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Research Note

Enhancing the barrier properties of colloidosomes using silica nanoparticle aggregates

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ABSTRACT

Recent interest is focused on microcapsules stabilized using colloidal nanoparticles – termed 'colloidosomes – for encapsulation applications in food, drug and cosmetic industries. However, due to electrostatic repulsion between similarly charged particles, shells composed of single-type nanoparticles tend to be monolayer-thick and relatively permeable. We investigated a self-assembly method for controlling the permeability of colloidal shells using aggregates composed of oppositely charged silica nanoparticles. Using a combination of rapid fluorescence based method and theoretical diffusion models, we found that colloidosomes whose shells contained colloidal silica aggregates displayed lower permeability to peroxyl radicals than ones stabilized by single type of silica nanoparticles. Furthermore, the permeability varied as a function of the ratio of oppositely charged silica nanoparticles in the shell. The ability to control the permeability of colloidosomes, while using a simple self-assembly synthesis method, will enable enhanced control over release kinetics and oxidative stability of encapsulants.

1. Introduction

Colloidosomes are microcapsules stabilized by shells composed of colloidal particles (Dan, 2012; Dinsmore et al., 2002; Lee and Weitz, 2008; Velev et al., 1996). Colloidosomes are being widely investigated for encapsulation applications in food, pharmaceutical and cosmetic applications (Lee and Weitz, 2008; Shilpi et al., 2007; Tikekar et al., 2013). The permeability of colloidal shells has been found to depend on the thickness of the shell, as well as the packing density and size of the colloidal particles in the shell (Dan, 2012; Kim et al., 2007; Rosenberg and Dan, 2011a; Rosenberg and Dan, 2010, 2011b; Thompson et al., 2010; Wang et al., 2011; Yow and Routh, 2009). Typically, colloidosome synthesis utilizes self-assembly of charged colloidal particles at interfaces (e.g. oil/water, hydrogel/water, gas/water) (Dan, 2012). In systems composed of one type of particles, the repulsive electrostatic interactions between particles affect the shell characteristics in two ways: first, electrostatic repulsion reduces the maximum packing density that may be obtained. As a result, the shells formed are, largely, a monolayer thick. Increasing the packing density or the shell thickness therefore requires additional processes such as sintering (Dan, 2012).

We examined a simple method to reduce the permeability of colloidal shells by synthesis of shells composed of self-assembled silica nanoparticle aggregates (Fig. 1). These self-assembled silica aggregates were formed through electrostatic attraction between oppositely charged nanoparticles mixed in various weight proportions in the aqueous phase. Colloidosomes were subsequently prepared using these silica aggregates as interfacial materials. Due to electrostatic screening, the packing density in such aggregates should be higher than in single-type particle systems (Islam et al., 1995; Piechowiak et al., 2010). Furthermore, the aggregates can be multi-layered, thereby increasing the local shell thickness (Fig. 1). Thus, their incorporation into colloidosome shells should reduce the permeability, when compared to shells composed of one type of particles. Yet, the synthesis method remains simple, i.e. self-assembly. We tested this hypothesis using a combination of fluorescence based method to measure permeability and theoretical diffusion models.

2. Materials and methods

2.1. Materials

LUDOX®HS-30 colloidal silica solution (30% w/v), LUDOX®CL colloidal silica solution (30% w/v), sodium azide, 2,2′-azobis(2-methylpropionamidine)dihydrochloride (AAPH), chloroform, hydrochloric acid (37%), sodium hydroxide were obtained from

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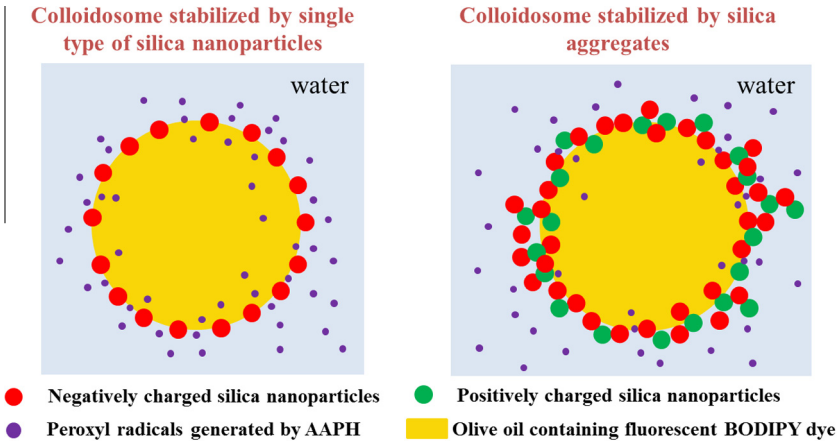

Fig. 1. Schematic representation of approach used to reduce colloidosome permeability.

Sigma–Aldrich (St. Louis, MO). Olive oil was obtained from Trader Joe's (Philadelphia, PA). BODIPY®665/676 was obtained from Invitrogen Inc. (Grand Island, NY).

2.2. Synthesis of nanoparticle aggregates

Four percentage LUDOX®HS-30 (anionic) colloidal silica solution and 4% LUDOX®CL (cationic) colloidal silica solution were prepared in water by diluting the stock solutions. To prepare nanoparticle aggregates, the anionic and cationic silica nanoparticle solutions were mixed in 6:1 or 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. 4% LUDOX® HS-30 solution adjusted to pH of 6.5 was also prepared to synthesize control colloidosomes.

2.3. Synthesis of colloidosomes

The lipid phase was prepared by mixing BODIPY®665/676 dye (3 μg/g lipid phase prepared in chloroform) with olive oil (5% w/v aqueous phase). Coarse colloidosomes were prepared by mixing aqueous phase containing silica aggregates and lipid phase using a high-speed disperser (Ultra-Turrax model T25, IKA Works, Wilmington, NC) set at 8000 rpm for 2 min. These were sonicated (Ultrasonic processor Q55, Qsonica, Newtown, CT) at 60% amplitude for 3 min to obtain stable colloidosomes. 0.1% sodium azide was added to prevent microbial growth. Control colloidosomes were prepared in the exact same manner except the aqueous phase consisted of anionic 4% LUDOX®HS-30 colloidal silica solution only.

2.4. Particle size and zeta potential measurement

Particle size and zeta potential of the silica nanoparticles, aggregates and colloidosomes were measured using a particle size and zeta potential analyzer (Malvern-Zetasizer, MA). The settings were – material oil, dispersant water, measurement angle – 90°, measurement duration automatic. Particle refractive index for silica suspensions was 1.537 and for oil droplets was 1.45.

2.5. Fluorescence imaging

Fluorescence images of colloidosomes stabilized by silica nanoparticles, 6:1 silica aggregates and 2:1 silica aggregates and encapsulated with fluorescent BODIPY® 665/676 dye were obtained using a confocal microscope with 60 × oil immersion lens (numerical aperture 1.35). The samples were diluted by mixing one part of colloidosome solution with one part of water to enable visualization of individual particles. The excitation and emission wavelengths were 635 and 647 nm respectively. Images were analyzed using ImageJ image analysis software (NIH, open source). The distribution of fluorescent dye within the colloidosomes was measured using a line-scan function of ImageJ.

2.6. Measurement of peroxyl radical permeability across colloidosome interface

We followed a procedure developed previously (Bricarello et al., 2012; Tikekar and Nitin, 2011, 2012): Peroxyl radicals were generated by dissolving 40 mM AAPH in ultrapure water. It was further diluted to 20 mM by mixing 100 μL of samples with 100 μL of AAPH solution, immediately after which, the samples were placed in the plate-reader (Spectramax M5, Molecular 10 Devices, Carlsbad CA) to measure fluorescence intensity. The values were obtained at an interval of 20 min for a period of 20 h. The excitation and emission wavelengths were 620 nm and 675 nm respectively. The relative fluorescence intensity was calculated using the following equation:

$$\text{Relative fluorescence intensity} = (I_{t\ AAPH}/I_{0\ AAPH}) \times 100/(I_{t\ control}/I_{0\ control}) \quad (1)$$

where $I_{t\ AAPH}$ is the fluorescence intensity of the sample after 't' minutes upon exposure to AAPH, $I_{0\ AAPH}$ is the fluorescence intensity of the sample immediately after adding AAPH, $I_{t\ control}$ is the fluorescence intensity of control after 't' minutes, $I_{0\ control}$ is the fluorescence intensity of control immediately after adding AAPH.

2.7. Theoretical model

Colloidosomes are composed of two regions: core, and colloidal shell (Fig. 1). Solutions for diffusion in such systems have been previously derived (Crank, 1975); The fraction $f(t)$ of diffusant into the core is given by

$$f(t) = 1 - \frac{\sum_{n=1}^{\infty} \frac{\exp\{-Dt\beta_n^2/a^2\}}{\beta_n^2(\beta_n^2+L^2-L)}}{\sum_{n=1}^{\infty} \frac{1}{\beta_n^2(\beta_n^2+L^2-L)}} \quad (2)$$

where t is time, D is the diffusion coefficient in the core medium, a is the diameter of the core, and L is the effective, dimensionless shell