Synthesis of low-melting-point metallic nanoparticles with an ultrasonic nanoemulsion method

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\textbf{A B S T R A C T}

A one-step, economical nanoemulsion method has been introduced to synthesize low-melting-point metallic nanoparticles. This nanoemulsion technique exploits the extremely high shear rates generated by the ultrasonic agitation and the relatively large viscosity of the continuous phase – polyalphaolefin (PAO), to rupture the molten metal down to diameter below 100 nm. Field’s metal nanoparticles and Indium nanoparticles of respective average diameters of 15 nm and 30 nm have been obtained. The nanoparticles size and shape are determined by transmission electron microscopy (TEM). Their phase transition behavior is examined using a differential scanning calorimeter (DSC). It is found that these nanoparticles dispersed in PAO can undergo reversible, melting-freezing phase transition, and exhibit a relatively large hysteresis. The experimental results suggest that the nanoemulsion method is a viable route for mass production of low-melting nanoparticles.

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1. Introduction

Various methods have been developed to synthesize nanoscale materials and structures in the past decades \cite{1–15}. Among them, ultrasound has recently been explored with important uses in synthesis of nanoparticles \cite{1–3}. Most applications of ultrasound are based on the chemical effects of ultrasonication such as high local temperature and pressure generated by acoustic cavitation. For example, the sonochemical decomposition, reduction, oxidation and coprecipitation of precursors have been able to produce nanostructures in various forms \cite{19,14–16}. Another class of ultrasonic applications relies on its physical effects – very strong shear rates – to break the dispersed phase to small droplets in another immiscible, continuous phase through a capillary instability \cite{17,18}. The resulting suspensions are often called “miniemulsions”, if the droplet diameter is in the range of 100 nm–1 \textmu m \cite{19,20}. The miniemulsions technology is rapidly attracting interests in the field of nanostructure solid materials due to its inherent advantages, which include low cost, minimal byproduct formation and ability to be scaled up for bulk production. However, how to go beyond conventional miniemulsion methods into the realm of nanoemulsions to make particles/droplets 100 nm or less in diameter has been much less studied to date.

In this paper, we present a nanoemulsion technique that preserves the advantages of the miniemulsion route but is able to produce particles with diameter less than 100 nm under an extremely high shear generated by an ultrasonic horn. As an example, Indium (melting point: 156.6 °C) and Field’s metal (by weight: 32.5% Bi, 51% In, 16.5% Sn; melting point: 63.2 °C) nanoparticles are prepared using this nanoemulsion technique. In addition, the phase transition behavior of these as-prepared nanoparticles is examined using a differential scanning calorimeter (DSC).

2. Methods and materials

A large number of factors could affect the droplet size in the emulsification technique. These include selecting an appropriate composition, controlling the reaction temperature, choosing the order of addition of the components, and applying the shear in an effective manner. However, the fundamental relationship governing how the dispersed phase can be ruptured in another immiscible liquid under a shear stress is given simply by Taylor’s formula \cite{21}:

\[ d \approx 2\sigma/(\eta_c\dot{\gamma}). \]

where \( d \) is the droplet diameter, \( \sigma \) is the interfacial tension between the droplet and continuous phase, \( \eta_c \) is the viscosity of the continuous phase, and \( \dot{\gamma} \) is the shear rate. Based on Taylor’s formula, it is possible to estimate the shear rate required to form nanoemulsions. Assuming \( \eta_c = 1 \) cP, the viscosity of water at room temperature, and \( \sigma = 10 \) dyn/cm, a shear rate of \( \dot{\gamma} \approx 10^3 s^{-1} \) would be needed to generate 20 nm-diameter droplets. Such a high shear rate is generally out of the range of most common mixing devices such as

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high-speed blenders. In our experiment, a high-intensity ultrasonic device (VCX 750, Sonics & Materials, Inc.) is used, which is equipped with a focusing Ti horn with a power density of more than 70 W/cm². This focusing horn agitates the emulsion at ultrasonic frequency (20 kHz) and causes an extremely high shear rate and cavitation that break up droplets. In addition to the high shear rates, the viscous polyalphaolefin (PAO) oil, instead of water, is used as the continuous phase during the ultrasonication. It can be seen from Taylor’s formula that raising the viscosity of the continuous phase, \( \eta_c \), leads to a lower requirement of shear rate, \( \gamma_c \), for creating nanoemulsions. The viscosity of PAO, as well as common solvents, is plotted in Fig. 1. It is observed that the viscosity of these materials monotonically decreases with increasing temperature. PAO is selected in this experiment due to its relatively high viscosity and chemical inertness to the molten metals (e.g., Indium).

The experimental setup for preparing nanoparticles is shown in Fig. 2. PAO and metal are placed in a three-necked flask that can be heated up by a silicone oil bath. The process of nanoemulsion formation in this experiment is illustrated in Fig. 3. First, 0.5 ml of a low-melting metal (Field’s metal or Indium) was added to 100 ml PAO oil in the reaction vessel, and then the mixture was heated 20°C above the metal melting temperature by using a silicone oil thermal bath. A thermocouple was immersed in the mixture to monitor its temperature. After the metal was completely melted and the setting temperature was reached, 4 ml polyalphaolefin aminoester as the polymer surfactant was immediately injected into the reaction vessel. The significant excess of surfactant would enable new surface area of the ruptured droplets to be rapidly coated during emulsification, therefore limiting shear-induced coalescence. The molten metal was dispersed in the PAO using a magnetic stirrer for 2 h to create microscale droplets. This pre-mixed microscale emulsion was then exposed to high-intensity ultrasound radiation (VCX 750, Sonics & Materials, Inc.) for more than 2 h till stable nanoemulsions were formed. The Ultrasonic transducer was cooled by forced air-convection. The emitted sound field was very strong in the vicinity of the horn tip, but attenuated rapidly with distance. An extended ultrasonic treatment is required for all droplets to experience the highest shear rate leading to a reasonably uniform distribution of their size. Once the nanoemulsion was cooled to room temperature, solidified Field’s metal or Indium nanoparticles were obtained.

3. Results and discussion

The size distribution of the Field’s metal and Indium nanoparticles was examined using the Transmission electron microscopy (TEM, JEOL 2100F). To prepare TEM samples, 5 \( \mu l \) nanoemulsion was transferred from the reaction vessel and dissolved in 5 ml toluene. One small drop of the toluene solution was placed on the carbon-coated copper grids. The toluene evaporated rapidly and only nanoparticles were left atop the copper grids. TEM bright field (BF) images of Field’s and Indium nanoparticles are shown in Fig. 4a and b, respectively. These nanoparticles are spherical because the liquid nanodroplets have a positive interfacial tension (i.e., surface energy) in the emulsification process. In addition, these nanoparticles are highly dispersed. The polymer surfactants appear to provide sufficient steric stabilization despite the strong cohesion forces among molten metal nanodroplets. Well-dispersed nanoparticles are highly desired in many applications such as thermal fluids and electronics packaging [6,12,13,25].

The nanoparticles size distributions were extracted from the TEM images. The average diameter of the Field’s and Indium nanoparticles is 15 nm and 30 nm, respectively. These two types of nanoparticles were created using the same procedure except for

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**Fig. 1.** Dynamic viscosity of PAO, Isopar M, water, and cyclohexane as a function of temperature [22–24].

**Fig. 2.** Experimental setup for preparing low-melting-point metallic nanoparticles.

**Fig. 3.** Schematic illustrating the formation of nanoemulsion: (a) PAO and molten metals are in the reaction vessel. These two liquids are immiscible and phase separate, (b) the polymer surfactant is soluble in PAO and preferentially adsorbs at the interface, (c) the mixture is stirred using a magnetic stirrer and the bulk molten metal breaks into microscale droplets and (d) the microscale emulsion is exposed to high-intensity ultrasound radiation till nanoemulsion is formed.
the emulsification temperature: 84 °C for Field’s metal and 177 °C for Indium. It can be seen from Fig. 1 that the temperature affects strongly the viscosity of PAO oil, e.g. \( \eta_{c} = 2.3 \text{ cP at } T = 84 \degree C \) and \( \eta_{c} = 0.9 \text{ cP at } T = 177 \degree C \). This viscosity change could primarily account for the size difference of the Field’s and Indium nanoparticles, according to Taylor’s formula. In other words, the nanoparticle size could be regulated by changing the reaction temperature in order to vary the viscosity of continuous phase.

Knowledge of the phase change behavior of these low-melting metallic nanoparticles is critical for their applications such as thermal fluids, energy storage, and electronics packaging [6,12,13,25–28]. In this experiment, the melting–freezing phase transition of the as-prepared Field’s metal and Indium nanoparticles was measured using a Differential Scanning Calorimeter (DSC, Model TA-Q100). DSC measurements were taken at an ordinary cyclic ramp mode, and the scan rate was 10 °C/min. Fig. 5a and b shows the cyclic DSC heating and cooling curves for the nanoemulsions containing Field’s metal and Indium nanoparticles, respectively. For comparison, the data for corresponding bulk materials are also plotted.

A relatively large melting–freezing hysteresis, about 45 °C for Field’s metal nanoparticles and about 50 °C for Indium nanoparticles, can be seen in Fig. 5a and b. Based on the classical nucleation theory, the melting and freezing of these nanoparticles are intimately tied to the interface energies between the solid metal nanoparticles and the oil matrix, the liquid metal and oil matrix, and the solid and liquid metals (\( \gamma_{SM}, \gamma_{SL}, \) and \( \gamma_{LM} \), respectively) [29]. The observed \( T_m \) slightly below the bulk value implies that \( \gamma_{SM} > \gamma_{SL} + \gamma_{LM} \) (or \( \gamma_{LM} < \gamma_{SM} + \gamma_{SL} \)), where \( \gamma \) is the interfacial energy. In this case, the solid nanoparticles will premelt or nucleate at the interfaces with the continuous oil phase. In contrast to melting, a relatively large freezing-point depression was found for these as-prepared nanoparticles dispersed in PAO oil, about 45.4 °C for the Field’s metal nanoparticles and 51.2 °C for Indium nanoparticles. This is probably due to \( \gamma_{LM} < \gamma_{SM} + \gamma_{SL} \). In this situation, the molten phase would not “presolidify” at the interfaces, instead, it would require critical nuclei inside these nanoparticles, i.e. homogeneous nucleation. So, these liquid nanoparticles could be supercooled to tens of degrees below the bulk melting temperature till critical nuclei associated with solidifying are reached. This characteristic might provide a way to tailor the phase transition behavior of nanoparticles by varying their interfacial energy or size for different applications.

4. Conclusion

In conclusion, a convenient nanoemulsion method, which exploits the high shearing capability of ultrasonication, has been introduced to prepare low-melting metallic nanoparticles. As an example, this technique was used to fabricate Field’s metal and Indium nanoparticles in the PAO oil, and their average diameter was
found by TEM to be about 15 nm and 30 nm, respectively. A relatively large melting-freezing hysteresis is observed in these as-prepared nanoparticles, which can be explained using the classic nucleation theory with different interfacial energy.

This nanoemulsion method could become a general route to synthesize well-dispersed nanoparticles of low-melting materials, such as metals, salts, and polymers. The nanoparticle size may be effectively regulated by changing the synthesis temperature in order to vary the viscosity of the continuous phase. These nanoparticles and their dispersions are expected to have wide applications in thermal fluids, energy storage, electronics packaging, medical diagnostics, and various other fields.

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References


