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Controlled release of astaxanthin from nanoporous silicified-phospholipids assembled boron nitride complex for cosmetic applications

Hye Sun Lee[a,b], Dae Kyung Sung[a], Sung Hyun Kim[a], Won Il Choi[a], Ee Tag Hwang[a], Doo Jin Choi[b], Jeong Ho Chang[a,*]

[a] Center for Convergence Bio-ceramic Materials, Korea Institute of Ceramic Engineering and Technology (KICET), Chungbuk 28160, South Korea
[b] Department of Materials Science and Engineering, Yonsei University, Seoul 03722, South Korea

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ABSTRACT

Nanoporous silicified-phospholipids assembled boron nitride (nSPLs@BN) powder was prepared and demonstrated for use in controlled release of anti-oxidant astaxanthin (AX) as a cosmetic application. The nanoporous silicified phospholipids (nSPLs) were obtained by the silicification with tetraethyl orthosilicate (TEOS) of the hydrophilic region of phospholipid bilayers. This process involved the co-assembly of chemically active phospholipid bilayers within the porous silica matrix. In addition, nSPLs@BN was characterized using several analytical techniques and tested to assess their efficiency as drug delivery systems. We calculated the maximum release amounts as a function of time and various pH. The release rate of AX from the nSPLs@BN for the initial 24 h was 10.7 μmol/(h mg) at pH 7.4. Furthermore, we determined the antioxidant activity (K_D) for the released AX with DPPH (1,1-diphenyl-2-picryl-hydrazyl) radical and the result was 34.6%.

1. Introduction

Liposomes have been widely used as a bio-surfactants and vesicles for delivery of cosmetics and drugs in a variety of industries for a long time [1,2]. Especially, liposomes are just utilized as a functional carriers or scaffolds to entrap the active ingredients effectively and release them on the skin in the field of cosmetics [3,4]. Liposomes are also called phospholipid vesicles, and they are composed of amphipathic molecules such as hydrophobic acyl (or fatty acid) chains and hydrophilic head groups [5]. In aqueous solution, phospholipids spontaneously form bilayers that have strong affinity with the cell membranes. The encapsulation of active ingredients of the liposome vesicles is usually performed in the hydrophobic regions using an impregnation process [6].

Drug delivery systems (DDS) are considered as a major innovation for increasing the bioavailability and stability of drug transport. The phospholipids based drug delivery systems have been found promising for better and more effective drug delivery, and have provided much more appropriate and systematic drug delivery for clinical medicines and cosmetics [7]. The use of phospholipids vesicles for delivery of active ingredient compounds has been described [8]; however, their use in cosmetic or drug delivery formulations are not efficacious. This is due to great flexibility of the vesicles in aqueous solution and mismatch between the loading capacity of the active ingredients and that of the micelles [9,10]. Moreover, silica-based surfaces and mica are the prototypes of solid supports that are currently used to form solid-supported lipid bilayers, in which they have provided indications for some differences in the SLB-formation process on these supports and the influence of the vesicle size on rupture. A detailed experimental and theoretical study is achieved during the SLBs formation [11–15]. Even though many issues regarding the formation of SLBs have been reported recently, the role of the inorganic solid support during vesicle formation remains poor understood [16–18].

To overcome these disadvantages of the using liposomes, we synthesized silicified liposomes by silicification with tetraethyl orthosilicate on the hydrophilic regions of lecithin vesicles. Moreover, the stability of these silicified phospholipids was enhanced by coupling with some inorganic or supported lipid bilayer (SLB) material such as sericite or mica [19]. Especially, boron Nitride (BN) has become a popular cosmetic ingredient because of its unique combination of silky feel, skin adhesion, and proccessability. It is widely used in a variety of formulations including; concealers, eye

* Corresponding author. Tel.: +82 55 792 2750.
E-mail address: jhchang@kicet.re.kr (J.H. Chang).

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preparations, lipsticks, and skin care products. However, there are no trials for the complexation with phospholipids.

Astaxanthin (AX) is a carotenoid pigment found in many animals and plants, and the compound can be purified in large quantity from the yeast species *Xanthophyllomyces dendrorhous* (*Phaffia rhodozyma*) [20]. In recent decades, the commercial use of AX by the cosmetic, nutraceutical, and pharmaceutical industries has attracted attention because of its higher antioxidant activity is higher than that of other carotenoids [21]. Although AX has strong antioxidant properties, it has the drawbacks of lower bioavailability and less stability when exposed to heat and light [22–24].

In this study, we designed the nanoporous silicified phospholipids assembled boron nitride (nSPLs@BN) powder and used it to demonstrate controlled release of the anti-oxidant astaxanthin (AX) as a drug delivery system for practical application in cosmetic fields. We are interested in increasing the stability and durability of drug carriers for potential applications in cosmetic fields using boron nitride as an SLB. Moreover, we calculated the maximum release amounts and the antioxidant activity (K_D) for the released AX with DPPH (1,1-diphenyl-2-picryl-hydrazyl) as a function of time.

2. Materials and methods

2.1. Preparation of nSPLs and nSPLs@BN powders

nSPLs, Mg@BN and nSPLs@BN were prepared by previous report with slight modification [9]. In brief, 1 g of hydrogenated lecithin was dissolved in deionized water in 98 mL at 80 °C. After complete dissolution, this phospholipids solution was treated by a high-pressure homogenizer to form nano-emulsions. And then, 20 g of TEOS was dropwise added into the solution to form a silicification. The prepared nSPLs were slowly dropped on the deionized water containing magnesium-grafted boron nitride at room temperature. The nSPLs coated boron nitride (nSPLs@BN) powder was obtained by the agitation of nSPLs and magnesium chelated BN powder for 24 h. Finally, the powder was filtered with deionized water and then dried under vacuum for 24 h at 25 °C.

2.2. Controlled release of AX form AX-loaded nSPLs@BN powders

AX was chosen as an anti-oxidant model drug and loaded on the nSPL@BN powders. nSPL@BN was immersed with constant agitation overnight in AX saturated solution at room temperature. After complete immersion, AX-nSPL@BN mixture was centrifuged to remove unloaded AX and dried under vacuum for 24 h at 25 °C. The controlled release of AX from the AX-nSPL@BN was achieved in phosphate buffered saline (pH 7.4, 10 mL), and was performed in a room-temperature. The total quantity of AX released from the AX-nSPL@BN was determined using a UV–Vis. spectrophotometer over different time intervals. After each measurement, the PBS buffer was replaced. Furthermore, the DPPH radical scavenging activity of AX-nSPLs@BN was carried out [24,25]. AX-nSPLs@BN was dissolved in 10 mM of PBS (pH 7.4). 0.15 M of DPPH solution in ethanol was prepared. Then, DPPH solution was mixed with the same volume of AX-nSPLs@BN solution. Radical scavenging capacity of AX-nSPLs@BN was measured with a UV–Vis spectrophotometer at different time intervals. Spectrophotometric measurements were done at 517 nm. The antioxidant activity (K_D) was calculated by determining the decrease in the absorbance by using the following equation:

$$K_D(\%) = 100 - \left[\frac{\mathrm{Abs}_0 - \mathrm{Abs}_1}{\mathrm{Abs}_0} \times 100\right] \quad (1)$$

where Abs_0 is the absorbance value at the 517 nm of the control sample, and Abs_1 is the absorbance of the samples. All measurements were done under dim light.

Table 1
Physicochemical properties of BN, magnesium chelated boron nitride powders (Mg@BN), phospholipids-coated boron nitride powders (PLs@BN), and nanoporous silicified phospholipids-coated boron nitride powders (nSPLs@BN).

Sample	V_T[a] (cm^3/g)	S_{BET}[b] (m^2/g)
BN	161.64	2.34
Mg@BN	3.96	0.01
PLs@BN	0.00	0.00
nSPLs@BN	0.00	0.00

[a] Total pore volume (V_T) was estimated at a relative pressure.
[b] Specific surface area (S_{BET}) computed using BET equation in relative pressure of $p/p_0 = 0.05 - 0.3$.

2.3. Instrumental analysis

The specific surface area (S_{BET}) and the pore volume were determined by the Brauner–Emmet–Teller (BET) with nitrogen adsorption and desorption isotherms (Micromeritics Tristar II, USA) after sample was pretreated at 100 °C overnight. The pore size distributions were calculated from analyzing the adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method. The pore volume was taken at the five points of P/P_0.

The morphology of each samples were observed by field emission scanning electron microscopy (FE-SEM) at 10.0 kV acceleration voltage (JEOL, JSM-6700F, Japan). Fourier transform infrared spectroscopy (FT-IR) analysis was performed using KBr pellets (JASCO V-460 FT-IR plus model). Ultraviolet–visible (UV–Vis) measurements were performed on a JASCO V-550 plus model.

3. Results and discussion

3.1. Characterization of nSPLs@BN

The preparation of nSPLs@BN is shown in Scheme 1, which shows the overall concept and the experimental procedure and can be described with respect to various applicators of phospholipids. Spherical micelles of lecithin were firstly synthesized at critical micelle concentrations. Lecithin has an amphiphile domain that self-assembles into nanoscale supramolecular assemblies in aqueous solution [26]. These vesicles of the nSPLs were formed via amphiphilic surfactants during the formation of nanoporous inorganic materials, and the pore size and distance depends on having silicate layers of porous structure [27]. The synthesis of the nSPLs was achieved by a TEOS based sol–gel reaction. The steps are explained for the preparation of nanoporous silicified-phospholipids-coated BN (nSPLS@BN): (a) boron nitride powders (BN), (b) magnesium chelated boron nitride powders (Mg@BN), (c) phospholipids-coated boron nitride powders (PLs@BN), and (d) nanoporous silicified phospholipids-coated boron nitride powders (nSPLs@BN) domain in the phospholipids with the silica precursor TEOS.

The FE-SEM images of (a) BN, (b) Mg@BN, (c) PLs@BN, and (d) nSPLs@BN are shown in Fig. 1, respectively. These figures show that BN has irregular morphology. This result is accord with results previously reported [9]. When Mg was chelated on the BN particles, the morphology of Mg@BN was not significantly different from the BN. This changed after the phospholipids and silicification coating processes. The image of the PLs@BN revealed the disappearance of the ordered lamellar structure seen in BN, and which resulted from coating with liquid phospholipids (Fig. 1c).

Table 1 shows the N_2 adsorption–desorption isotherm, which demonstrates the surface activation and the fixation of phospho-

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