Improving the supercooling degree of titanium dioxide nanofluids with sodium dodecylsulfate

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HIGHLIGHTS

- Effect of SDS on reducing supercooling degree of TiO_2/H_2O nanofluid is found.
- The effect of SDS depends on SDS-to-TiO_2 mass ratio and SDS concentration.
- The greatest effect of SDS is achieved when SDS adsorbed on TiO_2 reaches saturation.

ARTICLE INFO

ABSTRACT

The solidification processes of titanium (TiO_2) nanofluids and deionized water (DW) were measured by differential scanning calorimetry to explore the effect of sodium dodecylsulfate (SDS) surfactants on the supercooling degree of TiO_2 nanofluids. The supercooling degrees of TiO_2 nanofluids without surfactants were approximately 11.5% lower than that of DW, and the values did not change significantly with nanoparticle concentration. However, the addition of SDS surfactants could reduce the supercooling degree of TiO_2 nanofluids. With increasing surfactant-to-nanoparticle mass ratio and SDS concentration, the reduction in the supercooling degrees of TiO_2 nanofluids increased to a maximum value of approximately 30.6%. These phenomena indicated that the surfactants served an important function in enhancing heterogeneous nucleation in TiO_2 nanofluids. The theoretical analysis of heterogeneous nucleation associated with surfactants revealed that the surfactants reduced the free energy change required for nucleation in TiO_2 nanofluids by changing the contact angle of nanoparticles. The supercooling degree of TiO_2 nanofluids was found to be closely related to the adsorption density of SDS, that is, large adsorption densities resulted in low supercooling degrees. When the saturation adsorption density of SDS on TiO_2 nanoparticles was reached, the reduction in the supercooling degree of TiO_2 nanofluids caused by surfactants was at its maximum.

1. Introduction

Efficient and reliable thermal storage systems are important requirements for many applications, especially when the demand and supply of electricity is erratic [1]. Among the existing thermal energy storage methods, latent heat storage using a phase-change material (PCM) has recently gained increasing attention for its large heat storage capacity and small temperature swing. The

characteristics of PCMs serve an important function in the development of latent heat storage systems [2,3]. Water is widely used as a PCM because it is chemically stable, cheap, easily acquired, and environmentally friendly. However, the most serious problem encountered when using water as PCM is the avoidance of the supercooling phenomenon during water solidification. A lower degree of supercooling results in a better coefficient of performance of the refrigeration system [4].

Nanofluids, a term first proposed by Choi and coworkers at Argonne National Laboratory, consist of small fractions of nanoscale solid particles (nanoparticles) in base fluids such as water, ethylene glycol, oil and etc. [5]. Water-based nanofluids are produced by incorporating nanoparticles into water. They have the potential to offer higher thermal conductivity [6–8] and lower supercooling

degree [9–11] compared to the water itself. Although the melting enthalpy reduction of water-based nanofluids cannot be avoided because the phase change of nanoparticles does not occur at the operational temperatures, it can be alleviated to some extent by using low-density nanoparticles or lowering nanoparticle concentration [12]. Therefore, the use of water-based nanofluids to replace water may offer the potential to increase the performance of refrigeration systems. At present, nanofluids are expensive and their applications in industry seem uneconomical. But as the nanoparticle synthesis techniques are scaled up to industrial production levels by more and more companies, the nanofluids will become easy to manufacture in the near future, and then there will be potential economic advantages in using water-based nanofluids as PCMs in thermal storage systems.

Undoubtedly, an important prerequisite is to maintain the good dispersion stability of nanofluids in applications. Considering that particles in the order of nanometers can easily form agglomerates with significantly larger dimensions because of strong van der Waals attraction, surfactants are often used in nanofluid preparation [13]. Many studies have already demonstrated that the dispersion stability of nanofluids can be significantly improved through electrostatic, steric, or electrosteric stabilization by surfactants [14–16]. However, the role of surfactants playing in the solidification of nanofluids has received little attention in the literature up to now. Wu et al. used sodium dodecylbenzenesulfonate (SDBS) to prepare Al_2O_3–H_2O nanofluids, and found that the addition of 0.2 wt% Al_2O_3 nanoparticles remarkably decreases the supercooling degree of water by 70.9% [11], They simply attributed this finding to the heterogeneous nucleation effect of Al_2O_3 nanoparticles. However, Zhang et al. found that without surfactants, the supercooling degrees of α-Al_2O_3–H_2O and γ-Al_2O_3–H_2O nanofluids with the same nanoparticle concentration of 0.3% were only about 33.3% and 15.2% of the supercooling degree of water, respectively [9]. We therefore inferred that the greater reduction (70.9%) in the supercooling degree of Al_2O_3–H_2O nanofluid observed by Wu et al. was probably due to the existence of surfactant SDBS. In water-based nanofluids, some surfactants are able to absorb on the nanoparticle surfaces, and the others may be free and just dissociate in the water. We had confirmed that only surfactant SDS had little impact on the supercooling degree of water by testing the SDS aqueous suspensions without nanoparticles in our exploratory experiments. It is well known that the contact angle of foreign substrate is one of the main factors affecting the free energy change required for water nucleation [17]. We therefore speculated that the surfactants absorbed on nanoparticles might affect the supercooling degree of water-based nanofluids during solidification by changing the contact angle of solid nanoparticles. Further confirmatory studies are very necessary.

In this research, TiO_2 nanofluids with and without surfactants were prepared using a two-step method. SDS was used as surfactant to stabilize the dispersion of TiO_2 nanoparticles in deionized water (DW). The effects of nanoparticle concentration, surfactant-to-nanoparticle (SN) mass ratio, and SDS concentration on nucleation in TiO_2 nanofluids were investigated by differential scanning calorimetry (DSC). Discussions on the nucleation mechanism concerning surfactant adsorption were conducted to determine how and why surfactants affect the supercooling degree of nanofluids.

2. Material and methods

2.1. Material

TiO_2 nanoparticles (10–20 in diameter, Shanghai Huzheng Nanotechnology Co., Ltd., China) were used as additives, and SDS (Guangdong Xilong Chemical materials Co., Ltd., China) was used as surfactant in the present study. As it is know, there are many impurities in the tap water which may affect the nucleation of water. The effects of these impurities and nanoparticles may be competitive or cooperative. Thus, the deionized water (DW) was chosen to be the base fluid in the study in order to exclude other uncertain influencing factors which might affect our judgement on the effect of surfactant on nucleation of water on nanoparticles. In the experiments, SDS surfactants were first added into DW, followed by TiO_2 nanoparticles. The mixture was homogenized by continuous stirring with a magnetic bar and then sonicated with an ultrasonic vibrator (ultrasonic 250 model, He-Yu Technology Co., China) at a frequency of 80 kHz for 1 h. Ice was added to prevent the increase in temperature of suspensions due to the continuous ultrasonic treatment. The temperature of suspensions was monitored and maintained at approximately 25 °C. In the present study, three series of TiO_2 nanofluids were prepared: the SN mass ratio series with a TiO_2 concentration of 0.7 wt% and SN mass ratios of 0.07, 0.14, 0.43, 0.72, 1, and 1.43; the SDS concentration series with an SN mass ratio of 1 and SDS concentrations of 0.05, 0.1, 0.3, 0.5, 0.7, and 1.0 wt%; and the TiO_2 concentration series without surfactants with nanoparticle concentrations of 0.1, 0.3, 0.5, 0.7, and 1.0 wt%. A transmission electron microscope (JEM-100CXII, JEOL Ltd., Japan) was used to measure the TiO_2 nanofluids. As shown in Fig. 1, TiO_2 nanopartilces were bonded together to form aggregates. These aggregates were approximately spherical in shape, and had large sizes around 300 nm. The SDS aqueous solution was prepared by dissolving the SDS in DW. The solution was weighted using an electronic balance with an accuracy of ±0.1 mg (AUY220, Shimadzu Corporation, Japan), and the desired solution volume was obtained through successive dilutions, given that the concentrations of SDS are very small, ranging from 0.4 mmol/L to 12.0 mmol/L.

2.2. Methods

2.2.1. Particle size measurements

The particle sizes of TiO_2 nanofluids were measured at 25 °C using dynamic light scattering (DLS) at a scattering angle of 173° with a Zetasizer Nano ZS particle size analyzer (Malvern Instruments Ltd., England). The size measurements were repeated six times, and the reproducibility of data fell within an error of 2.5%.
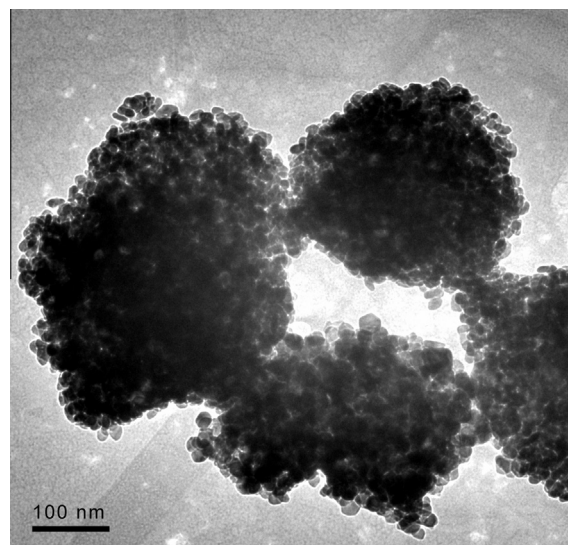

Fig. 1. TEM micrograph of nano-aggregates dispersed in TiO_2 nanofluid with 1 wt% surfactant concentration.