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Orientation of charged clay nanotubes in evaporating droplet meniscus

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ABSTRACT

During drying, an aqueous suspension of strongly charged halloysite clay nanotubes concentrates at the edge of the droplet ("coffee-ring" effect) which provides alignment of the tubes along the liquid-substrate contact line. First, the surface charge of the nanotubes was enhanced by polyanion adsorption inside of the lumen to compensate for the internal positive charges. This increased the magnitude of the ξ-potential of the tubes from −36 to −81 mV and stabilized the colloids. Then, colloidal halloysite was dropped onto the substrate, dried at 65 °C and after a concentration of ~0.05 mg mL^{-1} was reached, the alignment of nanotubes occurred starting from the droplet edges. The process was described with Onsager's theory, in which longer nanorods, which have higher surface charge, give better ordering after a critical concentration is reached. This study indicates a new application of halloysite clay nanotubes in polymeric composites with anisotropic properties, microchannel orientation, and production of coatings with aligned nanotubes.

1. Introduction

The self-assembly of nanoparticles is a perspective route to developing devices that exploit the properties of anisotropic materials properties, ranging from electronics to biomaterials. The controlled assembly of elongated particles such as carbon nanotubes, ZnO and DNA nanowires allows for their preferential alignment along a spatial direction [1–4]. This process enhances the electrical, electrochemical, optical and electromechanical properties along the orientation line [2,5–8]. Nano-fibers and tubes organize into ordered structures either through external stimuli or interparticle interactions; electrical, magnetic or mechanical forces, and liquid flow can induce the ordering [2,5,6,9–13]. Most of the methods based on external forces require specialized equipment and they are limited in their ability to fabricate uniformly aligned nanostructures over a large area. On the other hand, self-assembly can be achieved by specific interactions between the nano-objects as is used in spin coating, inject printing and drop casting [8,9,14–18]. Recently, evaporation-induced self-assembly on solid surfaces has received attention due to the ease of fabricating highly organized structures [14–17]. Drying a droplet of nanoparticle dispersion drives the formation of ordered patterns on the substrate, which depends on the mode of solvent evaporation [17]. The pattern that is formed is often a ring-like deposit ("coffee ring") along the edge of the initial droplet. In the absence of Marangoni flow and natural convection during evaporation, when the contact line of the drying droplet is pinned, there is an outward and radial hydrodynamic flow that prevents shrinkage of the droplet, which would replenish the liquid evaporating from the edge [17,19]. This flow carries the suspended particles from the center to the droplet periphery, causing the formation of a dense ring-like deposition. When a critical colloid concentration is reached the anisotropic particles near the edge transition from the isotropic to the liquid crystal phase and align parallel to the edge, as was observed for carbon nanotubes [14,20], gold [21] and iron oxide [22] nanoparticles. The explanation for this phenomenon is based on the classic Onsager's theory of high aspect ratio rigid rods forming orientation and position ordered liquid crystalline phases [1,23]. A recent review [17] reported that the droplet-casting method was successfully used for the self-assembly of polymers, proteins, graphene and nanoparticles, such as carbon nanotubes and metal oxides. No results were yet reported for nanoclays, which are appealing natural materials for environmental friendly composites. Among the clays, halloysite is interesting for applications because of its large surface area, tunable surface chemistry and hollow tubular morphology [24,25].

Halloysite clay, which is rolled kaolinite sheets, has a tubular shape with different external and internal surface chemistry and

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high aspect ratio of about 10–30. The sizes of halloysite nanotubes (HNTs) are within 600–1500 nm in length, 10–20 nm in inner diameter, and 50–60 nm in outer diameter depending on the deposit and milling process. Halloysite has a positive alumina inner lumen and a negative silica outer surface allowing its selective functionalization [26,27] and the encapsulation of chemically and biologically active compounds [24,25,28]. The toxicity of halloysite nanotubes was analyzed for human breast cells and human epithelial adenocarcinoma cells [29]. The viability of the halloysite-treated cells (up to 0.5 mg mL^{-1}) was preserved (up to 70% of viable cells), however, at higher concentrations of HNTs, cell death was induced. A low toxicity of chitosan-based scaffolds for tissue engineering was also demonstrated by monitoring the growth of fibroblasts on nanocomposites [30]. No significant effects of fibroblasts attachment and development on chitosan-doped scaffold were observed. Therefore, halloysite is considered as safe for very high concentration up 1 mg mL^{-1} of cell culture or tissue. These properties lead to halloysite application in functional polymeric composites with controlled release of anticorrosion, antimicrobial and flame-retardant agents and for wastewater treatment [24,25,28,31–36]. Halloysite can be dispersed in aqueous solutions by modifying the inner lumen with anionic surfactants to greatly enhance the surface charge of the nanotubes [26,27]. Halloysite can form liquid crystalline phases when dispersed in aqueous solution [37].

Here we present a strategy to produce aligned halloysite structures by using evaporation-induced droplet-casting method. The nanotubes cavity was functionalized with poly(styrene sulfonate) to enhance its surface charge resulting in high colloidal stability which allows for the halloysite orientational self-assembly. The influence of the nanotubes length, charge and the concentration on orientation was analyzed. Onsager's theory and "coffee-ring" phenomenon were employed to explain the alignment self-assembly of halloysite nanotubes.

2. Experimental and methods

2.1. Materials

Two types of halloysite nanotubes with different lengths were selected to observe the orientation phenomenon: halloysite with shorter length of ca 0.6 μm and length/diameter ratio of ca 15 which underwent to two-step milling was obtained from Applied Minerals Inc. (s-HNT), and none-milled pristine halloysite with full length of ca 1.5 μm and length/diameter ratio of ca 30 was purchased from China Henan Province (1-HNT). Polystyrene sulfonate sodium salt (PSS, MW 70,000) and sodium chloride (NaCl, 99.99%) were purchased from Sigma–Aldrich and were used without further treatments. Sodium hydroxide (NaOH, 1 M) and hydrochloric acid (HCl, 1 M), prepared from analytical grade chemicals were purchased from Sigma–Aldrich and used for pH adjustments.

2.2. Preparation of PSS/HNTs hybrid for surface charge enhancing

2 g of PSS was dispersed in 100 mL of deionized water in a flask and stirred for 30 min to form a homogenous suspension. Then, s-HNTs or l-HNTs (2 g) were added gradually under continuous stirring in this solution, magnetically stirred for 48 h at room temperature and left standing for 1 h to precipitate aggregates. The individual HNTs were dispersed in the bulk, while the impurities and aggregations precipitated at the flask bottom. The supernatant dispersion was collected and then centrifuged at 5000 rpm for 10 min. The precipitated halloysite was washed 3–4 times with deionized water until it became neutral. Finally, the obtained solid was dried in a vacuum drier for 24 h and crushed into powder by mortar before use. The samples were denoted as PSS/s-HNTs and PSS/l-HNTs, respectively.

2.3. Droplet-casting method

Pristine HNTs and PSS-functionalized HNTs aqueous dispersions were prepared by adding HNTs, PSS/s-HNTs or PSS/l-HNTs into deionized water and ultrasonicated with power level of 70 W per gallon for 5 min (the concentrations ranged from 0.01 to 100 mg mL^{-1}). These aqueous dispersions can be considered physically stable because the ξ-potential of both pristine and functionalized halloysite is above 30 mV (in absolute value). The "droplet-drying" process was carried out by dropping 20–100 μL of the dispersions onto a silicon wafer substrate and drying it at selected temperatures (25, 65, and 90 °C). Ionic force and pH of the dispersions were changed by adding NaCl, NaOH and HCl, respectively.

2.4. Instrumentation

2.4.1. Zeta-potential and dynamic light scattering

ξ-potential and dynamic light scattering (DLS) measurements were taken by using microelectrophoretic ZetaPlus Potential Analyzer (Brookhaven Instruments) at 25.0 ± 0.1 °C. For this, diluted aqueous dispersions of pristine and functionalized halloysite (ca. 1 μg mL^{-1}) were transferred into the special cell and electric field was applied causing the movement of negatively charged nanotubes toward cathode. ξ-potential of the particles was determined by Smoluchowski formula. For all of the systems, the field-time autocorrelation functions were well described by a mono-exponential decay process, which provides the rate (Γ) correlated with the apparent diffusion coefficient $D_t = \Gamma/q^2$, where $q = 4\pi n\lambda^{-1}\sin(\theta/2)$ is the scattering vector, being n the water refractive index, θ the scattering angle (90°) and λ the wavelength (632.8 nm).

2.4.2. Thermogravimetry

Experiments were performed by using a TGA Q50 (TA Instruments) under nitrogen flow of 25 cm^3 min^{-1} for the sample and 10 cm^3 min^{-1} for the balance. The explored temperature interval ranged between 25 and 900 °C at a heating rate of 10 °C min^{-1}. The loading of the polymer in the PSS/HNTs hybrid was determined from the residual mass at 600 °C by taking into account the water content as reported in the literature [26,27].

2.4.3. Contact angle

Contact angle experiments were performed by using an optical contact angle apparatus (OCA 20, Data Physics Instruments) equipped with a high-resolution CCD camera and a high-performance digitizing adapter. SCA 20 software (Data Physics Instruments) was used. For the study of the evaporation kinetics, a sessile droplet (volume was 10.0 ± 0.5 μL) of modified halloysite dispersion was deposited on the silicon wafer substrate. The concentration of the dispersion was 6 mg mL^{-1} and temperature 25.0 ± 0.1 °C both for the support and the injecting syringe. During the water evaporation, the evolution of the contact angle, contact radius and droplet volume were monitored. Images were collected 25 times per second up to 15 min. The wettability of l-HNTs and PSS/l-HNTs solid pellets was also determined by measuring their initial contact angle with the sessile drop method.

2.4.4. Polarizing optical and scanning electron microscopies

The orientational processes were investigated using an Olympus BX-50 polarized light microscope under crossed polarizers during a 360° rotation of the sample. Images were captured with a microscope-mounted digital camera (Olympus C-4000 Zoom). After drying the droplet on silicon wafer, it was mounted on a specimen holder (stub) glued with carbon tap for scanning electron