Journal of Colloid and Interface Science 475 (2016) 196–202

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

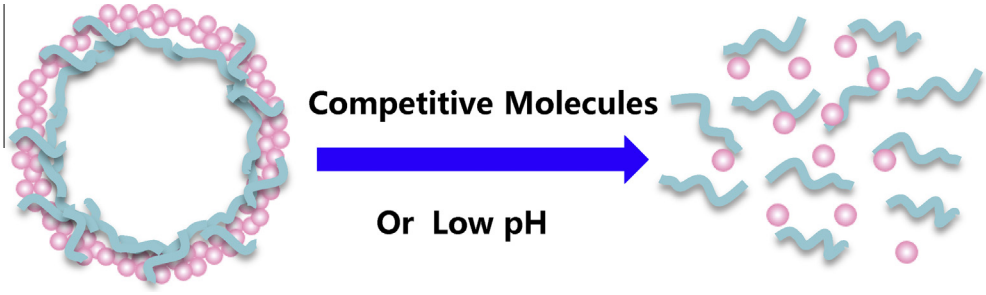
journal homepage: www.elsevier.com/locate/jcis

Dual-responsive colloidal microcapsules based on host-guest interaction on solid templates

Guangyu Li, Zhirui Dong, Yuting Zhu, Weijun Tong *, Changyou Gao

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 March 2016
Revised 28 April 2016
Accepted 28 April 2016
Available online 6 May 2016

Keywords:
Colloidal microcapsules
Host-guest interaction
Dual-responsive
Self-assembly

ABSTRACT

Colloidal microcapsules (MCs) have received considerable attention in the fields of microencapsulation, drug delivery as well as microreactors due to their unique nanoparticles-composed structure. In this study, dual-responsive colloidal MCs based on host-guest interaction were successfully fabricated via a layer-by-layer assembly method on sacrificial solid templates. Ferrocene-modified polyethylenimine (PEI-Fc) and cyclodextrin-modified polystyrene nanoparticles (PS-CD NPs) were used as building blocks for assembly. The colloidal MCs could be disassembled into nano-components upon addition of competitive adamantane (Ad) molecules or in the solution with a pH lower than 4.

1. Introduction

Colloidal microcapsules (MCs) are a novel class of microcapsules whose shell consists of coagulated or fused colloid particles [1]. Due to their hollow structure and tailored building colloidal particles of the shell, the colloidal MCs have many applications such as bio-imaging [2], enzyme catalysis [3], and controlled release [4,5]. Routes to fabricating colloidal MCs are mainly based on self-assembly of colloidal particles onto the interface of two immiscible liquid to form Pickering emulsions [6], which are usually produced through ultra-homogenizer and thereby possess large dispersion of emulsion droplets [7,8]. A narrow size distribution is important for the loading and controlled release of cargos. Thus, recently the microfluidic technique which can fabricate very uniform emulsions with controlled structures has been employed for the fabrication of colloidal MCs [9,10]. However, the yield of the microfluidic technique still needs further improvement.

To obtain stable colloidal MCs, the colloidal particles at the interface should be locked and then the MCs can survive after emulsion template removal. Methods of permanently locking together such layer of particles include thermal annealing [11], addition of polyelectrolytes [12], formation of covalent bonds [13] as well as gelation of the internal phase [14,15]. Through these

* Corresponding author.
E-mail address: tongwj@zju.edu.cn (W. Tong).

http://dx.doi.org/10.1016/j.jcis.2016.04.050
0021-9797/

methods, Pickering emulsions can be transformed into stable and robust colloidosomes, yet most of them lose the dynamic response. Recently, Scherman et al. fabricated colloidosomes based on host-guest interaction and achieved actively cargo release upon competitive molecular adding [4]. So far most of these works have been focused on the release of cargos from colloidal MCs without concern of nanoparticles (NPs) in the shells, which can also be the potential carriers for drugs. Because of their smaller size as compared with the microscale capsules, when the NPs in the shells of colloidal MCs or microparticles are disassembled in blood flow, they will experience lower drag forces, and hence attach more effectively to the nearby blood vessel wall [16]. According to this concept, microsize NP aggregates are fabricated to break into NPs and target to thrombus at obstruction of blood vessel due to the localized abnormal high fluid shear stress [16]. Thus the controlled disassembly of colloidal MCs may supply a new way to deliver both the encapsulated cargos and the NPs themselves to desired location.

Herein, as a proof-of-concept we describe dual-responsive colloidal MCs based on host-guest interaction between ferrocene (Fc) and cyclodextrin (CD). Polystyrene (PS) NPs are surface-modified with CD, and polyethylenimine (PEI) is grafted with Fc. These two building blocks are layer-by-layer assembled on solid particles. After template removal, hollow colloidal MCs can be obtained (Scheme 1). The PS NPs can be disassembled from the capsule shell under acidic condition or competitive molecule adding. Compared with traditional emulsion template, layer-by-layer assembly on solid template can achieve stable MCs with uniform size at large scale. Moreover, the colloidal MCs in this work can respond to dual-stimuli to realize controllable disassembly for potential delivery applications.

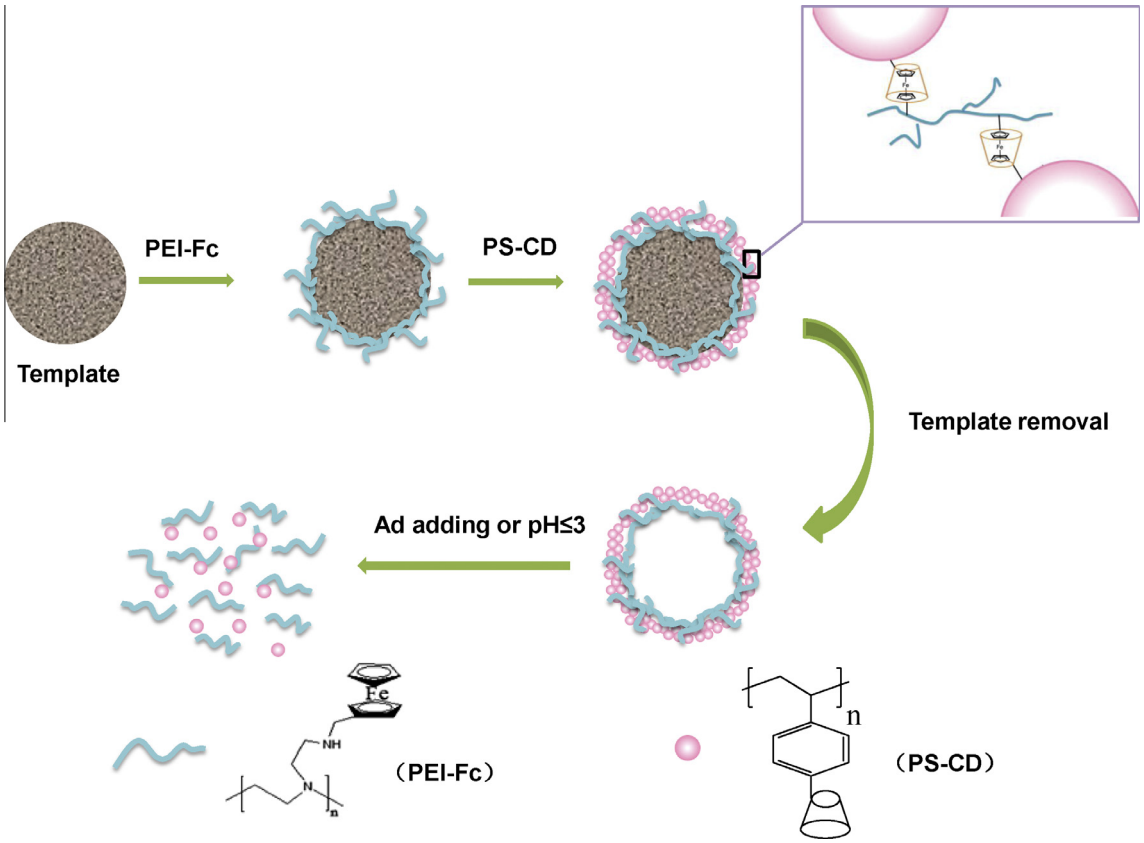
2. Experimental section

2.1. Materials

Branched polyethylenimine (PEI, average Mw ≈ 25,000), ferrocenecarboxaldehyde (Fc-CHO), amantadine hydrochloride (Ad), fluorescein isothiocyanate (FITC), and rhodamine isothiocyanate (RITC) were purchased from Sigma-Aldrich. $NaBH_4$, p-toluenesulfonyl chloride, and $MnSO_4$ were purchased from Aladdin. HNO_3, H_2SO_4, NaCl, NH_4HCO_3, styrene, ethylene diamine tetraacetic acid (EDTA), $(NH_4)_2S_2O_8$, methanol, $Na_2S_2O_4$, and β-cyclodextrin (β-CD) were purchased from Sinopharm group Co. Ld. Styrene was purified with a gel column before use. All other chemicals were of analytical grade and used without further treatment. The water used in all experiments was prepared via a Millipore Milli-Q purification system and had a resistivity higher than 18 MΩ cm^{-1}.

2.2. Synthesis of PEI-Fc

PEI-Fc was prepared according to literature [17]. Briefly, PEI (0.87 g) was dissolved in 25 mL methanol, into which Fc-CHO (0.37 g) dissolved in 5 mL methanol was added dropwise under constant agitation. After 2 h, $NaBH_4$ (0.07 g) was added into the mixed solution and stirred for 1 h. Then, the methanol was removed by a rotary evaporator and the residue was dried in a vacuum drier for 12 h. The raw product was extracted with benzene and washed with diethyl ether. After being dried under vacuum for 24 h, the product was extracted with distilled water and purified by membrane dialysis against deionized water for two weeks in dark. The final product was freeze-dried for later use.



Scheme 1. Schematic illustration of the fabrication and disassembly process of host-guest based colloidal MCs. Briefly, the colloidal MCs were fabricated via layer-by-layer method on solid templates. Fc modified PEI was the first layer assembled and CD modified PS nanoparticles were then assembled through host-guest interaction. Colloidal MCs were obtained after templates removal. Upon Ad adding or at low pH condition, these colloidal MCs can break up into nanocomponents.