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An assembly of organic-inorganic composites using halloysite clay nanotubes

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ABSTRACT

Halloysite is natural tubular clay suitable as a component of biocompatible nanosystems with specific functionalities. The selective modification of halloysite inner/outer surfaces can be achieved by exploiting supramolecular and covalent interactions resulting in controlled colloidal stability adjusted to the solvent polarity. The functionalized halloysite nanotubes can be employed as reinforcing filler for polymers as well as carriers for the sustained release of active molecules, such as antioxidants, flame-retardants, corrosion inhibitors, biocides and drugs. The tubular morphology makes halloysite a perspective template for core-shell metal supports for mesoporous catalysts. The catalysts can be incorporated with selective and unselective metal binding on the nanotubes' outer surface or in the inner lumens. Micropatterns of self-assembled nanotubes have been realized by the droplet casting method. The selective modification of halloysite has been exploited to increase the nanotubes' ordering in the produced patterns. Pickering emulsions, induced by the self-assembly of halloysite nanotubes on oil-water interface, can be used for petroleum spill bioremediation and catalysis.

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1. Introduction

Clays are well known as safe and human-friendly materials with a wide range of applications that have been used for many centuries. Nowadays, the knowledge of clay minerals allows for this raw material to be improved with nanoscale morphological features, controlling clay particle size, shape and surface chemistry. Among natural clays, halloysite nanotubes are attracting a great interest from researchers in chemistry, physics, engineering and biology. The success of halloysite as an emerging nanomaterial is explained by its low toxicity, biocompatibility, tubes' high aspect ratio, empty inner cavity and different inner-outer surface chemistry [1]. Several *in vivo* and *in vitro* tests have shown biocompatibility of halloysite, which can be employed as carriers for sustained drug delivery for pharmaceutical and tissue engineering applications [2,3]. The most available halloysites (in thousand tons of a pure product) are from the deposits in Northland (New Zealand) and Dragon Mine (Utah – USA). Geological settings in Europe, China, Turkey, and Australia also allow for smaller scale halloysite supply.

From the mineralogical view-point, halloysite is a naturally-occurring two-layered aluminosilicate, characterized by a hollow tubular structure (Fig. 1). Its size depends on the deposit and varies from 50 to 70 nm in external diameter, and 10 to 20 nm diameter for the lumen. The tubes' lengths range within 0.5–1.5 μm . Their walls are formed by the rolling of 15–20 aluminosilicate layers. The presence of water molecules in the interlayers determines a decrease of the spacing in the multilayer walls from 1.0 (swollen) to 0.7 nm (in dry) states. The water molecules bind to the wall layers acting as glue between them. The reason why flat kaolinite sheets roll into halloysite tubes is still unknown, although many efforts have been devoted to this - from computational chemistry to experimental observation of some morphological features and defects [4]. One can suppose that the neighboring alumina and silica layers together with their interlayer water molecules create a packing disorder causing them to curve and roll up, forming multilayer tubes. As displayed in Fig. 1c, modeling of multilayers spiral of halloysite nanotubes was achieved by computational SCC-DFTB simulations [5].

Halloysite was revealed to be efficient filler for polymers allowing for fabrication of functional hybrid materials with excellent thermo-mechanical properties [6,7,8,9]. Typically, addition of 3–5 wt% halloysite to polymers increases the composite mechanical strength by 30–50% [1]. The thermal stabilization effect can be attributed to the entrapment of degraded products of polymers inside the nanotubes lumens [10]. The

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