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Review

Recent Advances on Surface Modification of Halloysite Nanotubes for Multifunctional Applications

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Abstract: Halloysite nanotubes (HNTs) are natural occurring mineral clay nanotubes that have excellent application potential in different fields. However, HNTs are heterogeneous in size, surface charge and formation of surfacial hydrogen bond, which lead to weak affinity and aggregation at a certain extent. It is very important to modify the HNTs' surface to expand its applications. In this review, the structural characteristics, performance and the related applications of surface-modified HNTs are reviewed. We focus on the surface-modified variation of HNTs, the effects of surface modification on the materials and related applications in various regions. In addition, future prospects and the meaning of surface modification were also discussed in HNTs studies. This review provides a reference for the application of HNTs modifications in the field of new nanomaterials.

Keywords: halloysite nanotubes; surface modification; structural characteristics; controlled release; biocompatibility

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1. Introduction

HNTs are naturally occurring mineral clay nanotubes with particular hollow shapes. There are various morphologies of HNTs such as tubes, platy particles and spheres [1] with 500-1500 nm in length and 15 nm and 50 nm in lumen and external diameter, respectively [2]. HNTs possess a high surface area of 184.9 m^2/g and a large pore volume of 0.353cm^3/g and they are easy to carry and delivery drugs [3,4]. For example, a schematic diagram of antibacterial drug loaded HNTs is shown in Fig.1. Chemical composition of HNTs is similar to kaolin. However, the unit layers are isolated by monolayers of water molecules in HNTs. The HNTs hold the molecular formula of $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$ [5] and the HNTs are composed of Al, O and Si with the atomic proportion 1:4.6:1 [6]. The aluminosilicate clay nanotubes have a Al:Si ratio of 1:1.

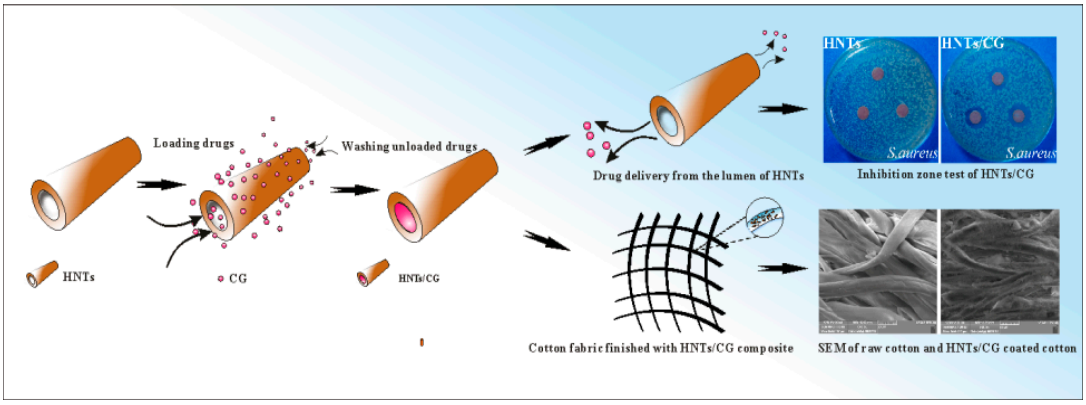

Fig. 1. Illustration of the preparation of HNTs/CG composite, drug release from the lumen of HNTs, and the application on cotton fabric.

There are two main polymorphs for HNT anhydrous form and hydrated form with spacing interlayers of 7 or 10 Å [7]. HNTs present a negative charge of ca -50 mV as shown by zeta-potential at pH of 6-7 [8]. HNTs exhibit a positively-charged surface at a pH of 8.5 [9] which possess a negative charge with ca −32±2 mV in water [10]. The external surface of HNTs is composed of silicon oxygen tetrahedron. The internal lumen is composed of alumina oxygen octahedrons. The outer surface is distributed mainly with Si-O-Si group. The inner surface is composed of Al-OH [11]. Because of the multilayer structure, most of the hydroxyl groups exist within the lumen and only a few in the outer surface [12].

As a widely used environmentally friendly clay material, HNTs have a good biocompatibility [13]. HNTs were confirmed to be non-toxic *in vivo* [10] and *in vitro* [14]. HNTs have a high specific surface area and strong surface adsorption. However, HNTs showed a weak affinity when were used to synthesize composites, drug delivery and molecular adsorbents because of the weak intermolecular forces such as van der Waals force and hydrogen bonding. To improve the performance of HNTs, surface modification is very desirable. For example, modified HNTs can be used as nanofillers in composite polymers to enhance mechanical strength [15] and as nanocarries to realize sustained drug delivery. In addition, it is also used as an adsorbent material to absorb or remove the dyes from aqueous solution [16] or as catalysts [17] to catalyze the reaction.

2. Surface modification of HNTs and the relevant properties

Surface modification of HNTs means that the HNTs maintains the original properties and meanwhile still bring about 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, free radical modification, and etc. The HNTs can be selectively modified according to the different demands.

2.1 Surfactant modification

Surfactant modification refers to the presence of non-polar lipophilic groups and polar hydrophilic groups in the surfactant molecules. HNTs can be successfully modified via electrostatic interactions [18]. The surfactants are able to be adsorbed selectively at the internal or external surface to maintain different hydrophilic/hydrophobic balances due to the charge characteristics of HNTs [19] and prepared into the amphipathic 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 [23] prepared high-impact polystyrene nanospheres by emulsion polymerization. In this system, sodium dodecyl sulfate (SDS) was added to aqueous solution containing HNTs. SDS was regarded as an emulsifier to form a molecular layer on the surface of

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HNTs, so that the surface of HNTs has a strong hydrophilicity to enhance the dispersion in aqueous solution. In addition, Wang et al [24] used the surfactant of hexadecyltrimethylammonium bromide (HDTMA) to modify the HNTs and prepared a new adsorbent for the removal of Cr (VI) from the aqueous solution. The composite had the maximum adsorption rate for Cr (VI) which reached to 90% in 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 react with the HNTs through physical or chemical bonding. Modifications of HNTs have a superior hydrophobic property, so that they can be better dispersed in the polymer to enhance the interface interaction. Guo et al [25] synthesized a high strength nanocomposite (polyamide 6/halloysite) by combining HNTs with 3-(trimethoxy silyl) propyl methacrylate. The results showed that the nanocomposites significantly improved its mechanical and thermal properties. Meanwhile, Wan et al prepared high-performance nanocomposite combined 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 better dispersion and strong capacitance.

2.3 Intercalation modification

Intercalation modification refers to that small molecules reacting with HNTs via the hydroxyl groups in order to improve the performance of HNTs. Tang et al [27] used the phenylphosphonic acid (PPA) to unfold and intercalate the HNTs, and mixed the product with epoxy to form the halloysite-epoxy nancomposites. The modified HNTs achieved better dispersion, large contact area among nanocomposites and significantly promoted micro-cracks and plastic deformation took shape at the interface. Deng et al [28] treated the HNTs with potassium acetate (PA) and ball mill homogenisation to improve particle dispersion. It was demonstrated that the modified HNTs could 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 that the surface of HNTs is coated with a layer of polymer or inorganic material by means of the electrostatic adsorption to achieve the purpose of changing HNTs performance. Li et al [29] prepared drug-loaded porous microspheres (Hal-CTS/Asp) by thorough emulsification in the water/oil microemulsion. The HNTs were coated with chitosan (CTS) and aspirin (Asp) molecules adsorbed to the inside of the microspheres as a model drug. The results indicated that the microspheres had the characteristics of a high surface area and large-interconnected pores, which was conducive to the adsorption of aspirin. The modified HNTs had an excellent loading capacity (42.4 wt %) which was twenty times higher than unmodified ones (2.1 wt %). Meanwhile, the special microspheres showed low drug release rate and pH sensitivity compared with the pristine HNTs. Liu et al [30] successfully prepared alginate/HNTs composite tissue engineering scaffolds by electrostatic adsorption. 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 monomer on the inner or outer surface. The functionalized HNTs have improved hydrophobicity and dispersibility in organic solvents. Liu et al [31] prepared modified HNTs by grafting the polymethyl methacrylate (PMMA) via radical polymerization and then compounding with poly(vinyl chloride) (PVC) to form composites with higher toughness, strength and modulus. The results showed that the modified HNTs have uniform dispersed in PVC aqueous solution. The modified HNTs could effectively improve the mechanical properties. Li et al [32] reported a kind of functionalized HNTs modified by

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polymers via atom transfer radial polymerization (ATRP) and cross-linked with polystyrene (PS) and polyacrylonitrile (PAN), respectively. The results indicated that the composites showed excellent wettability for 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 materials, magnetic facility, flame retardant, optics, scaffolds for tissue engineering and electronics. Meanwhile, the nanocomposites exhibit complex template and tedious preparation process. It is imperative to find effective modules and efficient production processes. Due to high specific surface area and unique surface chemical properties, HNTs are widely used to improve polymer's property. In the meanwhile, the low surface charge and weak interfacial interaction could be problematic [33].Surface modified HNTs not only demand well disperse and strong interfacial interactions [34], but also to provide abundant bond formation [35]. HNTs showed better interactions among clay–polymer nanocomposites by chemically or physically pretreatment [36]. Functionalization of nanotubes composite polymer will achieve a win-win situation.

HNTs have been used extensively for enhancing properties of ploymers. Parthajit et al [5] had successfully modified the HNTs by graft N-(b-aminoethyl)-c-aminopropyltri-methoxysilane, the modified and unmodified HNTs mingle with nonpolar polypropylene (PP) and polar polyoxymethylene (POM) by utilizing immiscible blend system, respectively. The results indicated that pure polymer blend and B-HNT nanocomposites always form obvious agglomeration due to the weak interface interaction between the polymer and HNTs. However, they present different phenomena to the B-MHNT nanocomposites that disperse well in the polymer blend. This suggests that modified B-MHNTs obtained a better dispersion compared to the unmodified (B-HNTs) in blend matrix. Meanwhile, the functionalized HNTs are used to enhance the chemical interactions as natural rubber (NR) filler [37]. The bis (triethoxysilylpropyl)-tetrasulphide was used to modify the HNTs by way of silane coupling agent. In general, the natural rubber composites with modified HNTs (NR-HNTs-Si) showed excellent physical properties and thermal stability compared with the unmodified HNTs nanocomposite (NR-HNTs) and natural rubber-silica (NR-Si). The HNTs were modified with polyrhodanine (PRD) by the way of oxidative polymerization to prepared styrene butadiene rubber (SBR)[38]. The results indicated that the tensile strength of SBR/PRD-HNTs composites have significant reinforce compared with unmodified HNTs increased by 117% and 87%, respectively. HNTs also can be treated with γ-irradiation [39] to enhance the strength of epoxy nanoconposites. Compared with untreatments, the treatments have significant effect on tensile strength and Young's modulus which rose by 46% and 38%, respectively, because of uniform dispersion and abundant hydroxy.

3. 2 As the nanocarriers for drug delivery

HNTs are environmentally friendly natural nanomaterials with low cost, high porosity, adjustable surface chemistry structure [40], good biocompatibility [41] and large surface area. HNTs have huge development prospects in the field of drug capacity as a sustained manner. Hence, HNTs attracted a lot of attention in biological medicine, biological science and technology. HNTs were used as multi-purpose excipient to improve stability of drugs and achieve controlled release [42]. They possess special periodic multilayer with the structure of 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 different surfaces.

Some meaningful research advances were successively reviewed in the drug delivery of HNTs. For example, the chemical or physical modified HNTs as nanocontainers for encapsulation the

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bioactive molecules, such as dexamethasone, tetracycline, furosemide, gentamicin and nifedipineas. The loaded capacities and sustained drug delivery were demonstrated by Yuri M. Lvov et al [44]. Except for drugs, the protein or nucleic acids also be loaded into the lumen surface of HNTs [45]. In addition, the outer surface covalent modified HNTs have improved the loading capacities of bioactive molecules such as DNA, proteins and other macromolecules [46]

The modified HNTs showed better effect of drug loading than unmodified ones. Weng et al. [47] used octadecylphosphonic acid (ODP) to modify halloysite nanotubes (halloysite-ODP) to load ferrocene by cross linking method. The results showed that halloysite-ODP exert more as colloidal stability in the aqueous suspension than the unmodified HNTs. Comparing with HNTs, the halloysite-ODP possesses higher adsorption capacity and faster assimilate for hydrophobic molecules of ferrocene. There have small initial burst release for unmodified HNTs because of the dissolved ferrocene to the HNTs surface. Halloysite-ODP showed a two-step release with a non-Fickian model.

Besides, HNTs were modified with γ-aminopropyltriethoxysilane (γ-APTES) to 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 at different pH values. In addition, the functionalized HNTs cross linked with the APTES to load ibuprofen [49], because of the low loading capacity and burst release of HNTs. The results showed that the modified HNTs possess higher capacity to load ibuprofen increasing by 25.4% [50]. The release behavior of ibuprofen indicated that the modified and unmodified HNTs put up 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 pointed out that HNTs are natural occurring hollow tubes, within 10-150nm diameter, 500-1500nm length, HNT shave large specific surface area and high aspect ratio [51]. The main hydroxyl groups exist the inexternal surface of the HNTs convenient for graft some organics. HNTs have extensive applications for separated and absorbed various metal ions in industrial due to these special properties [52]. Ruijun et al. [53] used two-step methods to modify HNTs with APTES and murexide. The results indicated that HNTs-Mu were ten-fold absorbed higher than original HNTs for Pb (II) at a pH of 1. The phenomena were shown that the HNTs-Mu provided available sites for anionic metal complexes. The functionalized HNTs also used to adsorb Cr (VI) to remove it from aqueous solution [54]. In this work, the functionalized HNTs were successfully 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 the models of Langmuir. Meanwhile, the HNTs were modified with 2-methacryloyloxyethyl phosphorylcholine (MPC) to adsorbed BSA with the method of phase inversion [55]. The modified HNTs of absorption 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 feeder adopts the modified HNTs to adsorb Zearalenone at the sow reproduction and piglet growth stage [56]. The HNTs were modified with stearyldimethylbenzylammonium chloride (SKC).The results demonstrated that functionalized HNTs conspicuously reduced the damage compared with Zearalenone-treated one in the aspects of colostrum and milk ($p<0.05$). The modified HNTs possessed superior adsorb property than the unmodified ones for Zearalenone i*n vivo* [57]. The results summarized that the modified HNTs have obviously improve composite ability with Zearalenone than the HNTs in the gastrointestinal tract.

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3.4 As the catalysts

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

It is reported that the HNTs were modified with APTES and HCl to prepared mod functionalized HNTs (HNTs-NH_2·HCl) as metal nanoparticles to product H_2 [61]. The results pointed out that the HNTs-NH_2·HCl catalysts obtain higher reaction values of HRG than the HNTs catalysts with the value 813.08mL $min^{-1}g^{-1}{}_{catalyst}$ and 630.80mL·min^{-1}·$g^{-1}{}_{catalyst}$, respectively. The modified HNTs have the activation energy of 30.41 kJ·mol^{-1},the enthalpy of 27.93 kJ·mol^{-1}, the entropy of −163.27 J·mol^{-1}·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 220.5mL·min^{-1} $g^{-1}{}_{catalyst}$.

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

3.5 As the potential consolidants

Material cultural heritages are the legacy of human history. There have historical value and cultural heritage for mankind. Cultural relics are involve various fields such as history, art and scientific. 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 special environment such as anoxic, low temperatures and humid. The materials become fragile and loss mechanical resistance because of the extreme deteriorating environment. It is necessary to consolidate the thermal and mechanical properties to protect them. The HNTs are expected to the meaningful and promising protective agents for material cultural heritages by the way of improved the mechanical properties.

Giuseppe Cavallaro et al. [63] modified the HNTs with Rosin by chemical treatment. The results proved that the HNTs endowed better mechanical properties and thermal stability. The thermal and mechanical properties of Rosin were sufficiently improved by the mount of HNTs. This conferred to the HNTs/Rosin nanocomposites were innovative protocol for consolidating waterlogged archaeological woods. In addition, Giuseppe Cavallaro et al. [64] used the nanocomposites to enhance the thermal and mechanical properties between HNTs and beeswax by direct blending. The experiments indicated that the HNTs were homogeneously dispersed and significantly reduced thermal degradation of Rosin. Except for the consolidation of waterlogged archaeological, HNTs were used to compounded the $Ca(OH)_2$and then placed end-stoppers to preserve paper [65]. They have proved that the HNTs/$Ca(OH)_2$ nanocomposites could improve the mechanical performance and balance the pH alteration with the addition of nanotubes. In view of the above mentioned 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 current advance about modified HNTs which mainly focused on catalysts, adsorbent and drug delivery system. Although the modified HNTs have obtained a lot of extraordinary achievements in various fields such as biomedical applications, industrial catalysts, nanofillers and scaffolds for tissue engineering. The core challenges are need to

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further research such as surface utilized percentage, transport pathway and uptake mechanism *in vivo*.

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

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