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Smart Nanocontainers: Preparation, Loading/Release Processes and Applications

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Abstract

This article presents a review on smart nanocontainers, dealing with various aspects, such as their definition, classification, preparative methods, loading/release processes and recent applications. It covers advanced applications in the areas of smart coatings, drug delivery, molecular biology, environment, anticorrosion, agri-food, gas storage.

Keywords: Nanomaterials; Nanocontainer; Nanocapsules; Nanoshell; Nanocarriers; Nanotube; Nanolayers; Drug delivery; Corrosion inhibitors; Catalysts; Argi-food; Gas storage.

Introduction

Definition

Nanocontainer is a nanosized volume (in at least one dimension), which contained the active substances in its interior (hollow structure) or in inner cavities (porous structure). The smart nanocontainers are typically related with the smart releasing property for their embedded active substances. These smart releases could be obtained by using the smart coatings as their outer nanoshells. In this regard, the active agents could be released from nanocontainers by external or internal stimuli, which referred to the chemical/physical/biochemical changes within or surrounding of the nanocontainer.

The loading capacity of nanocontainers can be enhanced by using both hollow and porous nanostructures. In a specific context, nanocontainer can refer to the nanoshells (with its nano-space), i.e. nanocapsule. Various forms of nanoshells such as metallic, carbonaceous, inorganic and polymeric types have been synthesized. These nanoshells could prevent the direct contact between the active agents and the adjacent local environments. In addition, the multi-walled shells can also be envisaged to engineer the specific and desired functionality.

On the other hand, in the drug-delivery applications, nanocontainer might also be referred to nanocarrier, as a transport module for the active drugs. It is very important to enhance the drug bioavailability, and to protect the drug from chemical or metabolic alterations on their delivering pathways towards the target cells.

Classification

Nanocontainer can be classified by their nanostructures or their synthetic methods. Regarding the nanostructures, nanocontainer can be divided into 3 main groups including: i) nanoparticles based nanomaterials (three-dimensional nanostructure) [1-4], ii) nanotubes (one dimension) [5-8], and iii) nanolayers based nanomaterials (two-dimensional nanostructure) [9-11]. Similarly, in terms of synthetic materials, nanocontainers consist of organic or inorganic scaffolds in which the encapsulation of active substances has been carried out. In addition, the mixed (hybrid) metal-organic nanocontainers [12], nano-MOFs (metal-organic frameworks) [13, 14] and gold/polymer core/shell [15-17], have also been achieved. The organic nanocontainers include polymeric [18-24], lipid [25-28] and protein nanocapsules [29-30]. A variety of inorganic nanocontainers have been synthesized, such as silica-based nanomaterials [1-3], layered double hydroxides (LDHs) [10-11], ceramic-based [31], carbon-based nanocontainers (nanotubes/nanohorns) [8, 32] and gold-based nanomaterials (nanocages) [33-34].

Methods for Synthesis of Nanocontainer

Inorganic nanocontainers

Hollow nanostructures

Organic hollow nanocontainers could be synthesized by using template-assisted methods. In these methods, a thin layer of organic material is coated on the template to form the core-shell nanostructures. This template core is then removed by using the selective etching or by calcination. Based on the type of templates, there are the soft and hard templating methods. The hard templates are made generally by inorganic materials [35] (like anodic aluminum oxide [36], silica [37], carbon [38]), whereas the soft templates can refer to the organic surfactants [39] and long-chain polymers [35] (eg. amphiphilic molecules containing hydrophilic head and hydrophobic chain) [40]. In practical application, for large scale and low cost, self-templating methods have recently been developed, as the direct synthesis without using the external templates. These new self-templating methods included the surface-protected etching [41], the Kirkendall effect [42], and galvanic replacement [43].

Porous nanostructures

Porous structured nanocontainers are mainly based on mesoporous silica and zirconia. Mesoporous nanosilica could be synthesized by several methods, such as sol-gel method (Stöber process) [44, 45], spray drying [46], or using template of micellar rods [47] with supramolecular assemblies of surfactants [48].

Hollow mesoporous nanostructures are also reported for drug delivery. Hollow mesoporous zirconia could be prepared by using

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silica nanoparticles as template [49]. Whereas, the hollow mesoporous silica [50] could be synthesized from iron silicate, by selective etching of iron oxide.

Organic nanocontainers

Polymeric nanocontainers

Smart hollow polymeric nanocontainers can be used effectively for drug delivery applications. They could be prepared by using the layer-by-layer (LbL) deposition of smart (stimuli-responsive) polymeric coatings on sacrificial templates [51].

Polymeric nanocontainers could be prepared by various methods, such as suspension polymerization [52], emulsion polymerization [53], self-assembly [54], core-shell precursors [55], dendrimer [56, 57].

Lipid nanocapsules

Lipid nanocapsules are reported as new platform for nanomedicine [58]. Lipid nanocapsules are the hybrid of polymeric nanocapsules and liposomes. They could be typically prepared by PIT (phase inversion temperature) process using nonionic surfactants, oily and aqueous phases.

Protein nanocapsules

Protein nanocapsules could be prepared by various emulsification methods, such as single/double emulsions [59, 60], polymerization [61], phase separation/coacervation [62], spray drying/spray congealing [63, 64] and ultrasonic emulsification [65].

Loading and Release Processes

Regarding the loading process, active substances can be loaded into nanocontainers during [66] or after [67-69] the synthesis process. After the synthesis, nanocontainers could be directly loaded with the active agents [67-68] or using the assisted loading transfer process [69]. In some cases, the loading process will be followed by the closing of the pores [70] or by the formation of the nanotube-end stoppers [71-72]. For the release process, the active agents could be released from nanocontainers by external or internal stimuli, which referred to the chemical/physical/biochemical changes within or surrounding of the nanocontainer. For instance, various controlled release methodologies of active agents have been reported, such as desorption controlled release [73], pH-controlled release [1, 34, 70], temperature-responsive control [22], ion-exchange control [74, 75], redox-responsive control of release [76, 77], light-responsive controlled-release [78, 79] and release under mechanical rapture [80, 81].

Applications

Various kinds of active agents could be embedded inside the nanocontainer, such as drugs, self-healing agents, corrosion inhibitors, catalysts, fertilizers, pesticides, biocides, antioxidants, nutrients, gases.

Agri-food productions

It was reported that nanocontainers could enhance the efficiency of fertilizers [82] and insect pest control [83, 84]. Bio char-based fertilizers can be applied at low doses and low costs [85, 86]. Various types of effective nano-fertilizers are also reported, such as cochleate nanotubes based fertilizers [87], nanoporous zeolites [88]. As smart fertilizers, their active ingredients could be released "on demand" (conditional release) [89]. In addition, nanocontainers can be used for delivery of antioxidants/nutrients to foods [90] or for food preservation/ fortification [91].

Anticorrosion

Various inhibitors have been loaded into nanocontainers, such as benzotriazole [92], mercaptobenzothiazole [68, 93], mercaptobenzimidazole [94], hydroxyquinoline [95], dodecylamine [96], molybdate salts [97]. Several biocides have been loaded into the nanocontainers, such as zinc pyrithione and copper pyrithione [98], benzalkonium chloride [99], mercaptobenzothiazole and 4,5-Dichloro-2-octyl-4-isothiazolin-3-one (DCOIT) [100], commercial antifouling compounds [101].

Drug delivery, cell imaging and hyperthermia

In pharmaceutical applications, nanocontainers have advantages over their micro counterparts, such as more efficient drug detoxification, increased specificity of drugs, higher intracellular uptake, better stability, fewer/less side effects and higher biocompatible with tissues, cells, and other biological environments. It was reported that various types of drug could be loaded into nanocontainers, such as anticancer [102], chemotherapeutic drug [103], retroviral drugs (against AIDS) [104], Alzheimer's disease [105], infectious and inflammatory diseases [106], wound healing drug [107], intracellular drug [108], transdermal drug [109], pulmonary drug [110].

In addition, nanocontainers can be also used for cell imaging [111, 112] and hyperthermia [113, 114] applications.

Molecular biology

The compartmentalized biomimetic nanocontainers could be used for artificial cell-like systems [115]. These nano-compartments are typically based on lipid vesicles (liposomes) and synthetic analogs of liposomes (polymersomes) [116]. Their applications include synthetic vesicles [117] and (enzyme) nanoreactors [118].

Gas storage

Hydrogen could be stored in carbonaceou nanoconatainers (upon compression at low temperature) [119-121] and in metallic nanocontainers (at room temperature) [122, 123]. In case of Pd hollow spheres, Pd nanoshells could play the dual catalytic role (dissociation/recombination of hydrogen molecule), that enhanced their storage capacity [122]. Other kinds of gases, like methane [124], argon [125] and oxygen [7], could also be stored in nanotubes based containers.

Environment

By removing various kinds of organic and inorganic pollutants, carbon nanotubes based adsorbents can be used effectively in wastewater treatment [126, 127]. In addition, carbon nanotube membranes can be used for water purification [128].

Air remediation under visible light irradiation could be obtained by using TiO_2/CNTs nanohybrids [129, 130].

Smart coatings

In coating technology, the smart nanocontainers have the ability to release encapsulated active agents via the controlled ways. This makes coatings uniquely well suited for the applications in corrosion protection, self-healing, detection, delivery of bioactive species, fire retardant and antifouling [131]. By the presence of nanocontainers, smart coatings can respond simultaneously either to the changes of coating integrity, or to the variations in the surrounding environment.

The domains of application for smart nanocontainers are expected to be much larger in the future. Researchers now is trying to shed more light on the underlying phenomenal and fundamental mechanisms through which active agents release from nanocontainers, thus provide guidance for their molecular design in the new promising applications.

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