Practical Synthesis of Nanomaterials and Nanostructures

A. Rae, J. Matteson and V. Dansoh

NanoMaterials Innovation Center
200 N. Main St, Alfred NY 14802, USA;
arae@nanomic.org, jmatteson@nanomic.org, vdansoh@nanomic.org

ABSTRACT

Nanoparticle and nanostructured coating synthesis is commonly hampered by complex processes or the need to use precursors which may not yet be registered under TSCA or REACH. There are, however, simple and practical processes using conventional equipment and raw materials that can be safe, economic and cost-effective. This review is illustrated by the authors' experience of scaling a range of metals, ceramics, oxides and non-oxides using a range of synthesis methods including microwave, combustion synthesis, milling, plasma and freeze drying..

Keywords: nanomaterials, nanostructures, printed electronics

1. INTRODUCTION

The National Nanotechnology Initiative – www.nano.gov – has supported a significant scientific and technical effort in the USA that is now being translated into manufacturing. According to Government statistics, over $18B has been invested in novel materials and systems. These production and processing technologies are applicable to both nano-sized and near-nano materials. Some are new techniques; some are modifications or new applications of older techniques, often applied in different ways or at a different scale than traditional methods.

Aside from semiconductor processing where nanotechnology has been the norm for many years, nanotechnology is steadily becoming mainstream in many product areas – quietly, without much fanfare, and not as quickly as many of us would expect. From automotive polish to sunscreen to shower curtains, new applications are appearing in a wide range of consumer and industrial products. However, we still have not seen the wave of disruptive applications that were predicted; we are seeing incremental improvements in existing products.

Why are we not seeing disruptive applications commercializing faster? There are challenges in terms of technology transfer, company formation, the economic climate and the sheer time it takes to get new materials and systems qualified. The business model of being a small nanomaterial supplier in particular is broken. Without market pull and an infrastructure to support the materials (in the case of printed electronics, ink makers and equipment makers) a materials maker is often waiting for serendipity to grow the business. Nanomaterials and nanostructures can be the basis for many new product areas – and someone has to make them – profitably. “Hot” areas like carbon nanotubes and graphene already have production capacity greatly exceeding demand, yet relatively small volume costs can deter new users.

Let’s look at a number of ways to make nanomaterials and then ways to assemble them into useful structures using printed electronics as a model market.

2. NANOMATERIAL SYNTHESIS

While this is not an exhaustive list of resources or techniques, it gives an idea of the types of equipment and processes used to produce. These process are all operated at the Nanomaterials Innovation Center in Alfred NY and are tailored to produce small particles without the opportunity for crystal growth.

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Precipitation

Ultrasonic processing systems are designed for dispersing, homogenizing, de-agglomeration, particle size reduction, sono-chemistry, emulsification, or emulsification of liquids in flow or batch operation. Multiple precipitation nuclei and high local energy concentrations can allow novel precipitations to occur. This technique has been used to successfully produce both nano-sized pure metals and alloys such as SAC (tin-silver-copper).

Figure 1. Ultrasonic mixer / reactor (in batch mode).

Vapor Phase Synthesis

Plasma synthesis us one of the leading ways to produce powders from solution or other types of liquid feed – for example it is has been used to produce millions of tons of titanium dioxide pigment by reacting titanium tetrachloride in an oxygen flame. This microwave plasma torch can operate using a variety of gases or mixture of gases and is capable of pyrolyzing chemically prepared stoichiometric solutions to temperatures as high as 5000°K.

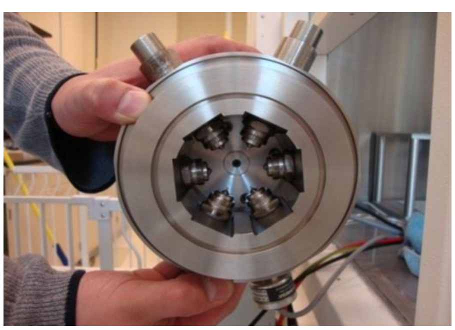

Figure 2. Plasma synthesis reaction chamber.

The carbon nanotube system is a laboratory sized catalyzed Chemical Vapor Deposition (CVD) system capable of enabling synthesis of single-walled and multi-walled carbon nanotubes. Carbon feedstock is provided from the decomposition of gases such as methane or ethylene while processing temperatures of 800°C - 1000°C for SWNT and 550°C - 750°C for MWNT encourage the growth of nanotubes on catalyst sites on the selected substrate. The unit is also capable of depositing graphene.

Figure 3. Carbon nanotube synthesis.

Drying

Where drying is unavoidable (normally it is preferable to supply wet material and to disperse nanomaterials from a solution or slurry form into the polymer, ink or other vehicle desired by the client) processes include conventional tray drying ovens plus an atmosphere-controlled spray drier and a freeze dryer. The spray dryer shown is an explosion proof (solvent-capable) system. Used primarily as a process tool for investigating new mixtures of binders, plasticizers, and chemistries, it is used with nanomaterials to create large (mm sized) flowable agglomerates of nanoparticles containing readily removable binders. This greatly facilitates normal ceramic or metal processing routes.

Figure 4. Spray dryer.

Freeze dried materials are formed by evaporating ice from slurries or frozen blocks under vacuum. This is especially useful for reactive mixtures or to shape materials into a mold with a polymer binder that will be removed in subsequent heat treatment.

Figure 5. Freeze dryer.

Thermal treatment

Conventional and microwave processing can be used to process powders, shapes and have even been used for thermal; treatment of electronic assemblies. Microwave processing in air, vacuum or inert gases can provide rapid heating and cooling of materials, avoiding long thermal soaks which can cause crystal growth and property degradation. Selective heating can be obtained, as can very high temperatures >1600°C.

Figure 5. Active and passive microwave ovens.

3. SYNTHESIS OF USEFUL NANOSTRUCTURES FOR PRINTED ELEXTRONICS

Three examples of this are from printed electronics; the processing of copper oxide nanomaterials by Novacentrix (www.novacentrix.com) to directly form additive circuits, the high speed-speed printing of silver inks at Clemson University's Sonoco Institute of Packaging Design and Graphics (http://sonocoinstitute.com/) presented at FlexTech 2012, and electrophoretic / transfer printing of nanomaterials at the NSF Center for High-Rate NanoManufacturing (http://www.northeastern.edu/chn/).

Novacentrix Conductive Copper Processing

Photo-initiated sintering of copper particles produces impressive densification in 5 milliseconds resulting in high quality conductors on substrates including PET and paper.

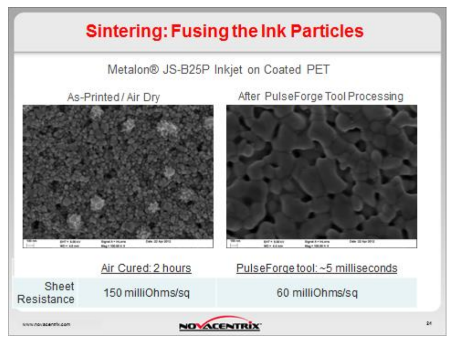

Figure 6. Sintered copper conductors on PET (courtesy Stan Farnsworth, Novacentrix)

This process does at last allow us to reach the long awaited goal of sub-5 cent RFID tags.

Flexographic Printing At Clemson University

An extensive designed experiment carried out by Dr. Bruce Kahn and the team at Clemson on the Omet Varyflex printing equipment, presented in detail at FlexTech 2012 (www.flextech.org) has revealed some surprising and favorable results. The printer is modular with 7 stations (flexure, gravure, rotary screen), can accommodate water, solvent and UV inks and can handle substrates 12-600 microns thick, up to 50cm wide and speeds up to 200m/min.

Results of the extensive designed experiments are impressive:

- High speed (200 m/min) and throughput (100 m^2/min)

- Inline complete curing (5 second residence time) at low temperature (120^{O} C)
- High conductivity (resistivity ~ 3X bulk Ag metal)
- Small feature sizes (<50 um wide, $\geq$ 80 nm thick)
- Increased performance (higher conductivity, larger aspect ratio, decreased sensitivity to anilox cell volume) with speed
- Practical application (transparent conductive grids)

Figure 7. Omet Varyflex 530 Press (Courtesy Bruce Kahn, Clemson University)

Electrophoretic Templating of Nanotube and Other Materials at the Center for High-Rate Nanomanufacturing.

Novel ways to develop circuits for sensor and other applications have been developed at the NSF Center for High-Rate Nanomanufacturing in Boston. Transfer printing and other techniques have been modified to produce circuit elements in a practical and reproducible way.

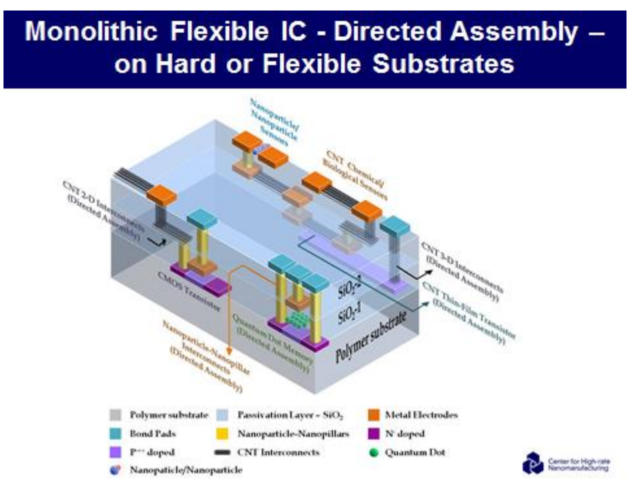

Figure 8. Functional Printed Device Schematic (Courtesy Ahmed Busnaina, Center for High Rate NanoManufacturing)

4. CONCLUSIONS

There are many ways to synthesize useful nanomaterials in a processable form and to form them into useful structures. As a result, we are starting to see practical applications in specific fields including printed electronics as well as more traditional fields such as catalysis and fillers for engineering polymers and elastomers.

Commercialization still presents challenges. The economic climate, the long qualification times at many stages in the supply chain and the sheer time taken to commercialize new markets mean that we are only seeing the most incremental products now, 10 years after the major investments in nanotechnology started worldwide. It may take another 5 years for the more disruptive opportunities, in sensors, electronic displays and medicine for example, to become mainstream.

5. ACKNOWLEDGEMENTS

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