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A facile method for fabricating room-temperature-film-formable casein-based hollow nanospheres

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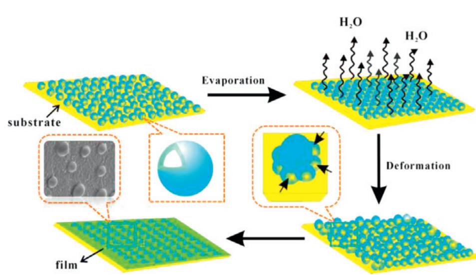
HIGHLIGHTS

- A novel and facile method for developing nanostrucured casein-based hollow spheres was proposed, which has been rarely reported.
- Casein, besides its matrix advanced function, also plays a key role in stabilizing and emulsifying the emulsion.
- The as-prepared hollow nanostructured coatings material displays good film-forming ability at room-temperature, which make it a good candidate for coating material.

GRAPHICAL ABSTRACT

The possible film-forming mechanism of casein-based hollow nanospheres.



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ABSTRACT

Room-temperature-film-formable casein-based hollow nanospheres, in which modified casein act as the shell and hollow interior as the core were innovatively prepared by alkali swelling process. Results of the TEM, AFM and DLS definitely confirmed the hollow structure and nano size of the as-prepared emulsion. The results also revealed that a film is easily formed on substrates like quartz glasses at room-temperature. The resultant thin films with hemispherical protrusions on surface make them good candidates in coating applications. A formation mechanism of coatings with this hollow nanosphere was then proposed accordingly.

1. Introduction

Over the past decades, organic materials with unique morphologies e.g., nanotubes [1], strawberry [2], core–shell [3] or hollow [4] have dramatically attracted a lot of attentions. In particular, the organic materials with hollow interior are of great interests for their wide applications in drug delivery system, catalysis, energy, adsorbent and coating fields because of excellent opacity, light mass, high specific surface area and the available interior spaces [5–9]. Given that the urgent voice of green chemistry principles, organic hollow spheres are experiencing a paradigm converting from synthetic polymer to natural polymer [10,11]. Natural Materials which can be derived from plants and other organisms are one of the types of such hollow structures.

So far, natural-based hollow polymers mainly focus on chitosan [12–14]. Besides, a few reports are related to starch [15], gelatin

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[16], pectin [17], polylactic acid [13,18] polysaccharide [11] and casein [19–21]. Among them, casein is actually of significance for practical applications [22] due to its exceptional surface-active stability, emulsifying ability and natural film-forming ability. In the case, casein-based micro- and nano-particles hold the most promise in food, drugs and cosmetics since they have remarkable superiority in biocompatibility, biodegradability and metabolism [19]. To better meet the requirement of the industries, several researchers used casein as substrate to fabricate hollow polymer material for broader applications. For instance, Liu et al. [10] reported a molecular self-assembly method to produce hollow protein nanospheres in aqueous solution. The resultant hollow protein showed extraordinary capability to penetrate cell barriers in an energy-independent fashion. Xu et al. [20] developed microwave synthesis route of hollow magnetic supraparticles by employing casein-micelle as a structure-directing agent. Zhang et al. [21] prepared hollow capsules under the action of self-assembly of caseins in the presence of sessile air bubbles temples. Their findings are interesting. However, the above synthesis of casein-based hollow nanospheres needs to satisfy certain conditions, for example, high-performed coatings since their limited access to film-forming property. Therefore, it is expected to study a way, which is facile, inexpensive, low-energy friendly and feasible in industry, to synthesize of casein-based hollow nanospheres.

As is known, seeded emulsion polymerization is one of the most widely used industrial methods [23] for fabricating well-dispersed hollow nanospheres, whilst alkali swelling is the predominant method to trigger the formation of multi-hollow structure [24]. To our knowledge, the described means to synthesize casein-based hollow nanospheres to date has scarcely investigated by alkali swelling route. Additionally, few works have been done on the correlation between structure and performance of casein-based films. Müller-Buschbaum et al. and Gebhardt et al. [25,26] was established a link between the casein micelle structure and casein film using characterization techniques including grazing-incidence small-angle neutron scattering (GISANS) and atomic force microscopy (AFM), which gives us good inspiration. In our previous study, we have investigated a series of researches on chitosan, casein and collagen [27]. For example, casein-based coatings have been successfully designed for leather finishing, drug delivery system and ink binders [6,28,29], which laid a good foundation for the further study. Driven by the case and motivated by the above mentioned literature, herein, we report casein-based hollow nanospheres through seeded emulsion polymerization, followed by alkali swelling. The as-prepared spheres are expected to have special room-temperature-film-formable ability with special hollow interior. It would be a good candidate for fascinating and promising functional coatings.

2. Experimental

2.1. Materials

Casein was purchased from Zhejiang Huatian Ltd. Triethanolamine, methyl acrylic acid (MAA) were supplied by Tianjin Fuchen Chemical Engineering Co., Ltd. Caprolactam was obtained from Shanghai Guoyao Chemical reagents Co., Ltd. Ammonium persulfate (APS), Absolute ethyl alcohol were supplied by Tianjin Hongyan Chemical Engineering Co., Ltd. Butylacrylate (BA) and methyl methacrylate (MMA) werepurchased from Tianjin Kemio Chemical Reagents Co., Ltd. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Tianjin Dalu Chemical Co., Ltd. Hydrofluoric acid (HF), a kind of dangerous chemical, was provided by Tianjin Binhai kedi Chemical Co., Ltd. All the chemicals were of analytical grade and used without further treatment.

2.2. Synthesis of casein-based core–shell nanospheres

Casein-based core–shell nanospheres were synthesized by seeded emulsion polymerization from MMA, BA, and MAA in the presence of APS. CA-CPL was firstly prepared according to our previous study [29]. In a 250 mL round-bottomed flask equipped with a mechanical stirrer, a temperature controller, and a condenser. This solution was kept stirring under $65 \pm 2\,°C$. When the temperature was raised to $75 \pm 2\,°C$,2 g mixture of acrylate monomers, including MMA, MAA, and BA and 10 g aqueous solution of APS was added to the flask. After 1 h of polymerization at $75 \pm 2\,°C$, the seed emulsion was obtained. Then, 0.30 g of APS dissolved in 10 mL of distilled deionized water, 1.5 g of BA, 3.0 g of MMA, and 1.5 g of MAA were drop wise added into the system with an appropriate dropping rate, respectively. After the temperature was heated to $80 \pm 2\,°C$, the reaction was allowed for 1.0 h. 4 g of BA, 2 g of MMA and initiator solution of 0.3 g of APS dissolved in 9.0 g of distilled deionized water were simultaneously fed to the system, and the reaction was allowed for 1.0 h. Finally, the system was cooled down to room temperature to obtain casein-based core–shell nanospheres.

2.3. Fabrication of casein-based hollow nanospheres

Casein-based hollow nanospheres were obtained by subsequent alkali swelling of casein-based core–shell nanospheres. In brief, 50 g of casein-based core–shell nanospheres were charged into a reactor which was immersed in a water bath at 90 °C, and the initial pH value of the nanospheres was accurately adjusted to 9.0–11.0 with 20 wt% aqueous sodium hydroxide under stirring at around 300 rpm. After 1.0 h ~ 5.0 h, the latex was cooled down to ambient temperature. Thus, casein-based hollow nanospheres were obtained.

2.4. Film Preparation of casein-based nanospheres

Before deposition, the substrate, quartz glass with $50\,mm \times 20\,mm \times 1\,mm$ in size, was cleaned in deionized water and ethanol ultrasonically and then dried with a stream of nitrogen. Firstly, 2 g of as-prepared emulsion was spread uniformly on quartz glass. After being dried up at room-temperature until constant weight was obtained, the films were conditioned under standard atmospheric conditions for 24 h prior to UV–vis tests.

2. 5 Characterization of casein-based nanospheres

Before tests, the samples have to be purified by five times of centrifugation-dispersion cycles using hydrofluoric acid, hydrochloric acid and deionized water. After being drying up, the simples were ground into powder. Prior to FT-IR characterization, casein-based powders were prepared by being dried in an infrared-ray oven until their weight reached constant. A pure KBr disk was pressed, and its IR spectrum was measured and determined to be IR-transparent. Then, KBr was mixed with the same dose of as-produced powders and pressed in a disk-shaped probing sample for IR measurements. Then, the chemical structure of the casein-based powders were determined by an IR Prestige-21 FT-IR spectrometer (Shimadzu, Japan) in the spectra range from $4000\,cm^{-1}$ to $400\,cm^{-1}$ with resolution of $4\,cm^{-1}$ and a forward and reverse moving mirrors speed of 10 and 6.2 kHz, respectively were used. The mean particles diameter and morphology of the as-prepared powers were characterized using a S4800 SEM instrument (Hitachi, Japan) equipped with an energy-dispersive X-ray (EDAX) 32 system simultaneously. Before tested, the nanospheres samples were sputter-coated with gold to enhance their surface conductivity before scanning at an acceleration voltage of 5 kV. The nanosphere samples were diluted to 0.1% using deionized