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Shape and Aggregation Control of Nanoparticles: Not Shaken, Not Stirred

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Abstract: The aggregation of nanoparticles during synthesis, particularly the effect of mechanical agitation, is investigated from a viewpoint of nucleation using a conjugated polymer, polyaniline, as an example. Homogeneous nucleation of polyaniline results in nanofibers, while heterogeneous nucleation leads to granular particulates. Mechanical agitation, which is a common method for disrupting aggregates, instead dramatically triggers aggregation during the synthetic process and favors the formation of granular particulates. Correlating the shape and aggregation of polyaniline nanoparticles with the mode of nucleation, a new aggregation mechanism is proposed in which aggregation is triggered by heterogeneous nucleation. The mechanism may be quite general as indicated by experiments with other materials such as silica nanoparticles. Highly dispersible polyaniline nanofibers can now be reproducibly prepared from a conventional reaction simply by not mechanically agitating the reaction and carrying it out at an elevated temperature. This work may prove to be of great value in reproducibly synthesizing nanoparticles with well-controlled sizes and shapes and in effectively preventing aggregation in chemical, pharmaceutical, and materials production processes.

Introduction

Aggregation, a common yet complex phenomenon for small particles, is problematic in the production and use of many chemical and pharmaceutical products. Aggregation makes it especially difficult to explore the properties and applications of nanostructured materials. In many synthetic processes for particles, especially surfactant-free chemical reactions, aggregation occurs immediately as particles are generated. In conventional studies, aggregation has been simply ascribed to the direct mutual attraction between particles via van der Waals forces or chemical bonding.[1] Strategies for preventing aggregation mainly come from conventional colloid science in which particles are coated with foreign capping agents and/or the surface charges are tailored to separate them via electrostatic repulsions.[1] Here, we provide a new understanding of aggregation in chemical reactions by studying the shape and aggregation of polyaniline nanoparticles in the conventional chemical oxidative polymerization of aniline.

Polyaniline is one of the most useful conducting polymers due to its facile synthesis, environmental stability, and simple acid/base doping/dedoping chemistry.[2] Since its electrical conducting mechanism was explored in the 1980s, this electroactive polymer has been extensively investigated for many applications including antistatic and anticorrosion coatings, chemical sensors, and electrodes for light-emitting diodes, capacitors, and batteries.[2] Arguably, the simplest method for synthesizing bulk polyaniline is the chemical polymerization of aniline with an oxidant, ammonium peroxydisulfate, in an acidic aqueous solution. Because polymerization is an exothermic process, it has long been recommended that this reaction be carried out at low temperatures with one reactant slowly added into the other under vigorous stirring.[3] The resulting polyaniline is highly aggregated and therefore unsatisfactory for most applications.

To make dispersible polyaniline nanoparticles, many methods have been developed such as emulsion and dispersion polymerizations and a large number of surfactants and templates have been tested to improve the processability of this polymer.[4] One-dimensional polyaniline nanostructures such as nanotubes and nanofibers have also received great interest in recent years.[5−10] Our group and others have recently demonstrated that

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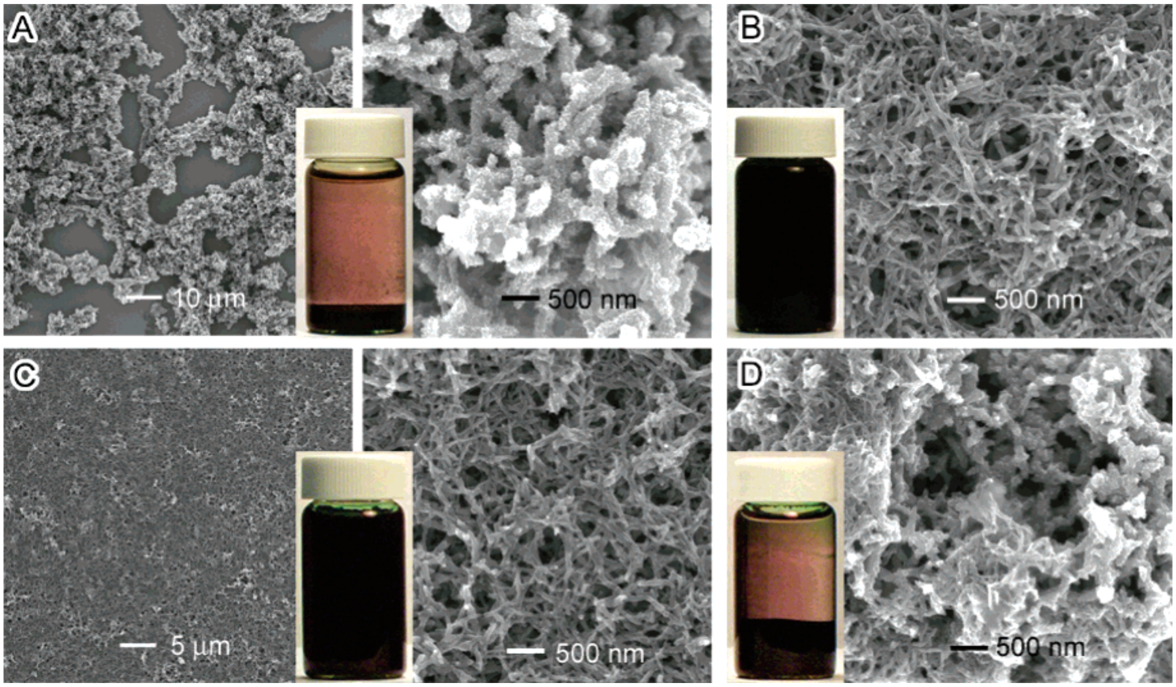

Figure 1. SEM images of polyaniline synthesized by reacting 0.3 mL of aniline in 10 mL of 1.0 M HCl with 0.18 g of ammonium peroxydisulfate in 10 mL of 1.0 M HCl at 25 °C. (A) The ammonium peroxydisulfate solution was added dropwise into the aniline solution at ∼5 mL/h while stirring at 1100 rpm. (B) The ammonium peroxydisulfate solution was added dropwise into the aniline solution without stirring. (C) The two reactant solutions were mixed rapidly with vigorous shaking for ∼30 s and then left standing for 2 h. (D) The two reactant solutions were mixed rapidly and stirred at 1100 rpm for 2 h. The vials shown in the insets contain the resultant products after standing undisturbed for 36 h. Low-magnification SEM images (A and C, left) are presented to compare the quality of films cast from the corresponding dispersions of polyaniline particles.

polyaniline nanofibers can be readily obtained by interfacial polymerization[5] or simply by rapidly mixing an aqueous solution of aniline and an oxidant, instead of slow addition of one reactant to the other.[6,7] However, we often observe that the quality of the products such as the shape and stability of their dispersions varies with different synthetic batches. We have now determined that the reproducibility problems are mainly caused by mechanical stirring during synthesis. We show that mechanical agitation, usually a common method for disrupting aggregates, unexpectedly triggers aggregation of polyaniline during the course of synthesis. This is contrary to our everyday experience in which stirring or shaking helps disrupt aggregation, for example, shaking orange juice rich in pulp.

Aggregation during synthesis is involved in a series of complicated processes such as chemical reactions, nucleation and growth, and precipitation, which often makes it difficult to study the actual aggregation mechanism in chemical reactions. In the presence of mechanical agitation, the formation and aggregation of nanoparticles becomes even more complicated. In the literature, it has been occasionally mentioned that some synthetic reactions for nanostructures including polyaniline nanofibers need to be performed without mechanical disturbance.[7,11] However, the mechanism has not been clarified, possibly due to its complexity. Because mechanical agitation is used in almost every wet chemical reaction and solution-phase chemical synthesis has been proven to be an important method for preparing a large number of nanoparticles with well-controlled sizes and shapes,[12] it will be of great value to acquire an improved understanding about how mechanical agitation functions in a chemical reaction.

Recent advances in controlling the shapes of nanoparticles have inspired us to address the abnormal aggregation phenomenon of polyaniline nanoparticles from a new viewpoint. Shape control of nanoparticles, especially synthesis of one-dimensional nanostructures, has received growing interest in recent years.[12−14] Research in this field has created many novel nanostructures for a wide range of applications.[13,14] Recent work has shown that rationally mediating the nucleation and growth process, for example, via using capping agents or templates, is the key to controlling the shape and size of nanoparticles.[12,13] In other words, the shape of nanoparticles reflects the nucleation behavior of particles. In this work, we use the shape of polyaniline nanoparticles as an indicator of the nucleation mode to “observe” the formation of polyaniline aggregates. We demonstrate an important aspect to shape control of nanoparticles: a new understanding of a fundamental problem that is difficult to deal with using conventional methods, the nucleation and aggregation of particles under shear during chemical reactions. We demonstrate that irreversible aggregation of polyaniline nanoparticles that often occurs during the course of synthesis does not result directly from the mutual attraction of particles as traditional aggregation theory suggests. Instead, the behavior of nucleation of nanoparticles plays a crucial role in the aggregation of the resulting particulates. Mechanical agitation, which is a common

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method for disrupting aggregates, instead affects the nucleation process and dramatically triggers aggregation. By examining the shape evolution of polyaniline nanoparticles during synthesis, we have revealed an important aggregation mechanism for particles that may be associated with the synthetic processes of many materials.

Experimental Section

All chemicals were of analytical grade and used as received. In a typical procedure for preparing polyaniline, 0.3 mL of aniline monomer and 0.18 g of ammonium peroxydisulfate were dissolved in two vials containing 10 mL of 1.0 M HCl, respectively. The newly prepared solutions were then poured rapidly into a 30 mL glass vial and shaken vigorously for ~30 s. The mixtures were left still or stirred with an ordinary magnetic stirrer (Corning Inc.) at different speeds for 2 h. Stirrer bars (9.5 mm in diameter × 25 mm in length) were used for all reactions. The obtained mixtures were thoroughly purified by dialysis against 5.0 mM HCl. To deposit polyaniline films on glass slides via in-situ polymerization, 3.5 × 2.5 cm glass slides were treated by Piranha solution (H_2SO_4/H_2O_2) for 2 h, rinsed with deionized water, and then put into the newly mixed reaction solution for 2 h. The resulting films were thoroughly rinsed with flowing water to remove loosely attached particles and then immersed in 0.5 M HCl for 0.5 h and dried in air. UV−vis spectra were recorded on an HP 8453 spectrometer. To monitor the polymerization of aniline, the open-circuit potentials of the reaction solutions were monitored as a function of time on a single-compartment two-electrode cell: Pt/reaction solution//reference electrode.[15] A saturated calomel electrode (SCE) was used as the reference electrode.

SEM images were taken with a JEOL JSM-6700F Field Emission SEM microscope. A small drop of the resulting dispersion (~2 g/L) was cast on a silicon wafer and dried in air for SEM imaging. No gold was coated prior to SEM imaging. The particle size distribution was measured with a Beckman Coulter LS 13320 Laser Diffraction Particle Size Analyzer using 5 mM HCl as the working fluid. The multiwavelength analyzer is capable of simultaneously measuring particle sizes ranging from 40 nm to 2 mm. Before each measurement, the dispersion was diluted 10-fold with 5 mM HCl and vigorously shaken for ~30 s. It is necessary to use an aqueous solution of pH ~2.5 as the working fluid to achieve repeatable measurements. If pure water is used, polyaniline particles will be dedoped and aggregate, resulting in incorrect results. Note that the particle size measurement is based on the assumption that the particles are spherical. Although polyaniline particles are not spherical, the results are quite reliable for comparative analysis.

Silica nanoparticles were prepared using the classical Stober method. Ethanol (46 mL), tetraethyl orthosilicate (2.6 mL), water (9.3 mL), and ammonia hydroxide (2.0 mL, 29%) were mixed in a 100 mL bottle and shaken vigorously for ~1 min, and then the mixture was split into three equal portions and poured into three 30 mL bottles. These solutions were then stirred with a magnetic stirrer bar at different speeds for 4 h. For the low-temperature reactions, the reactants and bottles were precooled to 0 °C in an ice/water bath prior to mixing and the reaction mixtures were kept in an ice/water bath overnight. The particle size distributions were measured with the same particle analyzer, but deionized water was used as the working fluid.

Results and Discussion

Figure 1A shows scanning electron microscope (SEM) images of polyaniline particles synthesized via the conventional method in which the oxidant solution is added dropwise into the aniline solutions while an ordinary magnetic stirrer bar was used to agitate the reaction mixture at 1100 rpm. The product settles out quickly from the reaction solution, and films cast from its suspension are rough and discontinuous. A close look at the purified powder with SEM indicates that as-synthesized polyaniline consists of coral-like, granular particulates.

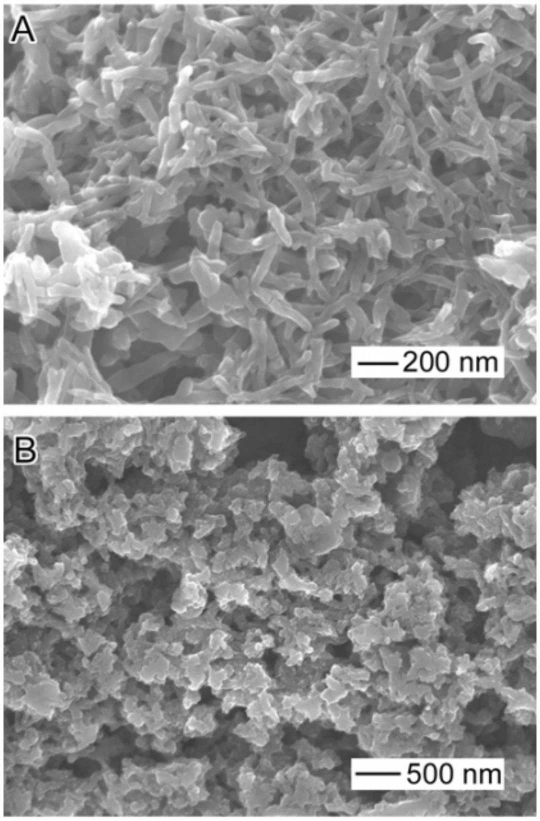

Figure 2. SEM images of polyaniline synthesized by reacting 0.3 mL of aniline in 10 mL toluene with 0.18 g of ammonium peroxydisulfate in 10 mL of 1.0 M HCl at 25 °C via interfacial polymerization. (A) No stirring is applied to the reaction. (B) The reaction is stirred at 1100 rpm.

Unexpectedly, we find that when no stirring is applied to the slow-addition polymerization process, the resulting product is composed mainly of smooth nanofibers (Figure 1B). The nanofibers are comparable in size and shape to those produced from reactions in which the reactants are rapidly mixed with vigorous stirring, but the stirring is stopped before the induction period of the polymerization ends (Figure 1C). However, if intense stirring is kept up during the entire polymerization process, the fibers obtained are highly aggregated and the number of granular nanoparticulates increases as a function of the stirring speed (Figure 1D).

We have also investigated the effect of stirring on the interfacial polymerization of polyaniline. As shown in Figure 2, no fibrillar structures appear in the product if the reaction is stirred at 1100 rpm. The resulting particles are also highly aggregated. We now realize that interfacial polymerization[5] may not occur as simply as previously assumed.[6] Because aniline is very soluble in acidic solutions, aniline dissolved in an organic phase can easily migrate into the aqueous acidic phase. Thus, the reaction is similar to conventional polymerization of aniline in which an aniline solution is added dropwise into the oxidant solution. The essential reason that high-quality polyaniline nanofibers form in this method is because the reaction is not stirred.

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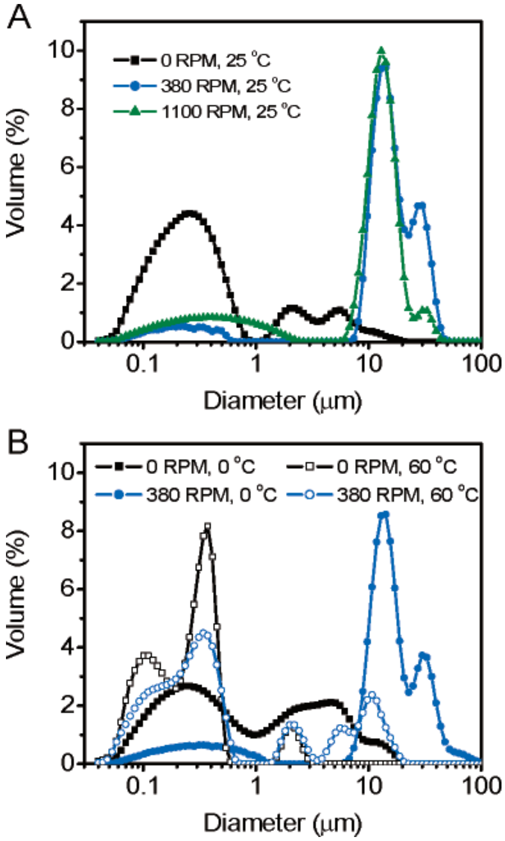

Figure 3. Size distributions of polyaniline particles prepared by rapidly mixing aniline and ammonium peroxydisulfate in acid at different temperatures with the indicated stirring speeds applied. Other synthetic conditions are the same as those given in Figure 1.

One can easily see the effect of stirring on aggregation by observing the settling speed of polyaniline precipitates and the volume of the resulting sediments (Figure 1, insets). In the absence of stirring, polyaniline nanofibers prepared under the conditions presented in Figure 1 remain suspended in the reaction solution without any noticeable sedimentation for months. However, if the reaction is stirred during the polymerization, the sedimentation is immediately observable when the stirring is stopped. The higher the stirring speed is, the faster the polyaniline particles settle out. Shaking the reaction solution gives a similar result. This phenomenon is also observed at different reaction temperatures and when different acids, for example, sulfuric, perchloric, or camphorsulfonic, are added into the reaction media.

The stirring-induced aggregation can be quantitatively characterized by particle size analysis. We have recently demonstrated that postsynthetic aggregation of polyaniline particles in an aqueous dispersion can be prevented via electrostatic repulsions if the pH is set properly.[16] With the interference due to postsynthetic aggregation minimized by adjusting the pH to an optimal window, the original particle sizes of the polyaniline products can be reliably measured with a light scattering-based particle size analyzer. Figure 3 shows the particle size distributions of the purified products prepared at different temperatures and stirring speeds. In all cases we have tested, a stirred reaction always results in a higher percentage of large particle sizes than a nonstirred reaction. For example, 80% of the polyaniline particles prepared without stirring at room temperature are less than 1 μm, while samples prepared under a stirring speed of 380 rpm contain only 9% of particles less than 1 μm and over 88% greater than 10 μm (Figure 3A). These results, together with the SEM observations, indicate that the big particles (>1 μm) are actually irreversible agglomerates of nanofibers and granular nanoparticulates.

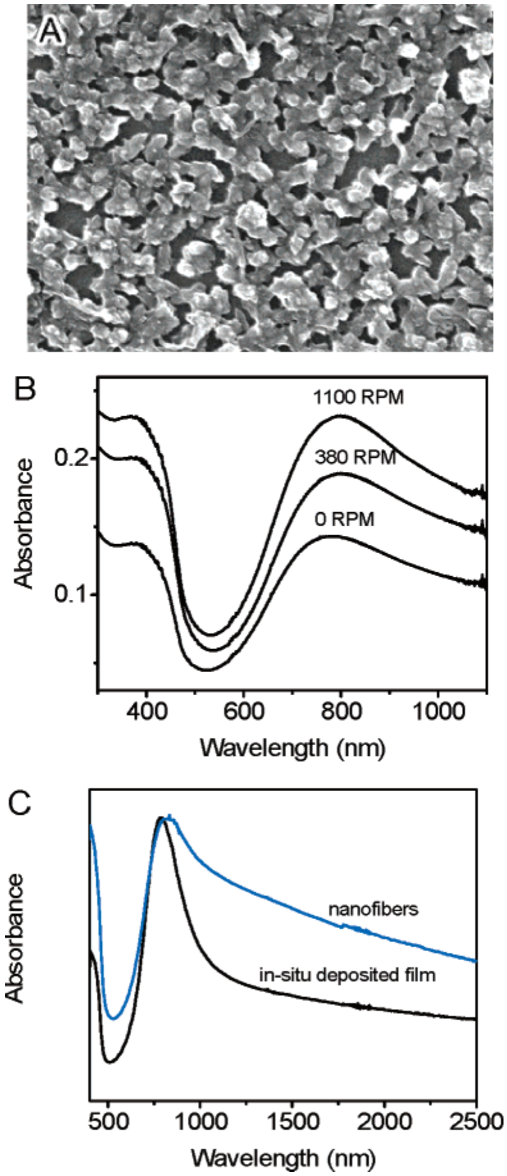

Figure 4. Morphology and structure of polyaniline films prepared via in-situ deposition. (A) SEM image of a film fabricated via in-situ deposition on a silicon wafer from the reaction given in Figure 1C at 25 °C. The film is composed of granular particulates ~200 nm in diameter. These particles appear to be formed by the fusion of smaller nanoparticles. (B) UV−vis spectra of the films fabricated via in-situ deposition from the reaction given in Figure 1C stirred at different speeds. (C) NIR spectra of a polyaniline film cast from a nanofiber dispersion and a film prepared via in-situ deposition from the same reaction. The films were doped by camphorsulfonic acid.

We first tried to interpret this stirring-induced aggregation phenomenon using the conventional coagulation theory of colloids. It is known in colloidal science that mechanical agitation can perform two opposite roles in the flocculation of colloidal particles.[17] First, mechanical shear can break up aggregated particulates and keep particles well dispersed in

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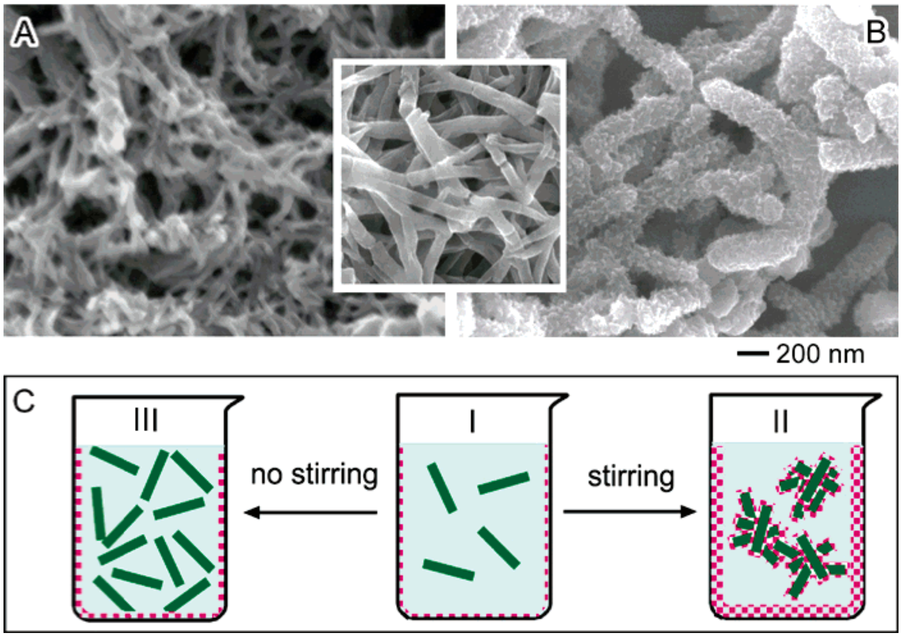

Figure 5. (A, B) SEM images of polyaniline samples taken from seeded-growth experiments, in which polyaniline nanofiber seeds of ∼120 nm in diameter (inset between (A) and (B)) are added into a conventional synthetic reaction of polyaniline. The reactions are carried out without stirring (A) and under stirring at 1100 rpm (B), respectively. (C) Schematic illustrations of the formation and aggregation of polyaniline particles. The green fibers and purple dots represent polyaniline particles that result from homogeneous and heterogeneous nucleation, respectively.

liquids, which is widely used in both academic and industrial laboratories. This effect may account for our observation that the particles synthesized at 1100 rpm are sometimes slightly smaller than those obtained at 380 rpm (Figure 3A). On the other hand, stirring could induce colloidal coagulation because stirring-induced shear can enhance the mutual collisions of particles in both intensity and probability. This latter phenomenon appears to occur with as-prepared polyaniline nanofibers. Sedimentation is observed if stable polyaniline suspensions prepared in the absence of mechanical disturbances are stirred after the polymerization is complete. However, as compared to the case of stirring applied during polymerization, the sedimentation induced by postsynthetic stirring is much less remarkable. Moreover, we find that once the sediments are purified and diluted, their particle size distributions are almost identical to the case without postsynthetic stirring, indicating that the aggregation induced by postsynthetic stirring is reversible and that shear-induced coagulation is not the key reason for the stirring-induced aggregation of polyaniline.

On the basis of a series of stirred experiments, we find that the stirring-induced agglomeration is strongly related to the nucleation and growth of polyaniline. Polyaniline is insoluble in water. The formation of polyaniline chains is always followed by a rapid precipitation of the polymer. In terms of classical nucleation (or precipitation) theory,[18] the molecules need to accumulate to a specific supersaturation level first and then experience nucleation and growth. The nuclei can be formed spontaneously (homogeneously) in the parent phase or they can be heterogeneously grown on other species such as reactor surfaces or other particles in solution.[19] Our observations indicate that both modes of nucleation occur with polyaniline and the mode that predominates is dependent on the experimental conditions. Of particular help to this study is that the shape of the polyaniline particles is found to be related to the mode of nucleation. We have studied the morphological evolution of polyaniline particles prepared in conventional polymerizations. Consistent with our previous observations,[6] at the initial stage of polymerization, as-formed particles are exclusively nanofibers, characterized by smooth surfaces and fairly uniform sizes. Because there are no heteronuclei available in the bulk solution at this stage, it is reasonable to attribute this fibrillar shape to the result of homogeneous nucleation.[20−22] As the polymerization proceeds under shear, granular nanoparticulates gradually grow on these nanofibers, leading to the formation of coral-like aggregates. It is worth noting that as the bulk polymerization proceeds, a polyaniline film will always be deposited on the reactor surface or other substrates in contact with the reaction solution. This film consists of granular nanoparticulates (Figure 4A) regardless of whether the reaction solution is stirred, again consistent with prior observations.[23] These results clearly indicate that the granular shape is related to the heterogeneous nucleation of polyaniline. The observation that a considerable amount of granular nanoparticulates appear in the product prepared with stirring suggests that stirring favors heterogeneous nucleation. This is also confirmed by the observation that the thickness of in-situ deposited films on substrates increases with stirring speed (Figure 4B).

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(20) This fibrillar shape has been observed with some other polymers, and a fibrillar crystallization mechanism has been proposed.[21] The formation of polyaniline nanofibers via homogeneous nucleation may involve a similar mechanism.[22] Heterogeneous nucleation appears to be primarily under thermodynamic control, producing spherical shapes due to minimization of surface area.[12b]

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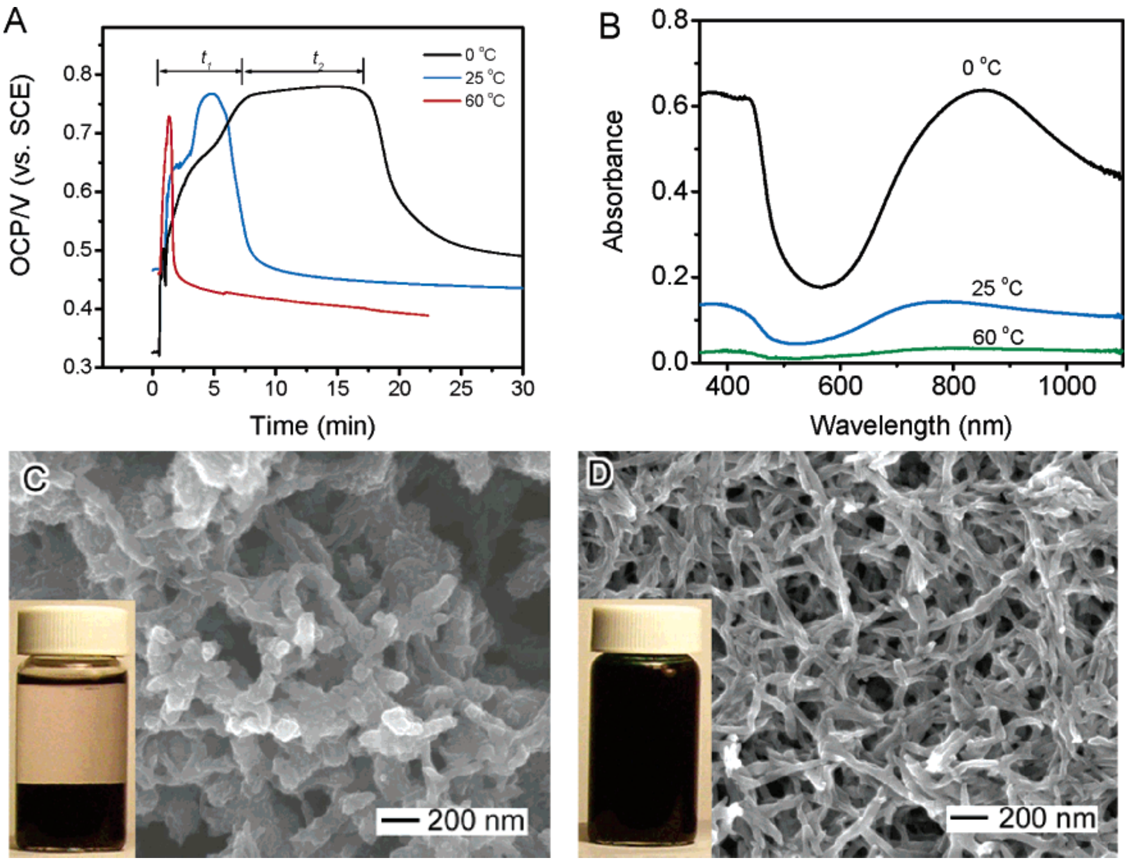

Figure 6. (A) Open-circuit potential (OPT) profile of the reaction given in Figure 1C at different temperatures. According to ref 15, the polymerization process occurs within t_1 and t_2, corresponding to the induction period (t_1) and the formation of pernigraniline (t_2), respectively. The faster is the reaction, the shorter is $t_1 + t_2$. (B) UV−vis spectra of the films fabricated via in-situ deposition from the reaction given in Figure 1C but with the reactions carried out at different temperatures. (C, D) SEM images of polyaniline synthesized from the same reaction except that it is carried out at 0 °C (C) and 60 °C (D), respectively. The vials shown in the insets contain the resultant products after standing undisturbed for 36 h.

To further examine the correlation between shape and nucleation mode of polyaniline, we have designed seeded-growth experiments in which pre-prepared nanofibers (∼120 nm in diameter) are added into an aniline solution in hydrochloric acid, and then a solution of ammonium peroxydisulfate is added dropwise. We find that if no stirring is used, a large amount of new nanofibers of ∼30 nm, characteristic of the nanofibers prepared in hydrochloric acid, appear in the product (Figure 5A), while the morphological change to the pre-added fibers is unremarkable. In contrast, if the reaction is stirred at 1100 rpm, granular nanoparticles will gradually grow on the pre-added fibers and the surface roughness and thickness of the pre-added fibers increase with the addition of the oxidant, leading to the formation of coral-like fibers (Figure 5B).

Mechanical agitation is known to affect the nucleation rate of some materials.[17] However, the mechanism of nucleation under unsteady conditions is not yet well understood. Nonetheless, recent theoretical simulations of nucleation behavior under shear using the crystallization of colloidal hard-spheres as a simplified model suggest that shear can cause a significant suppression of the homogeneous nucleation rate.[24] Nucleation is always connected with local changes in concentration and structure.[18] It has been suggested that the molecules to be nucleated will form transient nanoscale ordered regions or embryos prior to nucleation.[18] In our case, stirring could destroy these transient ordered regions or dilute local concentrations of polyaniline molecules, thereby decreasing the probability of homogeneous nucleation. We have noticed that the conformation of polymer chains in polymer nanofibers is slightly different from that of granular particles. As shown in Figure 4C, a film cast from a nanofiber dispersion exhibits higher absorbance in the near-infrared region (NIR) than a film prepared on a glass slide via in-situ deposition from the same reaction solution, indicative of a more extended conformation of the polymer chains in the nanofibers.[25] Mechanical shear is likely able to make the polymer chains in the solution more coiled, hindering homogeneous nucleation. On the other hand, mechanical shear could enhance collisions between embryonic nuclei and the preformed particles or the reactor surfaces, which may decrease the activation energy of heterogeneous nucleation and thereby facilitate this mode of nucleation. In addition, mechanical agitation also enhances mass transfer in the reaction solution and makes newly formed polyaniline molecules diffuse toward preformed particles faster, leading to greater probability of heterogeneous nucleation.

The successful observation of the nucleation behavior of polyaniline under shear enables us to propose a new aggregation mechanism for polyaniline particles (Figure 5C): At the initial stage (I), as polyaniline nanofibers form in solution via homogeneous nucleation, they will then be forced to collide

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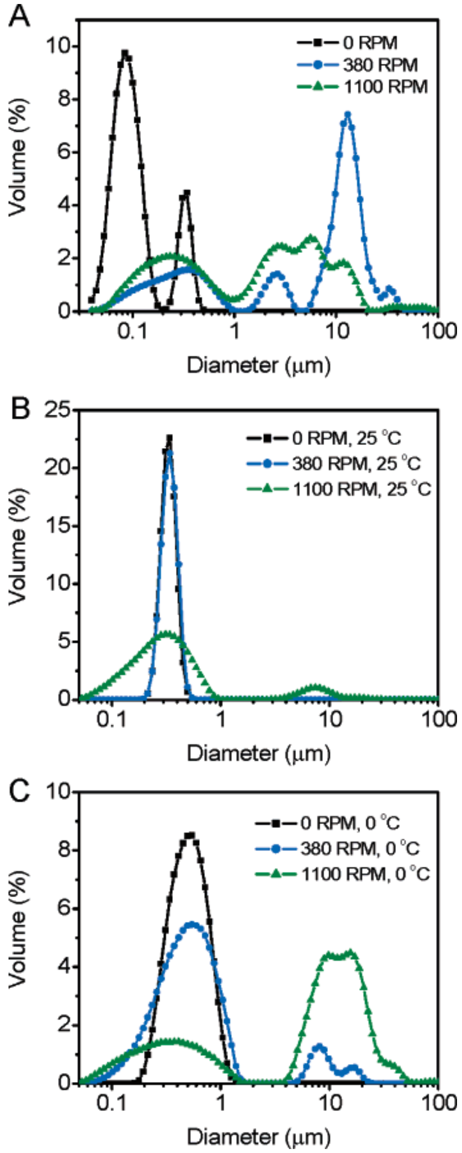

Figure 7. Effect of stirring on the particle size distributions of other particulate materials: (A) poly(*m*-toluidine). (B, C) Silica nanoparticles prepared using the Stober method at 25 and 0 °C, respectively.

into each other due to mechanical shear and Brownian motion. Under shear, heterogeneous nucleation occurs on the surfaces of these particles including the contact points of the preformed particles. The nuclei at the collision points will function like a nanoscale glue to link the particles together, causing aggregation of the preformed particles (III). Subsequent growth of the nuclei and the formation of new heteronuclei on their surfaces will further solidify the aggregation. In contrast, in the absence of stirring, heterogeneous nucleation is suppressed and the nanofibers are produced continuously and are therefore well dispersed (II).

The effect of the reaction temperature on the size of the resulting polyaniline particles further supports the concept that heterogeneous nucleation can induce aggregation. The nucleation behavior of polyaniline is highly dependent on the polymerization rate that is determined by the reaction temperature. As monitored by in situ open-circuit potentials (Figure 6A), the polymerization can complete ($t_1 + t_2$) within 1 min at 60 °C, while it will take more than 15 min to finish at 0 °C. This means that the transient concentration or the supersaturation level of polyaniline molecules at higher temperatures is much higher than that at lower temperatures. In other words, the formation of new embryonic nuclei is much faster at 60 °C than that at 0 °C. As new polyaniline molecules are rapidly produced at high temperatures, it is more likely that these embryonic nuclei evolve to create homogeneous nuclei before they can diffuse to heterogeneous nucleation sites to nucleate. Thus, more polyaniline molecules will precipitate via homogeneous nucleation at higher temperature, and the chance of heterogeneous nucleation will be decreased. This is consistent with the observation that the thickness of the in-situ deposited films is greatly increased with decreasing temperature (Figure 6B). As shown in Figure 6C, polyaniline fibers obtained in the absence of stirring at 0 °C have rough surfaces and are more like the sample shown in Figure 1A. In contrast, there are almost no granular particulates in the product prepared at 60 °C (Figure 6D). These results clearly indicate that low reaction temperatures favor heterogeneous nucleation. As a result, the percentage of larger particles in the product prepared at low temperature is higher than that obtained at high temperature either with or without stirring (Figure 3B). Note that in the absence of mechanical stirring, the collisions of particles in the reaction solution can only be induced by Brownian motion. Consequently, the effect of temperature on the aggregation is not as remarkable as stirring (Figure 3B).

The aggregation mechanism discovered for polyaniline appears to hold when we tested other materials. For example, stirring has the same effect on poly(*m*-toluidine) (Figure 7A). Analogously, this effect is also observed with inorganic nanoparticles such as silica colloids prepared using the classical Stober method.[26] As shown in Figure 7B, the particle size distributions of silica are insensitive to mild stirring at room temperature. However, the stirring-induced aggregation becomes noticeable once the stirring becomes intense (>380 rpm), and particularly when the reaction is carried out at lower temperatures (Figure 7C). The aggregation in these materials appears to involve the same mechanism as that in polyaniline. Unlike polyaniline, these materials have no sharp differences in the shape of the particles that result from different modes of nucleation. Without ascertaining the aggregation mechanism that we have discovered with polyaniline, it would be difficult to understand these aggregation phenomena in other materials.

It is worth pointing out that unlike aggregation due to the direct attraction via van der Waals forces, surface nucleation-induced aggregation is irreversible. From a thermodynamic point of view, as heterogeneous nucleation and subsequent growth proceed, the molecules acquire a configuration that is favorable to minimizing the interfacial energy between the nucleus and its substrate. As a result, the particles, especially small particles that result from heterogeneous nucleation, will strongly bond to their substrates. Note that the in-situ deposited films stick strongly to the substrates. In fact, spontaneous growth of films on a substrate from solution via heterogeneous nucleation has also been shown to be a simple route for fabricating robust ceramic films.[19]

Conclusions

Thanks to the unique feature that the shape of polyaniline nanoparticles is related to the mode of nucleation, we have

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(26) Stober, W.; Fink, A. *J. Colloid Interface Sci.* **1968**, *26*, 62.

revealed an important aggregation mechanism for nanoparticles during synthesis, one that appears to have long been overlooked. This work indicates that the aggregation of nanoparticles during synthetic processes can be triggered by heterogeneous nucleation. Mechanical agitation can facilitate heterogeneous nucleation, thereby inducing aggregation. Because heterogeneous nucleation is generally much more widespread both in nature and technology than homogeneous nucleation,[27] the surface nucleation-induced aggregation could also exist in many other synthetic processes involving particles to some extent. Because this nucleation-controlled aggregation is mechanistically different from aggregation induced by direct attraction of particles, conventional methods for preventing aggregation may not be effective and even may result in an inverse effect such as stirring-induced aggregation. In practice, if aggregation occurs in a reaction, one usually turns to the use of surfactants. As we have now demonstrated, it is actually unnecessary to use surfactants to prepare highly dispersible polyaniline nanofibers. In fact, we find that shear-induced aggregation still dominates if the concentration of added surfactants is not sufficiently high. Understanding this mechanism could be of great help in dealing effectively with aggregation problems in other chemical reactions.

This work clearly indicates the importance of engineering issues in the control of the shape and aggregation of nanoparticles even at the laboratory scale. The nucleation and growth process is crucial to prepare nanoparticles with controllable shapes and sizes.[12,13] Mechanical stirring is a routine operation in chemical reactions. Because stirring could affect nucleation and aggregation, this experimental factor needs to be considered when one carries out or repeats a synthetic process involving particles. Of particular importance is that stirring-induced shear in a fluid is strongly dependent on the stirring speed, the geometry and size of the reactor, as well as the structure of the stirring impellers. These factors may be especially important when a nanoparticle product is scaled up. Note that due to a lack of understanding of the nucleation behavior of polyaniline and particularly the effects of stirring, this simple idea that the conventional reaction for the synthesis of polyaniline is capable of producing highly dispersible nanofibers has been overlooked for decades. The processability issue of polyaniline, which has been pursued in the field for many years, can now be simply improved just by removing a routine operation, stirring, from the conventional reaction.

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