Colloids and Surfaces A: Physicochem. Eng. Aspects 410 (2012) 38–44

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Electrophoretic deposition of composite chitosan–halloysite nanotube–hydroxyapatite films

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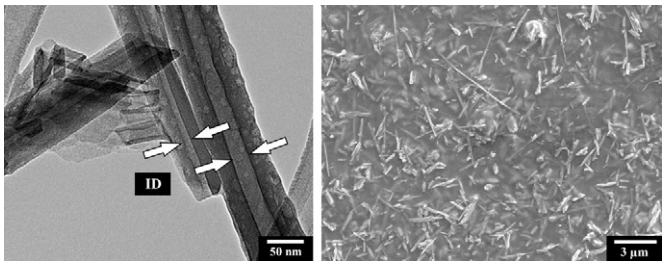
HIGHLIGHTS

- Halloysite nanotubes were electrosterically dispersed using chitosan.
- Electrophoretic deposition was developed for the fabrication of composite films.
- Chitosan–halloysite–hydroxyapatite films were deposited.
- The method allowed fabrication of monolayer, multilayer of functionally graded films.
- The films provided corrosion protection of stainless steel substrates.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 April 2012
Received in revised form 2 June 2012
Accepted 4 June 2012
Available online 19 June 2012

Keywords:
Halloysite
Nanotube
Hydroxyapatite
Nanoparticle
Chitosan
Electrophoresis
Film

ABSTRACT

Electrophoretic deposition (EPD) method has been developed for the deposition of halloysite nanotubes (HNT) and fabrication of composite chitosan–HNT and chitosan–HNT–hydroxyapatite(HA) films. The use of chitosan as a dispersing and charging agent for both HNT and HA allowed the formation of chitosan–HNT–HA monolayers, films of graded composition and multilayer laminates, containing different layers. The quartz crystal microbalance method was used for the investigation of the deposition kinetics. The composite films were studied by X-ray diffraction, thermogravimetric analysis, differential thermal analysis and electron microscopy. The deposition yield, thickness of the films or individual layers and their composition can be varied. The results of potentiodynamic studies in the simulated body fluid solutions showed that the films provided corrosion protection of the stainless steel substrates. The composite films are promising materials for fabrication of biomedical implants with advanced functional properties.

1. Introduction

Halloysite nanotubes (HNT) are of increasing interest for the nanotechnology of advanced materials in areas as diverse as catalysis, drug delivery, biomedical implants, corrosion protection of metals, biosensors, organic synthesis, flame retardant coatings, specific ion adsorbents, materials for sustained release of herbicides and anti-microbials, energy storage devices and other areas [1–5].

HNT are natural clay minerals with nanotubular layered structures, containing silica and alumina layers [2,6]. The chemical formula of HNT can be expressed as $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ ($n = 0$–2)[2]. The outer layer of the HNT is mainly SiO_2 while the inner cylinder core consists of Al_2O_3. It is known that silica and alumina have isoelectric points of 2 and 9, respectively [7–9]. Therefore, the electrokinetic behavior of halloysite at pH 7 is defined by the negative surface potential of SiO_2, with a small contribution from the positive Al_2O_3 inner surface [1]. The positive (below pH 9) charge of the inner lumen promoted loading of HNT with anionic molecules or macromolecules, which at the same time repelled from the negatively charged outer surfaces [2].

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http://dx.doi.org/10.1016/j.colsurfa.2012.06.011

A wide range of active agents, including drugs, can be entrapped within the inner lumen, as well as within void spaces of the multilayered aluminosilicate shells [2]. This entrapment can be followed by the retention and release of the agents, making halloysite a nanomaterial well suited for macromolecular delivery applications. There is an increasing interest in the use of HNT as biocompatible containers for controlled drug release and other biomedical applications [10–12]. HNT were loaded with corrosion inhibitors for the fabrication of protective coatings with advanced mechanical properties [13]. HNT were utilized as nanotemplates and nanoscale reaction vessels for the synthesis of nanomaterials [2,14]. The use of HNT lumens as nanotemplates offers promising possibilities for the synthesis of molecular wires and nanorods [2]. Recently HNT lumens were utilized for enzyme-catalyzed inorganic synthesis [2]. HNT were used as supports for immobilization of inorganic and organic catalysts [15–18] and magnetic nanoparticles [19]. HNT, loaded with corrosion inhibitors and coated with polyelectrolyte multilayers, were introduced into the silica–zirconia-based hybrid films [20], which showed good corrosion protection. The HNT reinforced composites showed advanced mechanical properties and high flame retardancy [2,21].

Significant interest has been generated in polymer–HNT composite films and coatings [2]. The incorporation of HNT into the polymer films resulted in advanced mechanical and flame retardant properties [2,22,23]. Polymer–HNT composites were utilized for the fabrication of thin film biosensors [24], supercapacitors [3], biomedical implant materials and protective coatings [2]. Recent studies showed that HNT are not toxic for cells [10] and can be used for the fabrication of biocomposites with important functional properties. HNT can be loaded with drugs, antimicrobial agents and other functional materials for the fabrication of advanced polymer–HNT films with controlled release of the materials [2]. The use of HNT for the biopolymer film reinforcement offers advantage of biocompatibility and low cost [6,10] compared to carbon nanotube reinforced biopolymer films [25,26]. Various methods have been developed for the fabrication of polymer–HNT composite films and coatings, including solution casting [24,27], painting [13] and self-assembly [6].

Electrophoretic deposition (EPD) is an attractive method for the deposition of composite films, containing HNT. This method is widely used for the deposition of inorganic materials, polymers and composites [28–30]. EPD is based on the electrophoretic motion of colloidal particles or polymer macromolecules under the influence of an electric field and deposit formation at the electrode surface [31–33]. EPD allows the fabrication of uniform films of controlled thickness and offers many processing advantages, such as high deposition rate and the possibility of deposition on substrates of complex shape [34–36]. Moreover, EPD is well suited for the fabrication of composite films [37,38]. Therefore, it would be important to apply the EPD method for the fabrication of polymer films, containing HNT.

The goal of this investigation was the EPD of composite films, containing HNT. Chitosan was used for charging and dispersing of HNT in the suspensions for EPD of chitosan–HNT films. The use of chitosan as a charging, dispersing and film forming agent allowed the deposition of composite films, containing HNT and hydroxyapatite (HA) in a chitosan matrix. HA provided improved bioactivity and biocompatibility to the composites. The films were obtained as monolayers, multilayers or functionally graded composites. Experimental data were presented on the microstructure and properties of the composite films. The composite films prepared by EPD are promising materials for biomedical applications. The method developed in this investigation paves the way for the fabrication of other composite films containing HNT in a polymer matrix for various applications.

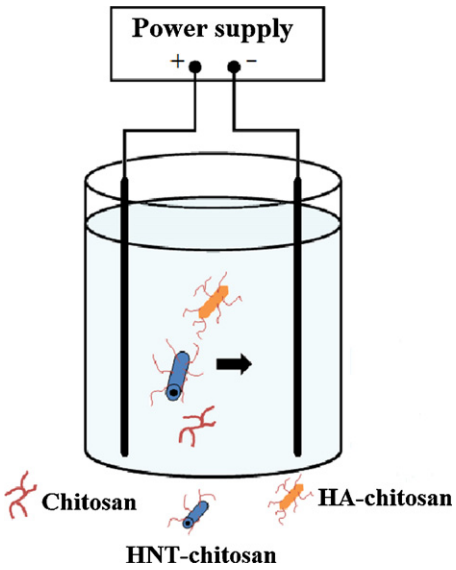

Fig. 1. Schematic of EPD cell, showing electrophoretic motion of chitosan macromolecules, HNT and HA particles with adsorbed chitosan.

2. Experimental procedures

The following chemicals were purchased from Aldrich: chitosan (M_w = 200,000) with a degree of deacetylation of 85%, acetic acid, $Ca(NO_3)_2{\cdot}4H_2O$, $(NH_4)_2HPO_4$, NH_4OH and HNT. Chitosan was protonated and dissolved in an acetic acid solution [30]. The procedure for the preparation of stoichiometric HA nanoparticles for EPD was based on that described in a previous work [39]. Precipitation was performed at a temperature of 70 °C by a slow addition of 0.6 M ammonium phosphate solution into 1.0 M calcium nitrate solution. The pH of the solutions was adjusted to 11 with NH_4OH. Stirring was performed for 8 h at 70 °C and 24 h at room temperature. The precipitate was washed with water and finally with isopropyl alcohol. It has been previously reported [40,41] that the average length of the needle-shaped HA crystals, prepared by this method, is about 150 nm and the average aspect ratio is 8. The long axis of the needles corresponded to the *c*-axis of the hexagonal HA structure.

EPD was performed from 0.1 to 0.5 g L^{-1} chitosan solutions in a mixed ethanol–water (17% water) solvent containing 0–0.6 g L^{-1} HNT and 0–1 g L^{-1} HA. The schematic of the EPD cell is shown in Fig. 1. The EPD cell included a substrate and Pt counterelectrode. The distance between the substrate and counterelectrode was 15 mm. The deposition was performed at a constant voltage in the range of 3–40 V, the deposition time was varied in the range of 1–10 min. The films were obtained on various conductive substrates, such as Pt, 304 stainless steel foils and platinized silicon wafers. The deposition process has been investigated using a quartz crystal microbalance (QCM 922, Princeton Applied Research) controlled by a computer. The deposit mass Δm was calculated using Sauerbrey's equation [42,43]:

$$-\Delta F = \frac{2F_0^2}{A\sqrt{\rho_q \mu_q}} \times \Delta m \quad (1)$$

where ΔF is the frequency decrease of the QCM, F_0 is the parent frequency of QCM (9 MHz), A is the area of the gold electrode (0.2 cm^2), ρ_q is the density of quartz (2.65 g cm^{-3}) and μ_q is the shear modulus of quartz (2.95×10^{11} dyne cm^{-2}).

Film adhesion was tested according to the ASTM D3359 standard. Electron microscopy investigations were performed using a JEOL 2010F transmission electron microscope (TEM) and a JEOL JSM-7000F scanning electron microscope (SEM). Thick deposits