

Article

Dry Sintered Metal Coating of Halloysite Nanotubes

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Abstract: Halloysite nanotubes (HNTs) are a naturally-occurring aluminosilicate whose dimensions measure microns in length and tens of nanometers in diameter. Bonding defects between the alumina and silica lead to net negative and positive charges on the exterior and interior lumen, respectively. HNTs have been shown to enhance the material properties of polymer matrices and enable the sustained release of loaded chemicals, drugs, and growth factors. Due to the net charges, these nanotubes can also be readily coated in layered-depositions using the HNT exterior lumen's net negative charge as the basis for assembly. These coatings are primarily done through wet chemical processes, the majority of which are limited in their use of desired chemicals, due to the polarity of the halloysite. Furthermore, this restriction in the type of chemicals used often requires the use of more toxic chemicals in place of greener options, and typically necessitates the use of a significantly longer chemical process to achieve the desired coating. In this study, we show that HNTs can be coated with metal acetylacetonates—compounds primarily employed in the synthesis of nanoparticles, as metal catalysts, and as NMR shift reagents—through a dry sintering process. This method was capable of thermally decaying the metal acetylacetonate, resulting in a free positively-charged metal ion that readily bonded to the negatively-charged HNT exterior, resulting in metallic coatings forming on the HNT surface. Our coating method may enable greater deposition of coated material onto these nanotubes as required for a desired application. Furthermore, the use of chemical processes using toxic chemicals is not required, thus eliminating exposure to toxic chemicals and costs associated with the disposal of the resultant chemical waste.

Keywords: 3D printing; filaments; additive manufacturing; halloysite

1. Introduction

Halloysite nanotubes (HNTs) are naturally-occurring aluminosilicates that measure microns in length and tens of nanometers in diameter [1–4]. Bonding defects between the alumina and silica lead to net negative and positive charges on the exterior and interior lumen, respectively [5,6]. HNTs are capable of enhancing the material properties of many polymer matrices [7–10]. HNTs have been widely used as a nanostructured reinforcement material for polymers that exhibit low mechanical strengths [7,8]. Modification of these nanotubes through surface coatings and other preparations can further enhance the strength and dispersion of the HNTs within the polymer [9,10]. HNTs also enable the sustained release of loaded chemicals, drugs, and growth factors [11–14]. Due to the net charges, HNTs can also be readily coated with polyelectrolytes, polymers, etc. using the net negative charge

of the exterior surface as the basis for assembly [15,16]. Through added layers deposited onto the HNTs, the pattern of released substances can be further controlled, enabling delayed or inhibited release [13–16].

For coating of the HNT surface, a layering method is commonly used to achieve the desired coatings onto the exterior surface, using the inherent charge differential between the layers of the nanotubes as the basis for these coatings [16,17]. Due to the aforementioned polarity of the nanotubes, solvents used are limited, and the nature of the method requires a much longer and more drawn out process that demands full drying of the prepared HNTs between successively added layers. In particular, the demands of preparing samples with cobalt to achieve a catalytic sheath require manufacture in a vacuum after sample preparation via double solvent impregnation of the cobalt salt [18]. Similarly, the HNT coating in polyamide requires the use of fully-hydrolyzed silane to enable full coating of the polyamide onto the nanotube surface [19,20].

In this study, we show a method of coating these nanotubes with metals through dry sintering of the HNTs with metal acetylacetonates—compounds primarily used in the synthesis of nanoparticles, metal catalysts, and as NMR shift reagents. We found that this method was capable of thermally decaying the metal acetylacetonate molecules, resulting in a free positively-charged metal ion that readily bonds to the negatively-charged exterior of the halloysite. Our results show that through sintering, metallic coatings can be achieved on these nanotubes of the desired metal using the associated metal acetylacetonate compound. We anticipate that our method of coating these tubes through a dry sintering process will enable compatibility with a wider range of materials to be coated onto these nanotubes as necessitated by the application without requiring the use of exotic chemical processes.

2. Materials and Methods

2.1. Materials

Iron (III) acetylacetonate (99.9% pure) and Nickel (II) acetylacetonate (95%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Barium acetylacetonate (99%) was ordered from Fischer Scientific Company (Hampton, NH, USA). Purity grades are based on trace metals analysis. Lab plastics and reaction vessels were purchased from MidSci, St. Louis, MO, USA. The scanning electron microscope (SEM) imaging and energy-dispersive X-ray spectroscopy (EDS) were performed on a Hitachi S-4800 SEM/EDS system (Schaumburg, IL, USA). Additional imaging was done using an FEI Tecnai G2 F30 Twin (Hillsboro, OR, USA) and a Libra 120 Transmission Electron Microscope (TEM) manufactured by ZEISS (Peabody, Oberkochen, Germany).

2.2. Methods

2.2.1. Metal Sintering of Halloysite Nanotubes

Most metal acetylacetonates degrade completely at 300 °C, outgassing acetone and carbon dioxide and leaving behind positively-charged metal ions. Due to the negatively-charged outer lumen of the halloysite, these metal ions should readily bond to the outer surface, allowing for a one-step sintering coating.

Halloysite was allowed to dry overnight at 60 °C. The halloysite was then weighed and mixed with an equal amount of a metal acetate or metal acetylacetonate. Metal acetylacetonates were mixed with halloysite in a 1:1 ratio by weight. Halloysite (100 mg) and the associated acetylacetonate were weighed, mixed in a VWR borosilicate glass container, and then vortexed for one minute. Powders were moderately mixed in a mortar and pestle, and the powders were then placed into 5 mL VWR borosilicate glass containers and vortexed vigorously for one minute.

A Vulcan oven was used for the sintering process. These heating/cooling rates were chosen arbitrarily, as nothing happens below 150 °C, increasing linearly with added heat after that. Containers were then placed in a Vulcan oven and programmed to heat to 300 °C at a rate of 12.8 °C/min, then held

at this temperature for four hours. The program was then set to cool the contents to room temperature at 5 °C/min. This resulted in a sintering reaction, which coated the halloysite nanotube in a metal shell or deposited metal clusters onto portions of the nanotube.

After sintering, the glass tubes were vortexed or ground by mortar and pestle to break up clumps of material. The raw material is moderately clumped, but breaks down to a fine powder with minimal vortexing or additional processing. Multiple batches of each nanoparticle were fabricated and characterized through the following methods to verify the consistency of the process. Conditions were kept as sterile as possible, and new borosilicate glass containers were used for different HNT metal coatings to ensure no cross contamination of additives occurred.

2.2.2. Scanning Electron Microscopy (SEM)

SEM was used to examine the surface morphology of the coated halloysite and to visually confirm the presence of a coated additive. Since halloysite has a characteristically smooth outer coating and distinct separateness between adjacent tubes, any difference was easily confirmed, and will lead to verification of the deposited material after sintering.

2.2.3. Transmission Electron Microscopy (TEM)

TEM was chosen due to the low-density elements present in the raw halloysite samples. Through the deposition of higher-density elements, a change in the visual nature should occur, showing the presence of the higher-density materials. Further, boundaries of the HNTs are easily identified through this method, allowing for the location of the material deposited to be confirmed as on the surface rather than as nanoparticulates dispersed throughout the sample.

2.2.4. Energy Dispersive X-ray Spectroscopy (EDS)

EDS was used to verify that the compounds associated with the acetylacetonate bond truly degraded into vapors and were not a part of the material deposition onto the HNTs. Measured peaks represent a mean of multiple samples ($n = 6$) that were tested via this method. It was found that the hypothesized degradation at 300 °C did fully occur after the four hour temperature exposure, resulting in the desired free positive metal ions that subsequently bonded to the halloysite surface.

3. Results and Discussion

Metal acetylacetonates provide a means of generating positive metal ions through thermal degradation of the acetylacetonate bond that interact readily with the native negative charges on the outer halloysite surface, allowing for coating of the metals without the use of wet chemical processes, flowed gas, or vacuum (Figure 1). Furthermore, the decay products are non-toxic, negating the need for filtration of the out gassed products during fabrication and allowing for a much easier path to a full-scale manufacturing operation without the need for environmental permits [21].

The metals chosen for this process were among many that had readily-available acetylacetonate compounds that could be used, but all have use in important applications. Barium acetylacetonate was selected, as barium sulfates are commonly used as a contrast agent in biomedical applications due to the strong mass attenuation coefficient of barium at the energies of medical grade photons. Additionally, barium titanate nanowires have been used as mechanical components in accelerometers due to their piezoelectric nature [22]. New fabrication techniques in halloysite could generate a host of new microelectromechanical (MEMS) devices. Iron acetylacetonate was chosen due to the potential magnetic qualities that could be achieved. The traditional layer-by-layer approach typically used in the creation of magnetic sheaths for the nanotubes provide very thin layers and typically use cobalt or nickel for the magnetic material [23,24]. Nickel has many potential uses as a catalyst, and as such, nickel acetylacetonate was used to obtain nickel coatings on the tubes for a potentially greater surface area. Nickel and iron also show promise as battery materials when nanostructured [25,26].

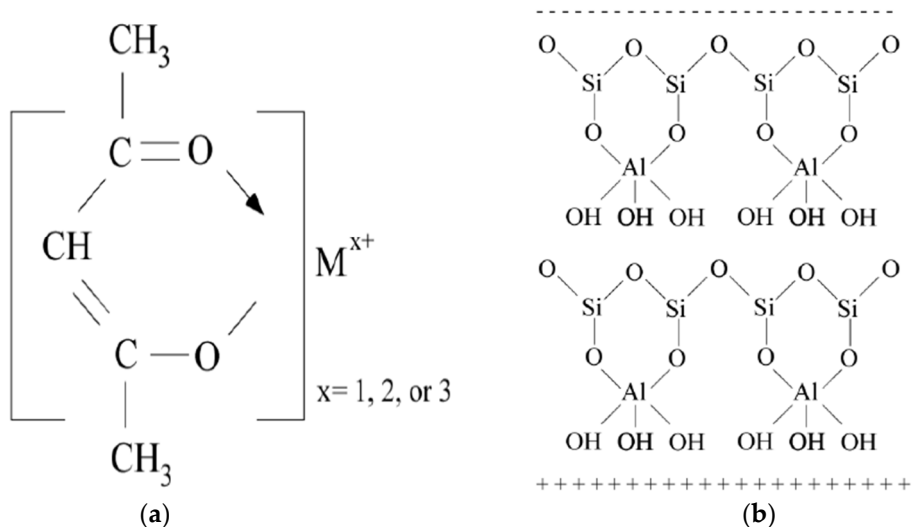


Figure 1. Chemical bonding structures for metal acetylacetonates (a) and HNTs (b).

Raw HNTs are transparent to the TEM, consisting of low-density thin-walled materials. With the introduction of heavier metals, the transparency is overcome. Shown in Figure 2 are transmission electron microscope (TEM) images taken of the resulting metal-coated halloysite after the above-described process. Here, the differing charges of the metal ions dictate the characteristics of the metal coating during the sintering process. For the barium and nickel (B,D), tight bonding to the external lumen of the halloysite is observed (Figure 2).

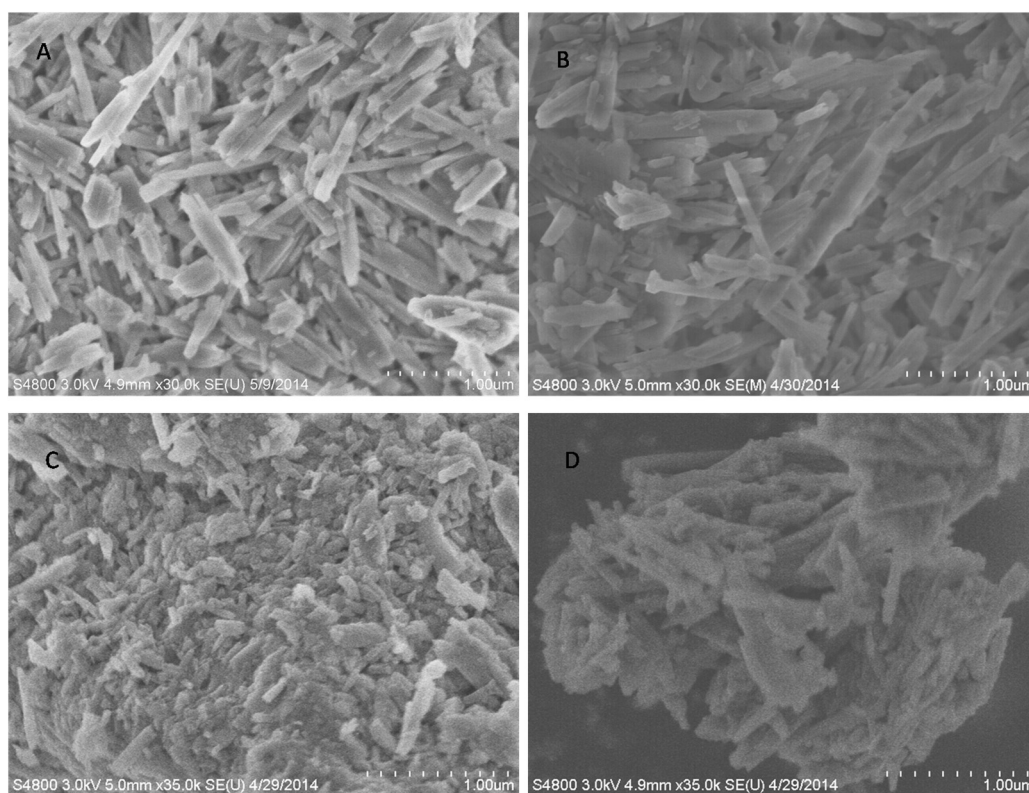


Figure 2. TEM of (A) raw HNTs, (B) barium sintered HNTs, (C) iron sintered HNTs, and (D) nickel sintered HNTs.

This is likely due to the M^{2+} -charge state of these metal ions, allowing for both bonds to be linked to the negatively-charged oxygen found on the surface of the halloysite. In contrast, the iron (C) (a Fe^{3+} ion) is seen to clump rather than evenly disperse along the length of the nanotube. This is due to the extra bond on the ion that is unable to bond fully onto the exterior lumen. Two of the available bonds oxidize onto the surface of the halloysite, while the remaining bond oxidizes, as the sample was not done under vacuum. This leads to another 1-oxygen bond on the surface of the iron, which attracts another iron ion, leading to two free 1-oxygen bonds. As the iron continues to oxide together, the clumps seen in Figure 2B are formed.

In considering larger bulk samples of the halloysite, scanning electron microscope (SEM) images were taken and are shown in Figure 3. The raw halloysite (a) exhibits a lighter nature, and can be seen to be distinct tubules; however, as the metals are applied, there is a contrast in the samples correlated directly to the increased density of the material. This allows visual confirmation of the coating material to be achieved as the metals (barium, iron, nickel) are significantly denser than the aluminum, silicon, and oxygen composing the raw halloysite. The barium-coated tubes (b) have tight sheaths, but can still be seen as individual tubes. The iron-coated tubes (c) can be seen to aggregate with individual tubes on top of the sample. The nickel-coated tubes (d) can also be seen to maintain the individual tubes as with the barium. However, the nickel does not form as thick of a sheath as the barium. This is attributed to the smaller size of the nickel ions as compared to the barium, allowing the nickel to bond in the nanotube pores.

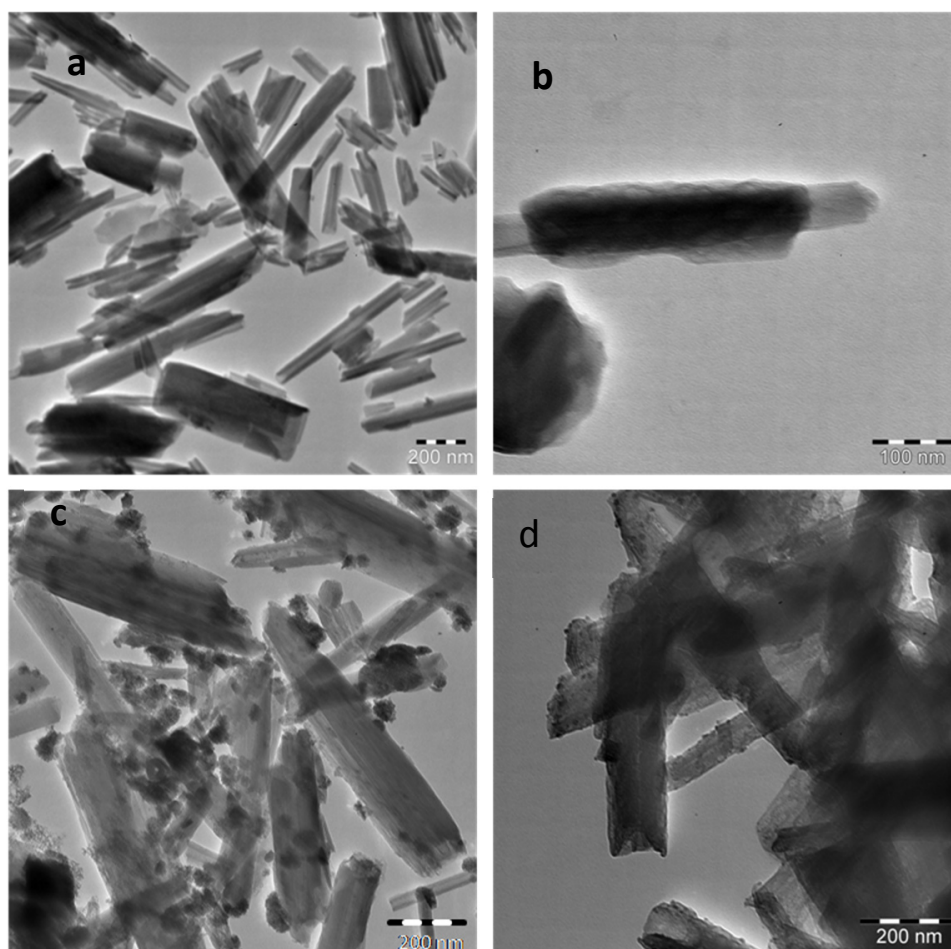


Figure 3. SEM of (a) raw HNTs, (b) barium sintered HNTs, (c) iron sintered HNTs, and (d) nickel sintered HNTs.

To verify the metallic coatings of the nanotubes, EDS (Energy Dispersive X-ray Spectroscopy) analysis was performed to test for the elements present in the sample (Figure 4). The raw halloysite (a) shows the aluminum, silicon, and oxygen expected of the aluminosilicate nanotubes. The subsequent three (b–d) show definitive peaks for the elements sintered, ensuring their presence in the samples. Multiple EDS characterizations were performed, and all peaks found were similar to the ones presented in Figure 4. Slight changes were noted due to the relative nature of the sample and the small sample window of the EDS; however, the peaks present during the analysis confirmed the presence of the suspected metal dopant.

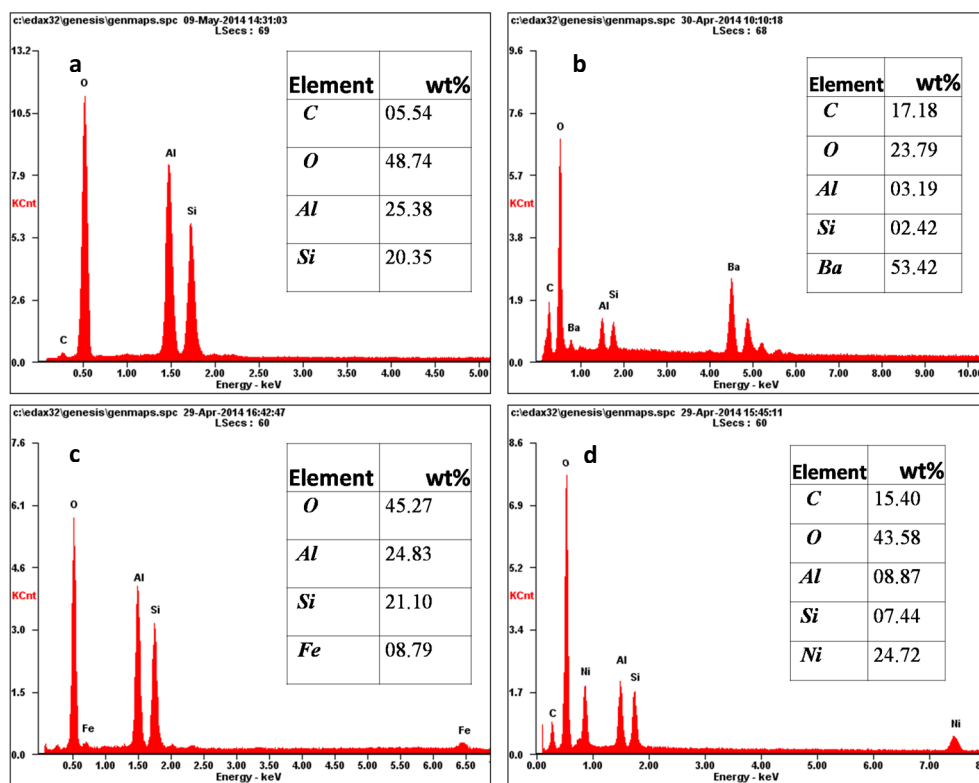


Figure 4. EDS of (a) raw HNTs, (b) barium sintered HNTs, (c) iron sintered HNTs, and (d) nickel sintered HNTs.

We have also been successful in sintering copper and lithium onto the surface of the HNTs; copper for its potential as a conductive sheath for micro-fabricated antennas and theranostic applications, and lithium for its common use in neutron detection or time-release coatings for bipolar treatments. EDS data for the lithium are inconclusive, due to the light weight of the element and the use of a beryllium lens for the system that filters out the respective signal. However, copper did show definitive elemental mapping. Imaging revealed that copper acted as nickel did, and this is attributed to the 2+ ion involved in that reaction. Images of the lithium proved to be cloudier than raw halloysite, indicating that deposition did occur onto the external surface of the nanotubes.

In this study, dry sintering of metal acetylacetonates mixed with halloysite was shown as a viable method for coating HNTs in the desired metal due to the HNTs' inherent net negative surface charge. The metal acetylacetonate coating was confirmed via SEM, TEM, and EDS, where visual and elemental analysis showed concrete deposition of the material. Metal nanoparticles (NPs), such as silver NPs, copper NPs, gold NPs, and others, can be directly deposited onto the surfaces of HNTs. Over the last five years, a number of methods have been developed for the metallization of HNTs. For example, Chu et al. [27] and Geckler and Hasan [28] describe processes used to bind gold compounds to the surface of halloysite. Methods that load HNTs with copper [29,30] and

silver [3] for use as an antibacterial agent have also been recently developed. All these fabrication methods include lengthy and multi-step processes that include metal-salts or organic compounds, complexing and reducing agents, high temperatures, and expensive equipment to achieve metallization of HNT surfaces.

Our method has the advantages of lower cost, simpler fabrication conditions, low energy consumption, environmental protection, and does not require the use of caustic or toxic compounds. Halloysite has been extensively studied for the reinforcement of medical grade polymer matrices [17,31,32] and in the sustained release of anti-corrosion agents [33], antibiotics [32,34,35], growth factors [15], and chemotherapeutic compounds [17]. Halloysite nanotube-supported metal nanoparticles have potential uses in biomedical devices, antimicrobial surfaces, theranostic delivery systems, radiation absorptive composites, plastic/elastomer composites, electronic components, and as industrial catalysts. As an example, the addition of the contrast agent to halloysite rather than the polymer matrix could potentially provide greater mechanical enhancement rather than barium added directly to the polymer. Furthermore, the imaging characterization showed that the coatings did not cap the nanotubes, allowing for even greater potential use when combined with the sustained release of loaded chemicals from the HNT lumen, and varied applications where subsequent layers can be coated over the metal sheaths obtained.

4. Conclusions

There exist many techniques for the surface modification of HNTs with metal compounds. Existing fabrication methods include lengthy multi-step processes that include metal-salts or organic compounds, reducing agents, high temperatures, and expensive equipment to achieve metallization of the halloysite surface. We describe a nanotube coating method through dry sintering of metal acetylacetonates, compounds primarily used in the synthesis of nanoparticles, metal catalysts, and NMR shift reagents. Our results suggest that our method is capable of thermally decaying the metal acetylacetonates, resulting in a free positively-charged metal ion that readily bonds to the negatively-charged halloysite exterior. We further show that through the sintering method, metallic nanotube coatings can be easily achieved, enabling a broader amount of material coated as necessitated by the application, without requiring the use of exotic chemical processes. We anticipate our method of coating these tubes through a dry method will enable a broader amount of material to be coated onto these nanotubes as necessitated by the application, without requiring the use of exotic chemical processes.

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Conflicts of Interest: The authors declare no conflict of interest

Abbreviations

The following abbreviations are used in this manuscript:

EDS	Energy Dispersive X-ray Spectroscopy
HNT	halloysite nanotube
NMR	Nuclear Magnetic Resonance
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

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