Soft and Functional Materials

Multi-scale model-driven methodology for design of materials, processes, and devices

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TATA CONSULTANCY SERVICES

IN BRIEF

Materials play an important role in our day-to-day life across food, personal care, health care, or structural products. A majority of soft and functional materials are produced on an industrial scale and used routinely. However, several challenges are faced during the design and development of new products and delivery systems. We describe here TCS' research on modeling, simulation, and synthesis of soft and functional materials and their applications in energy storage and drug delivery.

Materials that can be easily deformed by thermal stress or fluctuations at room temperature are referred to as soft materials, for example, polymers, gels, colloids, granular materials, and most soft biological materials. Materials having native properties of their own like magnetism, piezoelectricity, ferroelectricity, or energy storage functions are referred to as functional materials, for example, ceramics, metals, polymers, and some organic molecules. While a majority of these soft and functional materials are produced on an industrial scale and used routinely, several challenges are faced during the design and development of new products and their delivery systems. A few such challenges are:

- Scaling up production of nanoparticles and their suspensions
- Coatings that can withstand high-temperature and high-pressure environments
- Controlled and targeted delivery of active molecules like drugs, fragrances, etc.
- Insilico testing of health and personal care products to avoid animal testing

Design and development of new products and delivery systems require extensive time, effort, and money. Modeling, simulation, and optimization can greatly help reduce development and testing time as well as cost to market. Since these materials are utilized in different forms in diverse applications, it becomes necessary to develop a multi-scale modeling approach, as depicted in Figure 1. For example, in the design of drug delivery devices like inhalers, it is necessary to understand the behavior of

Modeling, simulation, and optimization reduce time and cost to market in the development of new products

Fact File

TCS Research: Research and Innovation for Manufacturing and Engineering

Outcomes: Modeling frameworks for synthesis of nanoparticles and for design of drug release devices; Experimental protocols for synthesis of nanoparticles and nanofibers

Principal Investigator: Venkataramana Runkana

Academic Partners: IIT Kanpur, IIT Bombay

Techniques Used: Multi-scale Modeling; Model-based Optimization; Bench-scale Experiments

Industries Benefited: Chemicals, Materials, Semiconductors, Life Sciences

Patents: Filed–14; Granted–7

Papers: Journal articles–15; Conference papers–40

Synthesizing electrodes from materials that are stable in liquid electrolytes, higher energy densities can be achieved

molecules through molecular dynamics (MD) simulations. Information from these simulations is used to design particles or carriers for a drug molecule through population balance modeling (PBM). The flow of particles through the inhaler using discrete element modeling (DEM) and computational fluid dynamics (CFD) is then simulated for designing the device or the delivery system. Similarly, a multi-scale modeling approach is required not only for the design of equipment such as furnaces, but also for understanding their performance.

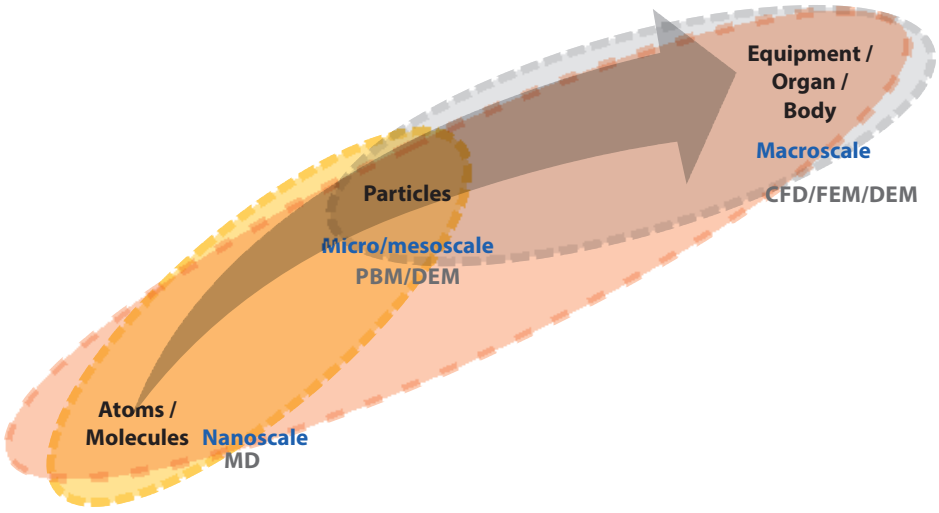

Figure 1: *Multi-scale modeling of materials, processes, and delivery systems*

Energy Storage and Functional Nanofibers

The demand for renewable energy sources calls for efficient and reliable electrochemical energy storage devices. Lithium-ion batteries and supercapacitors are the most assuring candidates. Supercapacitors are preferred over lithium-ion batteries in applications like electric and fuel cell vehicles, smart electric grids, pace makers, etc. as they acquire higher power density, faster charge/discharge times, and better cycling stability. Moreover, they are safe and environmentally friendly. However, they suffer from low-energy density which hinders their usefulness. One of the challenges is the development of electrode materials for supercapacitors with high-power and energy densities compared to batteries. Nanofibers are suitable for this, and electrospinning (see Figure 2) is probably the most convenient technique for producing nanofibers continuously.

In collaboration with Indian Institute of Technology, Kanpur, we have synthesized novel hierarchical nickel molybdate nanostructures, carbon–nickel molybdate (NM) composite nanofibers and nickel–zinc ferrite (NZF)–carbon nanotube (CNT)–carbon nanofiber (CNF) composites for making electrodes for supercapacitors.

- First, we synthesized solid, porous, and hollow nanofibers and microplates of NM. An asymmetric supercapacitor fabricated from hollow NM nanofibers had a high specific capacity of 175 C/g (at current density of 1 A/g) and a capacity retention of 97% after 5000 cycles. At this current density, the device delivers an energy density of 39 W-h/kg and a power density of 798 W/kg.

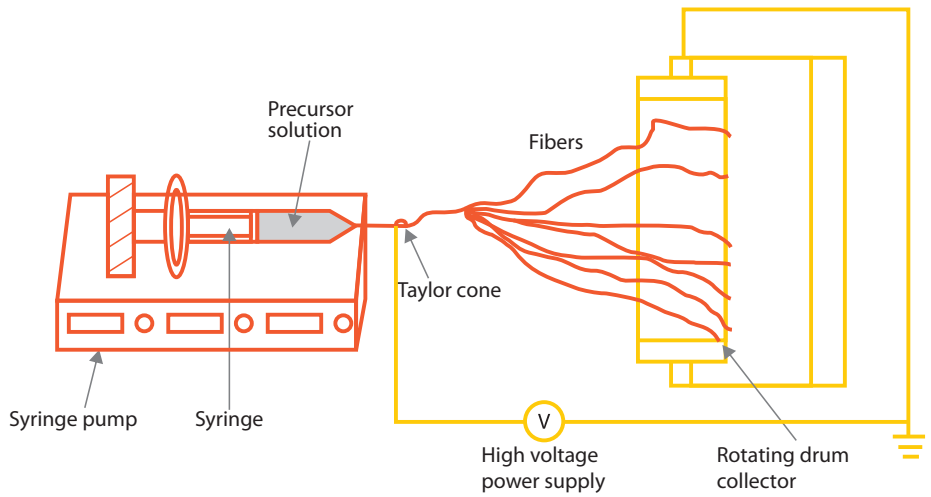

Figure 2: *Schematic of synthesis of nanofibers by electrospinning*

- Second, we synthesized four different electrospun composite nanostructures, with different ratios of NM to carbon. An asymmetric supercapacitor fabricated from a composite with 50 % wt NM had a specific capacity of 135 C/g (at current density of 1 A/gm) and a capacity retention of 92% after 3000 cycles.
- We have also synthesized a ternary nanocomposite consisting of NZF ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) nanoparticles and multi-walled carbon nanotubes (CNT) dispersed uniformly in hollow carbon nanofibers (HCNF). These NZF–HCNF–CNT composite nanofibers (with 30% weight of NZF) exhibited a specific capacity of 335 C/gm (at 1 A/g), much greater than pure NZF fibers (180 C/g) and hollow carbon nanofibers (96 C/gm). A capacity retention of 90% after 3000 cycles was achieved with these fibers, while pure NZF fibers had only 62%.

The practical application of our 50-NiMo-HCNF//AC asymmetric supercapacitor was shown by arranging three as-prepared supercapacitor cells in series and illuminating a red light emitting diode (LED). The superior performance of all these materials could be attributed to their mesoporous surface with high specific surface area (~105 m^2/g), the hollow core, and the interconnectedness of the fibers.

These electrodes can be used in electric vehicles for quick charging, engine start-up, and power bursts. The future challenge is to synthesize materials with improved surface properties so that energy density can be improved further. Generally, materials with abundance of mesopores (pore size ~2–50 nm) and nanopores (pore size ~2 nm) exhibit high specific capacity. However, controlling the pore size distribution is a challenge. An alternate way to increase energy density is to increase the working voltage of the electrolyte. We employed aqueous electrolytes which produced a maximum voltage of 1 V. Organic electrolytes and ionic liquid electrolytes can operate at higher voltages of 2 V and 3 V, respectively. By synthesizing electrodes from materials that are stable in these electrolytes, higher energy densities can be achieved. Hybrid storage devices made from supercapacitors and lithium-ion batteries are also promising since they produce higher levels of energy and power densities. Such devices can be assembled from electrodes that are fabricated from high-capacity battery materials and high-rate capacitive materials.

Nanomaterials: Model-based Production Processes

Nanostructured materials such as carbon black, metal oxides (titanium dioxide, fumed silica, ceria, zinc oxide, and alumina), and other high-purity materials (advanced ceramics, semiconductors, super alloys, and thin films) have diverse industrial applications in pigments, catalysts, and optical waveguides. The final product particle properties (size, shape, and distribution) determine the end application of a product. For example, nearly-uniform titanium dioxide particles are used for making paints and pigments, whereas aggregates of large nanoparticles are required for optical fibers. Despite their widespread application, control and optimization of the final product particle properties and large-scale production of nanoparticles is still a major challenge. Both liquid phase (sol-gel, coprecipitation, microemulsions, hydrothermal synthesis, etc.) and gas phase (aerosol flame synthesis, laser ablation, and electrospray synthesis) methods have been successfully demonstrated on a laboratory scale to produce diverse nanomaterials. However, these methods are not yet completely viable on a commercial scale owing to the difficulty in scaling up these processes.

We have established bench-scale facilities in our laboratories to produce nanoparticles of titania, ceria, silica, etc. through both liquid phase (hydrothermal) and gas phase (flame aerosol) synthesis methods, and developed a comprehensive modeling framework, combining computational fluid dynamics, population balance modeling, thermodynamics, and reaction kinetics, for process design and for scale-up (see Figure 3).

Development of novel materials such as core-shell metal complexes (ceria/titania, ceria/silica, Pt/titania, Pt/silica, etc) with relatively inexpensive precursors; design and development of novel methods to produce these materials on large scale are key challenges in this field. Model-based design and development, in conjunction with data from laboratory experimental studies, plays an important role in enabling the production of novel nanomaterials.

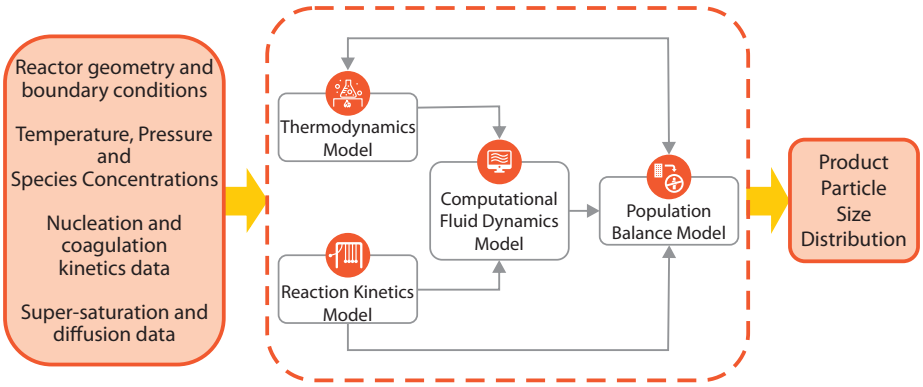

Figure 3: *Comprehensive mathematical modeling framework for nanoparticle production*

Drug Delivery Systems

The design and development of smart materials is an important and emerging field that is expected to have far-reaching implications in health care, especially as drug carriers, medical implants, artificial organs, and so on. Traditional carriers of drug molecules result in limited drug efficacy, undesirable temporal changes in drug concentration, and patient noncompliance. Polymeric systems such as biodegradable particles, stimuli-responsive hydrogels, and fibers have been identified to possess desirable properties that can provide targeted and controlled drug release. Designing these novel drug carriers is a challenge since selecting the correct polymer or polymer blend, functional agent, quantity, in addition to the carrier's shape and dimension, is critical.

Oral drug delivery is considered the most preferred method of patient compliance. We have devised a model-driven approach to design pH-sensitive hydrogels for oral delivery as illustrated in Figure 4. Our mechanistic model estimates the charge distribution of the hydrogel, its deformation in response to swelling pressure and elastic forces exerted by the elastic nature of cross-linking molecules, and migration of ions and drug in response to changes in environmental condition. The model was parameterized in terms of experimentally tunable formulation parameters such as cross-linking ratio, dimensions of hydrogel, and polymer concentration to enable its use as an in silico experimentation tool. The strategy was also extended for design of glucose-sensitive hydrogels.

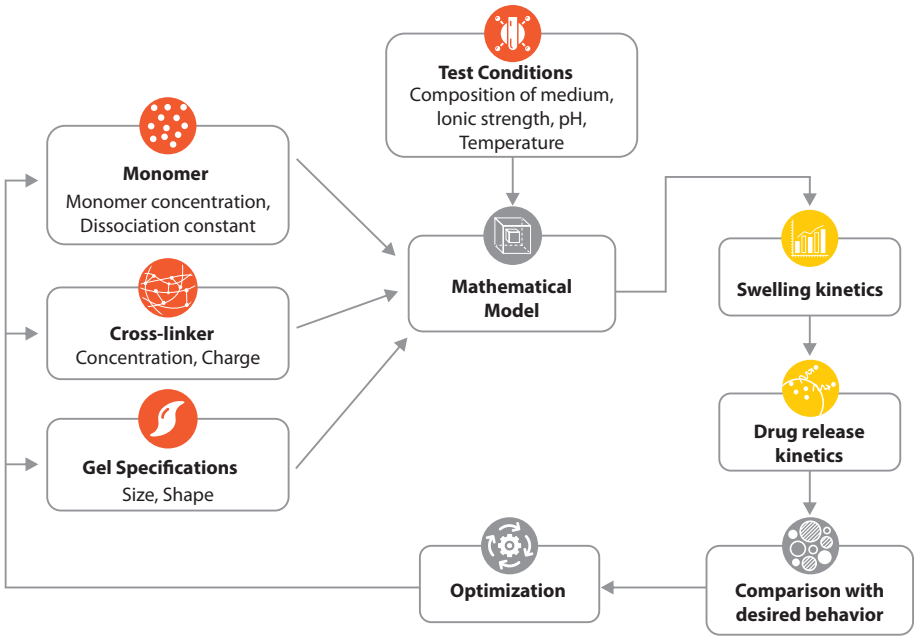

Figure 4: *Model driven methodology to design stimuli-sensitive polymer hydrogels or particles*

Looking into the Future

The long-term need is the development of an integrated knowledge-based platform that could be employed by researchers as well as practitioners for designing and developing new processes, functional materials, and novel delivery systems for applications in health care, foods, cosmetics, and agrochemicals. Here, we articulate our thoughts and ideas on the development of such a platform, for example, the design and development of materials and delivery systems for health care.

A major challenge for the pharmaceutical industry is designing delivery systems for proteins and peptides and their corresponding drug formulation. The drug pre-formulation process requires the characterization of a drug's physical, chemical, and mechanical properties so as to choose what other ingredients (known as excipients) should be used in the preparation. In protein pre-formulation, the important aspect is to understand the solution behavior of a given protein under a wide range of stress conditions such as freeze/thaw, temperature, shear

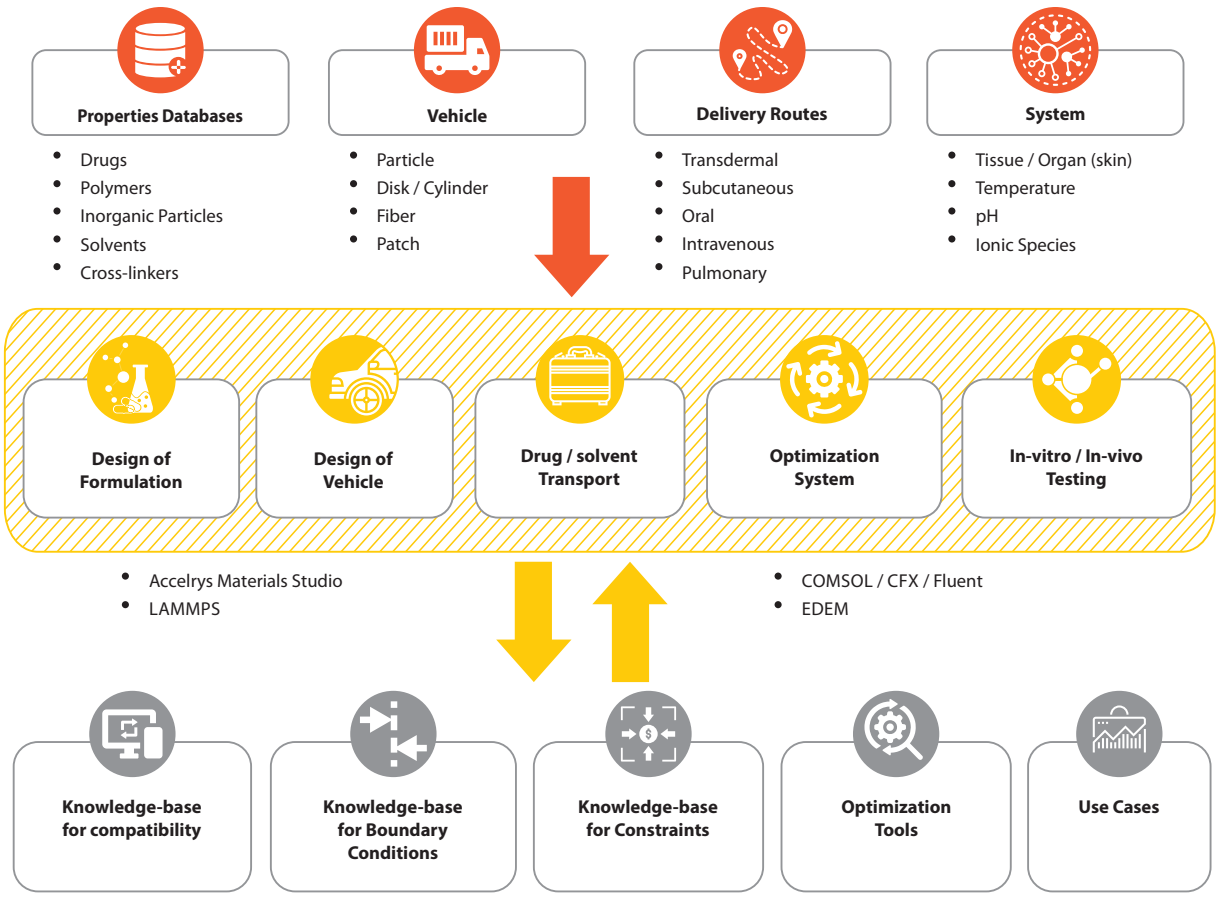

Figure 5: *Framework for an integrated, knowledge-based design and development platform for creating soft, functional materials and their delivery systems in healthcare*

stress, mechanisms of degradation, and therefore its mitigation. It is also necessary to consider factors such as particle size, polymorphism, pH, and solubility, as all of these can influence bioavailability and hence the activity of a drug. The drug formulation and its carrier depend on the drug and its properties, properties of the potential carrier, delivery route, and disease, among other factors.

While design of formulations is carried out using software tools such as Materials Studio, computational fluid dynamics software tools such as Fluent and COMSOL are utilized for undertaking release simulations. However, these activities are carried out independently and are not solved in a coupled or integrated manner. Simulations related to drug formulation, drug release, and in vitro or in vivo testing require modeling at multiple levels of scale, starting all the way from atomistic simulations at the nanoscale to the drug transport at the macro-scale. The framework for such an integrated knowledge-based platform with multi-scale modeling capabilities is depicted in Figure 5, which addresses some of the challenges mentioned above, taking into account the necessary inputs, for the design and development of soft and functional materials and their delivery systems or devices.

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Venkataramana Runkana is a Chief Scientist at TCS Research and Innovation and heads the Research Programme for Manufacturing & Engineering and Industrial Services Business Units in TCS. He has more than 27 years of experience in process modeling, simulation, and optimization, advanced data analytics and digital twins, process development, scale-up and design, nanomaterials and drug delivery systems. Venkat received the TCS Distinguished Scientist Award in 2014 and was an AICTE - INAE Distinguished Visiting Professor at IIT Kanpur during 2013–2018. He is a chemical engineer and holds a Ph.D. from Columbia University, New York.

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