Universidade do Minho

Escola de Engenharia

Semana da Escola de Engenharia
October 24 - 27, 2011

DEVELOPMENT AND CHARACTERIZATION OF POLYELECTROLYTE NANOCAPSULES FOR CONTROLLED RELEASE OF BIOACTIVE COMPOUNDS

Ana C. Pinheiro, António A. Vicente, Manuel A. Coimbra
Department of Biological Engineering
E-mail: anapinheiro@deb.uminho.pt

KEYWORDS

Nanocapsules, Self-assembly, Polyelectrolytes

ABSTRACT

Layer-by-Layer (LbL) assembly is based on the electrostatic interaction between oppositely charged polyelectrolytes alternatively adsorbed onto an appropriate template. Nanocapsules prepared through LbL technique can be specially engineered with controlled sizes, composition and functionality, and can be used as carriers for bioactive compounds. The present work aims at developing biodegradable hollow nanocapsules through LbL assembly of chitosan and fucoidan. The chitosan/fucoidan capsules are envisaged as a nanocarrier system for e.g. oxidation-sensitive active compounds, which would benefit from the shelter provided by the capsules. Such systems have possible applications in food and pharmaceutical industries.

INTRODUCTION

Nanoencapsulation systems exhibit high potential as carriers of bioactive substances. Core-shell nanoparticles can be produced through the deposition of polyelectrolyte layers onto colloidal nanoparticles and by removing the core, by dissolution or decomposition, from the core-shell structure, it is possible to obtain hollow nanocapsules with different properties, depending on the polyelectrolytes used. Layer-by-Layer (LbL) deposition technique is one of the most powerful methods to create multilayer nanocapsules. LbL assembly is based on the electrostatic interaction between oppositely charged polyelectrolytes alternatively adsorbed onto an appropriate template (Decher & Schlenoff, 2003). Nanocapsules prepared through LbL can be specially engineered with controlled sizes, composition and functionality, and can be used as carriers of bioactive compounds. The multilayer nanocapsules have promising applications in the release of bioactive compounds in the pharmaceutical and food industries; however for these applications to be possible, biofunctionality and non-toxic materials are the most fundamental conditions to be met. Therefore, biopolymers such as chitosan, a cationic polysaccharide with antimicrobial activity, and fucoidan, an anionic sulfated polysaccharide with various bioactive properties (such as antioxidant activity) are good candidates for the formation of functional multilayers. In this work, biodegradable hollow nanocapsules were built through the alternate deposition of 10 chitosan/fucoidan layers on polystyrene (PS) nanoparticles, used as templates, followed by removal of the PS core. The obtained multilayer nanocapsules were characterized by means of ζ-potential, quartz crystal microbalance (QCM) measurements, Fourier transform infrared (FTIR) and transmission electron microscopy (TEM).

METHODS

Preparation of nanocapsules

The chitosan/fucoidan multilayers were assembled on the PS nanoparticles by LbL deposition technique. The multilayer build-up was carried out according to (Ye, Wang, Liu & Tong, 2005) with some modifications. Briefly, 1 ml of chitosan solution (1 mg/ml, pH 3) in 1 % of lactic acid was added drop-by-drop to 0.5 ml of polystyrene suspension (0.5 % v/v), under gentle agitation and the mixture was incubated for 15 min. The excess of the polysaccharide was removed by two repeated cycles of centrifugation (14000 rpm, 20 min)/ washing /redispertion in water/sonication (40 KHz, 60 min). This procedure was repeated, this time using fucoidan (1 mg/ml, pH 7) as a polyelectrolyte. The alternate deposition of chitosan and fucoidan was repeated until the deposition of 10 layers. In order to remove the core of the polystyrene particles, the chitosan/fucoidan nanoparticles were treated with THF for 12 h. The suspension was then centrifuged at 14000 rpm for 15 min to remove the THF. This procedure was repeated two times and the resulting nanocapsules were washed three times with water, centrifuged and redispersed in water.

Characterization of nanospheres and nanocapsules

The ζ-potential of the coated polystyrene nanoparticles was determined by dynamic light scattering (DLS; Zetasizer Nano ZS, Malvern Instruments, UK). Real time deposition of chitosan and fucoidan was recorded by a Quartz Crystal Microbalance (QCM 200 purchased from Stanford Research Systems, SRS, USA), equipped with AT-cut quartz crystals (5 MHz) with optically flat polished titanium/gold electrodes on contact and liquid sides. Three replicates were performed. The morphology and the size of the nanocapsules were studied by transmission electron microscopy (TEM, EM 902A, Zeiss, West Germany). In order to confirm the removal of the polystyrene core, FTIR analyses were carried out with a Perkin Elmer 16 PC spectrometer (Perkin Elmer, Boston, MA, USA).

RESULTS & CONCLUSIONS

ζ-potential values alternated between positive and negative values after the deposition of chitosan and fucoidan, respectively, indicating the successfully deposition of these polysaccharides on the polystyrene nanoparticles. The real-time build-up of chitosan and fucoidan nanolayered assemblies was monitored by QCM and a frequency decrease was observed after each polyelectrolyte deposition, indicating that mass was being deposited, and also the adsorption equilibrium was attained and stable layers were obtained. The removal of the PS templates from the core-shell particles was confirmed by the disappearance of the characteristic bands (at 3000-3103, 756 and 698 cm^{-1}) of the PS residue in the FTIR spectrum. TEM showed that the core-shell nanoparticles exhibit a rough surface and some aggregation occurred, due to the irregular deposition of chitosan and fucoidan chains on the spherical surface of the polystyrene nanoparticles and that the hollow nanocapsules maintained their integrity and their spherical shape. Chitosan/fucoidan capsules are envisaged as a nanocarrier system of bioactive compounds and have possible applications in food and pharmaceutical industries.

ACKNOWLEDGEMENTS

The financial support from Fundação para a Ciência e Tecnologia (FCT) trough the PhD grant SFRH/BD/48120/2008 given to Ana C. Pinheiro is gratefully acknowledged.

REFERENCES

Decher, G., & Schlenoff, J. B. (2003). Polyelectrolyte Multilayers, an Overview. Weinheim Wiley-VCH Verlag GmbH & Co. KGaA.

Ye, S., Wang, C., Liu, X., & Tong, Z. (2005). Multilayer nanocapsules of polysaccharide chitosan and alginate through layer-by-layer assembly directly on PS nanoparticles for release. Journal of Biomaterials Science, Polymer Edition, 16, 909-923.

AUTHOR BIOGRAPHY

ANA C. PINHEIRO was born in Braga and went to the University of Minho, where she studied Biological Engineering and obtained her Integrated Master Degree in Biological Engineering in 2007. She worked for two years as a researcher in a project before start her PhD in Centre of Biological Engineering at University of Minho in 2009. Her e-mail address is: anapinheiro@deb.uminho.pt
Her webpage can be found at: http://www.ceb.uminho.pt/pessoas/pid.aspx?id=243.