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A hybrid microreactor/microwave high-pressure flow system of a novel concept design and its application to the synthesis of silver nanoparticles

Satoshi Horikoshi [a],*, Takuya Sumi [a], Nick Serpone [b],*

[a] Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan
[b] Gruppo Fotochimico, Dipartimento di Chimica, Universita di Pavia, via Taramelli 10, Pavia 27100, Italy

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ABSTRACT

This article reports on a microreactor/microwave high-pressure flow hybrid apparatus of a novel concept design, which includes both the microreactor and a spiral reactor, and its efficient use in the synthesis of silver nanoparticles of relatively uniform sizes (4.3 ± 0.7 nm) under microwave irradiation. By contrast, under otherwise identical experimental conditions but with conventional heating, the nanoparticle size was non-uniform (8.3 ± 2.7 nm) and the spiral reactor walls were covered with a silver mirror deposit. Formation of the nanoparticles was monitored by UV–visible spectroscopy (plasmonic absorption band; LSPR), TEM and by small-angle X-ray scattering (SAXS). Both the spiral microreactor and the spiral quartz reactor of the hybrid system played an important role in the synthesis, with the microreactor providing the environment wherein mixing of the aqueous solution of $[Ag(NH_3)_2]^+$ and the solution of glucose (the reducing agent) and poly(N-vinyl-2-pyrrolidone) (PVP; stabilizer/dispersing agent) occurred. The microwaves provided the thermal energy to effect a uniform growth of the silver nanoparticles at temperatures above 120 °C. Mixing the two solutions by conventional methods (no microreactor) failed to yield such nanoparticles even under microwave irradiation and no formation of a silver mirror occurred in the inner walls of the spiral reactor.

1. Introduction

Metal and metal-oxide nanoparticles are found in a variety of highly promising applications in paints, electronic materials, as biological markers, and in optoelectronic devices, all of which require nanoparticles of fairly uniform size distribution. Industrially, synthetic methods are sought that avoid the use of strong reducing agents and that may be of particular interest to Green Chemistry. Microwaves have proven particularly useful in the synthesis of metal nanoparticles [1], as the microwaves afford control of particle size [2]. However, microwave-assisted chemistry may be problematic for process scale-up because of the limited penetration depth of the microwaves into the absorbing media [3]. Moreover, most syntheses reported have been carried out in batch-type reactors in which processes tend not to be particularly efficient as well as being inappropriate to produce large quantities of metal nanoparticles in a cost efficient manner, not to mention the lack of reproducible quality of products in fast batch processes [4]. Accordingly, a particularly attractive and efficient synthesis methodology should make use of flow-type reactor systems that involve microwave radiation to produce nanoparticles of noble metals in short times.

Reports on continuous processes for the production of metallic nanoparticles tend to be rather scarce [5]. Except for the heating method, but otherwise under identical conditions of reactant concentration, reaction temperature and time, and a flow rate of $10\,mL\,h^{-1}$, superior yields of silver nanoparticles were obtained by microwave heating compared to conventional heating. Contrary to microwave heating, an increase of the flow rate to $100\,mL\,h^{-1}$ caused no reaction to occur by conventional heating owing to a limited heat transfer from the reactor wall to the bulk reaction solution with the result that the temperature inside the reactor was insufficient for nanoparticle formation [6].

Different from batch-type reactors, flow-type microwave reactors present some advantageous features, such as (a) no need for stirring the reactants and (b) greater suitability for large-scale production by continuous processing [6]. However, nucleation and particle growth are less controlled and so size distribution tends not to be uniform, not least of which metal deposition can occur on the reactor's inner wall because of inhomogeneous heating. Nishioka et al. [6] recently reported a microwave-assisted polyol process to produce silver nanoparticles using a tubular PTFE flow

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* Corresponding author.
E-mail addresses: horikosi@sophia.ac.jp (S. Horikoshi), nick.serpone@concordia.ca, nick.serpone@unipv.it (N. Serpone).

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microreactor located at the center of a cylindrical aluminum resonance cavity operated under single-mode conditions. Germane to this, some have argued [7,8] that a method based on a microfluidic technology might offer significant advantages over conventional technologies for the synthesis of nanoparticles as a result of (i) the intrinsic small volume of microreactors that allow the use of expensive or toxic chemicals, (ii) the large surface area to volume ratio of microreactors offers enhanced heat and mass transfer compared to conventional reactors, and (iii) reactions that are too fast to be controlled in traditional reactors can easily be achieved in microreactors owing to a massively reduced time of the transport processes at the micrometer scale. Also, efficient mixing is a key advantage for preparing monodispersed nanoparticles in microreactors.

Nanoparticles of certain particle sizes, uniform narrow size distributions, and desired structures can be formed in a better controlled reaction in microreactors. Along similar lines, Pacławski et al. [9] found such a method promising for stabilizing and preparing gold nanoparticles with well-defined shape (spheres) and narrow size distribution. Recent achievements in the synthesis of nanoparticles in microfluidic reactors have been reviewed by Zhao et al. [7] who described and compared various strategies that included continuous flow, gas–liquid segmented flow, and droplet-based microreactors. Different categories of nanoparticles manufactured in microreactors that highlight the wide application of microfluidic systems in the development of novel nanomaterials were also summarized. An important aspect in fabricating nanoparticles is homogeneous mixing that occurs in the microreactor. With very few exceptions [6], many of the studies hitherto reported in nanoparticle syntheses have used a microreactor heated by a conventional method [3].

To understand the effect of segmented flow on the nanoparticle size distribution in a unidirectional expanding spiral microreactor, where secondary flows are prevalent in the absence of segmentation, Kumar et al. [10] reported a continuous flow synthesis of nanoparticles in microchannel reactors that overcame the limitations of traditional batch preparative methods in terms of reproducibility, narrow size distribution, and facile scale-up. In this regard, a miniature chemical platform provides controlled fluid transport, rapid chemical reactions, and cost-saving advantages over conventional reactors, so much so that microfluidics have been used [11] to improve the synthesis of metal nanostructures, semiconductor nanoparticles, quantum dots, metal oxides and core–shell structures. Other methods have witnessed a combination of ultrasounds and microwaves to synthesize semiconductors such as flower-like zinc oxide (ZnO) nanostructures together with Au/ZnO and Ag/ZnO nanocomposites, which exhibited enhanced photocatalytic efficiency subsequent to decorating the surfaces of these ZnO nanostructures with noble metal nanoparticles [12].

In a 2010 article [2] we reported on the effect(s) of 2.45-GHz microwaves in the synthesis of silver nanoparticles in aqueous media by reduction of the diaminesilver(I) complex, $[Ag(NH_3)_2]^+$, with carboxymethylcellulose (CMC) playing the dual role of reducing agent and stabilizer in both a batch-type reactor and a rudimentary (domestic microwave oven) continuous-flow reactor system with a particular emphasis on the characteristics of the microwaves in this process and the size distributions of the resulting nanoparticles. The flow-through microwave reactor system (flow rate, 600 mL min^{-1}) coupled to 1200-Watt microwave radiation generated silver nanoparticles with a size distribution spanning the range 0.7–2.8 nm (average size ca. 1.5 nm).

As part of our systematic studies into the development of microwave techniques [13], the present article reports on a microreactor/microwave high-pressure flow hybrid system of a novel concept design (than hitherto reported [3,4,6–8]) for the continuous synthesis of silver nanoparticles. Nanoparticulates of uniform size can be grown with a microreactor under homogeneous continuous mixing of the reagents with microwaves supplying consistent heating. In this regard, Comer and Organ [14] showed that capillaries coated internally with thin films of a metal displayed significant rate accelerations in such processes as the catalyzed Suzuki–Miyaura reactions with no exogenous catalyst added. Their system suffered none of the laminar flow problems that tend to plague microreactor technology, thus paving the way in the use of microwave-assisted, flow capillary synthesis as a powerful and efficient means to replace one-at-a-time microwave-assisted organic syntheses. However, when used in nanoparticle syntheses, the interior of such capillaries could be fouled by the produced nanoparticles. To avoid such issues, the system we report herein used separate components: a spiral microreactor for the efficient mixing of the reactants and a microwave-irradiated novel spiral quartz reactor with a resonator that ensures uniform heating and affords increased residence times.

2. Experimental

2.1. Experimental setup

An actual photograph of the microreactor/microwave hybrid system of a novel design used in the present study is displayed in Fig. 1a; a schematic model of the whole system is illustrated in Fig. 1b. The two solutions were introduced into the microreactor (YMC Co. Ltd. Deneb; Helix type) at a fixed flow rate of 0.5 mL min^{-1} using a syringe driver pump, after which the mixture was continually driven into the microwave's quartz spiral reactor using an HPLC pump (flow rate, 1 mL min^{-1}; Nihon Seimitsu Kagaku Co. Ltd., NP-KX-2010U). The 10-mL feed tank (sample storage in the schematic model) was connected between the microreactor and the HPLC pump. A Saida UMS Ltd. microwave resonance single-mode applicator was used with a microwave semiconductor generator connected to the resonator by a coaxial cable and a cable waveguide converter. The microwave input power was maintained at 30 W (2.45-GHz microwaves; continuous irradiation). Since the resonance efficiency of the applicator was remarkably high and the semiconductor generator provided a microwave frequency spanning a very narrow band at 2.45 GHz [13a], in contrast to single-mode applicators of commercial microwave devices, the sample solution could be heated efficiently even at low microwave input power.

In the experimental setup of Fig. 1, the electric field inside the resonator was monitored using an electric field monitor and a personal computer (PC). A change in the electric field, which may occur because of changes in dielectric loss arising from temperature changes of the solution, was compensated automatically by tuning the frequency on the microwave generator using the PC. As a consequence, the quartz spiral reactor and its contents could be microwave-irradiated uniformly throughout (see Fig. 1c and d). The distribution of the microwaves' electric field (2.45 GHz) in the resonator was simulated using the COMSOL Multiphysics 4.2a software (see Fig. 1e). Results showed that the electric field was concentrated at the center of the resonator, especially at the spiral reactor where the electric field intensity was the greatest.

The solvent medium used in our experiments consisted of water and an electrolyte (NaCl), so that the inner diameter of the spiral reactor was set at 3 mm in consideration of the penetration depth of the 2.45-GHz microwaves. Note that the penetration depth of the microwaves when using NaCl (0.125 M) as the electrolyte is 8.8 mm at 30 °C and 6.1 mm at 90 °C [15]. The pressure of the sample solution was set at 1 MPa using a back pressure regulator (Swagelok Co., KCB1H0A2A5P60000); the solution discharged from the regulator was sampled periodically.