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Synthesis of ZnO nanoparticles from microemulsions in a flow type microreactor

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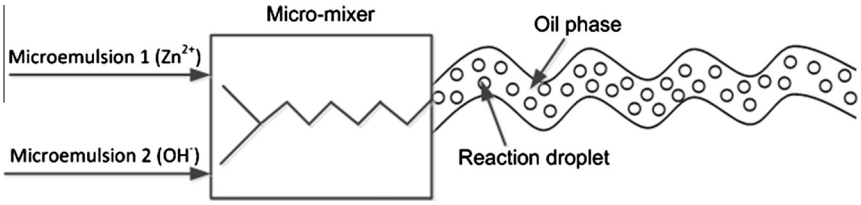
HIGHLIGHTS

- ZnO nanoparticles were synthesized from microemulsions in a microreactor.
- The microemulsion approach avoids the deposition of particles in the microchannels.
- $Zn(NO_3)_2$ was superior to $ZnSO_4$ and $ZnCl_2$ as the Zn^{2+} source.

GRAPHICAL ABSTRACT



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ABSTRACT

Zinc oxide (ZnO) nanoparticles were synthesized from microemulsions in a microchannel reactor system. The microemulsions provide confined space for the reactants, which is favorable for controllable reaction and nucleation, thus avoiding the formation of large particles. In addition, the microemulsions prevent the deposition of ZnO particles on the wall of the microchannels of the reactor. Three Zn^{2+} sources ($Zn(NO_3)_2$, $ZnSO_4$, and $ZnCl_2$) were tested in the synthesis of ZnO nanoparticles. Among them, $Zn(NO_3)_2$ showed best performance, yielding ZnO particles with the smallest average grain size. The effects of Zn^{2+} concentration, reaction temperature, and feed flow rate on the average particle size of ZnO nanoparticles were investigated. At optimal conditions, ZnO nanoparticles with average size of 16 nm were obtained. The synthesized ZnO nanoparticles were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), UV–vis absorption spectroscopy, and a laser particle size analyzer.

1. Introduction

ZnO is an important semiconductor material with extensive applications in electronics, photoelectronics, sensors, and optical devices [1–4]. The physical properties of ZnO nanoparticles are strongly dependent on the particle dimensions, including morphology and grain size distribution. Two types of synthetic approaches, vapor-phase synthesis and solution-phase synthesis, have been developed to fabricate ZnO nanoparticles. The vapor-phase approaches, such as vapor–liquid–solid growth [5], chemical vapor deposition [6], thermal decomposition [7], and thermal evaporation [8], have the advantage of simple operation and high-quality products, but generally require high temperatures and expensive equipments. Solution-phase approaches are more promising due to the low reaction temperature, low cost, and high efficiency. However, in the later approach, ZnO flowers and whiskers with large size (>100 nm) are often obtained, and the subsequent sedimentation or calcination leads to the aggregation of ZnO particles. In addition, the synthesis in a batch reactor is not effective in a large scale production. Therefore, new methods which facilitate the nucleation, growth, and particle size distribution in the synthesis of ZnO nanoparticles are highly desirable [9].

The microemulsion has found great applications in the synthesis of nanomaterials [10–12]. In the microemulsion approach, the reactants in aqueous solution are confined in the extremely small droplets, in which a uniform nucleation occurs. Additionally, the microemulsion helps to control the size and shape of the particles, preventing the nanoparticles from aggregation. Nevertheless, the microemulsion method suffers from low yield of nanoparticles and the difficulty of de-emulsification. As a consequence, the

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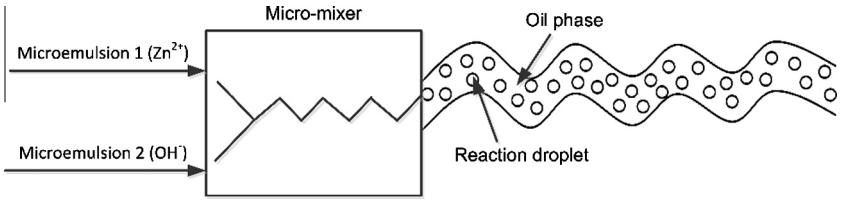

Fig. 1. Schematic diagram for the synthesis of nanoparticles by microemulsion in a microreactor.

reactor performance is generally low when the synthesis takes place in a batch reactor.

Recently, microchannel reactors have been utilized for producing nano-sized particles, including metals and alloys [13–18], metal salts [19,20], metal oxides [21], polymers [22], mesoporous materials [23], and zeolites [24]. The flow type microchannel reactors are able to intensify the mass and heat transfers as well as the mixing. The high surface-to-volume ratio in the microchannel reactors is favorable to enhance the response time and maintain isothermal conditions. Because the concentrations of reactants and temperature are homogeneous in the reaction zone, the obtained particles are uniform and reproducible.

When a single phase is involved, the velocity distribution in a microchannel is substantially broadened along the flow direction. Gunther et al. [25] compared the well mixing efficiency chaotic mixer with a liquid–liquid two phase mixer, and found that, when the fluid was mixed completely ($\geqslant$95%), the length of the channel required for the two-phase flow was 2–3 times shorter than for the single-phase flow. The computational fluid dynamics (CFD) simulations indicate that the enhancement of mass transfer can be interpreted in terms of an internal circulation flow within the plugs. As a consequence, narrow particle size distribution could be obtained in the synthesis of nanoparticles due to the enhanced mixing and the narrow residence time distribution in the segmented liquid–liquid flow [26]. Another important issue in the synthesis of solid materials in a microchannel is that the formed particles may nucleate and deposit on the microchannel walls, leading to runaway growth, clogging, and unstable reactor conditions. Jongen et al. [27] designed a complex liquid–liquid two phase slug-flow microreactor, which included an aqueous phase of the two reactants and an oil phase. The immiscible oil phase isolated the aqueous phase in droplets. Nanoparticles nucleate and grow in the isolated droplets, whereas the droplets will not contact with the microchannel walls when the oil-to-water volume ratio is carefully adjusted in a suitable range, preventing the solid particles from depositing on the walls.

In the present paper, ZnO nanoparticles were synthesized by mixing the Zn^{2+}-containing water-in-oil microemulsion with the NaOH-containing one in a micromixer followed by subsequent reaction in the relay tube (Fig. 1). The synthesis conditions were optimized, and the obtained ZnO nanoparticles were characterized.

2. Experimental

2.1. Synthesis

All of the chemicals were of analytical grade, and used without further purification (Tianjin Kermel Chemical Reagent Co. Ltd.). Deionized water was obtained from a water purification system.

The microemulsions were prepared in the following way. N-butanol, cetyltrimethyl ammonium bromide (CTAB), and n-octane were mixed at a mass ratio of 1.0:1.2:4.4 to form an organic phase. CTAB served as the surfactant, whereas n-butanol as the co-surfactant. An aqueous solution of Zn^{2+} ($Zn(NO_3)_2$, $ZnSO_4$, and $ZnCl_2$) were prepared by dissolving the salt in water under stirring. The solution of NaOH was prepared in a similar way. The microemulsion of Zn^{2+} (denoted as M(Zn^{2+})) were obtained by adding the aqueous solution of Zn^{2+} into the above organic phase under vigorous stirring with an aqueous mass fraction of 15%, and the mixture was stirred until it became transparent. The microemulsion of NaOH (denoted as M(NaOH)) was prepared by the same procedure with the same aqueous mass fraction.

The microreactor for the synthesis of ZnO nanoparticles is illustrated in Fig. 2. The micromixer (CPMM-R 300, microchannel size: 300 $\times$ 300 μm, Mainz, Germany) and the relay tube (stainless steel, i.d. 6.35 mm $\times$ 1.0 m) were immersed in an oil thermostat, whose temperature was adjusted by a temperature controller. M(Zn^{2+}) and M(NaOH) were fed separately to the two inlets of the micromixer by two syringe HPLC pumps. At a steady state, a white suspension was obtained at the outlet of the relay tube. The precipitates were collected by centrifugation at 4000 r/min for 10 min, and washed with ethanol, acetone, and water sequentially for three

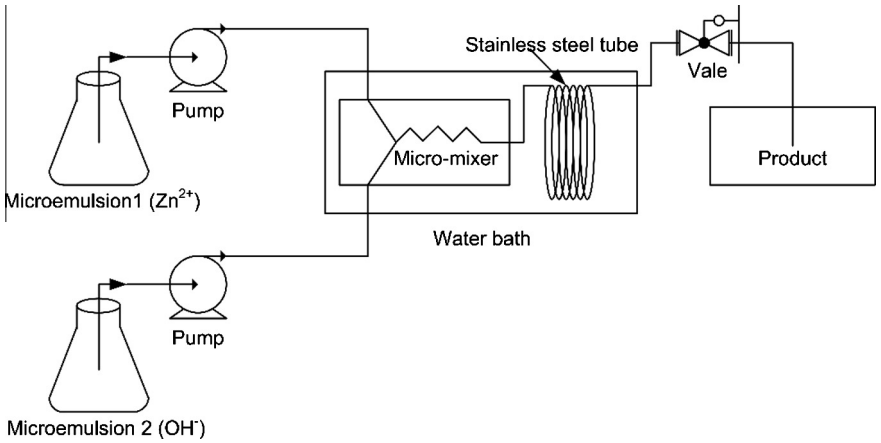

Fig. 2. The experimental setup for the flow type synthesis of ZnO nanoparticles.