LWT - Food Science and Technology 58 (2014) 667–671

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Research note

Enhanced stability of curcumin in colloidosomes stabilized by silica aggregates

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ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form
10 March 2014
Accepted 17 March 2014
Available online 25 March 2014

Keywords:
Colloidosome
Pickering emulsion
Curcumin
Oxidation
Encapsulation

ABSTRACT

A novel approach to develop colloidosomes with enhanced barrier properties that can reduce the oxidation of encapsulated bioactive compound is described. These novel colloidosomes were stabilized using silica aggregates. Silica aggregates were prepared based on electrostatic complexation between anionic and cationic silica nanoparticles and were subsequently used to stabilize sub-micron scale oil-in-water colloidosomes. Control colloidosomes stabilized using negative charged silica nanoparticles were also prepared. Particle size and ζ-potential results confirmed the formation of silica aggregates. Curcumin was used as a model encapsulant. Fluorescence microscopy results showed that curcumin was encapsulated within the lipid core of the colloidosomes. Curcumin showed significantly higher stability in colloidosomes stabilized by silica aggregates as compared to those stabilized by negative charged silica nanoparticles ($p < 0.05$). Enhanced stability of curcumin in silica aggregate stabilized colloidosomes could be attributed to higher interfacial thickness of silica aggregates compared to silica nanoparticles. The proposed approach can be a simple and efficient alternative to layer-by-layer assembly of interfacial materials.

1. Introduction

Stability of the encapsulants such as antioxidants and bioactive oils is a critical parameter in the design of encapsulation systems (Hu, McClements, & Decker, 2003; Mao, Dubot, Xiao, & McClements, 2013). Oxidation of encapsulated materials in emulsion based encapsulation systems is often triggered via free radical mediated oxidation processes. These free radicals can be generated in the vicinity of emulsion interface due to interactions of metal ions, high temperature, oxidants and light (Chaiyasit, Silvestre, McClements, & Decker, 2000; Coupland & McClements, 1996; Tikekar, Johnson, & Nitin, 2011; Waraho, McClements, & Decker, 2011) with the oil phase. Therefore, emulsions with enhanced barrier properties at the interface can significantly reduce the rate of oxidation of encapsulated bioactive compounds. To enhance the interfacial barrier properties, multi-layer coatings of biopolymers, have been deposited at the emulsion interface using the layer-by-layer coating process (Klinkesorn, Sophanodora, Chinachoti, McClements, & Decker, 2005; Mao et al., 2013). Despite flexibility in designing multi-layer coatings at the interface, the coating process itself can induce instability in emulsions due to flocculation of oil droplets induced by polymer coatings. Furthermore, the process of depositing multi-layer biopolymer coatings on emulsion droplets significantly enhances complexity of the formulation process by introducing additional separation steps for the removal of uncoated excess biopolymer at each stage of the layer-by-layer coating assembly (McClements, Decker, & Weiss, 2007).

Colloidosomes are microcapsules stabilized with a shell of colloidal particles. Similar to the emulsions, the core of these colloidosomes can consist of hydrophobic (oil) or hydrophilic materials. Furthermore, permeability of the interface of colloidosomes can be adjusted by high temperature fusing or sintering the colloidal polymeric particles such as polystyrene beads (Dan, 2012; Dinsmore et al., 2002; Lee & Weitz, 2008). However, such an approach may cause extensive degradation of temperature sensitive compounds such as flavors, and phytochemicals encapsulated in colloidosomes. Colloidosomes have also been stabilized by charged silica nanoparticles (Simovic & Prestidge, 2008; Tan et al., 2010; Tikekar, Pan, & Nitin, 2013). However, due to strong electrostatic charge on silica nanoparticles, these nanoparticles provide a limited interfacial coverage (Midmore, 1998) and may not offer optimum oxidative stability to the encapsulant.

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http://dx.doi.org/10.1016/j.lwt.2014.03.017
0023-6438/

To address these limitations, we investigated a novel approach to enhance the barrier properties by stabilizing colloidosomes using electrostatically aggregated silica nanoparticles. Silica aggregates were prepared by mixing anionic and cationic silica nanoparticles. Electrostatic attraction between oppositely charged nanoparticles led to formation of aggregates. These aggregates were subsequently used to stabilize sub-micron scale oil droplets in the aqueous phase. Fig. 1 shows the schematic representation of the proposed approach. We hypothesized that assembly of larger silica aggregates at the interface can enhance the barrier properties of the interface. Since oxidative stability of encapsulants is a function of the barrier properties of the interface (Pan, Tikekar, & Nitin, 2013; Tikekar & Nitin, 2011, 2012), we postulated that colloidosomes stabilized by silica aggregates will enhance the stability of encapsulant compared to colloidosomes stabilized by anionic silica nanoparticles. To test this hypothesis, stability of curcumin was compared in colloidosomes formed by either silica nanoparticles or silica aggregates. Curcumin is a yellow colored phenolic compound that naturally occurs in a common herb, turmeric (Curcuma longa) (Anand, Kunnumakkara, Newman, & Aggarwal, 2007). It is a hydrophobic bioactive compound with multitude of health benefits including antioxidant, antibacterial and anticancer activities (Aggarwal, Kumar, & Bharti, 2003; Bhawana, Basniwal, Buttar, Jain, & Jain, 2011; Maheshwari, Singh, Gaddipati, & Srimal, 2006). However, its efficacy is limited by its poor water solubility (0.6 μg/mL) (Kurien, Singh, Matsumoto, & Scofield, 2007). Therefore encapsulation of this compound in the oil phase of colloidosomes may enhance its delivery and bioactivity.

2. Materials and methods

2.1. Materials

All the chemicals were purchased from Sigma–Aldrich (St. Louis, MO). Olive oil was obtained from Trader Joe's (Philadelphia, PA).

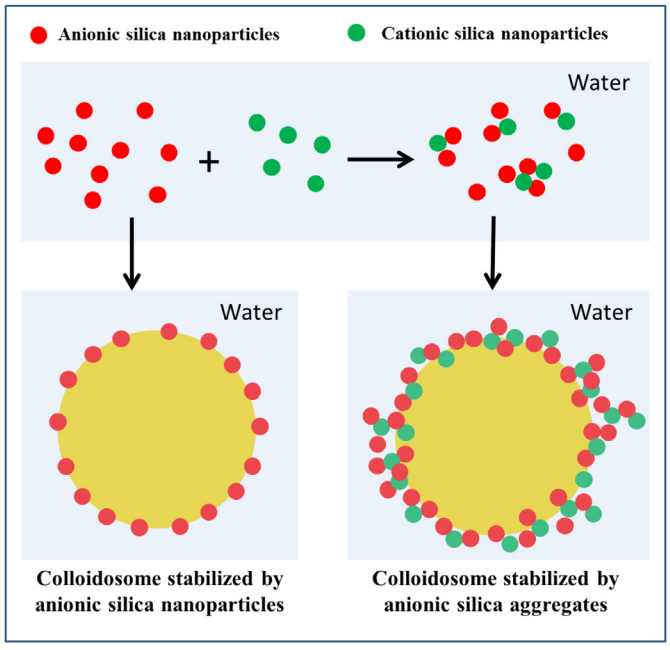

Fig. 1. Schematic representation of approach used in this study to stabilize colloidosomes.

2.2. Synthesis of silica aggregates

4 g/100 mL LUDOX®HS-30 (anionic) colloidal silica solution and 4 g/100 mL LUDOX®CL (cationic) colloidal silica solution were prepared in water by diluting the stock solutions (30 g/100 mL for LUDOX HS-30 and 30 g/100 mL for LUDOX-CL). To prepare nanoparticle aggregates, the anionic and cationic charged silica nanoparticle solutions were mixed in a 2:1 volume proportions respectively. The total volume of the aqueous phase was 50 mL. The solution was stirred for 30 min to facilitate aggregates formation. The pH of aqueous phase was adjusted to 6.5. LUDOX HS-30 (4 g/100 mL) solution adjusted to pH of 6.5 was also prepared to synthesize control colloidosomes.

2.3. Colloidosome preparation and characterization

The lipid phase was prepared by mixing 0.005 g of curcumin (1 mg/g of the oil) with olive oil at 80 °C for 20 min. The mixture was centrifuged at 14,000 *g* force for 10 min to remove insolubilized curcumin precipitated at the bottom of the centrifuge tube. The supernatant (olive oil containing solubilized curcumin) was subsequently used as the lipid phase. Coarse colloidosomes were prepared by mixing aqueous phase (pH 6.5 ± 0.1) containing either silica aggregates or silica nanoparticles and lipid phase (5 g/100 mL of aqueous phase) using a high-speed disperser (Ultra-Turrax model T25, IKA Works, Wilmington, NC) set at 8000 rpm for 2 min. These were subsequently sonicated (Ultrasonic processor Q55, Qsonica, Newtown, CT) at 60 percent amplitude for 3 min to obtain stable colloidosomes. 0.1 g/100 mL sodium azide was added to prevent microbial growth. The particle size and ζ-potential of the premixed silica suspensions and colloidosomes were measured using a particle size and zeta potential analyzer (Malvern Nano Series, Malvern Instruments Inc., Westborough, MA). Confocal microscopy was conducted to visualize distribution of encapsulated curcumin within colloidosomes using a Zeiss LSM 510 Meta confocal microscope. Confocal images of colloidosomes were obtained using a 63× oil objective with a numerical aperture of 1.4.

2.4. Curcumin stability in colloidosomes

Curcumin stability in colloidosomes was measured by storing the samples in the dark at 22 °C for a period of time (10 day) in presence of water soluble, peroxyl radical generating compound, 2,2′-azobis-2-methyl-propanimidamide, dihydrochloride (AAPH) (0.272 g/L or 1 mmol/L). Periodically, 200 μL of sample was pipetted out and mixed with 500 μL methanol to break the emulsion and extract curcumin. The mixture was centrifuged at 14,000 *g* force for 10 min. The supernatant was collected and absorbance was measured at 425 nm.

3. Results and discussion

3.1. Characterization of silica aggregates and colloidosomes

In this study, only aggregates prepared by blending anionic and cationic nanoparticles in 2:1 proportions respectively were considered because our earlier investigation showed that colloidosomes prepared with 2:1 silica aggregates had significantly higher oxidative barrier properties as compared to the colloidosomes prepared with 6:1silica aggregates (Zhao, Dan, Pan, Nitin, & Tikekar, 2013). Furthermore, our preliminary investigation in this study showed that colloidosomes prepared with silica aggregates at ratios greater than 2:1, such as 1:1, were not stable at a pH 6.5, possibly due to significant charge neutralization by blending anionic and cationic nanoparticles in 1:1 ratio. This possible