Sensors and Actuators B 242 (2017) 384–388

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

On-chip synthesis of ruthenium complex by microwave-induced reaction in a microchannel coupled with post-wall waveguide

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ARTICLE INFO

Article history:
Received 8 August 2016
Received in revised form 7 October 2016
Accepted 25 October 2016
Available online 29 October 2016

Keywords:
Lab-on-a-chip
MicroTAS
Microwave
Chemical reaction
Post-wall waveguide
Synthesis
Organic synthesis
Metal complex
Ruthenium complex
PTFE
Teflon
Pharmaceutical

ABSTRACT

We demonstrate the on-chip synthesis of a ruthenium complex based on a microwave-induced reaction in a microchannel coupled with a post-wall 24.15 GHz waveguide. The chip structure for continuous microwave irradiation of solvents and reactants comprises a post-wall waveguide and a microchannel that enters and exits the waveguide by passing between the metallic posts. To miniaturize the waveguide, it is designed to contain the 24.125 GHz industrial, scientific, and medical (ISM) band instead of the commonly used 2.45 GHz ISM band. Polytetrafluoroethylene (PTFE; $\varepsilon r = 2.1$) is used as a dielectric material through which the microwaves propagate because PTFE is suitable as chemical container owing to its high resistance to heat load (up to 300 °C) and its chemical inertness. Various microfluidic configurations such as curved channels and reservoirs may be integrated into the waveguide cavity between the post walls. For a microwave input power of 3.0 W, the water temperature in the microfluidic channel increases to 75.9 °C. We used such a chip to synthesize a ruthenium complex via a microwave-induced reaction in the microchannel inside the post-wall waveguide. For this synthesis, the microwave frequency and power in the waveguide were 24.15 GHz and 3.0 W, the irradiation time was 120.0–600.0 s, and the solvent temperature was 70 °C. After microwave irradiation of the microfluidic channel, the specific fluorescence emission spectrum of Tris (2,2′-bipyridyl) ruthenium(II) is observed. This work thus demonstrates the on-chip synthesis of a ruthenium complex with a high reaction rate and yield by using a microwave-induced reaction in a microchannel inside a post-wall waveguide designed to contain 24.15 GHz microwave radiation.

1. Introduction

Microwave heating [1–5] is recognized as the leading method for inducing chemical synthesis with very high reaction rates and yields [6–11]. These advantages are due to the specific effects of microwave radiation on molecular motion (for example, ion migration and dipole rotation), which accelerates the reaction steps [12–17]. Currently, commercially available microwave devices such as rectangular waveguides and multimode cavities are often used with high-power sources of ~100 W in the 2.45 GHz band [18–21]. However, to obtain multiple sequential and combinatorial chemical reactions with a small amount of source reagents and products in a reduced-size system, a promising approach is lab-on-a-chip (LOC) and microfluidics [22–29], including microreactor technology. Microreactors exploit the high surface-to-volume ratio and small diffusion length of molecules to create reactions; they thus provide precise temperature control and high reaction rates and yields. Microreactors are becoming ever smaller and are reaching the domain of microfluidics; they have been used not only for chemical reactions but also for biochemical reactions such as enzyme-catalyzed reactions, immune reactions, and cell cultivation [30–34]. In conventional microreactors or microfluidics, chemical synthesis is induced by external heating such as resistance heating, laser heating, or Peltier-effect heating [30,35,36]. These methods lead to chemical reactions with extremely low reaction rates, such as esterification of benzoic acid or the synthesis of metal complexes (these reactions have not yet been induced by using microfluidics). However, by microwave heating combined with microfluidics, extremely high reaction rates and yields should be possible in a more sequentially integrated

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http://dx.doi.org/10.1016/j.snb.2016.10.127

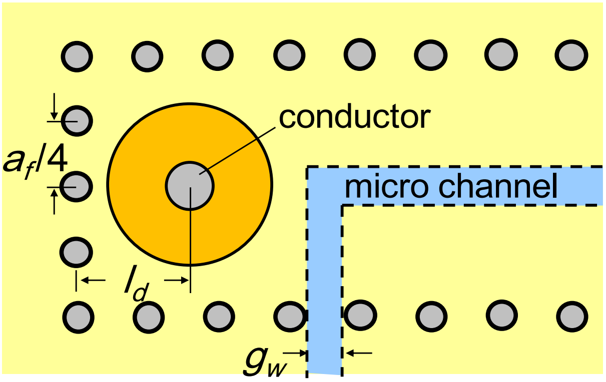

Fig. 1. Schematic diagram of basic structure for the continuous microwave irradiation using the post-wall waveguide with straight section. The height of the post-wall waveguide less than the wavelength leads the propagation mode to be TE10-like mode.

chemical-synthesis platform that offers extremely precise control of the reaction [37,11]. Unfortunately, few reports exist on microreactors wherein chemical and biochemical reactions are induced by microwaves. To address this issue, we demonstrate in the present work the on-chip synthesis of a ruthenium complex achieved by a microwave-induced reaction in a microfluidic channel inside a post-wall waveguide designed to confine 24.15 GHz microwave radiation. Two advantages of microwave heating compared with thermal heating are “inner heating,” which avoids heating the containment shell and “selective heating” of specific materials with high relative permittivity. To locally heat a chip, one approach is to combine a microwave guide with a microchannel. Although packaging a conventional rectangular waveguide with a microfluidics system is not easy, the two may be combined by using a post-wall waveguide. Circuit patterns are easily implemented with post-wall waveguides, which involve placing metallic posts periodically in a parallel-plate waveguide or on a grounded dielectric substrate. Such waveguides are either called post-wall waveguides [38,39] or substrate-integrated waveguides [40]. They have been used as feed waveguides for slot-array antennas, leakage-wave antennas, cruciform directional couplers [41], etc. In this work, we propose a chip-size structure that allows continuous microwave irradiation to drive radiation-induced chemical synthesis. The structure consists of a post-wall waveguide and a microchannel that passes between the metallic posts. To miniaturize the waveguides, the system uses the 24.125 GHz industrial, scientific, and medical (ISM) band instead of the commonly used 2.45 GHz ISM band. The temperature of water, ethanol, acetyl acetone, etc. under microwave irradiation are examined both numerically and experimentally by considering microwave sources of approximately 3 W. We also describe the on-chip synthesis of a ruthenium complex based on microwave-induced reactions in a microchannel inside a 24.15 GHz post-wall waveguide.

2. Design and experiment

2.1. Design: of microchip with microchannel combined with post-wall waveguide

The microchip design uses a post-wall waveguide with a microchannel arranged between the metallic posts. Fig. 1 shows a schematic illustration of the basic structure for allowing continuous microwave irradiation by using a straight post-wall waveguide. The space between the top and bottom metallic plates is filled with a dielectric material of relative permittivity εr, and metallic posts of radius *r* are fixed at intervals *af/4* and spacing *s* (see Fig. 1). With the proper choice of *af* and *s* and the proper waveguide arrangement, microwave leakage from the gaps between the posts can be sufficiently suppressed. In general, because the height of the post-wall waveguide is less than the wavelength of the microwave radiation, the propagation mode is a TE10-like mode, which is very similar to the TE10 mode of a conventional waveguide.

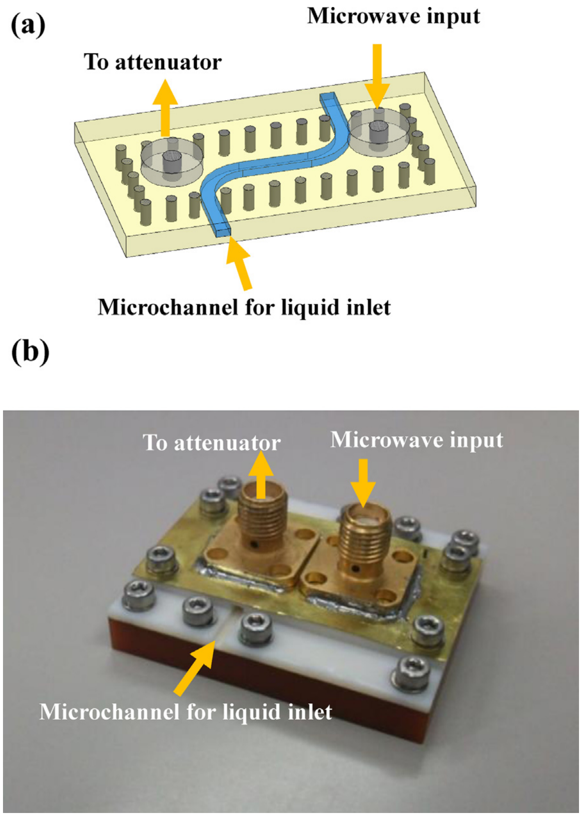

Fig. 2. (a) Perspective diagram of designed structure of microchannel embedded in the post-wall waveguide. (b) Photograph of fabricated structure of microchip of which microchannel is embedded in the post-wall waveguide. A micro liquid channel that flows into the post-wall waveguide is introduced in the space of dielectric medium material (PTFE).

Fig. 2(a) shows a perspective drawing of the microchannel embedded in the post-wall waveguide. A microfluidic channel in the space between the dielectric material (polytetrafluoroethylene; PTFE) passes through the post-wall waveguide, as shown in the image of the fabricated device [Fig. 2(b)]. Note that the microfluidic channel easily passes through the gaps between the metallic posts, which simultaneously confine the microwave energy.

This device combines the following functions: (1) injection of solvent and solute into the microfluidics channel, (2) microwave irradiation of liquid in the post-wall waveguide, and (3) continuous removal of chemical products from post-wall waveguide. The microfluidic channel itself can be fabricated by machining grooves in the dielectric material. Various microfluidic configurations such as curved channels and reservoirs may be inserted between the post-walls. In addition, the post-wall waveguide can be configured to concentrate the electromagnet field by forming an iris, a cavity structure, etc. In this work, the post-wall waveguide is designed to contain the 24.125 GHz ISM band. We use PTFE $(\varepsilon r = 2.1)$ as a dielectric material for microwave propagation because it is an excellent chemical container due to its chemical inertness and high resistance to heat load (up to 300 °C).

The radius *r* of the metallic posts is 0.365 mm, and the width *af* and spacing *s* of the guide are 6.8 and 1.8 mm, respectively. The height *h* of the post wall is 3.0 mm. These dimensions give a 16 GHz