Journal of Industrial and Engineering Chemistry xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Customized microfluidic reactor based on droplet formation for the synthesis of monodispersed silver nanoparticles

Cheol Hwan Kwak[a,1], Sung-Min Kang[a,1], Euiyoung Jung[b,1], Yuvaraj Haldorai[c,d], Young-Kyu Han[c], Woo-Sik Kim[b], Taekyung Yu[b,*], Yun Suk Huh[a,*]

[a] WCSL of Integrated Human Airway-on-a-Chip, Department of Biological Engineering, Biohybrid Systems Research Center (BSRC), Inha University, 100 Inha-ro, Incheon 22212, Republic of Korea
[b] Department of Chemical Engineering, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 17104, Republic of Korea
[c] Department of Energy and Materials Engineering, Dongguk University-Seoul, 30 Pildong-ro 1-gil, Jung-gu, Seoul 04620, Republic of Korea
[d] Department of Nanoscience and Technology, Bharathiar University, Coimbatore, 641046, India

ARTICLE INFO

Article history:
Received 3 December 2017
Received in revised form 25 February 2018
Accepted 26 February 2018
Available online xxx

Keywords:
Customized microfluidic device
Silver nanoparticle
Droplet formation
T-junction
Static mixer

ABSTRACT

A customized droplet-based microfluidic reactor was fabricated for the synthesis of silver nanoparticles (Ag NPs) using silver nitrate ($AgNO_3$) and branched polyethyleneimine (BPEI) as a precursor and a reducing agent, respectively. The effects of static mixing, temperature, and the volumetric flow rates of $AgNO_3$ and BPEI on the particle size were investigated. The use of a static mixer and the optimization of the reaction temperature enhanced the monodispersity of the Ag NPs. In addition, the size of the Ag NPs was manipulated by changing the flow rate ratio of $AgNO_3$ to BPEI at 60 °C for 60 min.

Introduction

Over the last decade, there has been significant advances in lab-on-a-chip technology in terms of the fabrication of various microstructures. The microfluidic devices that are being produced through this technology are being applied to a range of industrial fields, such as chemical synthesis [1], drug screening [2], and clinical assay [3]. On the other hand, chemical synthesis using microfluidic devices has a disadvantage; a Reynolds number of the fluid in a microscale channel is so small that uniform mixing is hardly achieved due to the formation of laminar flow [4].

One approach to improve this problem is the use of a droplet-based microfluidic system [5], which is based on the droplets formed using two or more fluids that do not mix with each other. This can also be used to manage and increase the reaction rate, which is promoted by mass transfer depending on convection and diffusion. Furthermore, each droplet can be used as an individual microreactor, so that the droplet-based microfluidic system can be used to synthesize complex uniform-sized materials, such as core-shell particles, quantum dots, and hydrogel microparticles [6].

Metal nanoparticles have been synthesized using microfluidic platforms, including specific microstructures, such as T-junctions [7], flow-focusing [8], micro valve [9], and sheath flow [10]. These platforms have been fabricated using a variety of polymers (e.g., PDMS, PMMA, and PC) [11]. However, the use of these polymers have several limitations. For example, the deformation of micro-channels occurs by the swelling of the polymer-based platform because of the organic solvent used in the synthesis of the nanoparticles [12]. In addition, the microfluidic platforms fabricated through soft lithography have limited flexibility in terms of customization. Once the microfluidic device has been manufactured, the structure cannot be adjusted [13]. Therefore, these types of microfluidic devices suppress the response to changes in the channel length and the structure of microfluidic devices for effective fluid mixing.

In the viewpoint of material synthesis, the microfluidic system has a problem of microstructure deformation by an organic solvent. To solve this problem, a microfluidic device was developed using materials with excellent solvent resistance (e.g., quartz, silica, and fluoropolymer) [14,15]. Furthermore, this technology was developed into a microfluidic system with advantages, such as easy fabrication, low cost, and lightweight [16,17]. To meet these

* Corresponding authors.
E-mail addresses: tkyu@khu.ac.kr (T. Yu), yunsuk.huh@inha.ac.kr (Y.S. Huh).
[1] These authors have contributed equally to this work.

https://doi.org/10.1016/j.jiec.2018.02.040
1226-086X/

requirements, the customized microfluidic reactor, which has similar advantages to those of the aforementioned modular microfluidic device, is proposed in this study.

Recently, a modular microfluidic device suggested the composition of one microfluidic system through the production and assembly of individual components with specific functions instead of the conventional PDMS-based microfluidic device [13,18,19]. The advantage of a modular microfluidic device is a simple reconfigurable device that enables the rapid assembly and surface-modification of a specific area.

In this study, silver nanoparticles (Ag NPs) were synthesized using the customized microfluidic reactor to evaluate the effective synthesis and size control of the nanoparticles in this microfluidic system. The customized microfluidic reactor was fabricated easily while allowing the simple customization of the system by assembling single functional microfluidic units that are commercially available. This microfluidic system overcame the limitations of the device reconfiguration in the PDMS-based microfluidic platform. The static mixer and T-junction in this microfluidic reactor were adjusted for mixing and droplet generation, respectively. In addition, fluoropolymer-based micro tubing was used as a microfluidic channel to prevent the deformation induced by the organic solvent. The effect of the static mixer, temperature, and the volumetric flow rates of the reactants on the particle size were investigated.

Materials and methods

Fabrication of customized droplet-based microfluidic reactor

The customized microfluidic reactor consisted of three functional elements: micro tubing (DuPont fluorinated ethylene propylene (FEP) tubing, 1/16″ OD, 0.030″ ID, IDEX, USA), two Tee connectors, and a static mixer. The first Tee connector (T-junction 1, Tee Assembly for 1/16″ OD, 0.020″ thru hole, IDEX, USA) was used for rapid mixing by introducing each of two solutions, an Ag precursor and reducing agent, to the static mixer. The second Tee connector (T-junction 2, Tee, 1/16″ OD, 0.75 mm ID, VICI, Switzerland) was used to generate the droplet. To mix the solutions, a precolumn filter (PreColumn PEEK 0.5 μm, IDEX, USA) was filled with a polyester porous sponge and used as a static mixer. All reagents were injected using microsyringe pumps (Legato 200, KD Scientific, USA).

Synthesis of Ag NPs using a droplet-based microfluidic reactor

In a typical experiment, silver nitrate ($AgNO_3$, ≥99.0%) and branched polyethyleneimine (BPEI, MW = 750,000, 50 wt% in H_2O) were purchased from Sigma–Aldrich Korea (Seoul, Korea), which were used as the precursor and a reducing agent, respectively. Aqueous $AgNO_3$ (33.8 mg mL^{-1}) and BPEI (5.07 mg mL^{-1}) solutions were prepared by dissolution in deionized water. For droplet formation, *n*-decane (Daejung, Korea) was used as a continuous oil phase. The microfluidic crystallization of Ag NPs was carried out at 60 °C for 60 min. The reaction was quenched by dropping the reaction product into a 50 mL conical tube filled with isopropyl alcohol (IPA). Finally, Ag NPs were collected by centrifugation at 12,000 relative centrifugal force for 40 min and washed three times with IPA to remove the unreacted reactants.

Characterization

X-ray diffraction (XRD, D/Max-2500, Rigaku, Japan) was carried out using Cu Kα radiation. The Ag NPs for XRD analysis were prepared by freeze-drying the colloidal Ag NPs overnight using a lyophilzer (FDS 8508, Ilshin Biobase, Korea) after removing the unreacted reactants using centrifugation. Thermogravimetric analysis (TGA, STA 409 PC/NETZSCH, Germany) was conducted at 25–800 °C at a rate of 10 °C min^{-1} using N_2 as the carrier gas. The morphology of the Ag NPs was examined by transmission electron microscopy (TEM, JEM-2100F JEOL, Japan). The purified colloidal Ag NPs (40 μL) were dropped onto a TEM grid (CF200-CU, Electron Microscopy Sciences) and dried overnight in a desiccator for TEM analysis. The optical properties of Ag NPs were analyzed using a

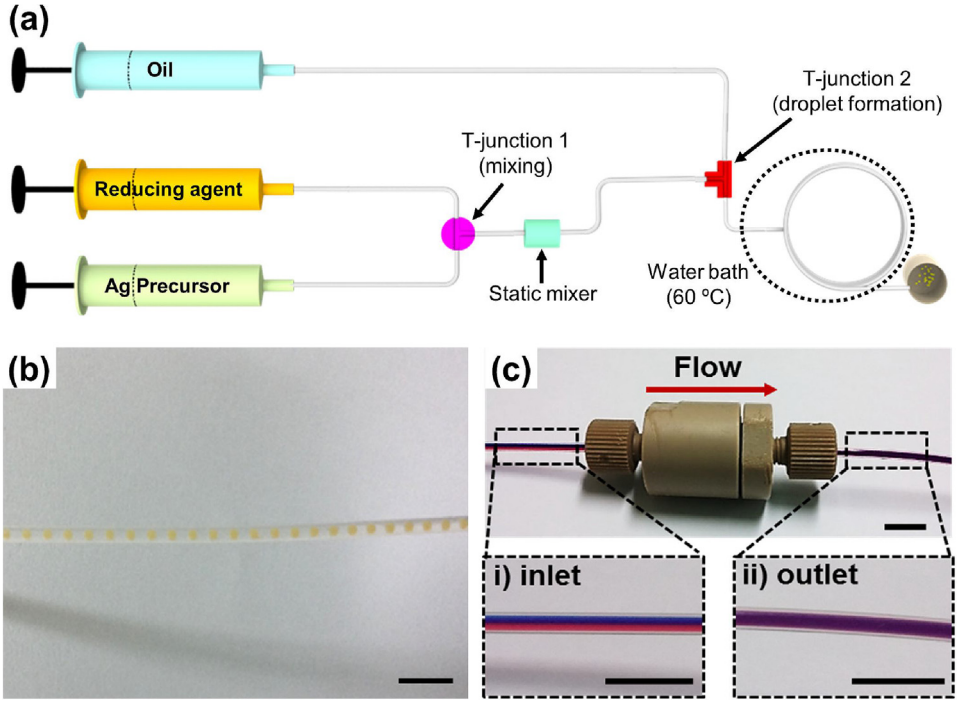

Fig. 1. Customized droplet-based microfluidic reactor fully integrated by T-junction, static mixer, and heating zone. (a) Schematic diagram illustrating the microfluidic reactor setup. Photograph of (b) droplets formed using the T-junction 2, and (c) static mixer for homogeneous mixing (scale bars are 1 cm).

Please cite this article in press as: C.H. Kwak, et al., Customized microfluidic reactor based on droplet formation for the synthesis of monodispersed silver nanoparticles, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.02.040