Review

Recent Advances on Surface Modification of Halloysite Nanotubes for Multifunctional Applications

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Featured Application: Authors are encouraged to provide a concise description of the specific application or a potential application of the work. This section is not mandatory.

Abstract: Halloysite nanotubes (HNTs) are natural occurring mineral clay nanotubes that have excellent potential application in different fields. However, HNTs are affected by size, surface electron and hydrogen bond formation on the surface which lead to weak affinity and reunion at certain extent. It is very significant to modify the HNTs' surface to expand its applications. In this review, the structural characteristics, performance and the related applications of surface modification HNTs are reviewed and summarized. We focus on the surface modify methods of HNTs, the effect of surface modification on materials and related applications in various regions. In addition, future prospects and the meaning of surface modification were also be discussed in HNTs studies. This review provided a reference for the application of HNTs modifications in new nanomaterials fields.

Keywords: halloysite nanotubes; surface modification; structural characteristics; application

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1. Introduction

HNTs are natural occurring mineral clay nanotubes with particular hollow shapes. There are various morphologies for HNTs, such as tubes, platy and spheres [1], and with 500 nm-1500 nm length, the lumen and external diameter respectively 15 nm and 50 nm [2]. HNTs possess a high surface area reached to 184.9 m^2/g and large pore volume reached to 0. 353 cm^3/g, and it is easy to form matrix membrane for gas separation [3, 4]. Chemical composition of HNTs is similar to kaolin. The unit layers are isolated by monolayer water molecules in HNTs. The HNTs hold the molecular formula of $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$ [5] and the HNTs is composed of Al, O and Si with the atomic proportion 1:4.6:1 [6]. The aluminosilicate clay nanotubes have Al:Si ration with 1:1. There are two main polymorphs for HNTs anhydrous form and hydrated form, interlayer spacing respectively 7 Å and 10 Å [7]. HNTs have a wide range of pH and the zeta-potential shown a negative electrical with ca -50 mV [8]. At pH 6-7, the zeta-potential of HNTs put up negative but exerts a positive surface at pH 8.5 [9] and a negative charge with ca −32±2 mV [10]. The external surface of HNTs is composted of silicon oxygen tetrahedron, the internal lumen is alumina oxygen octahedron, outer surface is the mainly distribution of Si-O-Si group, the inner surface is Al-OH [11]. Because of the multilayer structure, most of the hydroxyl exists within the lumen and only a few in the outer surface [12].

As a widely used environmentally friendly clay tubes, HNTs have good biocompatibility [13]. HNTs were confirmed to have non-toxic not only *in vivo* [10], but also *in vitro* [14]. HNTs with High specific surface area, strong surface adsorption and different chemistry of the inner and outer

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surface. However, HNTs showed a weak affinity when were used to synthesize composites, drug delivery and molecular adsorbents, because of the weak intermolecular force, such as Van der Waals forces and hydrogen bonding. To improve the performance of HNTs, a surface modification is very ideal. For example, the modified HNTs can be used as nanofillers to composite polymer thus to enhance mechanical strength [15] and as nanocarries to implement sustain drug delivery. In addition, it is also be regarded as adsorbent to absorb or remove the matter from aqueous solution [16] and served as catalysts [17] to the study of reaction.

2. Surface modification of HNTs and the relevant properties

Surface modification of HNTs means that it maintains the original properties and endows the new properties, such as hydrophilicity, biocompatibility, antistatic properties, dyeing performance. At present, many methods of surface modification of HNTs are reported, including surfactant modification, coupling agent modification, intercalation modification, surface coating modification and free radical modification, etc. The HNTs can be modified in the appropriate time according to the need for selective modification.

2.1 Surfactants modification

Surfactants modification refers to the presence of non-polar lipophilic groups and polar hydrophilic groups in the surfactant molecule. It has been extensively investigated the better dispersions stabilization by electrostatic forces [18]. Because of the charge characteristics of the HNTs, the surfactants are able to be adsorbed selectively into the internal or onto the external surface maintaining to different hydrophilic–hydrophobic balances [19] and prepared the hydrophilic / hydrophobic nanoparticles to obtain nanomaterials such as the oil recovery / solubilization of hydrophobic molecules. The negatively charged surfactants were adsorbed mostly into the internal lumen on account of the positively charged internal surface [20, 21, 22]. Yong Lin et al (2011) [23] prepared the high-impact polystyrene nanospheres by emulsion polymerization. In this system, the sodium dodecyl sulfate (SDS) was added to the aqueous solution containing the HNTs. SDS as an emulsifier to form a molecular layer on the surface of HNTs , so that the surface of HNTs has a strong hydrophilic to enhance the dispersion in aqueous solution. In addition, Wang et al (2010) [24] used the surfactant of hexadecyltrime-thylammonium bromide (HDTMA) to modify the HNTs and prepared a new adsorbent for the removal of Cr (VI) from the aqueous solution, and the adsorbent with the maximum adsorption rate of Cr (VI) reached to 90% in the 5 minutes.

2.2 Coupling agent modification

Grafted silane coupling agent onto the surface is the most common chemical modification method for HNTs. The silane coupling agent can be chemically reacted with the HNTs through physical or chemical bonding. By changing the performance of hydrophobicity, to improved the dispersibility and interfacial interaction between HNTs and polymers. Guo et al (2009) [25] synthesized a high strength nanocomposite (polyamide 6/halloysite) by combined with 3-(trimethoxy silyl) propyl methacrylate. The results showed that the nanocomposites significantly improve its mechanical and thermal properties. Meanwhile, Wan et al (2017) prepared high-performance nanocomposite by compounded with 3-aminophenoxy-phthalonitrile and poly (arylene ether nitrile) (PEN) based on HNTs [26]. It has been found that functionalized HNTs exhibit superior tensile strength and modulus because of the better dispersion and strong capacitance.

2.3 Intercalation modification

Intercalation modification refers to the small molecules reacted with HNTs between the hydroxyl groups and other groups, in order to improve the performance of HNTs. Tang et al (2011) [27] used the phenylphosphonic acid (PPA) to unfold and intercalate the HNTs, and mixed with epoxy to form the halloysite-epoxy nancomposites. The modified HNTs obtained a better dispersion, large contact area among nanocomposites and significantly promoted micro-cracks and plastic deformation take shape at the interface. Deng et al (2009) [28] treated the HNTs with potassium acetate (PA) and ball mill homogenisation to improve particle dispersion. It was demonstrated that the modified HNTs could observably enhance the properties of mechanical, interfacial debonding and provide opportunities for other substances to intercalate.

2.4 Surface coating modification

Surface coating modification refers to the surface of HNTs is coated with a layer of polymer or inorganic material by means of the electrostatic adsorption, so as to achieve the purpose of changing HNTs performance. Li et al. (2016) [29] prepared the drug-loaded porous microspheres (Hal-CTS/Asp) by the method of thoroughly emulsification in the water/oil microemulsion. The HNTs were coated with chitosan (CTS) and the aspirin (Asp) adsorbed inside the microspheres as a model drug. The results indicated that the microspheres had the characteristics of high surface area and the large-interconnected pores, which was conducive to the adsorption of aspirin. The modified HNTs had excellent loading capacity (42.4 wt %) which is twenty times higher than unmodified ones (2.1 wt %). Meanwhile, the special microspheres showed low drug release rate and pH sensitive compared with the pristine HNTs. Liu et al (2015) [30] successfully prepared a lot of alginate/HNTs composites tissue engineering scaffolds by electrostatic adsorption method. The scaffolds showed significant enhancement in thermal stability and cell-attachment properties.

2.5 Free radical modification

The surface of HNTs contains hydroxyl groups that could react with the monomer on the inner or outer surface. The functionlization HNTs can improve the hydrophobicity and their dispersibility in organic solvents, in order to obtain the stable composites. Liu et al (2011) [31] prepared the modified HNTs by grafting the polymethyl methacrylate (PMMA) via radical polymerization, and then compounded with poly (vinyl chloride) (PVC) to form higher toughness, strength and modulus composites. The results showed that the modified HNTs have uniform dispersed in PVC aqueous solution, and effectively improved the mechanical properties. Li et al (2008) [32] reported a kind of functionlization HNTs modified by polymers via atom transfer radial polymerization (ATRP) and crosslinked with polystyrene (PS) and polyacrylonitrile (PAN), respectively. The results indicated that the composites showing excellent wettability and can be used to entrap water droplets.

3. Application of Surface Modification of HNTs.

3.1 As the filler nanocomposites.

Composite materials are vital for the development of modern science and technology. They are widely used in magnetic material, magnetic facility, flame retardant, optics, scaffold for tissue engineering and electronics. Meanwhile the nanocomposites always need a complex template, tedious preparation process and high cost. It is imperative to find an effective modules and efficient fabrication. Due to high specific surface area and unique surface chemical properties, HNTs are widely used to improve polymer’s property. At the meanwhile, the low surface charges and weak interfacial could be problematic [33].

The modification on the surface of HNTs is to spread the basal spacing through insert the inorganic or organic groups between layers. The surface modified HNTs not only acquire well

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dispersibility and strong interfacial interaction [34], but also to provide abundant bond formation [35].

HNTs proposed a better interactions in clay–polymer nanocomposites by chemically or physically pretreatment [36]. The functionalization of nanotubes composite polymer will achieve a win-win situation.

HNTs have been used extensively for enhacing properties of ploymers. Parthajit et al (2013) [5] successful modified the HNTs by N-(b-aminoethyl)-c-aminopropyltri-methoxysilane, the modification and unmodification respectively mingle with nonpolar polypropylene (PP) and polar polyoxymethylene (POM) by utilizing the methods of immiscible blend system(B). The results indicate that pure polymer blend and B-HNT nanocomposites always form obvious agglomeration attribute to the weak interface interaction between the polymer and HNTs. Howeve it present different phenomenon to the B-MHNT nanocomposites that dispersed well in the polymer blend. This suggests that modification (B-MHNTs) obtain a better dispersion compared to the unmodified (B-HNTs) in blend matrix. Meanwhile, the functionalization HNTs are used to enhance the chemical interactions as a natural rubber (NR) filler [37]. The bis (triethoxysilylpropyl)-tetrasulphide was used to modified the HNTs by the way of silane coupling agent. In general the natural rubber composite with modified HNTs (NR-HNTs-Si) show an excellent physical properties and thermal stability compared with the unmodified HNTs nanocomposite (NR-HNTs) and natural rubber-silica (NR-Si). The HNs also modified with polyrhodanine (PRD) by the way of oxidative polymerization to Styrene butadiene rubber (SBR) [38]. The data indicate that the tensile strength and SBR/PRD-HNTs composites which PRD-HNTs composite SBR have significant reinforce compared with unmodified HNTs increased by 117% and 87%, respectively. HNTs also can be treated with the γ-irradiation [39] to enhance the strength of epoxy nanoconposites. Comparing with untreat ones, the treatment have significant effective on tensile strength and Young's modulus which raised to 46% and 38% respectively, because of the uniform dispersion, abundant hydroxy and chemical interaction.

3. 2 As the nanocarriers for drug delivery

HNTs are environmentally friendly natural nanomaterials with low cost. With high porosity, adjustable surface chemistry structure [40], good biocompatibility [41] the large surface area, HNTs have great development prospects in the field of drug capacity with a sustained manner. Thus made it attracted a great deal of interest in biological medicine, biological science and technology. HNTs can be used as a multi-purpose excipient to improve stability for sustained release of drugs [42]. It possess a special periodic multilayer with gibbsite octahedral (Al-OH) in internal surface and siloxane (Si-O-Si) on external surface [43]. HNTs have great application value in alternative modification with organic and inorganic functional molecules at diverse surface.

Some meaningful research advances in the drug delivery of HNTs were successively reviewed. For example, the use of chemically or physically modified HNTs as a nanocontainers for encapsulation the biologically active molecules, like dexamethasone, tetracycline, furosemide, gentamicin, and nifedipine as well as for their better loading capacities and yields drug delivery were demonstrated by Yuri M. Lvov et al [44]. And except for drugs, the protein and nucleic acids also loaded to the lumen surface [45]. In addition, the covalent modification of HNTs to the outer surface to improve the loading capacities such as DNA, proteins and other macromolecules [46]

The modified HNTs showed a better effect of drug loading than unmodified ones. Weng et al. (2012) [47] used octadecylphosphonic acid (ODP) modified halloysite nanotubes (halloysite-ODP) to load ferrocene with crosslinking method. The results showed that halloysite-ODP exert more ascolloidal stability in the aqueous suspension than the unmodified HNTs. Comparing HNTs, the

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halloysite-ODP possessed higher adsorption capacity and faster assimilate for hydrophobic molecules of ferrocene. There is a initial burst release for unmodified HNTs because of the inadequateinadequate between HNTs and ferrocene. But halloysite-ODP showed a two-step releasing with a non-Fickian model.

Besides, the HNTs modified with γ-aminopropyltriethoxysilane (γ-APTES) could enhance the ability of loading analgesic [48]. The results demonstrated that the modified HNTs showed much high capacity. Furthermore, the modified HNTs have a long time sustaining release reached to 115 h. In addition, the functionlization HNTs crosslink with the APTES used to load ibuprofen [49], for low loading capacity and burst release for HNTs. The result showed that the modified HNTs possess higher capacity to load ibuprofen increasing by 25.4% [50]. The releasing of ibuprofen indicated that the modified and unmodified HNTs put up a two-step release *in vitro*. However the modified HNTs showed slower releasing than unmodified ones due to strong electrostatic interactions.

3.3 As the adsorbent

As research point out that HNTs are natural occurring hollow tubes, within 10-150nm diameter, 500-1500nm length and with large specific surface area and high aspect ratio [51]. The primary hydroxyl groups exist inexternal surface providing convenience for the HNTs experiment with some organics. These special properties made nanotubes having extensive applications for separation and absorption material in industrial extraction to enhance the ability of absorb various metal ions (Peng et al., 2010) [52]. Ruijun et al (2012) [53] used two-step modification methods to synthesize functionalized HNTs react with APTES and murexide (Mu). The results indicate that HNTs-Mu were ten-fold absorption higher than original HNTs for Pb (II) at pH 1. The phenomenon shown that the HNTs-Mu uptake Pd (II) and provide available sites for anionic metal complexes. The functionalization HNTs also used to adsorb Cr (VI) and to remove it from aqueous solution (Wang et al., 2010) [54]. In the work, the functionalization HNTs were successful prepared by crossed with HDTMA. The results showed that the modified HNTs adsorbed nearly 90% of Cr (VI) within 5 minutes from aqueous solution with a Langmuir model. Meanwhile, the HNTs modified with 2-methacryloyloxyethyl phosphorylcholine (MPC) utilized to adsorb BSA with the method of phase inversion [55]. The modified HNTs of absorb capacity increased 87% compared with the pure membrane.

As we all known, Zearalenone has a strong toxicity damage to the reproductive system. It is necessary to remove the toxicant for the development of animals. The fodder also adopts the modified HNTs to adsorb Zearalenone in the sow reproduction and piglet growth stage [56]. The HNTs were modified with stearyldimethylbenzylammonium chloride (SKC), the results demonstrated that the functionalization HNTs conspicuous reduced the damage compared with Zearalenone-treated one in the aspect of colostrum and milk ($p<0.05$). *In vivo* test results showed that the modified HNTs possessed superior adsorb property than the unmodified ones for Zearalenone [57], and it can be summarized that in the gastrointestinal tract the modified HNTs have obvious composite ability with Zearalenone than the HNTs.

3.4 As the catalysts

There is no doubt that the rapid and efficient production is particularly important for the production. With the development of the industry, catalyst has been widely used to change the reaction rate [58] in the industry. The modified HNTs were used as catalyst, due to their large special surface area, high-activity and luxuriant surface hydroxyl groups [59]. The HNTs could be modified and synthesized the catalyst composites [60].

It is reported that the HNTs were modified with APTES and HCl to prepare a mod functionlization HNTs (HNTs-NH2·HCl) as metal nanoparticles to product H_2 [61]. And the results point out that the HRG values of HNTs-NH_2·HCl catalyst obtain a higher reaction than the HNTs catalyst with the value 813.08mL $min^{-1}g^{-1}{}_{catalyst}$ and 630.80mL·min^{-1}·$g^{-1}{}_{catalyst}$, respectively. The

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modified HNTs has the activation energy of 30.41 $kJ \cdot mol^{-1}$,enthalpy of 27.93 $kJ \cdot mol^{-1}$, entropy of −163.27 $J \cdot mol^{-1} \cdot K^{-1}$ and catalytic activity of 91%.In addition ,the modified HNTs catalysts have higher efficiency than the common H_2 generation rate which only keep 220.5$mL \cdot min^{-1}$ $g^{-1}{}_{catalyst}$.

The catalyze system (HNTs-APTMS-Mo-SL) has been synthesized by APTMS grafted on the HNTs and self-assembly way [62]. The results revealed that the functionalized catalyst could be filtered and maintain high-activity to catalyze the alkene epoxidation. It is hardly to loss catalytic activity even though repeated for at least eight times. The catalyst is easy to convert the active material such as the linear, aromatic alkenes and cyclic, and recycled in the catalyze reaction system. It is indicated that the catalytic mechanism of functionalized catalyst composited the Mo salen for epoxidation could be concluded for the interact bonding between Mo and the salen ligands.

3.5 As the potential consolidants

Material cultural heritage is the legacy of human history. It is a valuable historical and cultural heritage of mankind. Cultural relics have history, art and scientific value involving various fields. However, it is difficult to protect them such as ancient books and waterlogged archaeological woods due to the highly sensitivity and responsively to the environment. Most of them exist in a special environment such as anoxic, low temperatures and humid. The materials become very fragile and loss mechanical resistance because of the extreme deteriorating environment. So, it is necessary to consolidate the thermal and mechanical properties to protect them. And the HNTs are expected to be meaningful and promising protective agents for material cultural heritages at to improve the mechanical properties.

Giuseppe Cavallaro et al. (2017) [63] modified the HNTs with Rosin by chemically treatment. The result proved that the HNTs endow better mechanical properties and thermal stability and the thermal and mechanical properties of Rosin are sufficiently improved by the mount of HNTs. This conferred to the HNTs/Rosin nanocomposite an innovative protocol for consolidating waterlogged archaeological woods. In addition, Giuseppe Cavallaro et al. (2017) [64] also used the nanocomposite to enhance the thermal and mechanical properties between HNTs and beeswax by direct blending. The experiments indicated that the HNTs are homogeneously dispersed and significantly reduced thermal degradation of Rosin. Except for the consolidation of waterlogged archaeological, the HNTs can be used to preserve paper by compounded the $Ca(OH)_2$ and placed end-stoppers [65]. They proved that the HNTs/$Ca(OH)_2$ nanocomposites can improve the mechanical performance and balance the pH alteration with the addition of nanotubes. In view of the abovementioned research results, there have great application prospects for HNTs to consolidate waterlogged archaeological woods.

4. Conclusion and future applications.

In this review, we summarized the recent advance about modified HNTs, mainly focused on catalysts, adsorbent and drug delivery system. Although the modified HNTs have obtained a lot of extraordinary achievement in various fields, including biomedical application, industrial catalyst, nano composite filler and tissue engineering scaffolds, the surface utilization percentage and the transport pathway and uptake mechanism in the vivo still are the core challenges needed to further research.

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

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