

Laser pyrolysis - a platform technology to produce nanoscale materials for a range of product applications

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ABSTRACT

Laser pyrolysis, a gas phase process for the synthesis of nanomaterials, has been pioneered and developed as a viable nanoparticle manufacturing platform (NPMTM) by NanoGram Corporation. It has been successfully employed in producing various nanoscale materials including metals, simple and complex metal oxides, carbides, nitrides, rare-earth doped oxides, multi-elemental glasses among others. NPMTM processing routinely produces very high-quality nanoscale particles with high degree of crystallinity, generally spheroidal morphology and exceptionally tight particle size distributions. In this paper we will introduce and describe laser pyrolysis-based NPMTM process as a platform technology with demonstrated capability of scaling-up nanomaterials production to 1kg/hr using this technology. Nanoscale materials made by laser pyrolysis are currently being developed for a range of product applications such as phosphors for solid-state lighting applications, high-index fillers for optical polymer composites, cathode materials for lithium ion batteries. Nanomaterials from NPMTM process have already been commercialized in an exceptionally high-rate battery as cathode material for defibrillators batteries by a NanoGram spin-off company. In this paper we briefly present the capabilities of NPMTM processing by showing examples of complex materials currently being synthesized, and outline the levels of control available in the process to enable functional materials.

Keywords: laser pyrolysis, nanomaterials, production, processing platform, product applications

1 BACKGROUND

Nanoscale materials continue to generate ever increasing levels of interest for applications in a broad-range of fields. Concurrently a variety of synthesis methods are being explored and developed for the synthesis and production of nanoparticles. Process methods for producing nanoscale particles are broadly classified as liquid-phase methods, gas phase condensation methods, and dry grinding and size-reduction methods, and these include sol-gel process, mechanical or chemo-mechanical grinding, hydrothermal method, spray and flame pyrolysis process.

Gas phase processes such as flame pyrolysis have been scaled to produce tonnage quantities of simple ultra-fine and nanoscale materials such as carbon black, fumed silica, and titania. Similarly, liquid-phase processes have also been

established to produce materials such as colloidal silica at commercial scales. Large profitable businesses have been established around selling such materials and products based on their use. These include traditional applications such as fillers for automobile tires, slurries for chemical mechanical polishing, and printing inks and toners.

A growing number of newer high-value product applications are being developed and reported for nanoscale materials. These applications are in diverse areas such as electronics, energy conversion and storage, biomedical technology, and they rely on higher functionality available at nanoscale from a wider range of materials compositions and particle sizes down to the single nanometer scale. Such applications require materials with more stringent specifications of chemical purity, particle size and distribution. However, nanomaterials, especially of a broader range of complex compositions and tighter specifications, on which such applications depend, have not yet attained the status of standard commercial powder materials reached by carbon black and fumed silica. Majority of them are either only available in sample quantities or are of poor, inconsistent quality (1). Although a large number of small companies are trying to do business by developing and selling nanomaterials into a growing market (\$20.5B in 2010 (2)), rapid applications or product development based on complex materials by users of such materials will be severely impaired without significant efforts on the part of suppliers to a) maintain consistency or repeatability of the process and product, b) scale-up to produce commercial quantities, and c) develop standardized test methods and formats for reporting materials specifications. Product development invariably requires tailoring of nanomaterials which is not readily available with such materials suppliers.

We have developed laser pyrolysis process into an industrial platform - NPMTM process platform, to produce a broad range of complex nanoscale materials. Inherently, materials produced by laser pyrolysis process are in the range of 10-200nm in average particle size with remarkably narrow distributions. Unlike liquid-phase methods, a key advantage with laser pyrolysis is the ability to use the same process across production scales - from laboratory development quantities to production. We have demonstrated nanoparticle production scales of a 1kg/hr on the NPMTM process platform. NanoGram's capabilities and approach to product development with partner companies also provides the ability to take an integrated approach to developing the materials and the product application.

Laser pyrolysis offers linear scalability along the beam and the ability to maintain a short (ms) residence time for

reactant elements. This aspect of the process allows for a narrow size distribution of particle size. We are developing a broad portfolio of product applications using higher quality nanomaterials from NPM™ process.

In this talk we present some examples from portfolio of materials being developed by NanoGram that demonstrate excellent control of application-specific properties of the nanoparticles. Some of these include control of crystal structure to produce phase pure nanocrystalline rutile or anatase TiO₂ for transparent polymer nanocomposites, control of concentration and oxidation state of a rare-earth dopant ions to produce high quantum efficiency phosphors such as Eu:BaMgAl₁₀O₁₇ (BAM), Ce:Y₃Al₅O₁₂ (YAG), and complex composition and crystalline structure control for a range of other nanocrystalline materials. The paper will present the outstanding level of application-specific properties achievable by NPM™ processing.

2 NPM™ PROCESSING

Cannon et al (3) of MIT first reported laser pyrolysis as a method for producing highly uniform nanoscale particles. Over the past nine years NanoGram Corporation has developed process technology and several generations of equipment to transform laser pyrolysis into a viable platform to develop and manufacture nanoscale materials and films for use in a range of product applications. In the process developed by NanoGram shown schematically in Fig.1, a continuous-wave (CW) 10.6micron wavelength CO₂ laser PRC Laser Corporation, Landing NJ) is passed through a reactor to intersect an orthogonally flowing reactant stream fed through a nozzle which is elongated in the direction of the laser. An optical system made of lenses or mirrors mounted on the side of the reactor focuses the laser beam into a thin sheet, to form a well-defined and uniform laser reaction zone (LRZ). CO₂ lasers are proven and reliable workhorses in automotive industry, and they are available in powers up to 10kW.

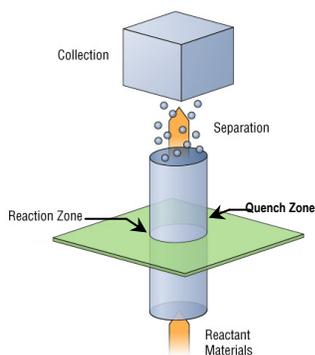


Fig.1. Schematic illustration of NPM™ process

Laser pyrolysis process is based on the resonance between the emission of a CW CO₂ laser and the infrared absorption band of a precursor or a component present in

incoming reactant stream (4), and subsequent transfer of energy to non laser-active molecules. There are a broad range of available materials that absorb at 10.6um (0.12eV). These can be categorized broadly as: i) precursors which directly produce the desired materials upon decomposition or chemical reactions following laser photolysis or pyrolysis, e.g. silane gas to produce silicon nanoparticles (5) ii) sensitizers that only absorb and transfer energy to heat/decompose reactants without producing products and or participating in the reaction, e.g. SF₆ to decompose iron carbonyl for Fe nanoparticles synthesis (6) iii) species that have the role of absorbing, decomposing and reacting to assist decomposition of precursors e.g. ethylene in the presence of oxygen to produce vanadium oxide from vanadium oxy-trichloride vapor (7).

Depending on the number of photons absorbed per molecule of the excitable species, either photolysis or pyrolysis can occur. In either case controlled chemical reactions are initiated, and depending on the precursors used, produce nanoparticles from the process. Short millisecond scale residence times, spatial uniformity of the reaction zone, continuous source of activation energy are the key attributes of the process which enable small footprint high production rate reactors, narrow particle size distribution, and the ability to produce several classes of compounds such as oxides, nitrides, carbides, sulfides etc.

We have developed intellectual property and know-how for design and operation of reactant delivery systems to uniformly deliver gases, vapors, or liquid-based aerosols containing dissolved precursors to the laser beam. These three precursor forms and their combinations allow delivery of a broad spectrum of elements and elemental combinations for production of nanomaterials of a wide range of complex compositions.

For examples presented in this paper, the materials produced by NPM™ process were characterized by various powder characterization techniques to determine the physical, chemical and crystalline properties of the nanoparticles. Phase purity and crystalline characteristics of the powders was determined using the XRD (Rigaku Miniflex). Diffraction patterns were recorded using Cu K α radiation from $\theta = 20$ to 80° , in steps of 0.01° with a collection time of 0.5s per step. Phase content and average crystallite size of the powders were determined by Rietveld Refinement and X-ray line broadening using the Scherrer equation respectively on the MDI Jade 7 software coupled with the Miniflex. Particle size and morphology was examined using routinely Transmission Electron Spectroscopy. Specific surface area of the powders was measured using the BET method (Micromeritics Tristar) based on the absorption of nitrogen and using a 3-point analysis. Transmission data on optical films were measured. Chemical analyses, namely EDX and XPS, were also performed on the powders to determine their chemical composition and purity. The particle size of the dispersed nanopowders was measured using dynamic light scattering (Malvern -Zetasizer Nano ZS). The surface charge

characteristic was determined by measuring the zeta potential of the dispersion using the same instrument

3 APPLICATIONS

3.1 High Refractive Index Nanocomposites

Refractive index of commercially available optical polymers can be raised from their typical value of 1.50 (for most acrylates, epoxies, silicones measured @559nm) by loading them with nanoparticles of a transparent high refractive index inorganic material. Attributes of polymer materials such as their processability and their mechanical properties render them very useful in a wide range of high-value applications such as packaging for electronic and opto-electronic devices, display films, and as micro-optic elements in various devices. Ability to raise the refractive index of polymers by preserving processability and enhancing mechanical properties is highly desirable in many of these applications. For e.g. high-index encapsulation can extract more light out of a light emitting diode (LED) device, To obtain high index while maintaining high transparency, it been shown both theoretically and in some experiments that the size of nanoparticles must be significantly below the wavelength of light, and the particles must be well dispersed with no aggregation. Using a volumetric average a 0.10 increase in index with rutile TiO₂ with an index of 2.62 requires a loading level of 23.5wt%, and for an increase of 0.20 it is 41.5wt%. To obtain such high-loading levels of nanoparticles with minimum aggregation, surface modification with organic molecules is required.

Highly uniform rutile titania nanoparticles are produced from vaporized titanium tetrachloride, and ethylene and oxygen as reactants. Fig.2 shows the ability of the NPMTM process to produce highly crystalline nanoparticles of either of the two most common phases of TiO₂ – anatase or rutile, or mixed phase. Rutile phase of titania is preferred for optical nanocomposites as anatase is photo-catalytic.

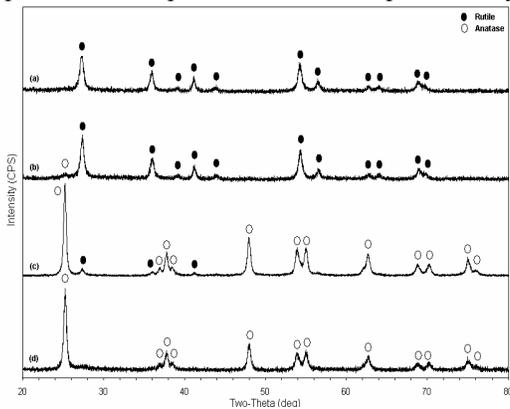


Fig.2 X-ray diffraction patterns of nanocrystalline TiO₂ showing progression from phase-pure anatase (bottom) to phase-pure rutile (preferred phase for high-index optical

nanocomposites) as a function of NPMTM process conditions

Rietveld analysis of x-ray scans of the powder samples showed achievable phase purity of up to 99% rutile at average particle size of 10nm and below, with no particles larger than about 20nm, in loosely agglomerated powder form. The switching between the anatase and rutile phases of the particles and the average particle size can be easily and repeatably achieved by varying reaction conditions in the laser reaction zone. This puts forth the flexibility of producing TiO₂ powders in the anatase and rutile phases at sub-20nm particle size. To our knowledge flame-pyrolysis which is well-established for titania does not readily produce phase-pure rutile, and generates a broader distribution, whereas sol-gel synthesis cannot achieve rutile phase. The uniformity and phase-purity of TiO₂ nanoparticles is uniquely possible by laser pyrolysis as available in the NPMTM process (Fig.3(a) & (b)).

The loosely agglomerated nature of the nanoparticles produced excellent dispersions in organic solvents that were very stable with up to 3wt% TiO₂. Dispersed average particle size measured by DLS was between 20-30nm with only mild ultra-sonication. Using such high-quality rutile nanoparticles we have developed high-transparency polymer nanocomposite films. Spin-coated films in the 2um thickness range show >90% transmission as seen in Fig. 4 for refractive index of 1.60 to 1.70 at 559nm, using a starting polymer of 1.50 index. They appear smooth, highly reflective and show excellent surface topography.

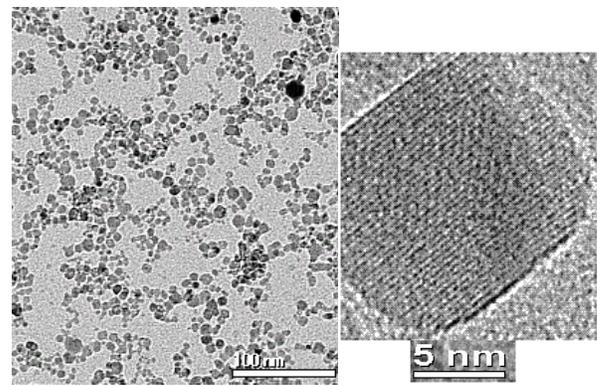


Fig. 3(a) Highly uniform crystalline rutile TiO₂ with an average particle size of <10nm (b) Typical rutile TiO₂ nanoparticle showing high degree of crystallinity

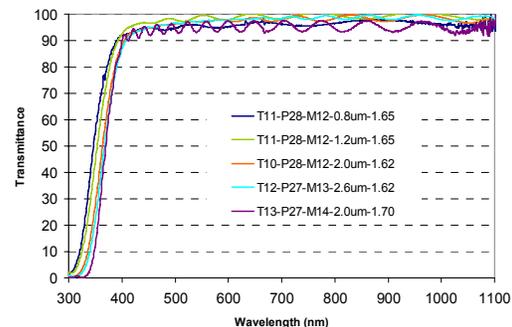


Fig. 4 Transmission spectra measured by UV-Vis spectrometer of rutile TiO₂-acrylate nanocomposite films showing refractive index from 1.62-1.70 (measured at 559nm) with a base polymer index 1.50. Films were spin-coated on silicon wafers for refractive index and thickness measurements and on glass slides for transmission data. Films show >90% transmission.

3.2 High Efficiency Nanophosphors

Phosphors are materials of great interest in general lighting, displays, and recently in LED devices for a variety of lighting applications. There is a growing interest in nanoscale inorganic phosphors on account of enhancements available from nanometric particles in their applications. Nanoscale particles could allow higher resolution printing in display screens, and could potentially produce higher brightness at lower excitation in cathodoluminescent materials.

NPMTM processing is being used to develop nanoscale phosphor materials for specific applications. We present here data on YAG and BAM phosphor nanoparticles.

To synthesize YAG phosphor nanoparticles using NPMTM process platform, liquid precursors containing dissolved precursors of yttrium, aluminum and cerium were atomized into a stream of fine droplets and were reacted with sensitizer gas and oxygen in the laser reaction zone to produce the nanoparticles. NPMTM process method allows precise control of dopant concentration in the nanophosphors. A range of process conditions and Ce doping levels were studied for the optimization of nano-YAG as shown in Fig.5. Quantum efficiency comparable to those measured for commercially available micron-sized particles were achieved for nanoparticle phosphors at average particle size of 40nm.

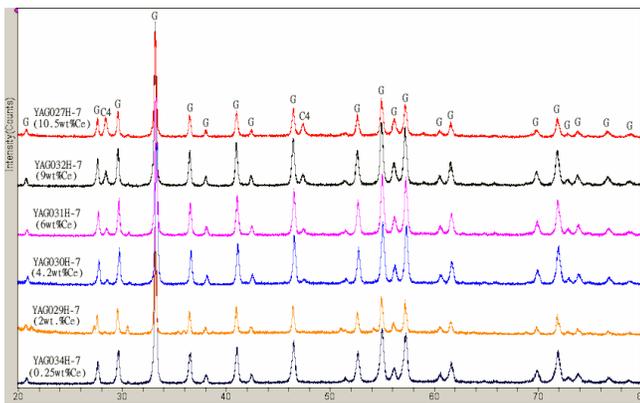


Fig. 5 X-ray diffraction scans of Ce:YAG nanoparticle phosphor produced by NPMTM process showing dopant concentration control. Data shows YAG peaks, and CeO₂ primary peak for samples with greater than 2wt% dopant concentration.

Similarly Eu:BAM phosphor was also produced by NPMTM process. Fig.6 x-ray diffraction data on nanoparticulate powders of this composition.

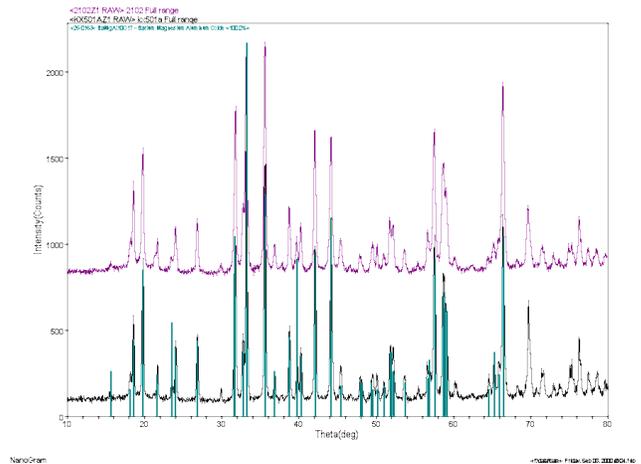


Fig. 6 X-ray diffraction scans of Eu:BAM nanoparticle phosphor; reference lines BAM for structure are in green

4 CONCLUSIONS

In this presentation we highlight laser pyrolysis as a viable nanomaterials manufacturing platform developed by NanoGram. NPMTM processing is set-up to produce highly uniform nanoparticles of complex compositions to develop and commercialize a range of product applications. We have presented examples of high-index transparent nanocomposites, nanophosphors.

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