Automated, Continuous Flow Reactor for the Mass Production of Photoluminescent Nanoparticles

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ABSTRACT

We demonstrate a fully automated, continuous flow process design for the mass production of photoluminescent nanoparticles. The design comprises advanced glass reactors which not only provide good mixing and good heat transfer during the entire reaction interval, but also allow on-line spectroscopic characterization from the radiation transparent reactor surface, without intruding into the reaction media. In addition to these unique features, the process possesses state of the art properties of recent flow reactor designs such as consecutive production line segments on which different reaction parameters can be applied. All the monitoring equipment, pumps, valves, thermostats, and etc. are computer controlled, so that, the characterization data can be used effectively to self-optimize the final product properties in an automated fashion.

Keywords: flow reactor, photoluminescent nanoparticle, quantum dot, automation

1 INTRODUCTION

Batch and flow reactors are two most common production methods employed widely in various chemical industries. The main advantage of flow reaction systems over batch reactors is the continuous production capability. Besides, particularly for the production of fine chemicals where efficient mass and heat transfer is crucial for homogenous reaction kinetics, flow reactor channels offer much to improve product quality without altering the production capacity in comparison to bulky batch systems. As an example to fine chemicals production, nanoparticle synthesis require good reaction kinetics control since small differences in elemental composition and particle geometry may have drastic effects on overall product properties. Accordingly, in the past 15 years, a number of efforts has been showed for developing flow reactor technologies which are suitable for mass production of nanoparticles with a feasible "scaling up without drawbacks in the product quality" perspective.

Flow reactors also offer various flexibilities for better process designs. One of the popular applications is separating the production line into different reaction segments, for instance, employing different heating regions for particle nucleation, growth and shell/coating addition step for a core/shell nanoparticle, a quenching step for stabilizing the final particles, and etc. To control the final product quality, spectroscopic characterization is required during or after each reaction step so that appropriate actions can be taken accordingly. Most of the time, employment of flow cells are required for this purpose since the polymeric or metal tubings used widely as reaction platforms in conventional flow reactors are either opaque or slightly transparent for in-line spectroscopic characterization. These flow cells are likely to lead to formation of dead volumes in the production line and have the risk of introducing regular product contaminations and quality control problems. To overcome these drawbacks, we have developed a process that makes use of glass reaction modules which are radiation transparent, and also have non-linear channel geometries which provide good mixing and good heat transfer during the entire reaction interval.

2 THE PRODUCTION PROCESS

2.1 Precursor System

Most nanoparticle productions comprise the reaction of precursors, which possess the main particle forming elements. The precursors, whether formed by a simple dissolution in the solvent, or after a chemical reaction such as complex formation with ligands, require a preparation step performed – most of the time – under inert atmosphere, before dosing into the flow reactor. To maintain the continuity of the production, we use a two heated-stirred vessel system, one is employed as a batch reactor for the preparation of the precursors and the other functions as a tank from which the precursors are pumped into the reactor. Vessels are connected to each other with a transfer pump, so that ready-to-use precursor can be transferred into the tank under inert atmosphere to maintain a minimum precursor level and used readily for the production. Accordingly, precursor preparation and dosing to the reactor can be performed simultaneously, without halting the continuous production.

2.2 Flow Reactor

For the production of fine nanoparticles having narrow particle size distribution, fast nucleation followed by a slower growth might be necessary, in most cases. From a quantity point of view, the completion of these reaction intervals must be sufficiently fast to provide a high production capacity for a kinetically fixed residence time in a mechanically fixed reactor volume (basically, flow rate equals reactor volume divided by residence time). From a

quality point of view, a good kinetic control is necessary to achieve product properties such as narrow particle size distribution at a desired average particle size. To achieve an optimization between quality and quantity for a nanoparticle production, the flow reactor must provide:

1. Efficient heat transfer
2. Good mixing

Efficiency of heat transfer is already crucial for highly endothermic or exothermic reactions. It is also very important for the reactions where instant temperature change is necessary between consecutive production line segments. An example to this case is application of a relatively low temperature for slow particle growth after a nucleation at high temperature. The efficiency of the heat transfer depends on both flow reactor design parameters such as the dimensions of the flow channels and the heat exchange surface area, and reactor material properties such as heat transfer coefficient.

Mixing quality is important for both higher production yields and achieving desired product qualities, and mostly depends on the reaction channel geometry for a given flow rate. Geometries which lead to plug flow inside the channels provide high levels of mixing. Particularly for reactions having short completion times (i.e. low residence time), each plug can be considered as separate continuously stirred tank reactors in which mixing quality becomes crucial even in the very early segments of the channel where the precursors first meet and start reacting.

In our system, we use Corning advanced glass flow reactors which have all the characteristics mentioned above.

2.3 Dosing Line

Transfer of the precursors into the flow reactor is also important particularly for highly reactive precursor species and reactions having fast kinetics. For such reactions, metering pumps which provide smooth material transfer with minimum pulsation (periodic change in flow rate due to the necessity of a suction state between two injection states) must be preferred since the pulsation frequency might lead to stoichiometry gradients in the very first plugs, where the particle nucleation might start depending on the reaction kinetics. Piston, HPLC, diaphragm and peristaltic pumps are known to have considerable pulsation levels, compared to annular gear pumps which have relatively low pulsation levels, or to syringe pumps with no pulsation at all (but inappropriate or less feasible for continuous production). Multiple head pumps are good candidates for reduced pulsation levels but may not be a cost efficient choice. Or one must consider using pulsation dampers in order to overcome the disadvantages of the corresponding pump technologies.

In addition to pulseless pumping, employment of mass flowmeters might also be critical for precise dosing of the precursors, since, for instance, even small levels of clogging in flow reactor channels (which have millimeter scale diameters) can lead to serious variations in pressure, which affects the precision of the volumetric dosing rates, thus the stoichiometric ratios and overall residence time. Whereas, a metering pump coupled with a mass flowmeter can demonstrate quite feasible and accurate dosing performances.

2.4 On-line Characterization

In flow reactor systems, on-line characterization of the flowing media is generally performed via flow cells, since the polymeric or metal tubings used commonly as reaction platforms in conventional flow reactors are either opaque or slightly transparent for on-line spectroscopic characterization. In our productions system, the advantage of using glass flow reactors is that they allow spectroscopic characterization from the outer surface of the reaction channels, by using optical fiber probes for transmitting light between the spectrometer and the sample (flowing media), corresponding to excitation of and emission from the photoluminescent nanoparticles. Accordingly, the location of the measurement point can be changed easily, like a medical doctor examining the patient with a stethoscope. The capability to easily collect data from various points on the reactor can provide very effective reaction kinetics studies; for instance, plenty of data corresponding to particle growth and nucleation separately can be collected and processed. Those data then can be used for achieving a better product quality through an intense optimization mechanism dealing (also) with intermediate particles within the production line (i.e. reaction channels), in contrast to self-optimizations performed according to the final properties of the product coming out of the flow reactor.

2.5 Processing of Characterization Data

The spectroscopic data corresponding to the emitted light from the photoluminescent nanoparticles are used by the automation system for two main purposes in our reactor systems:

1. To auto-optimize the product
2. To auto-decide between product and waste

For photoluminescent nanoparticles, product quality is considered mainly in terms of optical properties, such as average emission wavelength, full width at half maximum and the intensity of the emission. A computer software control loop feedback (i.e. PID) mechanism can automatically optimize the desired particle property by changing the process parameters according to predefined commands derived from kinetic trends from theoretical and experimental data.

In our system, the PID mechanism also have an algorithm to be able to decide between the product or waste; such that, change in parameters leads to a change in one of the spectroscopic data, for example in average emission wavelength, and this change continues until a steady state is achieved, characterized by a constant value versus time in the corresponding parameter. The automation

system collects the output as product if the steady state corresponds to the desired product property, and disposed it as waste for all other conditions. In addition, when multiple production recipes are run consecutively for the production of different particles of same elemental composition, the automation system can also perform such a production plan and collect different desired products separately.

3 CONCLUSION

Although new features introduce various useful options to a process design, they also bring about new challenges in terms of process control. Recent flow reactor systems introduced with computer control still leave many gaps in terms of automation since most decisions are left to operator. The superiority of our process is that all the monitoring equipments, pumps, valves, thermostats, and etc. work in coordination to realize a complex production plan of multiple recipes by self-optimizing each final product using strong characterization data from an effective on-line characterization system. Our unique approach in fully automated, continuous flow process design would bring new aspects to nanoparticle mass production.