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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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