

Interfacial Self-Assembly in Halloysite Nanotube Composites

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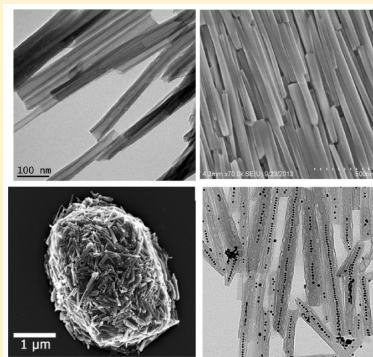
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ABSTRACT: A self-assembly of clay nanotubes in functional arrays for the production of organized organic/inorganic heterostructures is described. These 50-nm-diameter natural aluminosilicate nanotubes are biocompatible. Halloysite allows for 10–20 wt % chemical/drug loading into the inner lumen, and it gives an extended release for days and months (anticorrosion, self-healing, flame-retardant, antifouling, and antibacterial composites). The structured surfaces of the oriented nanotube micropatterns enhance interactions with biological cells, improving their capture and inducing differentiation in stem cells. An encapsulation of the cells with halloysite enables control of their growth and proliferation. This approach was also developed for spill petroleum bioremediation as a synergistic process with Pickering oil emulsification. We produced 2–5-nm-diameter particles (Au, Ag, Pt, Co, Ru, Cu–Ni, Fe₃O₄, ZrO₂, and CdS) selectively inside or outside the aluminosilicate clay nanotubes. The catalytic hydrogenation of benzene and phenol, hydrogen production, impacts of the metal core–shell architecture, the metal particle size, and the seeding density were optimized for high-efficiency processes, exceeding the competitive industrial formulations. These core–shell mesocatalysts are based on a safe and cheap natural clay nanomaterial and may be scaled up for industrial applications.



INTRODUCTION

For us, Helmuth Möhwald's research is founded on a self-organization strategy in the design of new functional materials with integrated nano/microstructures. First, there were his illuminating works on 2D self-assembly in Langmuir monolayer patterns on water surfaces with a deep understanding of the structures and phase transitions of these systems, followed by the study of Langmuir–Blodgett multilayer films with great physical interpretations. Then, his name was associated with other methods of interfacial assembly including layer-by-layer (LbL) nanoarchitecture based on the electrostatic attraction of positive and negative polyelectrolytes or other nanoparticles. Finally, his most cited papers on LbL microshells opened a new era in nano-encapsulation development.^{1–3}

I (Y.L.) regularly visited the Max Planck Institute for Colloids and Interface and collaborated with Helmuth's team on LbL materials. During these summer visits, we took long evening walks in Golm, talking about life and of course science, which was a major part of Helmuth's life. He challenged me to provide deeper work with better physical understanding. During such walks, we planned a strategy to develop a new research field: halloysite clay nanotube core–shell design. We planned to use a uniquely different inside/outside chemistry of these ceramic nanoscrolls for their use as containers for the sustained delivery of chemical inhibitors and drugs.^{4–6} A general nanoarchitectural development of halloysite systems by

placing different compounds (catalytic nanoparticles, fluorescent quantum dots, drugs, proteins, and DNA) in the tube lumens or onto their external surface was suggested. Many of these plans have been realized,^{7–12} but some of them are still being developed, for example, Langmuir–Blodgett multilayer films from hydrophobized halloysite.

In this article, we generalize the self-assembly of natural clay nanotubes in functional arrays to produce organized organic/inorganic/metal heterostructures. These halloysite nanotubes are biocompatible, which is logical considering the millions of years that living organisms coexisted with clays. Halloysite allows for 10–20 wt % chemical loading into the inner lumen, and it gives an extended release for days and months after application (anticorrosion, self-healing, flame-retardant, and antibacterial composites). The structured surfaces of the oriented nanotubes enhance the interactions with biological cells, improving their capture and inducing differentiation in stem cells. An encapsulation of biocells with halloysite enables continuous control of the microorganism's growth and proliferation. This approach was also developed for spill petroleum bioremediation as a synergistic process with Pickering oil emulsification and bacterial delivery. Quantum

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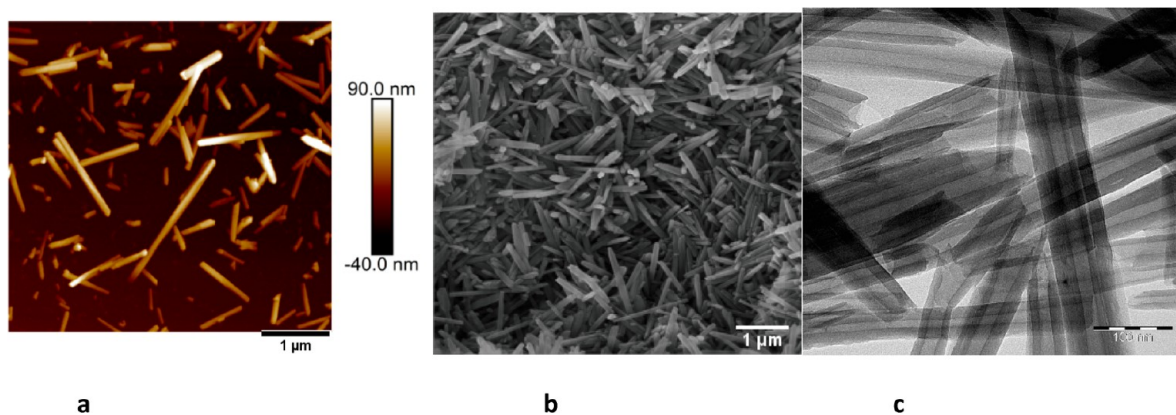


Figure 1. Halloysite nanotube images: (a–c) AFM, SEM, and TEM. (a) Reproduced with permission from ref 7, copyright Wiley, 2016.

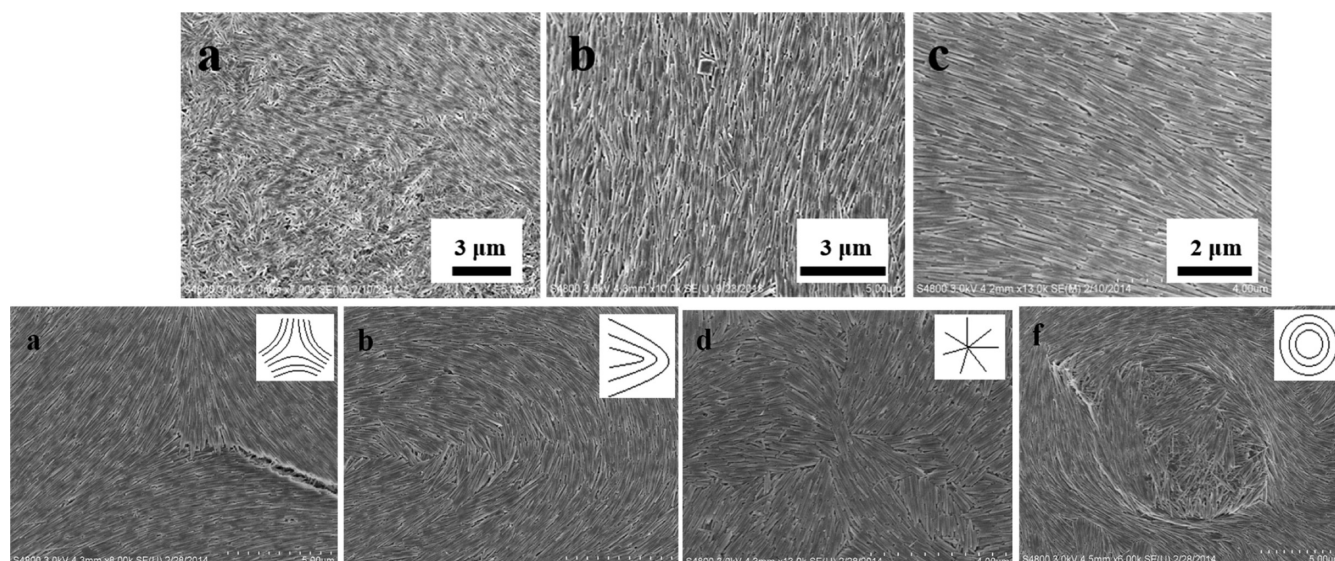


Figure 2. Halloysite orientation in a dried layer: (upper row, a–c) SEM images of droplet of 2 wt % PSS/HNT thermally dried at 25, 65, and 90 °C. Liquid-crystalline defects in halloysite ordering. SEM images of axial disclinations in a dried droplet of PSS/HNTs, drying at 65 °C: (lower row, a) the hyperbolic disclination, $m = -1/2$, (lower row, b) the parabolic disclination, $m = +1/2$, and (lower row, d and f) the circular disclination, $m = +1$. Reproduced with permission from ref 21, copyright Elsevier, 2014.

dots immobilized into the clay nanotubes were employed for cell labeling and imaging.

In the second part of our work, we describe the strategy for producing 2–5-nm-diameter metal particles (Au, Ag, Co, Ru, Cu–Ni, Fe_3O_4 , ZrO_2 , In_2O_3 , CdS, and CdSe) placed inside or outside of these aluminosilicate nanotubes, thus optimizing the catalysis. The catalytic hydrogenation of benzene and phenol, hydrogen production, impacts of the core–shell architecture, the metal particle size, and the seeding density were optimized for high-efficiency processes that exceed the competitive industrial formulations. The autoexhausting Cu–Ni/halloysite systems have shown high efficiency at 400 °C, demonstrating temperature stabilization of the catalyst encased in the nanotubes.^{1,8}

Halloysite is a naturally occurring aluminosilicate characterized by a hollow tubular structure (Figure 1). Its external diameter varies from 50 to 70 nm with a 10–20 nm diameter for the inner lumen. The tubes' lengths are within 0.5–1.5 μm , and the specific surface is ca. 60 m^2/g . Halloysite is formed by the rolling of 15–20 kaolinite layers and is characterized by multilayer wall packing with a periodicity of 0.72 nm in the dry states. The water molecules bind to the wet wall layers, acting

as glue between them.^{1,9,10} Contrary to other clays (e.g., kaolin and montmorillonite), halloysite does not require complicated exfoliation processes and may be easily dispersed in water. The outer and inner surface chemistries of halloysite are different: the external surface is composed of Si–O–Si groups, and the internal lumen consists of Al–OH groups. Considering positive–negative charges of alumina/silica surfaces, the whole nanotube ζ -potential of ca. –30 mV was qualitatively interpreted as their difference, providing for moderate aqueous colloidal stability in the pH range of 2 and 8.⁸ These characteristics make halloysite nanotubes excellent vehicles for carrying numerous types of cargo, when negatively charged molecules are sacked into the tube's lumen and positive ones are adsorbed on the tube's outer surface. The halloysite nanotube lumen can be enlarged by selective alumina etching with sulfuric acid at 80 °C, and these tubes may be cut shorter by strong ultrasonication.^{13,14}

The typical loading mechanisms for negative or neutral molecules are driven by precipitation from saturated solution into the positive (alumina) lumen. Vacuum applied to the sample helps the loading efficacy. The inner lumen of halloysite may be hydrophobized with octadecyl phosphonic

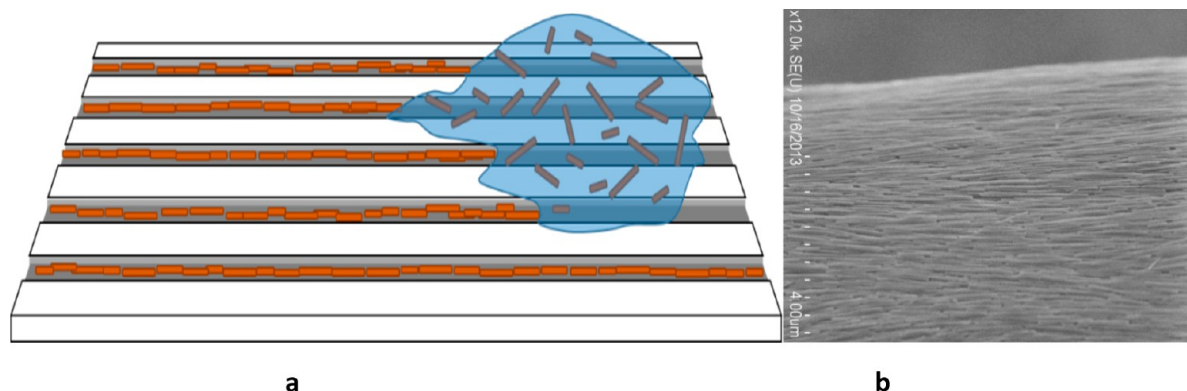


Figure 3. Halloysite orientation and capillary ordering: (a) scheme and (b) resulting SEM images of oriented PSS/HNT films in 5 μm channel, with an initial concentration of 5 wt %.

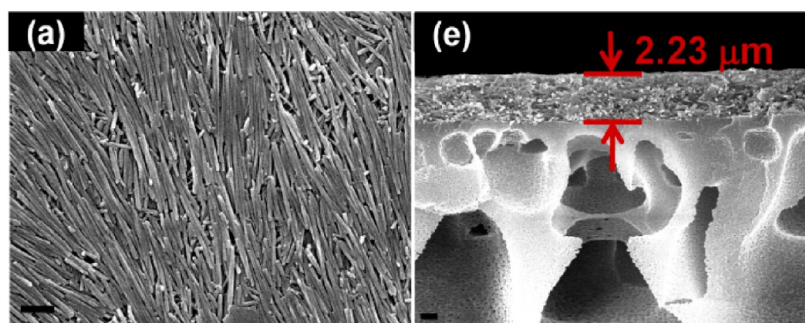


Figure 4. SEM image of the composite two-layer nano/microporous membrane (top view and cross section). Reproduced with permission from ref 25, copyright American Chemical Society, 2016.

acid¹⁵ or by the simple adsorption of an anionic surfactant such as sodium dodecanoate, resulting in tubule containers for the loading of hydrophobic molecules, including oil.^{16–18} Such encapsulation allowed us to convert water-insoluble dye into aqueous nanopigments and to encase insoluble drugs into water-dispersible nanotubes.¹² Beside the confinement within the halloysite hollow lumen, the adsorption onto the outside walls of the tubes as well as intercalation into wall interlayer spaces should be considered.⁸

Loaded (stuffed) nanotubes are useful for doping a polymer matrix, but it is even more interesting to create organized oriented arrays of the charged clay nanotubes, mimicking the ordering in nematic liquid crystals for inorganic ensembles. The silanization reactivity of halloysite nanotubes allows for their external modification, allowing for the external attachment of drugs and other molecules.¹⁹ Halloysite is an efficient filler for polymers, allowing the fabrication of functional hybrid materials with excellent thermomechanical properties.^{7–9} Typically, the addition of 3–5 wt % halloysite to polymers increases the composite mechanical strength by 30–50%. Halloysite undergoes dehydroxylation at 500 $^{\circ}\text{C}$, but it preserves the tubular shape and structural integrity up to 1200 $^{\circ}\text{C}$, converting to mullite at higher temperature. Its thermal stabilization effect can be attributed to the entrapment of degraded products of polymers inside the nanotubes' lumens.^{7,9}

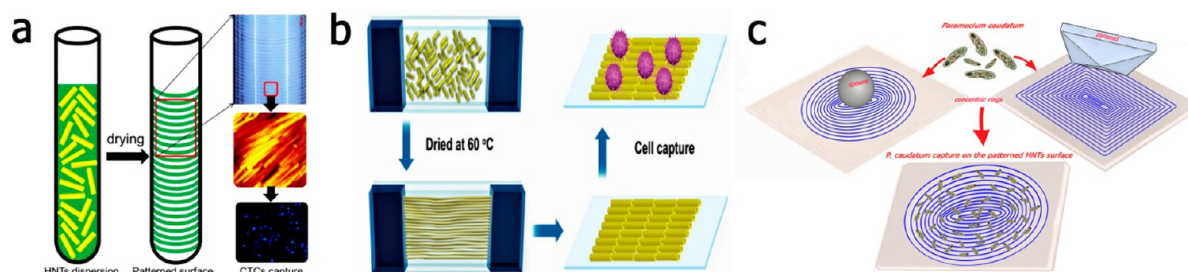
■ PRODUCTION OF ORIENTED ARRAYS OF CLAY NANOTUBES

In a highly concentrated dispersion, halloysite nanotubes reveal behavior similar to that of the liquid crystal ordering of

elongated nematic-type molecules.²⁰ Similar to nematic liquid crystals, halloysite nanotubes can orient themselves along a common axis. In the layer formed by a dried halloysite dispersion, one could see oriented patterns enhanced with higher tube charge. This high electrical potential of -70 mV was achieved by loading halloysite nanotubes with anionic compounds such as sodium polystyrene sulfonate: PSS-HNT (Figure 2). Four different types of disclination defects can be found in the halloysite film. Most of the disclinations have $m = 1/2$ or $-1/2$ due to high stability, and few disclinations with $m = 1$ could be initiated by short broken tubes.²¹

We suggested the use of this phenomenon to produce organized patterns of oriented nanotubes with the thermocontrolled evaporation of a halloysite aqueous dispersion.²¹ The nanotubes were found to orient along the edge of a drying droplet of a halloysite suspension following the phenomenon known as “coffee ring” formation. During drying, the three-phase contact line among the air, suspension, and solid substrate remains fixed, and evaporation pulls the fluid from the center of the droplet, pushing the suspended nanoparticles toward the periphery. The accumulation of tubes from the center to the circumference increases the tubes' concentration beyond a critical level governed by Onsager's theory for the orientation of highly charged nanorods.^{22,23} The alignment is enhanced by higher concentrations, temperature, surface charge, and the length of the tubes. When the local concentration at the droplet edge increases up to a critical concentration of ca. 10 wt % (which corresponds to 6–8 halloysite tubes/ μm^3), these nanotubes interact strongly and form a nematic liquid-crystalline phase.

Scheme 1. Organized Halloysite Patterns by Its Dispersion Thermoevaporation (a) in a Glass Capillary, (b) between Parallel Glass Slides, and (c) after Being Dropped onto Small Metal Ball or Pyramid^a



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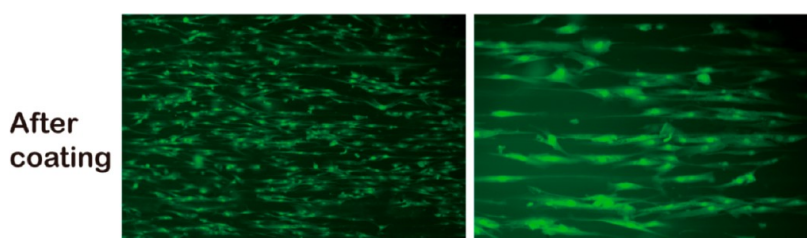


Figure 5. Stem cell orientation along the coated halloysite pattern, as shown by optical fluorescent images. Reproduced with permission from ref 28, copyright Elsevier, 2019.

We fabricated continuous aligned halloysite layers in microchannels using an evaporation technique and capillary forces. A microfluidic device was created by pressing a 5- μm -channel silicon wafer into a poly(dimethylsiloxane) plate and then covering with a glass slide. The halloysite suspension was injected into the microchannels, resulting in a high degree of nanotube alignment in the direction along the channels. Capillary force flow drives the nanotubes to align parallel to the microchannel.²¹ It would be very interesting to align the nanotube by writing with halloysite ink because the nanotubes tend to align along the mechanical shear force direction. This approach may be a simple method for the printing of aligned nanostructures, and recently we developed a deposition of oriented halloysite arrays by brush.²⁴

This technique was applied to the design of two-layer filters consisting of a microporous polymeric base coated with a few-micrometers-thick layer of oriented clay nanotubes loaded with polystyrenesulfonate (PSS).²⁵ The nanotubes are well-aligned on the polyacrylonitrile substrate, and this PSS-HNT coating with a well-arranged nanotube layer exhibited much better selectivity for dye/salt solution and also had very good water permeability (Figure 4). This sustainable antifouling nanocomposite membrane was efficient in the separation of salts from solutions.²⁵

CLAY NANOTUBE MICROPATTERNS FOR CELL CAPTURE AND ORIENTATION

The “coffee ring” effect for halloysite was extended to applications for forming periodic clay rings across the glass capillary tube.²⁶ The mechanism for the formation of such rings follows the same principle as the coffee ring effect because it begins with the formation of a fixed contact line. Halloysites modified with polystyrene sulfonate (PSS-HNTs) are highly charged and very stable in aqueous dispersions. As the halloysite dispersion inside a 1- to 2-mm-diameter capillary dries in hot air, the contact line is pinned along the

circumference of the capillary. Then the nanotubes start moving toward the contact line at the capillary wall. The evaporation of the solvent at the edge increases the concentration of halloysites in the liquid-crystal regime. The crowding at the contact line converts the halloysite into the nematic phase, aligning the nanotubes. After a moment when capillary forces cannot hold the mass, the contact line falls to a lower position (with the capillary kept vertical). The process of ring formation with halloysite attachment is repeated at this lower position, and thus we have regular halloysite rings with a periodicity of 0.2–0.5 mm on the capillary inner wall. Halloysite nanotubes were orientated along the rings perpendicular to the capillary axis.²⁶ The pattern of stripped capillary rings was used to create grooved p surfaces to capture cancer cells, and this device has shown a 6-fold higher efficiency than an untreated glass capillary (Scheme 1).

A 3D-printed polylactic acid pattern was functionalized by a polydopamine interlayer to firmly bond the halloysite nanotubes on the surfaces of the pattern to guide cell orientation. The successful introduction of halloysite into the pattern was verified by field emission scanning electron microscopy, X-ray photoelectron spectroscopy, the water contact angle, FTIR, and thermogravimetric analysis. In vitro human mesenchymal stem cell (hMSC) culture experiments proved that patterns with different strip widths exhibited different abilities to induce cell orientation.²⁸ The smaller the stripe width, the better the cell orientation, and with a layer height of 0.05 mm, the effect of inducing cell orientation was optimal (Figure 5).²⁸ This work provided a general routine for improving the cell affinity of the 3D-printed polymeric structure by a simple coating with a tubule nanoclay, which will have promising applications in cell culture scaffolds, wound healing materials, and biosensors.

Even more interesting is the drying of a halloysite aqueous dispersion dropped onto a 1 to 2 mm metal ball placed onto the solid support (glass). As a result of such a drying process, halloysite nanotubes self-assembled into concentric barriers with a periodicity of 0.1–0.2 mm and a height of 0.3–0.5 μm

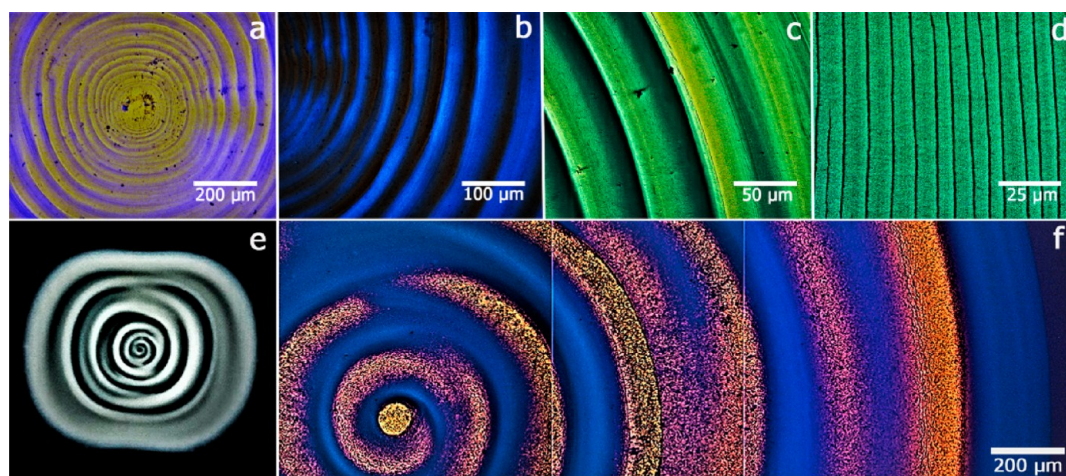


Figure 6. Images demonstrating the structure of concentric halloysite patterns formed on a glass surface during drying, made from a 1 wt % HNT-PSS suspension using a square pyramid visualized by (a and b) optical and (c and d) polarized optical microscopy. (e) Low-magnification images showing the structure of the concentric patterns and (f) an optical micrograph of rings formed from 2 wt % HNT-DNA using a metal sphere template.

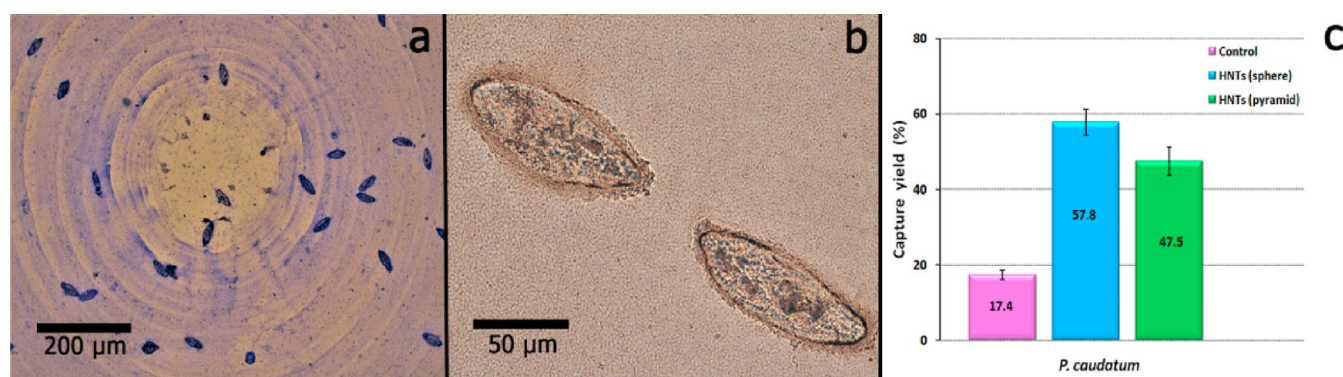


Figure 7. Capture of *P. caudatum* cells using a halloysite glass coating: (a) optical microscopy images of a concentric ring pattern formed from HNT-PSS using a metal sphere, (b) optical micrograph of *P. caudatum* cells captured on the halloysite ring, and (c) capture yield of the cells on concentric structures as compared to the control (clear glass).

(Figure 6). Tubes in such circular micropatterns are oriented in a tangential direction and allowed for the selective adsorption of the cells.²⁹ One can use a number of systematically placed metal balls which confine the drying process of the halloysite suspension and allow for the sophisticated design of halloysite micropatterns that resemble wave interference patterns. Such micropatterns or oriented halloysite allows for the selective adsorption of cells aligned with the tubes' orientation direction.

The nontoxicity of halloysite is its great advantage for various applications in the field of medicine or biology, implying the use of living organisms or their parts. The oriented cell growth is a long-sought-for and desirable aim of tissue engineering, where nanostructured scaffolds are needed to artificially reproduce the interface between the cell and its environment.³⁰ To prepare scaffolds guiding the growth of cells, techniques such as electrospinning and soft lithography can be used, but both of them have certain disadvantages. The electrospinning method involves the use of organic solvents and pore structures are difficult to control, while microchannels of poly(dimethylsiloxane) (PDMS) made by soft lithography can be deformed during applications.^{31–33}

The organized patterns created by self-organizing halloysite nanotubes is an easy and cheap alternative for making devices

capable of cell capture or orienting cell growth for diagnostic and tissue engineering purposes. When a dispersion of nonvolatile particles evaporates from a solid surface, it leaves a deposit, the structure of which depends on the route of liquid evaporation. The most common deposits are known as coffee rings because of the ringlike patterns left behind when a suspension drop dries. As liquid evaporates from the edge of the drop, it is replenished by liquid from the interior, and the appearing capillary flow transfers the dispersed material to the drop edge. Alternating pinning and depinning processes ("slick-slip" motion) taking place during solvent evaporation lead to the formation of irregular concentric rings. To make uniform periodic structures, the convective and evaporative flows inside the droplet must be controlled. When the suspension drop is forced to dry out in a restricted space, the temperature gradient is minimized and the drying dynamics is controlled, which allows us to obtain highly regular complex patterns.^{27,28} Different approaches to evaporative particle self-assembly in constrained environments can be utilized, such as cylindrical tubes, a two-plate configuration, curve-on-flat geometries, and others (Scheme 1).

Anisotropic particles such as halloysite nanotubes can be used to form concentric structures on flat surfaces ("sphere-on-flat" or more generally "curve-on-flat" configurations) to create

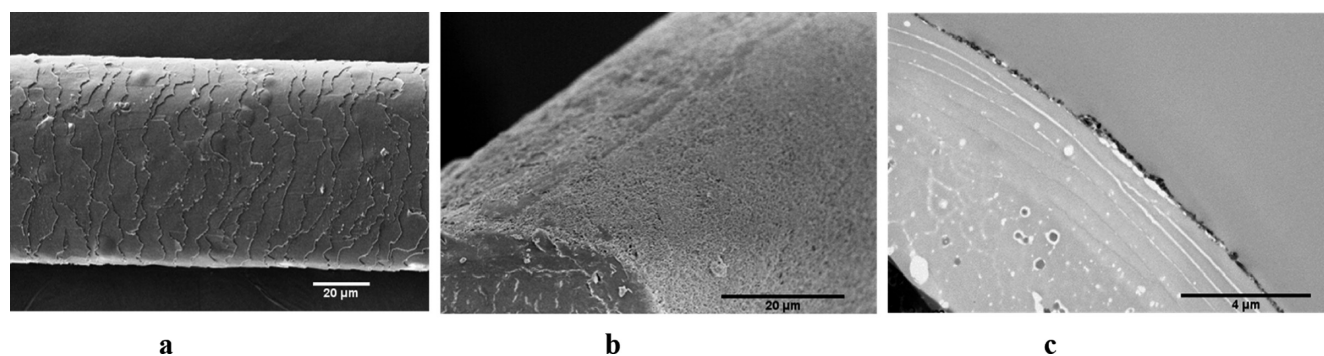


Figure 8. Human hair coating with halloysite clay nanotubes: (a and b) SEM images of original hair and hair coated with halloysite and (c) TEM cross-sectional view. Reproduced with permission from ref 34, copyright Royal Society of Chemistry, 2018.

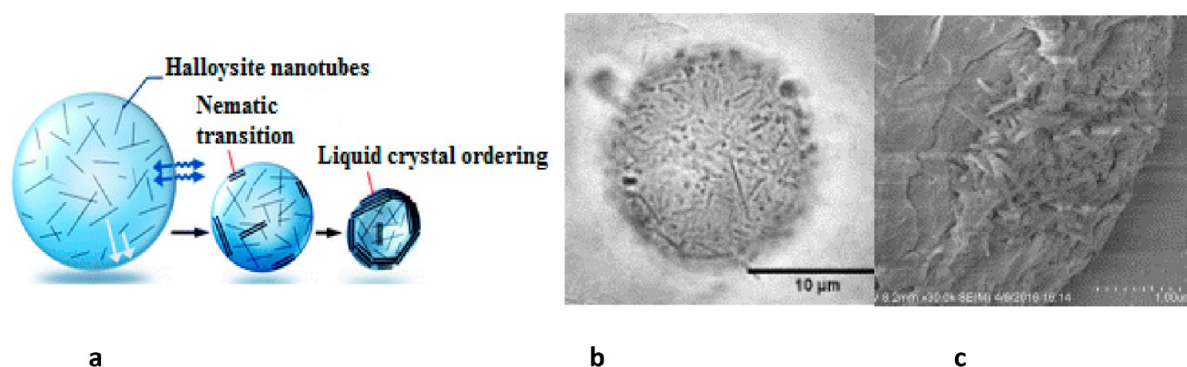


Figure 9. (a) Scheme of halloysite interfacial assembly on oil microdroplets and corresponding (b) optical and (c) cryo-SEM images. Reproduced with permission from ref 40, copyright Elsevier, 2018.

complex scaffolds directing the growth of cells. The geometry of the future cell scaffold can be predetermined by the form of the mold used during the process of suspension drying. Scheme 1 and Figure 6 demonstrate the formation of rectangular concentric structures when a small sphere and pyramid were used. The suspension concentration is of significance because as it increases the pattern becomes more distinct due to greater thickness and spacing between the rings.²⁷ The distance between the adjacent crests (or the groove width) is an important parameter for applications for capture and oriented cell growth and can be intentionally predesigned for the formation of cell-type-specific capture devices (Figure 6a–d).

The polymer precoating of halloysite can improve the suspension stability and formation of the ordered structures. Natural polyelectrolytes such as DNA can be applied to stabilize the nanoparticle suspension. When a 2 wt % aqueous suspension of halloysite covered with sonicated chicken erythrocyte double-stranded DNA was used to prepare a ring structure on a cover glass with a steel sphere template, more enduring and spiral-like patterns were formed (Figure 6e,f). The high stability of the micropatterns made of DNA-modified halloysite is beneficial both for extending guided cell culturing and for making various flow-type devices.

Another negatively charged polyelectrolyte, poly(styrenesulfonate), PSS was loaded into the small gap between the cover glass surface and a stainless-steel sphere ($d = 3$ mm), fixed above the glass by a magnet. For the creation of the rectangular structure, a glass pyramid glued to the glass slide was applied instead of the sphere. After drying at 65 °C, the obtained scaffolds were used to catch protozoa cells (*Paramecium caudatum*). *P. caudatum* cells were captured by rough

halloysite crests formed on the glass (Figure 7). However, the concentric ring structure was found to catch a larger number of protozoa cells than the rectangular one, where more frequent crests and narrower grooves created a rougher catching surface (Figure 7c).

Extending the halloysite self-assembly strategy, we reported the phenomenon of the spontaneous assembly of clay nanotubes on the hair surface. The platelike cuticles covering the surface of hair have a tendency to swell upon wetting with water. Narrow spaces between the cuticle and the bulk of hair expand and create spaces for halloysite alignment, similar to microchannels (Figure 3). A brief exposure of hair with an aqueous 2 wt % halloysite clay suspension allows the tubes to enter the swollen intercuticle spaces, and consequent drying aligns them from beneath the cuticle, outward toward the rest of the surface. This results in the formation of a micrometer-thick multilayer of this clay tubule on the surface (Figure 8). The self-assembly technique works with all mammal hairs, and the halloysite coating is resilient against washing. These nanotubes allow for loading chemicals into the inner lumens. Halloysite clay is a biocompatible material used for sustained drug delivery and dye-pigment formulations and can be loaded with chemicals into the lumen. We have further explored the feasibility of hair-surface engineering for hair color and health care including insecticide drug deposition. We also loaded halloysite with brown and blue dyes for hair color with the drug permethrin to demonstrate the potential in sustained antilice care. This technique may have many applications in human pharmacological and beauty formulations as well as in veterinary medicine.³⁴

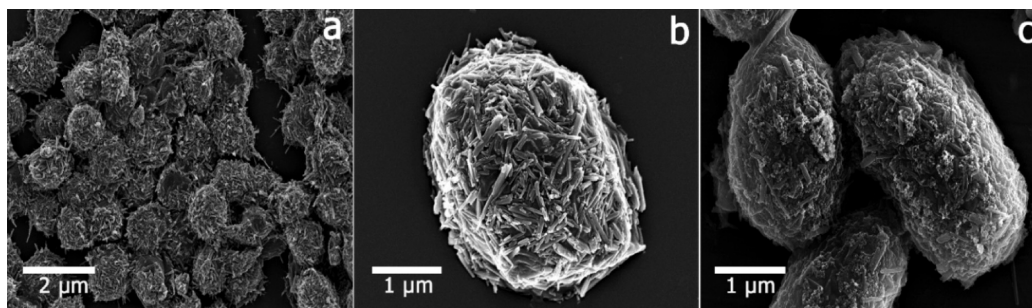


Figure 10. SEM images demonstrating the polyelectrolyte-mediated self-assembly of pristine halloysite nanotubes (a, b) with yeast cells/PAH/HNT/PAH/PSS architecture and the direct self-assembly of magnetite-modified halloysite (c) on *Saccharomyces cerevisiae* yeast cells.

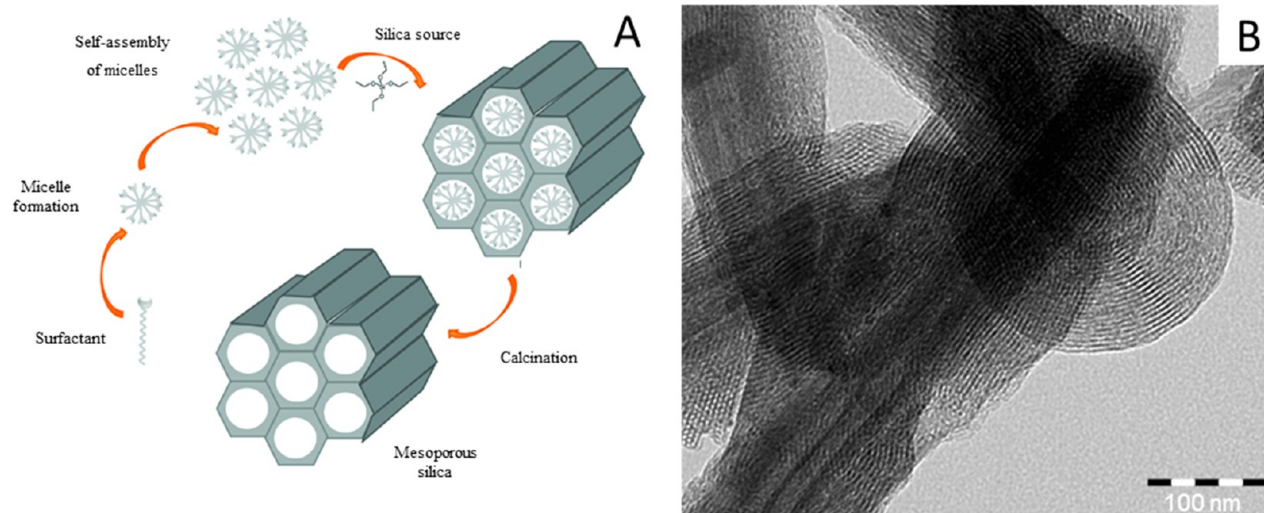


Figure 11. (A) Scheme of mesoporous silica MCM-41-type synthesis. (B) TEM of mesosilica assembled on halloysite, in a cross-sectional view. (A) Modified from Nam et al., *Materials* **2018**, *11*, 779, doi: 10.3390/ma11050779 with a CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

■ HALLOYSITE PICKERING EMULSION FOR OIL SPILL BIOREMEDIATION AND CATALYSIS

The above self-assemblies of halloysite were driven by capillary forces in a drying process on a solid substrates, but halloysites can also assemble on an oil–water interface. Solid micro-particles such as alumina and silica stabilized a paraffin–water interface and formed partial emulsions called Pickering emulsions. Halloysites, both pristine and with surface hydrophobization, form such stable oil–water emulsions.^{5,35,36} The nanotubes position themselves laterally on the oil–water interface, reducing the surface tension and stabilizing the microemulsions. Hydrophobizing the surface of halloysites increases the contact of the halloysites with the nonaqueous phase, providing more stability to the emulsions. The formation of microemulsions with droplets of 10 to 5 μm diameter was demonstrated with progressively hydrophobized halloysite (Figure 9).⁵ Pickering microemulsions with halloysite have been proven to have uses in biphasic catalysis and petroleum spill bioremediation, helping oil-eating bacteria *A. Borkumensis* to proliferate much better as compared to industrial petroleum spill emulsifier Corexit.³⁶

Higher hydrophobization of halloysite enables the encapsulation of water droplets inside a clay shell forming reversed Pickering-type microshells.³⁶ Such a droplet coated with halloysite with a contact angle greater than 120° is capturing 5–10 μL of water, forming liquid marbles.³⁶ In classic

Pickering emulsions, a hydrophobic layer of micro/nano-particles assembled onto the external surface balances the interface with oil, whereas in reversed liquid marbles, nanotubes retain water inside the marbles. These 0.5-mm-diameter marbles are pliable and mobile: a single one can be split into two, and they roll on flat surfaces. Apart from use as transport vesicles in microfluidic devices, marble integration with biomaterials can extend the potential applications. The growth of biofilm-producing bacterial species such as *Alcanivorax borkumensis* deposits a layer of exopolymer onto the inner walls of the marble, providing mechanical reinforcement for such encapsulation. In addition to stabilizing the liquid marble, the biofilm layer helps retain the bacterial activity in the encapsulated liquid medium. Such a viable microenvironment for the growth of microorganisms creates a novel strategy for encapsulating and storing bacteria at room temperature and can have far-reaching implications for bacterial storage.³⁷

Another interesting interfacial assembly of halloysite nanotubes is cell-surface engineering, an area of biotechnology aimed at the fabrication of organized shells on live micro-organisms.³⁸ These shells impart new functionality to the cells, offering mechanical and chemical protection and controlling the biological processes within the encapsulated species. Using polyelectrolyte self-assembly at the interfaces of cellular membranes (in the case of mammals) or cell walls (in the case of microorganisms) is one of the main instruments for

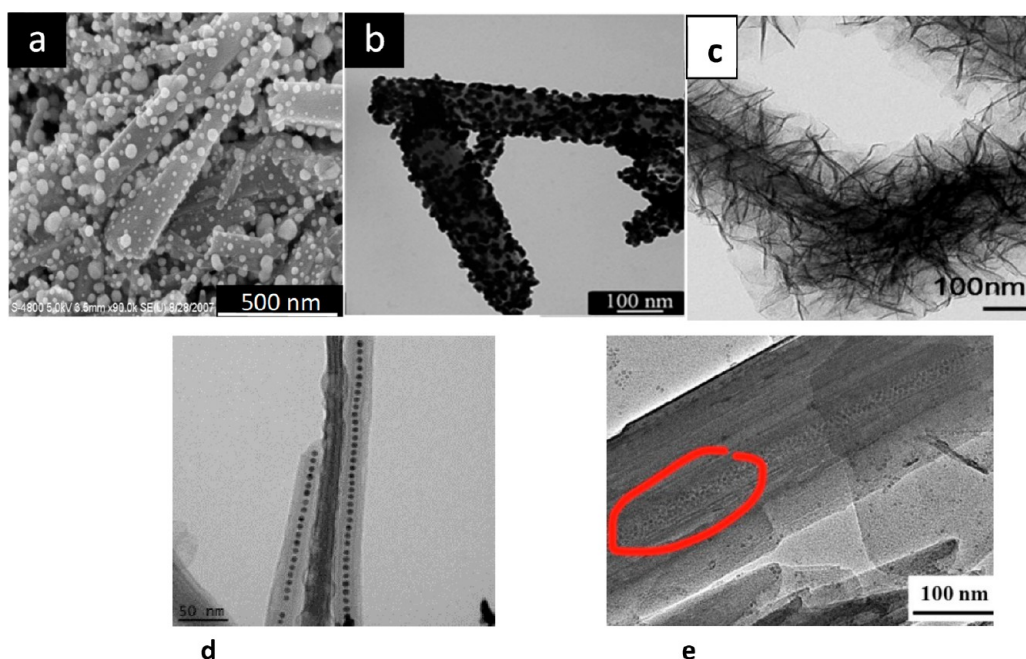


Figure 12. Decoration of the nanotube exterior with metal particles: (a–c) Ag and Au spheres and NiO sheets and TEM images of inner-lumen metal locations of (d) gold and (e) magnetite. (a and d) Reproduced with permission from refs 48 and 50, copyright American Chemical Society, 2011 and 2017. (b) Reproduced with permission from ref 57, copyright Royal Society of Chemistry, 2014. (c) Reproduced with permission from ref 58, copyright Elsevier, 2015.

biosurface engineering. The fabrication of polyelectrolyte multilayers results in the construction of several layers of oppositely charged polymer coatings, which can also be doped with several nano/microparticles, such as halloysite.³⁹ Anionic clay nanotubes were deposited on yeast cells modified with a polycation (poly(allylamine hydrochloride), PAH), providing mechanical protection and a nutrient surplus (halloysite was loaded with sucrose). Importantly, clay nanotubes did not induce any toxic effects in yeast. The typical scanning electron microscopy images demonstrating the “hedgehog-like” architecture of polycation/halloysite shells are shown in Figure 10a,b. An alteration of this approach has also been demonstrated using magnetite-PAH-modified halloysite capable of one-step direct deposition onto yeast cells (Figure 10c). Halloysite-coated live cells can be utilized as templates for the fabrication of microcapsules for drug delivery and also as versatile shells for living cells’ surface engineering, remarkably altering the properties of microbes.

Halloysite is the safest of clays and is nontoxic up to a very high concentration of 5 mg/mL, as proven with different cell cultures and animal models: from microworms, infusoria, and fish to mice, chickens, and piglets.^{11,40–42} Oral halloysite formulations efficiently treated piglets against mycotoxin poisoning with zearalenone and deoxynivalenol present in grain feed.¹¹ The toxicity of halloysite is typical of inorganics at higher concentrations, and much of the oxidative stress was attributed to the dissolution of Al^{3+} in the gastric pH. The inhibition of mouse growth and inflammation in the lungs occurred after the oral administration of a high dose of 50 mg/kg of body weight for 30 days.⁴¹ Recently, the potential inhalation exposure to halloysite was investigated in an industrial research laboratory, and no significant exposure risk was found.⁴² Overall, halloysite is a relatively safe nanomaterial which can be widely used in biomaterials.

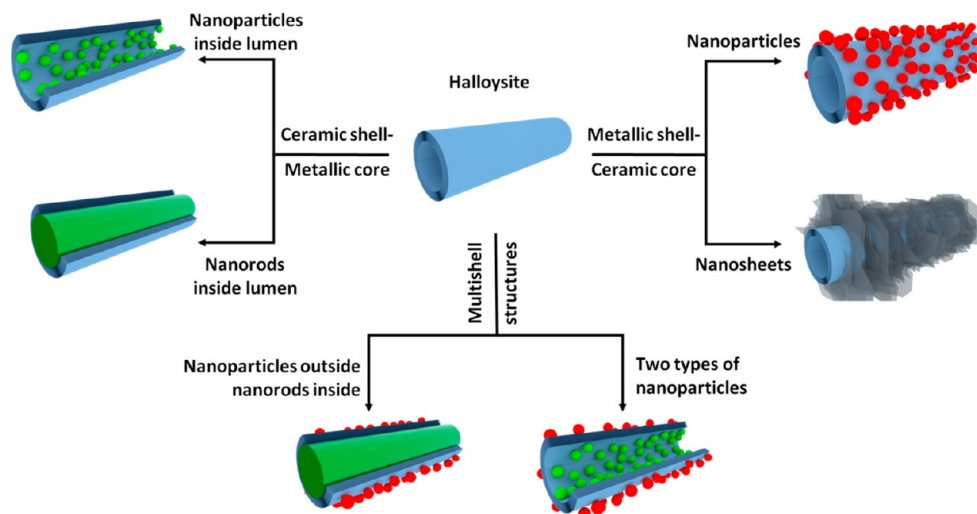
■ TEMPLATING MESOSILICA ON CLAY NANOTUBES

Ordered mesoporous molecular sieves of the MCM-41 type are a promising class of silica with regular nanopores and a specific surface area of up to 1000 m^2/g . (These materials were developed by Mobil Corporation.)⁴³ The synthesis of MCM-41 silica is based on the sol–gel method and the self-assembly of surfactant micelle array templates (Figure 11a). Depending on the amphiphiles, additional organic compounds, and the reaction parameters, the hexagonal mesophase is formed with a regular pore diameter distribution within 1.5–5 nm. These pores are larger than in crystalline zeolites, and MCM-41 materials possess new features for applications in catalysis, separation, and purification. This mesostructured silica is prospective in larger molecule processing in catalytic cracking and hydrocracking,^{44–46} but its commercial application is limited by the low-temperature and steaming stabilities.

We developed a new strategy for structured mesoporous silica synthesis by self-assembly onto halloysite nanotubes. Thanks to the negatively charged outer surface of halloysite, cationic cetyltrimethylammonium bromide (CTMAB) forms rodlike micelles around the nanotubes aligned into hexagonal arrays. After the silica precursor was added, these arrays were covered with silica layers, forming a mesostructured solid with surfactant. Aging or hydrothermal treatment leads to enhanced silicate condensation and packing into a highly ordered mesoporous phase with a favorable hexagonal arrangement. Finally, the organic template is removed by calcination at 550 °C in air, leading to the formation of a new architectural composite consisting of mesoporous silica assembled onto the clay nanotubes (Figure 11b,c). The mesoporous silica is formed around halloysite tubes with 100–120 nm concentric rings, resulting in a highly ordered structure with a pore diameter of 2.6 nm and a wall thickness of 1.6 nm.

Because of the high specific surface area (600–700 m^2/g) and enhanced thermostability this material has potential in

Scheme 2. Structure of a Tubule Core–Shell Metal Containing Halloysite Systems



thermal catalytic processes and separation and adsorption techniques. It could be applied as a catalyst support to exclude steric hindrance for bulky molecule conversion due to the large pores in halloysite (transport pores) and could provide high catalytic activity and selectivity at the expense of smaller MCM-41 silica mesopores. Reinforcement of the silica structure with halloysite nanotubes provides extremely high thermal and mechanical stability for these new composite materials.

METAL–CERAMIC CORE–SHELL TUBULE SYSTEMS FOR CATALYSIS

Self-assembly also takes place when metal–ceramic core–shell systems are produced using halloysite as a carrier. These tubule systems are different from the shell–metallic core particles that are usually based on sequential surface layering on spherical nanocrystals and did not employ hollow particles with internal modification.⁴⁷ Such systems mostly contain a gold core covered with organic or metal shells and did not use ceramic. We produced metal nanoparticles in the inner surface of clay nanotubes. It is difficult because of repulsion preventing the entry of positively charged ions into the same charge lumen. (For this task, inner/outer surfaces of the nanotubes have to be modified with organic ligands.) The charged halloysite surface attracts ions or molecules that form organized clusters shown on Figure 12. Numerous halloysite-supported metal nanoparticles have been synthesized: Ag-, Au-, Pt-, Co-, Cu-, Ru-, and CuNi.⁸ Depending on the procedure, different core–shell systems could be designed with a selective metal particle location inside or outside the nanotubes (Scheme 2). To produce nanoparticles outside the nanotubes, we carried out the synthesis in the presence of clay nanotubes and then washed the product. The size and shape of the metal particles deposited in the nanotube shell were different depending on the reaction conditions and reagent concentrations, ranging from spheres to “exotic” nanosheets for NiO (Figure 12c).

In most cases, a simple strategy of loading the reagents inside the tubes followed by a reduction reaction was exploited for inner-lumen synthesis.^{48–55} We know of only one that works when preformed carbon nanoparticles (quantum dots) were pulled inside the halloysite lumen.⁴⁹ In all other cases, highly concentrated precursor reagent was loaded inside the

tubes followed by the reaction producing particles. It is interesting that in only one case continuous silver nanorods were reported inside the halloysite, but in the majority of work, the nanotubes were stuffed with 2–5-nm-diameter spherical nanoparticles (Figure 12d,e). A simple mass estimation shows that one cannot produce densely packed metal nanoparticles inside the nanotube, consuming only reagents initially encased in halloysite, and that one needs an additional supply of the reagent. Therefore, in such nanoconfined metal nanoparticle synthesis a kind of molecular pump sucking reagents inside the clay tubes may work.

To improve the internal tubes' loading with the metal ions and to avoid undesirable precipitation (prevent aggregation) for building more sites for metal cluster crystallization, special modifications were applied. Figure 12b shows monodispersed gold nanoparticles bound through aminosilane (APTES) to the halloysite surface.⁵⁷ Enhanced selective intercalation of metal salts into halloysite is also possible. Metal ions surrounded by surfactants enter the tube lumen more easily than do positively charged initial metals, resulting in nice peapodlike structures (Figure 12d).^{50,51} Halloysite-encapsulated Fe₃O₄ was also achieved by loading a phenyl ether solution of iron(III) acetylacetonate and surfactants into the lumens, followed by heating to reflux under nitrogen (Figure 12e). The high-temperature solution-phase reaction in the lumens leads to 5 nm Fe₃O₄ particle formation, which provides for the nanotubes' magnetic performance with a specific saturation magnetization of ca. 6 emu/g.⁵⁶

The modification of the internal surface of halloysite nanotube with organic ligands also increases the metal ions' loading efficiency. Ligands pull ions inside the tubes, filling the lumen or other porous defects. Metal complexes were formed inside the tubes at a high concentration of up to 9 wt %, and after reduction or decomposition, they organize in particles.^{8,51–53} All of these structures could be applied in catalysis, and what is especially interesting is the ability to make nanoreactors with superior catalytic performance with catalytic centers placed inside nanotubes. The Cu–Ni nanoparticles encased in clay nanotubes have shown a high efficiency at 400 °C in autoexhausting the conversion of CO and NO, demonstrating temperature stabilization of the catalyst enclosed in the halloysite. The catalytic activity of nanoparticles synthesized in halloysite was investigated in

many organic oxidation reactions as well as in hydrogen production reactions. Such systems showed very good activity.^{53,55}

CONCLUSIONS

Here we described an architectural approach in materials design based on natural halloysite clay nanotubes. The interfacial halloysite arrays may be produced at solid–liquid interfaces, oil–water interfaces, or biosurfaces such as tissue scaffolds and microorganism surfaces (cell encapsulation). An orientation of charged nanorods/nanotubes in condensed systems, similar to that of nematic liquid crystals, was predicted by Nobel Prize winner L. Onsager, and halloysite clay nanotubes allowed for the experimental verification of this theory. Our strategy is based on the interfacial self-assembly of these nanotubes and building metal nanoparticle shells as well as the internal loading of their lumens. All biorelated applications of halloysite may have a synergetic effect due to possible loading with drugs followed by slow and controlled release.

Metal–ceramic core–shell tubule systems look very promising for mesocatalytic systems: metal nanoparticles may be placed selectively outside or inside the nanotubes, thus providing thermo- and aggregation resistance and the possibility to adjust the catalytic particle sizes. A perspective on combining in one catalytic system different metals (inside/outside) and the possibility to optimize Al_2O_3 , MnO_2 , and Fe_2O_3 content in such a tubule template promises even more elaborate catalysts. The placement of metal nanoparticles inside halloysite mesopores combined with the functionalization (hydrophobization) of the outer tubes' surface will result in nanoreactors for biphasic catalysis. Another direction is a combination of industrial mesosilica catalysts with halloysite nanotubes, making “fish-tissue”-like composites when 30–40 wt % embedded ceramic nanotubes provide strength and thermostability to often weak bulk nanosilica or zeolites. Finally, we underline that contrary to many other nanomaterials, halloysite nanotubes are safe, inexpensive, and available in thousand of tons natural material which is not harmful to the environment and in most cases allows for “green” water-based chemical processing.

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Notes

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