



## Preparation of nonaqueous silver nanosuspensions by in situ dispersion of the surface-modified nanoparticles



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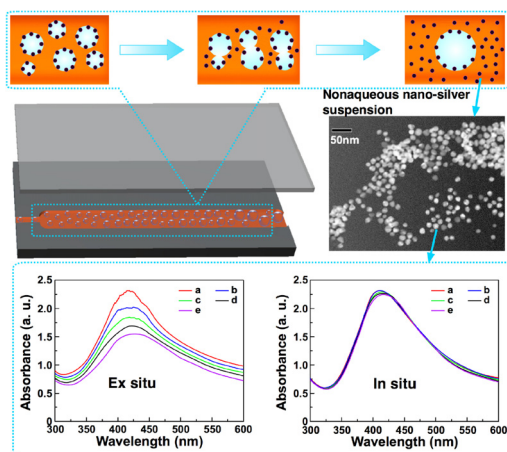
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### HIGHLIGHTS

- A method for in situ dispersing surface-modified Ag nanoparticles was developed.
- The dispersion process was intensified by microdroplet coalescence.
- A plate-type microchannel was constructed to initiate droplet coalescence.
- Nonaqueous suspensions were prepared with Ag nanoparticles of 10 nm.
- The dispersed Ag particles exhibited high monodispersity and excellent stability.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this study, we have developed an in situ dispersion method to prepare nonaqueous Ag nanosuspensions by controlling microdroplet coalescence. A plate-type microchannel was constructed to initiate droplet coalescence. Under optimal conditions, the hexane-based nano-silver suspension with a high particle concentration of 0.47 mol/L and an average particle size of 10 nm could be controllably prepared. The effects of various operation parameters on droplet coalescence and particle dispersion were experimentally investigated. The stability of the dispersed silver nanoparticles in suspensions was significantly enhanced due to the in situ dispersion, and no obvious agglomeration could be observed in the experiments.

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## 1. Introduction

Ag particles are receiving a great deal of attention for their nontoxicity and potential for hygienic applications [1,2]. Since

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**Notation**

M	Molar concentration, M corresponds to the specific material
$d_d$	Droplet size ( $\mu\text{m}$ )
$d_p$	Droplet size (nm)
$E_C$	Efficiency of droplet coalescence (%)
$E_T$	Efficiency of nanoparticle dispersion (%)
$m$	Mass of Ag nanoparticles (g)
$Q_C$	Flow rate of the continuous phase (mL/min)
$Q_D$	Flow rate of the dispersed phase (mL/min)
$u$	Average flow velocity (m/s)
$V$	Volume fraction (%)
$\gamma$	Interfacial tension (mN/m)
$\mu$	Viscosity (mPa s)

the nano-sized Ag particles have special antimicrobial properties for control of bacterial infections, a wide range of medical, biological, and pharmaceutical Ag-based products, such as creams, skin cleansing, and catheters, have been rapidly developed [3–5]. Generally, Ag nanoparticles are used in the form of organic nanosuspensions. The function of Ag nanoparticles can be greatly improved when the particles are uniform in size and stable in organic media, especially for antimicrobial processes or exhibiting physical changes in agglomeration [2,4–6]. Therefore, both the surface modification of Ag nanoparticles and the controllable preparation of organic nano-silver colloids have been widely investigated. Surfactants such as 2-diethylaminoethanethiol (DEAET) and 3-aminopropyl-triethoxysilane (APTES), and stabilizers such as polyvinylpyrrolidone (PVP) and sodium citrate, are increasingly applied to prevent the particles from agglomerating [6–8]. However, because of the high surface energy and correspondingly the high activity of Ag nanoparticles, traditional methods, which involve surface modification, particle separation, drying, and dispersion (into organic phase) processes, are often limited by particle stability and cannot be adapted to produce nanosuspensions of high nanoparticle concentrations. Moreover, during the drying and dispersion processes, unavoidable particle agglomeration renders the preparation of initial particles with small sizes and narrow size distributions worthless.

To reduce particle agglomeration, several groups have developed an in situ dispersion method to prepare Ag nanocolloids in organic solvents or monomer solutions, which integrated the preparation and dispersion simultaneously. For example, Chou and Lai [9] synthesized silver nanoparticles (10–30 nm) by using formaldehyde in an alkaline solution. In this process, intermediate  $\text{Ag}_2\text{O}$  was formed in the presence of hydroxyl ions and then converted to Ag nanocolloids. Andrade et al. [10] proposed to perform in situ dispersion of hydrophobic Ag nanoparticles with an average size of 38 nm. Results showed that the particles were highly dispersed in the monomer solution and uniformly distributed in the fabricated membrane. Similarly, the synthesis of highly monodispersed nonaqueous Ag nanocolloids of less than 10 nm through an in situ dispersion process was also studied by Yang et al. [11]. By virtue of the uniform particles, silver/polymer nanocomposites were fabricated by ultraviolet (UV) irradiation, which proved the in situ dispersion an effective tool for the synthesis of composite materials. Some other studies have also addressed the preparation of nonaqueous Ag nanosuspensions by in situ dispersion, mostly initiated by microdroplet coalescence in emulsions [12–15]. Correspondingly, the enhancement of droplet coalescence by applying external forces (such as electric field and light irradiation) has also been studied [16–18].

These studies have demonstrated that the in situ dispersion of surface-modified Ag nanoparticles is favorable for both the size uniformity and the particle stability in organic media. However, there still exist challenges in the interphase mass transfer of the hydrophobic nanoparticles from aqueous phase to organic phase [19,20]. Given that in situ dispersion of hydrophobic nanoparticles is generally performed in w/o emulsions, a number of microdroplets (1–1000  $\mu\text{m}$ ) are generated and further increase the interfacial energy [21–23]. Meanwhile, the surface-modified nanoparticles, whose surfaces are absorbed by surfactants, tend to gather at the water–oil interface and stabilize the emulsion. In this case, particle dispersion is greatly suppressed. However, if the interfacial energy of the system could be reduced, in other words, if the microdroplets could have coalesced in time, the hydrophobic particles would transfer directly into the oil phase and undesirable agglomeration at the phase interface would therefore be avoided.

In recent years, tuning the interfacial tension gradient in microchannels to enhance microdroplet coalescence has attracted considerable passion [24–26]. Depending on a high gradient of interfacial tension due to the opposite hydrophobicities of microchannel walls, for instance, between a stainless steel plate and a poly(methyl methacrylate) (PMMA) plate, the slip flow forms at one side while the regular flow remains at the other side [27]. The shift of the flow centerline offers high energy for droplet collision and coalescence. When droplet coalescence occurs, particles transfer smoothly into organic phase and the problem of particle sedimentation is also solved owing to the separation from the wall by the continuous flow. The microfluid-induced droplet coalescence offers potential for intensifying in situ dispersion of surface-modified nanoparticles. Therefore, we suggest introducing this strategy to the in situ dispersion of hydrophobic Ag nanoparticles into oil phase and preparing nanosuspensions with uniform and monodispersed particles.

Here, for the first time, we have developed a method to prepare nonaqueous Ag nanosuspensions based on in situ dispersion by microdroplet coalescence. A plate-type microchannel with channel walls of opposite hydrophobicities was used to direct the droplet coalescence. Surface-modified Ag nanoparticles with a small size and high monodispersity were prepared using the new method, and effects of operating parameters were experimentally investigated. Measurements were also conducted to evaluate the stability of the nanosuspensions.

## 2. Experimental

### 2.1. Materials

Silver nitrate ( $\text{AgNO}_3$ , 99.8%) and sodium hydroxide (NaOH, 96.0%) were purchased from Beijing Chemical Works, Co. Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ , 99.6%), *n*-hexane (99.5%), acetone (99.6%), ethanol (99.8%), and 3-amino-propyltriethoxysilane (96.0%) from Tianjin Yongda Chemical Reagent Co. were used without further purification. Dodecanethiol (98.5%) was purchased from Sigma-Aldrich Co. and used as received.

### 2.2. Apparatus

Two microchannels were used to conduct the generation of microdroplets and droplet coalescence (Fig. 1), respectively. Both the plates of the upstream microchannel and the bottom plate of the downstream microchannel were fabricated from polydimethylsiloxane (PDMS) plates using soft lithography technique. To seal the downstream microchannel, the PDMS plate was treated with a solution of sodium-naphthalene and then bonded with a glass plate. Prior to use, the sealed downstream microchannel was washed

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