

Structure controlling and process scale-up in the fabrication of nanomaterials

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Abstract Nanotechnology is already having a significant commercial impact, and will very certainly have a much greater impact in the future. The research on process engineering and scale-up will be very important for the commercial production and application of nanomaterials, because the properties and structure of nanomaterials are not only determined by the nucleation and growth process, but also strongly affected by the engineering properties, such as the mixing, the heat and mass transfer, and also the distribution of temperature, concentration, etc. This paper will present some research work in our laboratory on the fabrication of nanomaterials. Based on the chemical engineering principle and methods, many kinds of novel nanomaterials can be synthesized and their structure can be easily controlled through adjusting the parameters of the fluid mixing, and the distribution of temperature, residence time and concentration, etc. By using the micro-mixing, heat and mass transfer and reaction control methods, the host-guest nanocomposites have been assembled and assumed as the novel electroanalytical sensing nanobio-composite materials. Based on the principles of chemical engineering, the manufacturing technologies for magnetic powders, calcium carbonate, and titanium dioxide have been developed for commercial-scale production, and the largest production scale has reached 15 kt/year.

Keywords nanomaterials, assembly, structure controlling, scale-up, engineering properties

1 Introduction

Nanotechnology is concerned with the development and utilization of structures and devices with organizational features at the intermediate scale between individual molecules and about 100 nm where novel properties occur as compared to bulk materials. As a broad and interdisciplinary area of research and development activity, nanotechnology has been growing explosively worldwide in recent years. With the development of nanotechnology, potential revolution will be founded in the way materials and products are created, and the range and nature of functionalities can be accessed in the near future¹⁾. As an essential component of nanotechnology, nanomaterials have displayed comprehensive application in microelectronics, biology, medicine, etc. The critical control points of nanomaterials are the size and composition of the nanocluster composites, the interfaces and distributions of the nanocomponents. In recent years, the synthesis of nanomaterials witnessed a breakthrough, which developed from the simple synthesis and characterization in the design and control of structure at the nanoscale as well as forming the nanocomposites with a specific structure through assembly or other methods²⁾. However, for meeting commercial applications, scale-up production of nanomaterials is of great interest. The National Science and Technology Council of the US pointed out that the engineering magnification and process control of nanomaterials preparation and application is the key issue to be solved in the future³⁾. The chemistry discipline focuses on the research of the material synthesis and control at the micro-scale such as the molecular and atomic level, whereas the traditional chemical engineering discipline pays more attention to the macro-characteristics of the

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- 1) Committee on Technology of National Science and Technology Council, National Nanotechnology Initiative: Leading to the Next Industrial Revolution. February 2000, Washington DC, USA
- 2) Siegel R W, Hu E, Roco M C. Nanostructure Science and Technology, A World Wide Study, IWGN report. National Science and Technology Council, 1997
- 3) Siegel R W, Hu E, Roco M C. R&D Status and Trends in Nanoparticles, Nanostructured Materials and Nanodevices in the United States, January 1998

preparation processes. The fabrication of nanomaterials belongs to the mesoscopic field between the micro and macro scale. The president of the European Federation of Chemical Engineering, Professor Charpentier, indicated that multiscale controlling is the development direction of chemistry and process engineering in the future, and nanomaterials processing and structure control are the very important issues in chemical engineering [1]. The Key Laboratory for Ultrafine Materials of the Ministry of Education of East China University of Science and Technology has long been engaged in the research on crystal growth principles, how to control the material structure, as well as the scale-up regulations of the nanomaterial fabrication process for many novel nanomaterials.

2 Synthesis and structure control of nanomaterials

The major efforts in the chemical synthesis of nanomaterials can be grouped into two broad areas: gas phase synthesis and sol-gel processing. Nanomaterials with different morphologies and structures have been processed by both gas phase and sol-gel technologies. Metals, metal oxides, metal carbides and metal nitrides, and their composite nanoparticles were manufactured by chemical vapor synthesis [2–5], microwave plasma [6] and radio frequency plasma [7] chemical vapor deposition. Nano-sized metallic particles like Cu, Ag, Cr, Fe-Cr-V, etc., were synthesized by chemical reduction in liquid phase [8]. In the past few years, magnetic metal oxide nanoparticles and calcium carbonate nanoparticles with different structure and morphology synthesized by precipitation had been manufactured in commercial processes.

Because the application properties are determined mainly by the composition and structure of nanomaterials, the key in nanomaterial preparation is to control the scale, composition and structure of their basic unit and the interface characteristics and component distribution of the materials elements. At present, people generally use templates to control the structure and morphology of the nanomaterials. It would be very interesting to prepare

nanomaterials with a novel structure based on the chemical engineering principle and methods. Novel metal oxide nanomaterials, for example, nanoparticles [9–12], nanotubes [13,14], nanofibers [15], hollow nanostructured microspheres [16,17], and also core-shell nanocomposites [18] have been prepared by gas flame combustion through adjusting the parameters of fluid mixing, flame temperature and the residence time distribution. Figure 1 shows the nanomaterials that have been synthesized by gas flame combustion. By changing the feeding position, $\text{TiO}_2/\text{SiO}_2$ nanocomposite particles were prepared in premixed flame in the form of dispersing structure of TiO_2 nanocrystals depositing in amorphous SiO_2 matrix and core/shell structure of TiO_2 nanoparticles encapsulated by amorphous SiO_2 [18,19]. Based on the Joule-Thomson throttle cooling and high speed jet entrainment phenomena in the multi-jet reactor, novel $\gamma\text{-Al}_2\text{O}_3$ hollow nanospheres as well as $\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{Al}_2\text{O}_3/\text{SiO}_2$ hollow nanocomposites were successfully prepared; the particle size of these hollow nanostructures was in the range of 100–200 nm and the shell about 10–30 nm [17]. The formation mechanism of such hollow nanostructures conforms to the one-droplet-to-one-particle theory (ODOP), where hydrolysis and nucleation occur on the surface of the droplet when the surface concentration of the droplet is greater than the critical degree of super-saturation and its inner concentration is less than equilibrium concentration.

By the micro-area mass transfer and reaction control, a variety of novel nanostructure materials have been fabricated without any organic templates [20–25]. The hollow and solid ZnS nanospheres were synthesized by refluxing the aqueous solution of the reagents using thioacetamide (TAA) as a S^{2-} source with the temperature held at 103°C (Fig. 2) [20]. The spherical morphology has been formed through the oriented aggregation of the formed ZnS primary nanocrystals, and the morphology and size of the samples can be tuned easily by adjusting the experimental parameters properly. The probable reaction process for the formation of ZnS nanospheres can be summarized as Fig. 3.

Based on the same reactions, the MWCNT/ZnS heterostructures (Fig. 4) were synthesized by a mild solution-chemical reaction using TAA and $\text{Zn}(\text{CH}_3\text{COO})_2$

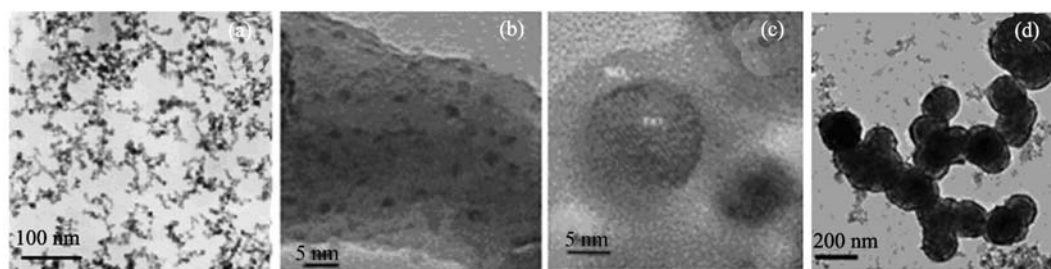


Fig. 1 Nanomaterials synthesized by gas flame combustion

(a) chain like aggregates of TiO_2 nanoparticles; (b) $\text{TiO}_2/\text{SiO}_2$ composites with dispersion structure; (c) $\text{TiO}_2/\text{SiO}_2$ composites with core-shell structure; (d) ball-in-shell structured TiO_2 nanomaterials

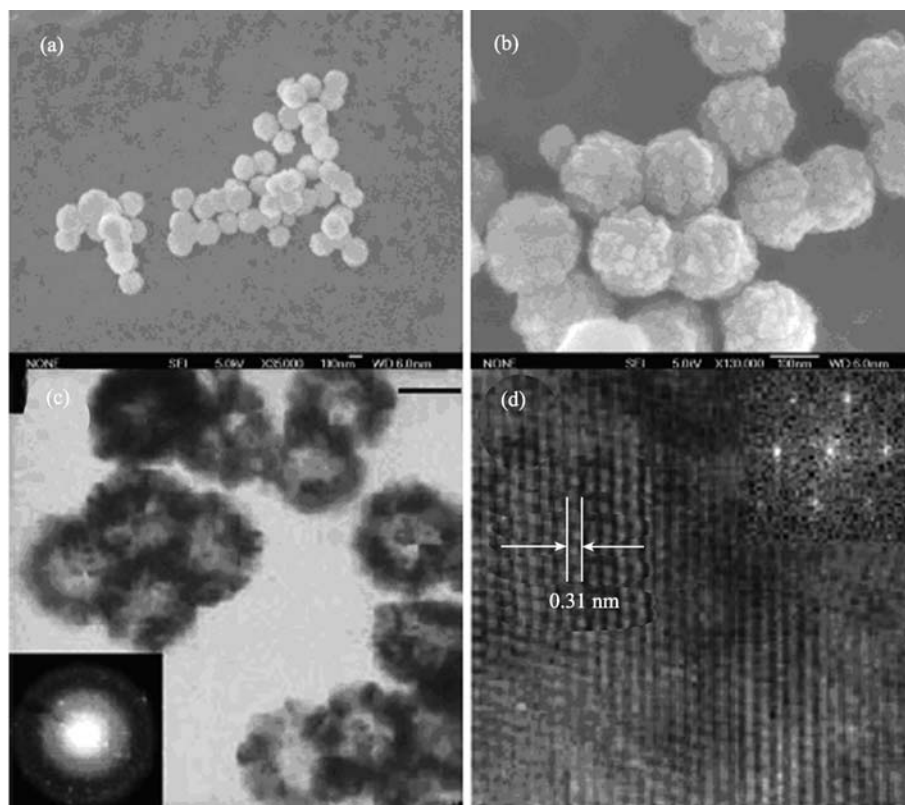


Fig. 2 SEM images of the hollow spheres (a, b); TEM images of the hollow and solid ZnS spheres (c), inset part is the corresponding ED pattern; HRTEM images of the hollow and solid sphere (d), inset part is the corresponding fast Fourier transform (FFT) pattern. The bar is 100 nm

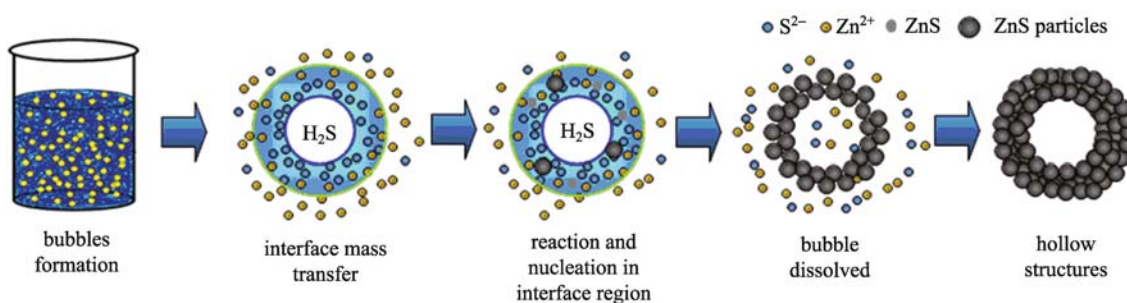
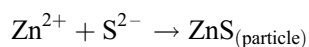
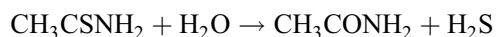


Fig. 3 Formation process for ZnS hollow spheres

as S^{2-} and Zn^{2+} sources, respectively, as well as using MWCNT as a substrate [21]. In comparison with previous studies on metal-sulfide nanoparticles, the probable reaction process for the formation of MWCNT/ZnS heterostructures can be summarized as follows.



Under the experimental conditions, the positive metal ions Zn^{2+} can be first adsorbed onto the surface of MWCNTs because of electrostatic attraction. The immobilization of Zn^{2+} ions allows heterogeneous nucleation along with the release of S^{2-} from TAA at elevated temperatures, which can be catalytic toward the decomposition of TAA, leading to the formation of primary ZnS particles around the sites. Such special structures may enrich the family of 1D nanomaterials and represent good candidates for further applications.

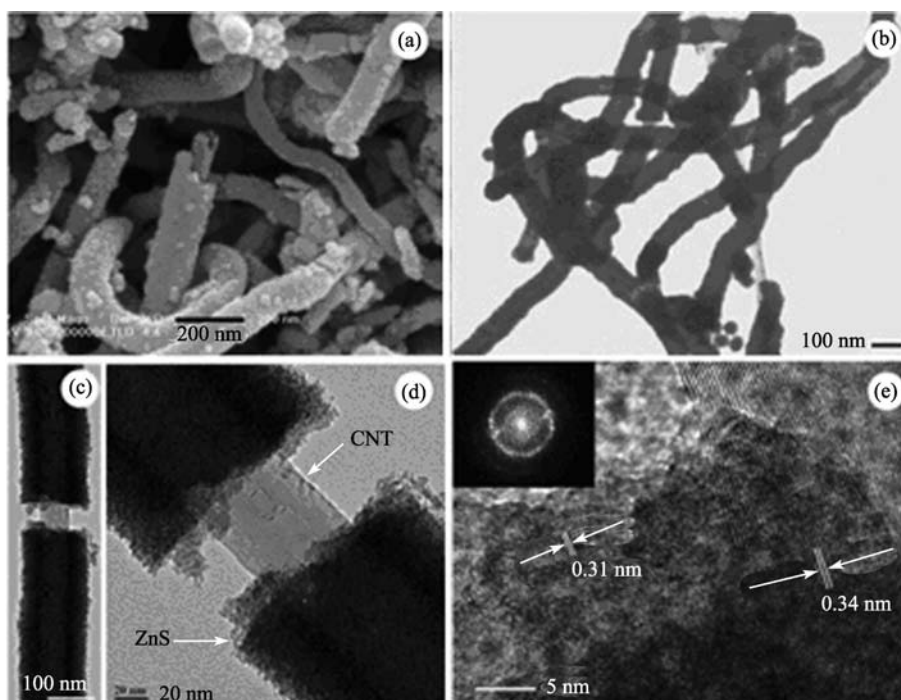


Fig. 4 SEM and TEM images of the formed MWCNT/ZnS heterostructures (a,b); selected high-magnification TEM images of the MWCNT/ZnS heterostructures exhibiting a discrete ZnS layer (c,d); HRTEM image of the formed MWCNT/ZnS heterostructures (e), inset part is the corresponding processed FFT

3 Confined assembly and application of nanocomposites

The confined reaction assembly of nanostructures in nanotube, mesoporous channel and dendrimer packaging has had great significance in recent years. The structure of the host-guest nanocomposites are determined not only by the nucleation and growth process, but also by the mixing, reaction and transmission characteristics in the micro-district. By using micro-mixing, heat and mass transfer and reaction control methods, many kinds of nanostructures have been assembled recently. For example, a nanoreactor has been built by using nanotube and synthesized carbon nanotube packaging Mg_3N_2/Ga semiconductor-metal heterojunction nanowire through carbonthermal reduction of MgB_2 and Ga_2O_3 [26], which is expected to be applied in electron-beam and temperature sensors, etc.

Because of their regular adjustable nanoporous structure, mesoporous materials can be used as a micro-reactor and provide the possibility for the preparation of the host-guest nanostructured composites, as well as facilitate the assembly of nanocluster materials into porous materials. For the preparation of the host-guest nanostructured composites, the intensification of mass transfer in the pores is very important because it is mainly the rate-controlling step of the assembly process. Through electrochemical synthesis, low-temperature chemical reaction, sensor technology, layers of electrostatic self-

assembly technology, and other physical chemical methods we successfully prepared magnetic composite microspheres, compound semiconductor fluorescent microspheres, flavor prolonged-release composite microspheres and fixed-peroxidase complex [27–33]. Figure 5 shows the process for the assembly of CdSe nanocrystals (NCs) in the pores of mesoporous silica (MS); the expanding of the pore size and the intensification of the mass transfer in the pores are very important for the assembly process. The semiconductor materials of CdSe nanocrystals (NCs) with an approximate diameter from 5.0 to 10 nm were synthesized in the pores of mesoporous silica (MS) through direct reaction between Cd ions and selenosulfate solution at low temperature (from -10°C to room temperature) [29]. By producing the electrostatic interactions between Cd^{2+} and negatively charged silica substrates, it could direct the assembly of nanoparticles inside the pore of MS spheres (CdSe/MS) with the purpose of creating functional composite semiconductor materials applied in the biological field.

There has been particular interest in materials where the conducting polymer is confined in the channels of the mesoporous host to produce novel structures, even on the molecular level. Encapsulation of the conducting polymer can improve the mechanical, thermal, and chemical stabilities of the assemblies, and possibly allowing individual molecular wires to be addressed. The semi-conducting polypyrrole was incorporated in the channels

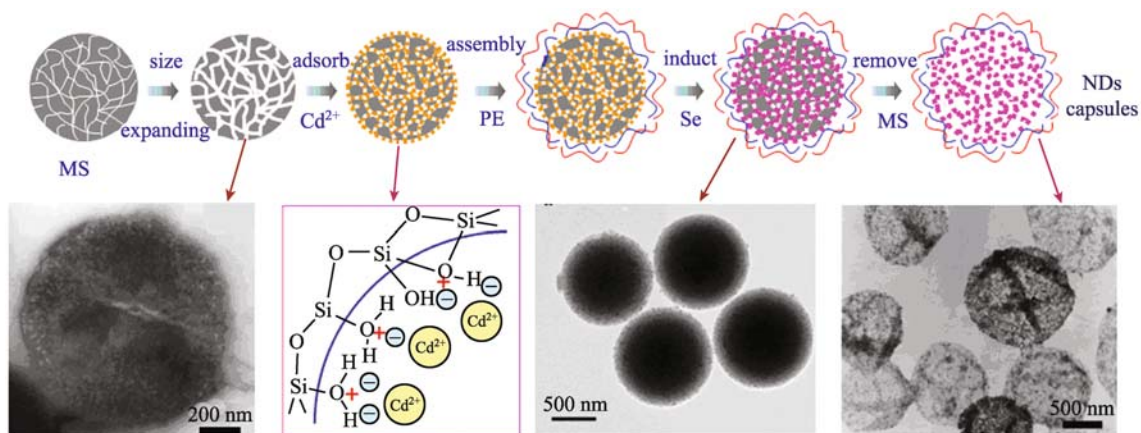


Fig. 5 Assembly process of CdSe in the pores of mesoporous silica

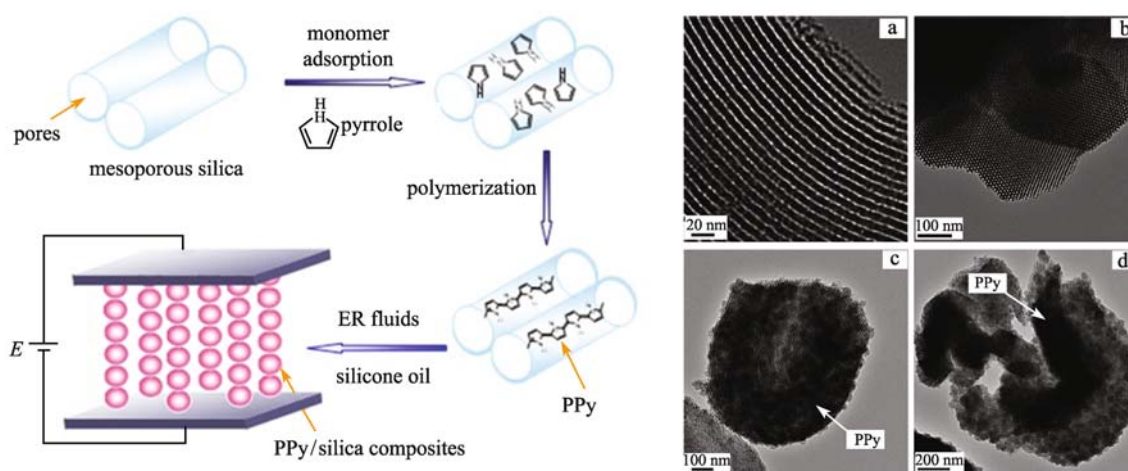


Fig. 6 Preparation process and HRTEM photograph of PPy/MCM-41 nanocomposites

of mesoporous silica by adsorption of pyrrole gas and subsequent oxidative polymerization using MCM-41 and SBA-15 hosts [34–36]. PPy confined in the channels was confirmed by different experiment techniques, and the basic characteristics of mesoporous materials are retained after incorporation of PPy and the structure of the channels is not destroyed (Fig. 6). However, encapsulated PPy in the channels significantly affects the structural properties of the hosts and specific surface area, pore size and pore volume of the hosts decrease to a certain extent. The amount of PPy loading increases with reaction temperature and much more amount of PPy is obtained in SBA-15 than in MCM-41 at the same temperature. It is worth noting that the conductivity of the mesoporous composite is lower than that of bulk PPy by 7 or 8 orders of magnitude.

Dendrimers are roughly spherical in shape, highly functionalized, sterically crowded on the exterior, and somewhat hollow in the interior. They can form nanosized particles with well-defined composition, structure and thickness. Partially quaternized poly(amidoamine)

(PAMAM) dendrimer having both quaternary ammonium groups and primary amines can be used as a polymeric template reservoir to prepare stable dendrimer-encapsulated nanoparticles. By using dendrimers as both monodisperse templates and stabilizers, many metal nanocrystals had been prepared by the confined reduction. Dendrimer encapsulated Pt nanoparticles with uniform size have been synthesized in our laboratory which assumed as the novel electroanalytical sensing nanobiocomposite material [37–45]. Figure 7 gives the assembly process and the dendrimer encapsulated Pt nanoparticles. Well dispersed Pt nanoparticles are formed by the method. The sensitive enzymed-based biosensor for glucose were obtained by introducing dendrimer encapsulated Pt nanoparticles via a layer-by-layer assembly method, the free amine groups located on each poly(amidoamine) dendrimer molecule were exploited to covalently attach enzyme to the dendrimer chains using carbodiimide coupling. The resultant enzyme electrodes have excellent sensitivity, limit of detection, linear response range to

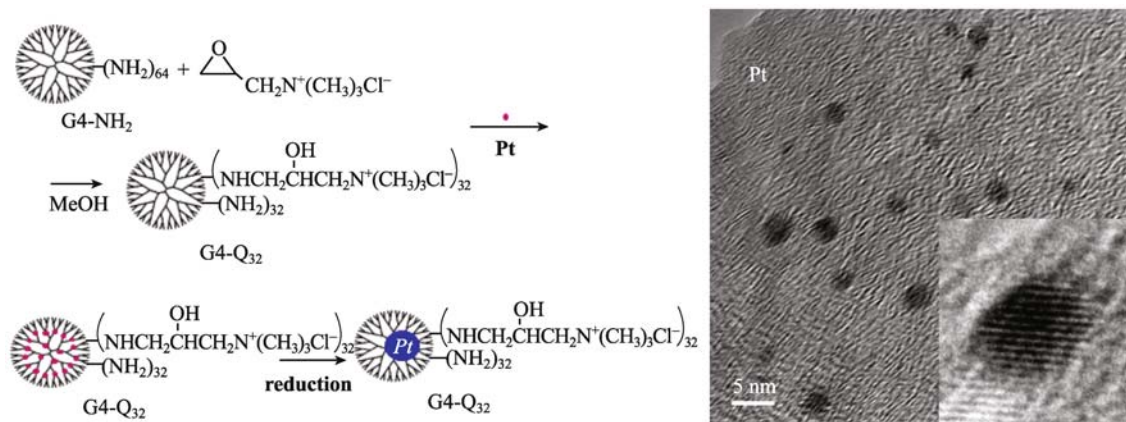


Fig. 7 Preparation process and HRTEM photograph of Pt nanodots in PAMAM dendrimer

glucose, fast response time and good reproducibility [44]. By electropolymerization of pyrrole onto glassy carbon electrodes, the (GLDH/Pt-DENs)_n/CNTs/Ppy hybrid film was obtained which showed a high electrocatalytic ability toward the oxidation of glutamate [39,40]. The sensitivities, and stabilities determined experimentally have demonstrated the potential of dendrimer encapsulated Pt nanoparticles as a novel candidate for enzymatic glucose biosensors.

4 Scale-up and manufacture technology

Nanomaterials synthesized at high rates have been a major research objective in the last few years. In order to ensure that the properties of nanomaterials synthesized in larger scale reactors are the same as nanomaterials synthesized in the laboratory reactors, fundamental transport mechanisms for mass, momentum and heat will require further investigation in order to understand the differences of nanomaterials formation at different reactors. The research work should include basic aspects of multiphase transport processes, such as interaction between phases, rheology, particle settling and fluidization, mixing and segregation, and then move to aerosol or colloidal reactors. The mixing properties, rheological behavior, and mass transfer properties for nanomaterials synthesis by chemical reaction in liquid phase were studied based on the three-phase system of nanosized acicular FeOOH and CaCO₃ [46–48]. Also, the engineering characteristics during the preparation of nanoparticles based on the fluidization chemical vapor deposition processes and the combustion processes of nanomaterials were studied [17,19,49,50].

Nanomaterials are formed through chemical reaction, nucleation and growth. The relative rates in the processes mainly determine the properties of the products. Mixing and mass transfer have a significant impact on chemical reaction rate. The morphologies of nanomaterials are also affected by rheological activities by changing the mixing

and mass transfer. On the other hand, if the reactors are scaled up, the concentration and temperature fields in the larger scale equipment should be controlled to be the same as in the smaller scale equipment. This has been proved in the process for preparing goethite nanoparticles by three-phase oxidation of ferrous hydroxide slurry [46]. Our studies indicated that the reaction slurries displayed strong shear-thinning behavior, which can be fitted to the power law equation at the middle-later stages, and these slurries processed yield stress at quietus but without thixotropy. The rheological behaviors of the reaction slurries were mainly caused by the formation mechanism and the morphology change of solid particles in the reaction slurries. The apparent reaction rates were limited by the rates of mass-transfer of oxygen into the liquids, which were strongly affected by the rheological behavior of the reaction slurries. The synthesis process for goethite was an oxygen transfer controlling process which can be scaled up according to the equal reaction rate. In the preparation processes of nanosized calcium carbonate, there may exist two mechanisms in its fast reaction: CO₂ absorption control and Ca(OH)₂ solution control [47,48]. In order to prepare nanoparticles with uniform and narrow distribution, Ca(OH)₂ solution should be controlled at the initial reaction stage with the reaction temperature increase, Ca(OH)₂ solution control disappear and turn into CO₂ absorption control completely. In our laboratory, the manufacturing technologies for aciculate γ -Fe₂O₃ nanoparticles, calcium carbonate, and titanium dioxide nanoparticles have been developed for commercial production, and the largest production scale has reached 15 kt/year.

5 Summary

Nanomaterials have been empirically synthesized for thousands of years, and have met their commercial applications in pigments, cosmetics, sunscreens, coatings, catalysis, etc. The chemical principles and methods give us

more ideas in the preparation and control of the structure of nanomaterials, and the research of process engineering properties should pay more attention on the commercial-scale production of nanomaterials. Based on the development of new technologies and methods for preparation of nanomaterials, the morphology and structure, as well as the mass transfer, chemical reaction, macro and micromixing, nucleation and growth of nanoparticles were studied systematically in our laboratory, and then the relationship between these properties and parameters was established according to the experimental results. By confined reaction assembly, many kinds of host-guest nanostructured composites were prepared for application in biosensors and electrorheological fluids. Based on the analysis of the chemical engineering properties for nanomaterials synthesis processes, the principles for the process scale-up and design of reactors were established for commercial production.

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