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Titania microparticles using a facile microfluidic mass-transfer control method

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HIGHLIGHTS

- Designed a droplet-based microreactor for achieving the synthesis of titania particles.
- Developed a microfluidic mass-transfer method for controlling reactions in droplet microfluidics.
- Nanoprecipitation inside droplet reactors was initiated by interfacial diffusion or mass transfer.
- Titania particles with different degrees of compactness were formed.
- This microfluidic mass-transfer control technique opens up a new synthesis approach.

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ABSTRACT

Droplet microfluidics has found many applications in chemical reactions. In most of the studies, however, reactions are performed in droplet-based reactors either through introducing various reagent streams into a single droplet, or upon coalescence or merging of two droplets encapsulating different reagents. Here we introduce a facile microfluidic mass-transfer control approach for synthesizing titania microparticles using droplets as microreactors. Droplets of a water soluble and stable titania precursor aqueous solution, titanium (IV) bis(ammonium lactato)-dihydroxide (TiBALDH), were dispersed in an oil continuous phase containing a small amount of ethanol, which can precipitate TiBALDH and produce titania. Precipitation was initiated and controlled by the mass-transfer of ethanol from the continuous phase into the droplets. Titania particles with different degrees of compactness were formed and well encapsulated inside the droplets by varying the concentrations of TiBALDH in the droplet phase and ethanol in the continuous phase. This paper provides a new approach for synthesizing nanoparticles or microparticles in droplet microfluidics based on a mass-transfer control approach.

1. Introduction

Microfluidics has attracted significant interest over the past two decades in various fields as diverse as chemistry, physics, biology and engineering (Stone et al., 2004; Whitesides et al., 2001; Zhao et al., 2011b; Zhao and Middelberg, 2011). Droplets formed within microfluidic channels are ideal microreactors for fabricating materials as well as conducting analysis and reactions by virtue of a number of unique properties, including precisely controlled small volume and composition, restricted dispersion and limited cross contamination (Fletcher et al., 2002; Nie et al., 2005; Song et al., 2006). To perform reactions in droplet-based microreactors, various techniques have been developed to introduce reagents into droplets. For example, reagents can be introduced through pumping two streams of reagents with a buffer stream in the middle to prevent premature mixing, and controlled mixing initiates reactions inside droplets (Song et al., 2003) (Fig. 1a). In addition, reactions start upon coalescence or merging of two droplets encapsulating different reagents (Chen et al., 2011; Mazutis et al., 2009) (Fig. 1b). However, both of these two common approaches suffer a number of problems. For rapid reactions, premature mixing as a result of two or three streams of solutions introduced from inlets is hard to avoid. Coalescence between droplet pairs is also not easy to control precisely. Therefore, alternative approaches are desirable to enable precise control of reactions inside droplet microreactors.

Titanium dioxide has attracted extensive interest because of its attractive chemical, electrochemical and optical properties and its widespread applications, including those in cosmetics and sunscreen, catalysis, dye-sensitized solar cells, and water treatment. However, the synthesis of titania particles suffers a number of difficulties,

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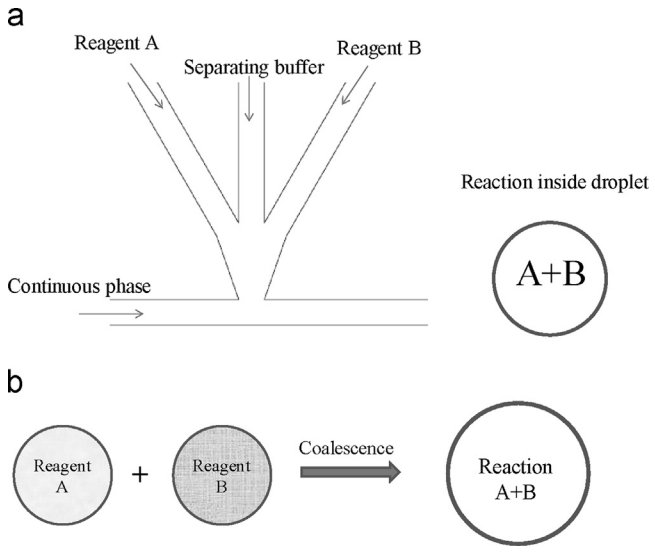

Fig. 1. Schematic illustration of reactions in droplet-based microreactors. (a) Reaction induced by introducing different reagents from separate streams and (b) reaction initiated by coalescence of droplets containing different reagents.

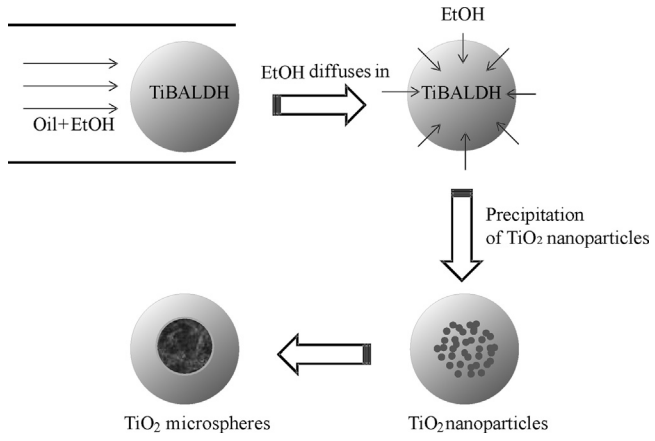

Fig. 2. Schematic illustration of synthesis of TiO_2 microspheres using the diffusion of ethanol from the continuous phase to the dispersed droplet phase.

because most titanium precursors (titanium alkoxides, titanium tetrachloride, etc.) are extremely sensitive to water, which renders the sol–gel reactions between titanium precursors and water too rapid to control. A microfluidic T-junction device has been demonstrated to produce TiO_2 microspheres (150–400 μm in diameter) by controlled aggregation of TiO_2 nanoparticles in uniform water droplets containing a titania nanoparticle suspension (Schunk et al., 2012). We also developed a facile ethanol-in-oil droplet-based microfluidic approach for making titania hollow spheres through controlled interfacial reaction (Zhao and Middelberg, 2013). The titania precursor titanium tetrabutoxide dissolved in the continuous oil phase reacts with water in the ethanol droplet through a controlled interfacial reaction. The vigorous reaction was slowed down by separating the two reactants into two different phases. Instead of using highly reactive titania precursors, we also demonstrated biomolecule-based biomimetic approaches to synthesize titania nanoparticles using a water soluble and stable precursor titanium(IV) bis(ammonium lactato)-dihydroxide (TiBALDH) under benign conditions, including neutral pH, ambient temperature, and the absence of caustic chemicals (Zhao et al., 2012b). TiBALDH is stable at ambient temperature in neutral solution, simplifying control over its reaction.

In this paper, we report a new facile microfluidic mass-transfer control approach for synthesizing titania microparticles using droplets as microreactors. As shown in Fig. 2, uniform TiBALDH droplets were formed in a flow-focusing microfluidic device with Miglyol oil containing a certain amount of ethanol as the continuous phase. With the diffusion of ethanol from the continuous phase to the dispersed aqueous droplet phase, the precipitation of titania is initiated, and titania particles are formed inside the droplet. Upon the aggregation of TiO_2 nanoparticles, TiO_2 microparticles with different degrees of compactness are formed and well encapsulated inside the droplets. The microfluidic mass-transfer control method represents a novel approach not only for making nanoparticles and microparticles, but also for making complex emulsions as reported previously (Zhao and Middelberg, 2009). The technique opens up a new synthesis approach through the control of mass transfer between the continuous and dispersed phases based on droplet-based microfluidics.

2. Experimental

2.1. Materials

Miglyol® 812 oil (AXO Industry SA, Wavre, Belgium) containing a small amount of ethanol and 0.05 wt% PEG-30 Dipolyhydroxystearate (Croda, Australia) was used as the continuous phase as it does not swell the PDMS microchannels, and TiBALDH aqueous solution was used as the dispersed phase. PEG-30 Dipolyhydroxystearate (ARLACEL P135), a gift from Croda, was used as the surfactant to stabilize the droplets. Water was obtained from a Milli-Q system (Millipore, North Ryde, Australia) equipped with a 0.22 μm filter and had a resistivity of >18.2 MΩ cm.

2.2. Microfluidic device

The microfluidic device was fabricated from poly(dimethylsiloxane) (PDMS) using standard soft-lithography and SU-8 photolithography techniques, and bonded to PDMS-coated glass coverslips to provide uniform surface properties on all walls of the channel as reported previously (Zhao et al., 2011a, 2012a). The flow-focusing microfluidic device is shown in Fig. 3a. The spiral microchannel was 200 μm wide and the downstream expansion channel was 800 μm wide. All the microchannels were 200 μm deep.

Experiments were performed in a flow-focusing microfluidic device with a combination of a flow-focusing geometry for droplet formation and a long spiral channel for droplet-based reaction (Fig. 1a). The continuous phase (oil phase with ethanol, 200 μL/h) flowed through the two side channels of 160 μm width, and the dispersed phase (containing TiBALDH, 20 μL/h) was introduced from the central channel of 40 μm width. The three streams met at the focusing part (width 200 μm). After droplets were sheared off at the flow-focusing part, they traveled along a spiral channel. To ensure enough time for the diffusion of ethanol and the precipitation of TiO_2, the spiral channel was designed with a length of 0.27 m.

2.3. Experimental setup

Two gas-tight SEG glass microsyringes (Analytical Science Pty Ltd., Ringwood, Australia) were filled with liquids and mounted on motor-driven syringe pumps (Harvard Pump 11 Plus, Harvard Apparatus, Holliston, Massachusetts). The PDMS device was linked to the syringes through polyethylene tubing. Images of droplet formation and nanoparticle precipitation were captured and recorded by a video camera (Powershot A640, Canon Inc., Tokyo, Japan) mounted on an inverted optical microscope (Eclipse TS100, Nikon Corporation, Tokyo, Japan).