Particuology 24 (2016) 1–17

Contents lists available at ScienceDirect

Particuology

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

Review

Recent advances in the production of controllable multiple emulsions using microfabricated devices

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ARTICLE INFO

Article history:
Received 20 September 2015
Received in revised form 12 October 2015
Accepted 18 October 2015
Available online 18 December 2015

Keywords:
Membrane emulsification
Microchannel emulsification
Droplet microfluidics
Microencapsulation
Multiple emulsions
Janus droplets

ABSTRACT

This review focuses on recent developments in the fabrication of multiple emulsions in micro-scale systems such as membranes, microchannel array, and microfluidic emulsification devices. Membrane and microchannel emulsification offer great potential to manufacture multiple emulsions with uniform drop sizes and high encapsulation efficiency of encapsulated active materials. Meanwhile, microfluidic devices enable an unprecedented level of control over the number, size, and type of internal droplets at each hierarchical level but suffer from low production scale. Microfluidic methods can be used to generate high-order multiple emulsions (triple, quadruple, and quintuple), non-spherical (discoidal and rod-like) drops, and asymmetric drops such as Janus and ternary drops with two or three distinct surface regions. Multiple emulsion droplets generated in microfabricated devices can be used as templates for vesicles like polymersomes, liposomes, and colloidosomes with multiple inner compartments for simultaneous encapsulation and release of incompatible active materials or reactants.

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http://dx.doi.org/10.1016/j.partic.2015.10.001

Introduction

A multiple (double or duplex) emulsion is an emulsion in an emulsion (Garti, 1997). Conventional multiple emulsions consist of numerous drops of an inner phase dispersed within larger drops of a middle phase, which are themselves dispersed in an outer phase (Fig. 1(a)). The middle phase must be immiscible with both the inner and outer phases. Two main types of multiple emulsions are water-in-oil-in-water ($W_1/O/W_2$) and oil-in-water-in-oil ($O_1/W/O_2$) emulsions. A $W_1/O/W_2$ emulsion consists of droplets of the inner water phase W_1 dispersed within oil drops, which are dispersed in the outer water phase W_2. In an $O_1/W/O_2$ emulsion, water drops enclosing smaller droplets of the oil phase O_1 are dispersed in the outer oil phase O_2. Multiple emulsions are used to encapsulate active species in food, cosmetics, and pharmaceuticals, in separation processes, and to synthesize microcapsules (Vladisavljević & Williams, 2005). Other types of multiple emulsions have also been prepared, such as oil-in-water-in-water ($O/W_1/W_2$) (Kim, Decker, & McClements, 2006) and ethanol-in-oil-in-water (E/O/W) (Nakajima, Nabetani, Ichikawa, & Xu, 2003).

Microfluidic emulsification allows precise fabrication of structured multiple emulsions with controlled drop morphology (Fig. 1(b)–(i)). Core–shell drops consist of a single drop of an inner phase coated by a thin layer of a middle phase (Fig. 1(b)). High-order multiple emulsions contain nested drops with concentric anion-like liquid shells around the core drop (Fig. 1(c)). Depending of the number of phases within each multiple emulsion drop, high-order multiple emulsions can be divided into triple ($W_1/O_2/W_3/O_4$ or $O_1/W_2/O_3/W_4$), quadruple ($W_1/O_2/W_3/O_4/W_5$ or $O_1/W_2/O_3/W_4/O_5$), and quintuple ($W_1/O_2/W_3/O_4/W_5/O_6$ or $O_1/W_2/O_3/W_4/O_5/W_6$) emulsions consisting of three, four, and five phases, respectively, incorporated within each complex drop (Abate & Weitz, 2009). High-order multiple emulsion drops are useful in the production of complex capsules for co-encapsulation and simultaneous or sequential release of multicomponent active species (Kim & Weitz, 2011).

The multiple emulsion drops shown in Fig. 1(d) consist of a controlled number of small inner drops encapsulated within each large drop. Typically, the number of inner drops can range from one to seven (Chu, Utada, Shah, Kim, & Weitz, 2007). Each inner drop can contain a controlled number of even smaller drops and the size and number of drops at each hierarchical level can be adjusted independently (Chu et al., 2007). Fig. 1(e) depicts triple emulsion drops consisting of four innermost drops in each middle

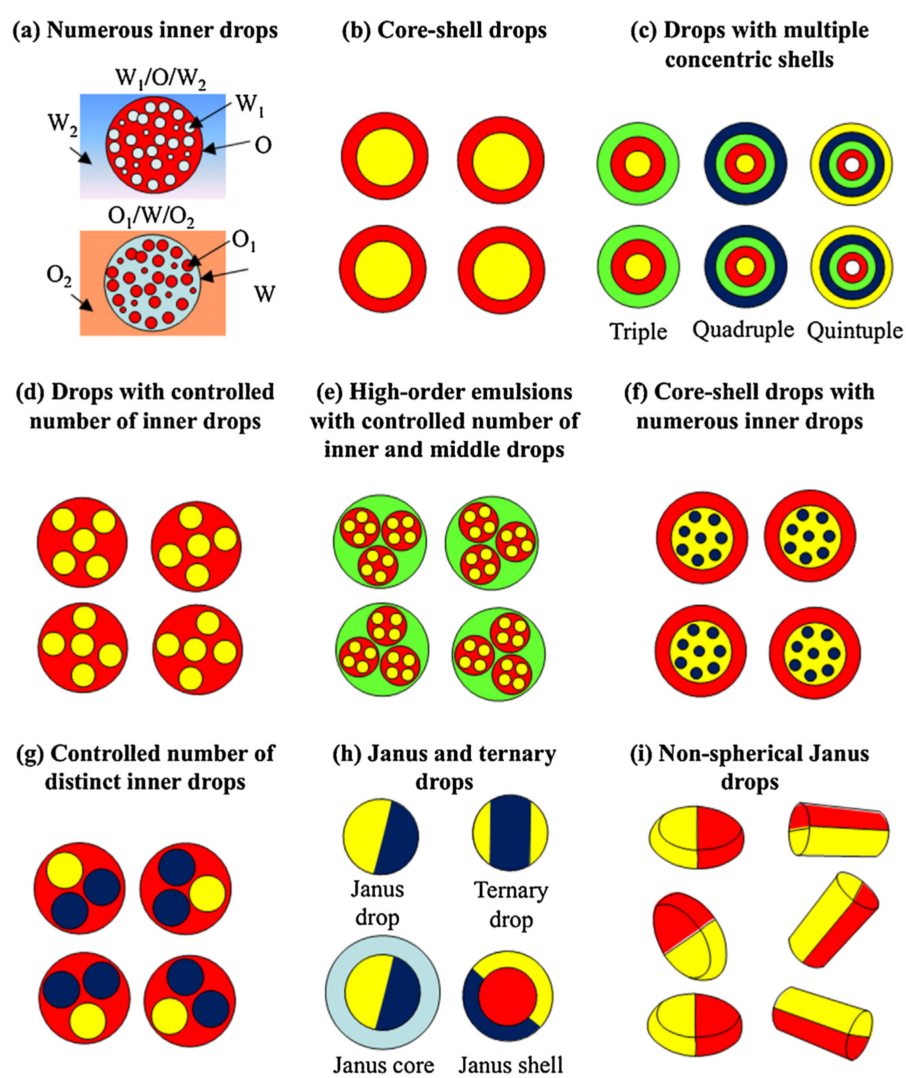

Fig. 1. Morphologies of multiple emulsion droplets: (a) numerous droplets of inner phase, (b) core–shell droplets (Vladisavljević, Shum, & Weitz, 2012a), (c) multiple concentric shells (Kim et al., 2011a), (d) droplets with a controlled number of inner droplets (2, 3, 4, . . .) (Chu et al., 2007), (e) high-order multiple emulsions with a controlled number of droplets at each level (Chu et al., 2007), (e) core–shell droplets with numerous inner droplets (Chu et al., 2007), (g) distinct inner droplets (Wang et al., 2011), (h) Janus and ternary droplets (Yang et al., 2012; Nie, Li, Seo, Xu, & Kumacheva, 2006), and (i) non-spherical Janus droplets (Shepherd et al., 2006).