

# Colloidal stability of halloysite clay nanotubes

Lorenzo Lisuzzo, Giuseppe Cavallaro, Filippo Parisi, Stefana Milioto, Giuseppe Lazzara\*

Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze pad 17, 90128 Palermo, Italy; \* Corresponding author: giuseppe.lazzara@unipa.it

The colloidal stability of halloysite clay nanotubes dispersion is reviewed showing the strategy and the mechanism to obtain stable systems in water and apolar solvents. The selective modification of halloysite inner/outer surfaces can be achieved by exploiting electrostatic interactions. The adsorption of anionic surfactants onto the halloysite cavity allows generating inorganic cylindrical micelles that can be separated from the solvent. On the other hand, the functionalization of halloysite shell by positively charged surfactants drives to obtain stable water-in-oil emulsions. The interactions with ionic and nonionic polymers alters the dispersability of halloysite due to electrostatic and steric effects that are strongly dependent on the nanoarchitecture of the hybrid systems.

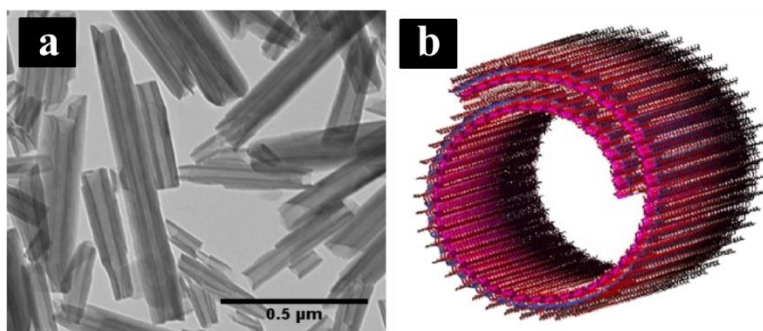
Modified nanotubes by selective interactions lead to the formation of colloidal systems with tuneable surface properties and controlled colloidal stability adjusted to the solvent polarity. These dispersions are perspectives nanocarriers for substances such as antioxidants, biocides, drugs and corrosion inhibitors, to be released in response to external stimuli.

**Keywords:** halloysite nanotubes; surfactants; colloidal stability; clay dispersion; polymers; biopolymers; Pickering emulsion.

## 1. Introduction

In recent years, nanoclays have been the object of particular interest for many scientists and researchers in chemistry, physics, engineering and biology due to their excellent properties as well as their sustainability [1–3]. For instance, they represent the starting point to the development of smart materials for drug delivery [4–9], food packaging [10–12], environmental remediation and wastewater treatment [13], cultural heritage [14–17] and additives for enhancing the performances of polymers [18,19]. Due to the large demand of applications, the physico-chemical properties of nanoparticles, and nanoclays particularly, have been manipulated in order to improve their stability in aqueous media [20,21]. Since the discovery of carbon nanotubes in 1991 [22], the tubular structure has been widely investigated in other types of particles including metal nanotubes [23,24], oxide nanotubes [25,26], semiconducting nanotubes [27], nitride nanotubes [28,29] and natural clay nanotubes, which have gained interest in the material science and nanotechnology for their large specific surface, high porosity and tunable surface chemistry.

This review will be focused on the strategies to prepare stable dispersions of halloysite clay nanotubes (HNTs) that are naturally-occurring two-layered aluminosilicate characterized by a hollow tubular structure with a spiral conformation (Figure 1) [1].



**Figure 1.** TEM halloysite image (a) adapted with permission from [3], copyright 2015 Wiley Publ. Modeling of the halloysite spiral ordering (b) adapted with permission from [30], copyright 2015 American Chemical Society

The HNTs size depends on the deposit and varies from 50 to 70 nm in external diameter, and from 10 to 20 nm diameter for the lumen [18,31]. The tubes' lengths range within 0.5–1.5 μm. The external surface of HNTs is composed of silicon oxygen tetrahedron meanwhile the internal lumen consists of alumina oxygen octahedrons [32], so the outer surface is distributed mainly with Si-O-Si group and the inner surface is composed of Al-OH [30,33]. Because of the multilayer structure, most of the hydroxyl groups exist within the lumen and only a few in the outer surface [34].

Considering the different chemistry in the inner/outer surface, the former is positively charged and the latter is negatively charged in water in a pH range between 2 and 8. Moreover, as a widely used environmentally friendly clay material, HNTs have a good biocompatibility [35] and they are non-toxic as evidenced by in vivo [36] and in vitro tests [37]. These characteristics make HNTs excellent vehicles for carrying numerous types of cargos, when negatively charged molecules are sacked into the tube's lumen and positive ones adsorbed on the tube's outer surface. The colloidal stability of HNTs is a key point that has been deeply investigated, in order to improve the nanoparticles manageability trough the several possible uses that could be made [38]. For instance, when stable colloidal dispersions are reached, both a higher specific surface and a greater cavity area of halloysite nanotubes could be obtained and extensively used in nanocatalysis [39–45], nanotemplate [46] and biological controlled release [47–49]. This purpose was pursued by some different strategies of manipulation of the physico-chemical properties that range from the direct study into aqueous media by the selective functionalization of halloysite outer/inner surface with ionic molecules (surfactants, polymers and biomacromolecules) to the evaluation of HNTs in generating Pickering emulsions.

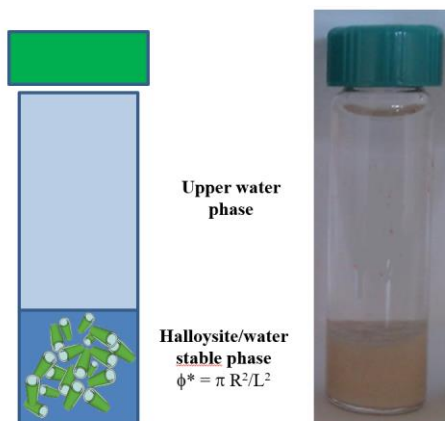
## **2. Halloysite nanotubes in water**

Due to their high aspect ratios, the anisotropic nanoparticles can form liquid crystalline phases, such as those observed for carbon nanotubes (CNTs) [50–52], graphene oxide (GO) [53,54], cellulose [55], which are recognized as key potential precursors for the fluid phase processing of particles into aligned materials with outstanding properties. Firstly, Luo et al. [56] have studied the liquid crystalline phase of HNTs in aqueous dispersions. It has been observed that the liquid crystalline phase starts to form at the HNTs concentration of 1 wt %, and a full liquid crystalline phase is achieved at the HNTs concentration of 25 wt %. Rheological measurements indicate a typical shear flow behavior for the HNT aqueous dispersions with concentrations above 20 wt % and the sol–gel transition occurs at the HNT concentration of 37 wt % [56]. Furthermore, the HNTs aqueous dispersions exhibit pH-induced gelation with more intense birefringence when hydrochloric acid (HCl) is added. These findings could facilitate the large-scale alignments of HNTs in the fluid phase and open the way to make the long-range ordered structures of HNT-based functional materials, offering the opportunities to uncover the complex phase transition behaviors for HNT dispersions with particular topologies [56]. The sedimentation behavior of halloysite in water is rather peculiar and a simple percolation model can explain it. It has been already observed in 1952 [57] that halloysite aqueous dispersions settle down with a large sedimentation volume. Recently, [58] this

peculiarity has been explained on the basis of geometric considerations allowing to predict the nanotubes volume fraction in the sedimentation volume ( $\Phi$ ) by considering the contact distance as

$$\Phi = \pi R^2/L^2 \quad (1)$$

where R and L are the external radius and the length of the nanotubes [58]. A scheme of the sedimentation behavior with optical image is presented in Figure 2.



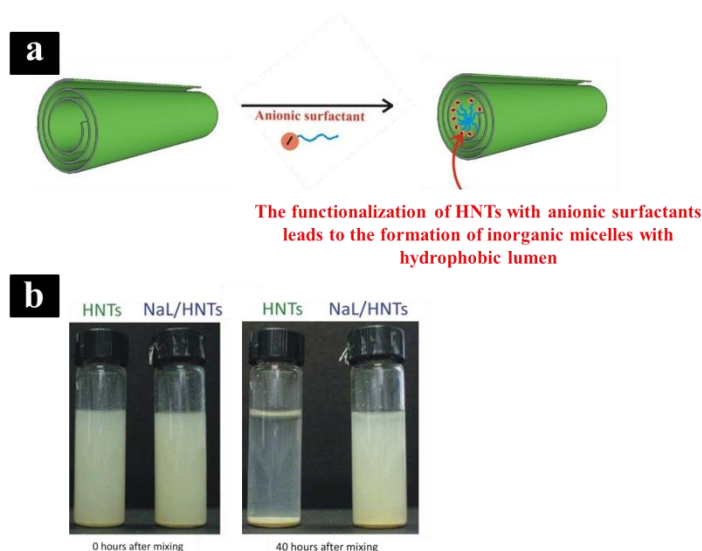
**Figure 2.** Scheme for the sedimentation volume of halloysite nanotubes. Halloysite concentration in the stable phase was  $\Phi=0.03$ .

### 3. Effect of surfactants on halloysite colloidal stability in polar and apolar solvents

Amphiphilic molecules are typically used to stabilize nanoparticles dispersions due to their surface active features. Regarding halloysite nanotubes, the choice of surfactant in terms of the headgroup charge is a key factor and it has a profound effect on their colloidal stability. Such a peculiarity is due to the charge separation in the inner and outer surface of halloysite.

#### 3.1 Anionic surfactants selective functionalization

It has been demonstrated that the adsorption of anionic surfactants (e.g. sodium alkanoates) occurs into the HNTs lumen and it increases the net negative charge of the nanotubes enhancing the electrostatic repulsions and consequently the dispersion stability [59,60]. It is noteworthy that the change of  $\zeta$  potential, that becomes more negative, predicts a better colloidal stability of the hybrid materials compared to the pristine nanotubes because of the low tendency to aggregate and the sedimentation is strongly slowed down by the surfactants [60] (Figure 3).



**Figure 3.** Scheme of HNTs functionalization with anionic surfactants (a) and photographs of pristine halloysite and nanotubes functionalized with sodium dodecanoate (NaL) in water (b) adapted with permission from [30,59], copyright 2015 American Chemical Society.

Moreover, it was observed that the colloidal stability of modified HNTs is not strictly correlated to the loading degree of the anionic surfactants into the HNT inner lumen as soon as the inner surface is fully covered.

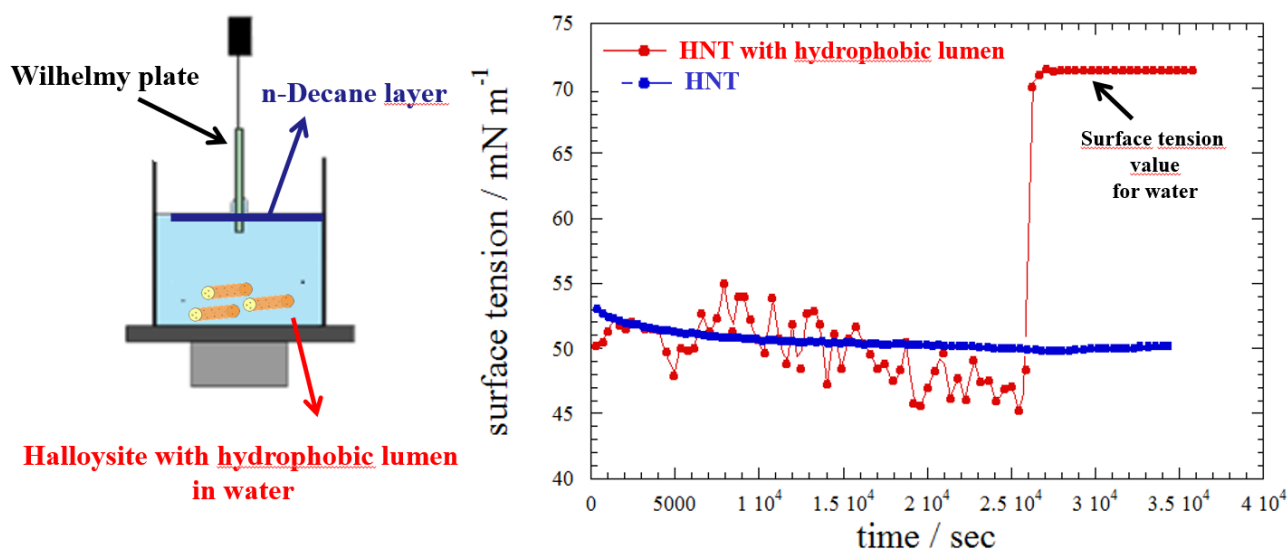
However, the very high surfactant content (close to 10% ) indicates the formation of self-organized structures in the cavity, for example double-layers that maintain the counterions and do not contribute to the charge increase of the nanoparticle and consequently to its electrostatic stabilization [60].

These findings are consistent with the DLVO theory that establishes that the stability of a colloidal suspension depends on the balance between attractive van der Waals forces and electrostatic repulsions caused by the double layer surrounding each particle [61]. Therefore, both  $\zeta$ -potential and width of the electric double layer contribute to the total repulsive force. This theory also envisages that a large ionic strength generates a screening of the electrostatic repulsions because of the reduction of the double layer [60].

Moreover, the structures of pristine halloysite nanotubes and ones functionalized by anionic surfactants (sodium dodecanoate and sodium dodecyl sulfate) were investigated by small angle neutron scattering (SANS) [62]. These experiments evidenced the structural organization of the surfactants adsorbed onto the HNT cavity and the influence of their headgroup, which affects

affects the surfactant organization and, consequently, the hydrophobic character of the HNT lumen and the net charge [62]. In particular, it was noted that only the carboxylate group promotes the formation of organized structures, such as densely packed multilayers of sodium dodecanoate within the halloysite cavity, as seen from a correlation peak in SANS curves [62].

Finally, the solubilization capacity of these functionalized nanotubes toward hydrophobic compounds has been demonstrated. Accordingly, the surfactant/HNTs hybrids can be considered as inorganic micelles useful for the solubilization of pollutants and delivery of compounds from different origin [59,60,62]. As sketched in Figure 4, surface tension experiments highlighted the removal capacity of sodium dodecanoate/HNTs composite towards n-decane (Figure 4)



**Figure 4.** Surface tension as a function of time for pristine halloysite and halloysite functionalized with sodium tetradecanoate dispersions in the presence of an n-Decane film on top of the aqueous phase. Adapted with permission from [60], copyright 2014 American Chemical Society.

Literature [63] reports a similar methodology where uniform and dispersed halloysite nanotubes were obtained using sodium dodecyl sulfate (SDS). The results indicated that SDS was adsorbed on the HNTs, which could enhance the dispersibility by the electrostatic effect; in fact, the zeta potential of dispersed HNTs became larger than that of the raw ones within the pH ranging from 2.5 to 11.9. The difference is higher under alkaline conditions, due to the adsorption of SDS molecules by electrostatic forces between surfactant molecules and HNTs, leading to ion exchange at the alumina surface [64]. It was also observed that there is no obvious difference between the zeta potential at different concentration of SDS (1.22 g/L and 1.48 g/L), which suggests that the well

dispersion effect does not depend on the more content of dispersant confirming the saturation effect. Therefore, the zeta potential of SDS/HNTs is always more negative than HNTs, and the high zeta potential is a condition of good colloidal stability of SDS/HNTs.

It was found that also perfluoroalkylated anionic surfactants, when adsorbed at the inner surface, formed kinetically stable dispersions due to the enhanced electrostatic repulsions exercised between the particles and these systems can be used as non-foaming oxygen nanocontainers in aqueous media [58]. Interestingly, the oxygen release from these hybrids can be tuned by specific external stimuli [58].

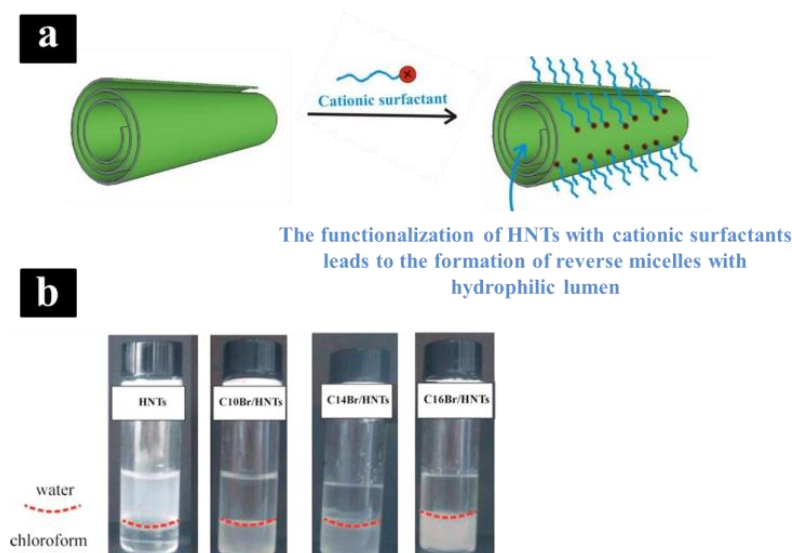
The determination of the translational diffusion coefficient and the charge of the hybrid materials showed that the concentration effect was negligible and the functionalized HNTs did not aggregate in water but they diffuse as single nanotubes [58]. To definitely rule out the presence of aggregates and to evidence eventual particle–particle interactions, the specific volume, the isoentropic compressibility of HNT and HNT/surfactants dispersed in water and the pair interaction parameters were determined. Data reflected that the nanoparticle–nanoparticle electrostatic interactions are enhanced in the hybrid material in agreement with the  $\zeta$ -potential results.

Above all, the sedimentation of the clay nanotubes assumes a crucial role in order to understand the colloidal stability and the sedimentation volume is a key parameter that, at least in water, is controlled by repulsive forces between particles [65]. For instance, the electrostatic repulsions are caused by the double layer surrounding each particle and by the particle charge. Therefore, if the particles repel to each other they remain independent until reaching the closest packing, which will represent the concentration in the sedimentation volume. If the particles do not strongly repel to each other, they are sticking together generating a smaller sedimentation volume [58]. The presence of anionic surfactants strongly affects the concentration of the sedimentated phase, which corresponds to the critical value above which the dispersion is stable because the highest packing of the nanotubes is reached and shorter distances between the nanoparticles are hindered by the electrostatic repulsions.

As concerns the hybrid HNT/anionic surfactants,  $\zeta$ -potential data evidenced an increase in the net charge and, therefore, the particle – particle repulsive interactions shift to longer range increasing the closest average distance between the functionalized nanoparticles. Moreover, it was revealed that each mole of adsorbed anionic surfactant neutralizes an equivalent number of positive charges of the inner lumen thus generating a linear increase in the net negative charge of HNT and therefore longer range interactions [61].

### 3.2 Cationic surfactant selective functionalization

Literature reports another easy strategy to obtain stable colloidal dispersions and it deals with the preparation of inorganic reverse micelles in non-aqueous media based on halloysite nanotubes and cationic surfactants, such as alkyltrimethylammonium bromides [66]. It is known that generally, a “reverse micelle” structure possesses a hydrophilic core and a hydrophobic shell that delineates a nanoscale droplet of aqueous phase from a nonpolar medium [67]. Because of their positive headgroup, the cationic surfactants are selectively adsorbed onto the HNTs external surface endowing to the formation of tubular nanoparticles with a hydrophobic shell and a hydrophilic cavity. The effect of the hydrophilic/hydrophobic balance on the properties of the obtained hybrid materials and their colloidal stability was studied in solvents with different polarity (water, 1-octanol, chloroform, and hexane) [66] (Figure 5).



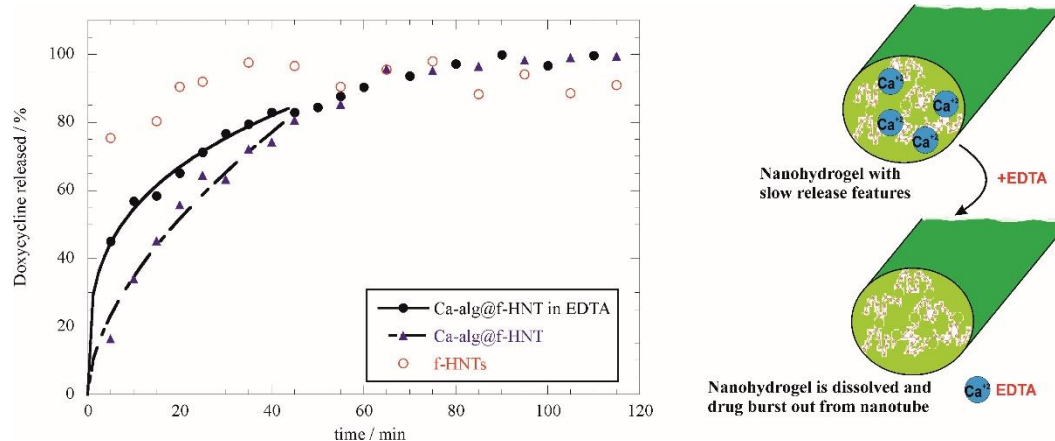
**Figure 5.** Scheme of HNTs functionalization with cationic surfactants (a) and partition of pristine and functionalized HNTs between the oil and the aqueous phases (b) adapted with permission from [66], copyright 2015 American Chemical Society.

The first evidence is that the charge of the modified HNTs is strongly dependent on the hydrocarbon length chain of the surfactant. In particular, the  $\zeta$  potential of the hybrids increases with the tails length of the adsorbed alkyltrimethylammonium bromide.

This allowed to assert that the enhancement of the surfactants hydrophobic character improves the adsorption efficiency due to stronger tail – tail hydrophobic interaction evidenced by FTIR [59] and, consequently, the neutralization of the HNTs negative sites thus determining an inversion of the HNTs charge. Dynamic Light Scattering in chloroform evidenced that the hybrid materials



present a faster dynamic behavior compared to the pristine HNTs, in agreement with the enhancement of the repulsive interactions between the nanoparticles. In other words, the very large hydrodynamic radius value for pristine HNTs in chloroform indicates the aggregation of nanotubes in this solvent whereas the presence of the surfactant confers hydrophobicity to the HNTs outer surface, and consequently, the colloidal stability of the nanotubes in nonpolar solvents is increased [66]. Briefly, the reported procedure allows to fabricate eco-compatible reverse micelles with different dispersibility in organic solvents and tunable hydrophobic/ hydrophilic interface that might be suitable for industrial or biological applications and to generate an aqueous nano-pool in organic media. Recently, this feature was used to confine hydrogel based on alginate inside the halloysite lumen generating a drug delivery system with sustained release sensitive to chemical stimuli (Figure 6).



**Figure 6.** Release profile of doxycycline from halloysite with hydrophobic shell, and confined hydrogel inside the halloysite lumen (Ca-alg@f-HNT) in water and in EDTA aqueous solution. Adapted with permission from [9], copyright 2018 American Chemical Society.

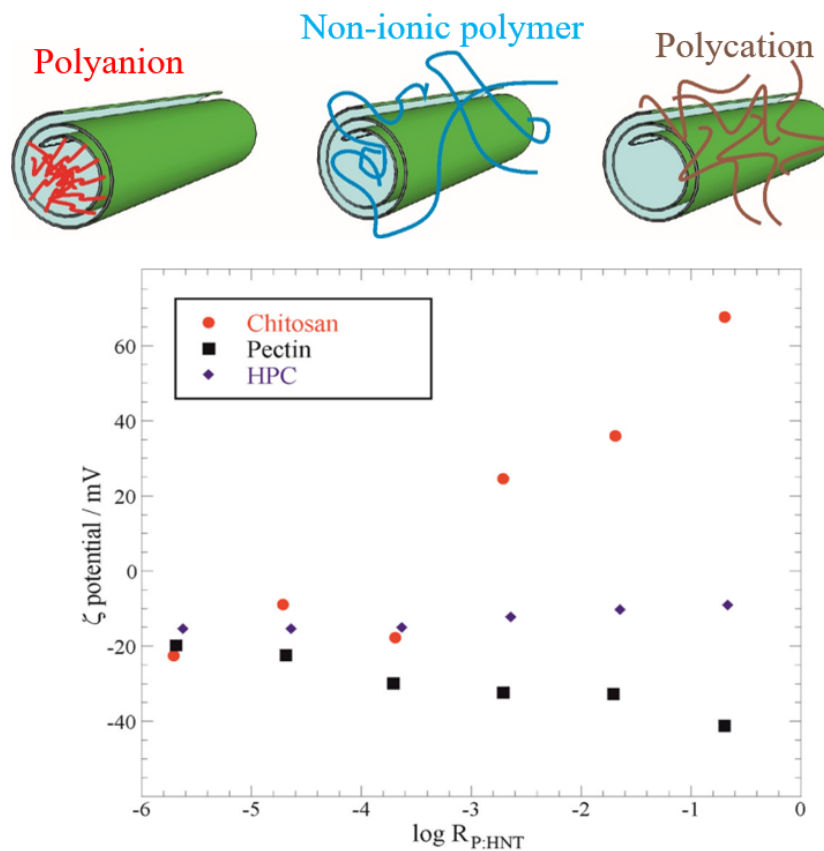
#### 4. Effect of biopolymers on halloysite colloidal stability in water

Another promising strategy for the preparation of stable colloidal dispersions is represented by the adsorption of biopolymers via non-covalent interactions with a resulting improvement in the biocompatibility of HNTs.

It is reported a facile and green method for preparing a supramolecular complex of amylose and HNT in solid state using just mechanical force [68]. The wrapping of amylose onto the HNTs external surface induced the formation of modified nanotubes with a peculiar core-shell structure. The stability of HNTs and amylose-HNTs in DMSO/H<sub>2</sub>O dispersions was studied for 24 h. Pure

HNTs fastly precipitated due to the high density and the long tubular structure of halloysite [69] whereas the amylose-HNT dispersion showed an excellent stability being that any sedimentation was observed within 24 hours. This behavior can be related to the high affinity between the polymer and the solvent mixture. Surprisingly, the stability of the hybrid system was maintained over a period of two weeks. This was probably dependent on the interaction between amylose and the outer surface of HNT [68].

Recent literature [70] reports studies on the adsorption of three biopolymers (anionic pectin, non ionic hydroxypropyl cellulose HPC and cationic chitosan) onto halloysite nanotubes in water using isothermal titration calorimetry (ITC) to determine the thermodynamic parameters. In addition, the combination of turbidimetry and  $\zeta$ -potential experiments provided the stability and the surface change properties of functionalized nanoparticles at two different pH values in order to understand the influence of the polymer and HNT charge density on the settling process of the nanotubes. Briefly, they found that the dispersion stability is dependent on particle dimensions, charge, viscosity of the medium, and interactions between components (HNTs/polymer). As expected, the addition of the nonionic HPC hardly alters the  $\zeta$ -potential values and, on the other hand, the addition of charged biopolymers shifted the  $\zeta$ -potential values toward negative and positive values for pectin and chitosan, respectively [70] (Figure 7). Moreover, the changes induced in the  $\zeta$ -potential values reflect the protonation equilibria of the biopolymer. Besides, HPC is the more efficient polymer in retarding the sedimentation. The  $\zeta$ -potential trends for chitosan- and pectin-based mixtures show that an electrostatic mechanism of nanotube stabilization exists. As a general feature, chitosan is efficient in stabilizing HNT dispersions under acidic pH, whereas pectin is recommended for the same purpose at basic pH values. In particular, pectin should adsorb within the HNT lumen onto the positively charged surface of alumina, altering the overall HNT charge toward more negative values. The opposite occurs for chitosan, which is selectively adsorbed on the outer silica surface. HPC is in a stretched conformation at the interface, and therefore its adsorption could be considered very efficient in creating a steric barrier around the nanotubes against agglomeration and precipitations. Finally, the stability of the dispersions is controlled by the interactions (electrostatic and steric) between the dispersed particles [70].



**Figure 7.** Scheme of adsorption site based on electrostatic interactions between polymers and halloysite surfaces and  $\zeta$ -Potential values for HNT/biopolymers dispersions as a function of the polymer/halloysite weight ratio adapted with permission from [70] copyright 2015 American Chemical Society.

Besides bio-derived macromolecules, the effect onto the colloidal stability has been studied also taking into account the functionalization with other types of polymers, for example the temperature responsive poly(N-isopropylacrylamide) [71,72]. Meanwhile PNIPAAm was grafted onto the external surface of modified HNT-NH<sub>2</sub> by an amine bond, it was found that PNIPAAm selectively adsorb onto the external surface by exploiting electrostatic interactions at pH = 6. More interestingly the physico-chemical properties of the modified nanotubes in the polymer/HNT are deeply changed in comparison with the pristine nanoclay, thus evidencing a transferring of the thermo responsiveness from polymers to halloysite in the hybrid system [71]. Since the dispersion are stable under the Lower critical solution temperature (LCST) and unstable above it, this allowed to prepare very versatile systems where the temperature of the colloidal stability can be controlled in order to have external-stimuli triggering solubilization and delivery of hydrophobic compounds.

The PNIPAAm/HNT system was loaded with curcumin providing a biocompatible and thermosensitive system for targeted release of active species in the intestine [72].

Lee et al. [73] reported the synthesis of HNT-based supramolecular complexes by the wrapping of DNA to the surface of halloysite. It is observed that pristine HNTs are insoluble in water, but they become highly water dispersible after interacting with DNA. It is reported that the interaction between DNA and HNTs induces a reorientation of the phosphate groups in DNA and an association of the phosphates in DNA with the outer surface of the nanotubes, which is composed of silica. Thus,  $\pi$ - $\pi$  interaction is supposed to be a critical force to determine the interaction between DNA and the outer surface of HNTs [73]. Most likely, this interpretation should be revised being that the enhanced colloidal stability is due to the neutralization of the inner positive charge that drives to an increase of the total net negative  $\zeta$ -potential enhancing the particle – particle repulsions.

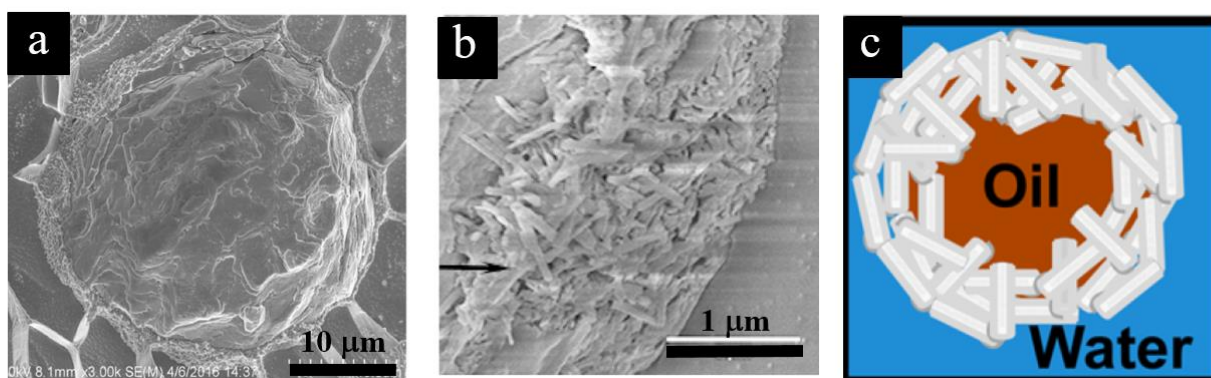
## 5. Pickering emulsion

Emulsions are dispersions of one liquid in another immiscible liquid in the form of small droplets. Typically, these systems are stabilized by the addition of emulsifiers that can be either surfactants, or solid particles. For instance it is known that interfacially-active solid particles can act as emulsifiers for stabilizing oil-in-water, as reported by the pioneering studies of Ramsden and Pickering [74,75], from which the name derives. In recent years, several experimental and theoretical studies have been carried out on solids-stabilized emulsions to understand the factors that affect the stability and the structure of the interface [76,77] for application in food and materials science.

Owoseni et al. [78] reported the halloysite effect in stabilizing oil-in-water emulsions. On this basis, HNTs can be considered as interfacially-active vehicles for delivering oil spill treatment. They evidenced that the increase of HNTs concentration leads to the formation of more stable emulsions. The formation of a rigid and protective interfacial film by the adsorption of HNTs at the oil–water interface provides steric hindrance to drop coalescence [79] (Figure 8). Since surfactants and interfacially-active particles can act synergistically to stabilize the emulsion, HNT were loaded and it was observed that the adsorption of surfactant molecules at the emulsions interface serves to lower the interfacial tension while the adsorption of particles provides a steric barrier to drop coalescence [78,80].

Similar observations were found by von Klitzing et al [81]. They prepared hydrophobized halloysite nanotubes for model petroleum and dodecene emulsification demonstrating the suitability of these systems for catalysis. They observed that an increase in halloysite concentration drives to denser packing at the oil/water interface, which stabilizes the droplets against coalescence allowing their architectural control. The oil-in-water emulsions allowed an efficient hydroformylation reaction using an aqueous Rh-catalyst. This gave efficient dodecene conversion to tridecanal with a simple aqueous catalyst separation from the product [81].

Besides, these systems were studied also for oil spill bioremediation exploiting the bacterial proliferation on HNTs [82]. It was observed that the oil/water interface is roughened and the oil degrading microorganisms are linked to these oil droplets better than to the ones without halloysite. The presence of halloysite enhances the metabolic activity demonstrating that HNTs-based dispersant systems are environmentally friendly and promising formulations to achieve 'bioremediation' through degradation of spilled crude oil [82].



**Figure 8.** Cryo-SEM images of HNT emulsions with oil showing halloysite on oil-water interface (a,b) adapted with permission from [82] copyright 2018 Elsevier and (c), scheme of the Pickering emulsion droplet adapted with permission from [78] copyright 2014 American Chemical Society.

## 6. Conclusions and perspectives

In this review, we summarized the current strategies that are followed in order to create stable colloidal dispersions of halloysite clay nanotubes. In particular, they range from their own liquid crystalline behavior in water to the selective functionalization of inner/outer surface by using differently charged molecules such as surfactants, polymers, biopolymers. Several advantages rise up from these methods, such as the possibility to obtain highly stable systems, reverse micelles, Pickering emulsions that can be applied for pollutants removal, oil spill, catalysis and controlled drug release.

Moreover, it is well known that the sample of halloysite could contain impurities (kaolinite above all) and could present high polydispersity in sizes. In this regards, this review represents a relevant background for designing separation and purification routes. In fact, one of the crucial challenges for further research in halloysite could be the “selective sedimentation” of nanoparticles of different length/radius in order to obtain halloysite samples with a reduced polydispersion degree.

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**Conflicts of Interest:** The authors declare that they have no conflicts of interest to this work.

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