continue to decrease. PRN design and formulation are projected to enhance the performance of charge collectors, separators and the active anode/cathode materials. The research and development of PRNs will also be targeted at thin film and flexible battery innovations for portable electronic device applications. Opportunities exist to create innovation alliances to accelerate the development of next generation PRN based electrodes, polymer electrolytes and separators for lithium batteries.

Hydrogen

Plasma reactor nanocomposites (PRNs) have the potential to store and release hydrogen to be used in polymer electrolyte membrane (PEM) fuel cell systems. Plasma reactor technology platforms offer the opportunity to synthesize and formulate metal hydride and silica nanocomposites that would be designed to store and release hydrogen at lower temperatures. The vision is to develop nanocomposites with plasma reactor nanoparticles possessing large surface area to volume ratios and catalytically enhanced hydrogen storage and release characteristics that would meet the needs of the automotive, aerospace, consumer electronics and defense industries for lower-weight and more robust storage modules.

ENERGY CONVERSION
Fuel Cells

PRNs can be integrated into PEM fuel cell systems both by nanostructured formulation of the proton exhange membrane and the electrochemically active catalyst nanocomposites. The R&D of plasma reactor nanoparticles for solid oxide fuel cells (SOFCs), that can withstand very high temperatures in excess of $800^{o}C$, will also grow as customers demand rapid starting and more energy-efficient fuel cells than can tolerate and run robustly on fuels such as propane, kerosene, diesel fuel and less-purified hydrogen. PRN technology innovation alliance opportunities exist for both solid oxide fuel cells and polymer electrolyte membrane fuel cell systems.

Photovoltaics

It is forecast that the highest growth rate of Plasma Reactor Nanocomposite (PRN) research and development for energy applications will be targeted at solar cell innovations during the next five years. Plasma reactor nanoparticle technology platforms are believed to have the potential to significantly impact photovoltaic systems by increasing the absorption rates of light via PRNs that tune the spectral absorption of light and the design of PRN based anti-reflection coatings. It is envisioned that PRNs will be increasingly utilized to improve the efficiency and reduce the cost of solar cells with enabling thin films and coatings. It is believed that PRNs will improve photovoltaic device "efficiency-to-cost ratios" for both inorganic semiconductor photovoltaic (PV) cells and organic polymer PV cells.

PRNs provide the large surface and interfacial areas that are necessary for enhanced photon absorption and for charge separation. Innovation alliance opportunities exist to develop and commercialize light sensitive and electrically conductive PRN coatings that can be painted onto various surfaces and can absorb photons more efficiently during dim light conditions. PRNs also offer the opportunity to enhance the performance of thin film technologies based on CdTe, CdSe CIGS and bulk heterojunction PV cells. Plasma reactor nanoparticle technology platforms can create new research pathways in the pursuit of novel molecular architectures that may improve the performance and cost effectiveness of second generation thin film PV cells and third generation based PV devices.

SUMMARY

Nanocomposites are an emerging new class of functional materials that hold the promise of facilitating breakthrough innovations in almost all energy market segments. Nanostructured materials and nanocomposites, and the devices engineered and manufactured from them are poised to revolutionize many industries. The Idaho National Laboratory is engaging in research and development of advanced modular hybrid plasma reactors for low cost production of nanoparticles. The advent of plasma reactor nanocomposites is providing additional degrees of freedom to design and produce nanocomposite that is predicted to accelerate application research and enable the formation of technology innovation alliances that will result in the commercial production of nanocomposites for alternative energy production devices such as fuel cells, photovoltaics and electrochemical double layer capacitors.

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