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Recent advances on surface modification of halloysite nanotubes for multifunctional applications

Yongtao Yang, Yun Chen, Fan Leng, Li Huang, Zijian Wang, Weiqun Tian*

Department of Biomedical Engineering, School of Basic Medical Sciences,

Wuhan University, Wuhan 430071, China.

*Corresponding author's E-mail: tian_weiqun@whu.edu.cn

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

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

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 at 0.353 cm^3/g [3] to form matrix membrane for gas separation [4]. HNTs chemical composition is similar to kaolin. However, 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 halloysite nanotubes is composted 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 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 surface. However, HNTs showed a weak affinity when used to synthesize composites, drug delivery and molecular adsorbents, because of the weak intermolecular force, like 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 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, which can be attributed to surfactant modification, coupling agent modification, intercalation modification, surface coating modification and free radical modification. The HNTs can be modified in the appropriate time according to the need for selective modification.

2.1 Surfactant modification

Surfactant modification refers to the presence of non-polar lipophilic groups and polar hydrophilic groups in the surfactant molecule. When the surfactant binds to the nanotubes, it has a better dispersion. Yong Lin et al (2011) [18] 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 and enhance the dispersion in aqueous solution. In addition, Wang et al (2010) [19] 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 was the most common chemical modification method for HNTs. The silane coupling agent can be chemically reacted with the HNTs by 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) [20] synthesized a high strength nanocomposite (polyamide 6/halloysite) by combined with 3-(trimethoxy silyl) propyl methacrylate. The results showed that the nanocomposites significantly improve mechanical and thermal properties. Meanwhile, Wan et al (2017) [21] prepared a kind of high-performance nanocomposites by compounded with 3-aminophenoxy-phthalonitrile and poly (arylene ether nitrile) (PEN) based on HNTs. 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 withHNTs between the hydroxyl groups and other groups, in order to improve the performance of HNTs. Tang et al (2011) [22] 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 the micro-cracks and plastic deformation take shape at the interface. Deng et al (2009) [23] treated the HNTs with potassium acetate (PA) and ball mill homogenisation to improved particle dispersion. It was demonstrated that the treatment HNTs could observably enhanced the properties of mechanical, interfacial debonding and provided 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) [24] 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 %) nearly 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) [25] 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 toobtain the stable composites. Liu et al (2011) [26] prepared the modified HNTs by grafted the polymethyl methacrylate(PMMA) via radical polymerization, and then compounded with poly(vinyl chloride) (PVC) to form the high toughness, strength and modulus composites. The results showed that the modified HNTs have an uniform dispersed in PVC aqueous solution, and effectively improve the mechanical properties. Li et al (2008) [27] 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 showed excellent wettability and can be used to entrap water droplets.

3. Application of Surface Modification of HNTs.

3.1 As the filler nocomposites.

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. But these nanocomposites always need a complex template, tedious preparation process and high cost. To find an effective modules and efficient fabrication will be imperative.

Due to high specific surface area and unique surface chemical properties, HNTs widely used to improve polymer's property. At the meanwhile, the low surface charges and weak interfacial could be problematic [28].

But if it is modification on the surface of HNTs to spread the basal spacing through insert the inorganic or organic groups between layers. The surface modified HNTs not only acquire well dispersibility and strong interfacial interaction [29], but also provide abundant bond formation [30]. The functionalization of nanotubes composite polymer will achieve a win-win situation.

HNTs have been used more and more 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

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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 [31]. The bis (triethoxysilylpropyl)-tetrasulphide was used to modified the HNTs by the way of silane coupling agent. It can be summarized that 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) [32]. 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 [33] to enhance the strength of epoxy nanoconposites. Comparing with untreat ones, the treatment have significant effective such as tensile strength and Young's modulus increasing 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 and low cost. With high porosity,adjustable surface chemistry structure [34], good biocompatibility [35] 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 that improved stability for sustained release of drugs [36].

It possess a special periodic multilayer with gibbsite octahedral (Al-OH) in internal surface and siloxane (Si-O-Si) on external surface [37]. HNTs have great application value in alternative modification with organic and inorganic functional molecules at diverse surface. The modified HNTs always obtain a better effect of drug loading than unmodified ones. Weng et al. (2012) [38] used octadecylphosphonic acid (ODP) modified halloysite nanotubes (halloysite-ODP) to load ferrocene with crosslinking method. The results showed that halloysite-ODP exerts more ascolloidal stability in the aqueous suspension than the unmodified HNTs. Comparing with HNTs, the 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 show a two-step release with a non-Fickian model.

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Besides, the HNTs modified with γ-aminopropyltriethoxysilane (γ-APTES) could enhance the ability of loading analgesic [39]. The results demonstrated that the modified HNTs were more than three times higher capacity compared to unmodified HNTs. 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 [40], for low loading capacity and burst release for HNTs. The date showed that the modified HNTs possess higher capacity to load ibuprofen increasing by 25.4% [41]. The release of ibuprofen indicated that the modified and unmodified HNTs put up a two-step release *in vitro*. However the modified HNTs showed slower release 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 [42]. The primary hydroxyl groups exist inexternal surface provided convenience for the HNTs experiment with some organics. These special properties made nanotubes have extensive applications for separation and absorption material in industrial extraction to enhance the ability of absorb various metal ions (Peng et al., 2010) [43]. Ruijun et al (2012) [44] used two-step modification methods to synthesize functionalized HNTs respectively react with APTES and murexide (Mu). The results indicate that HNTs-Mu were ten times 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 remove it from aqueous solution (Wang et al., 2010) [45]. In the work, the functionalization HNTs were successful prepared by crossed with HDTMA. The results showed that the modified HNTs adsorbed nearly ninety percent of Cr (VI) within five minutes from aqueous solution with a Langmuir model. Meanwhile, the halloysite nanotubes modified with 2-methacryloyloxyethyl phosphorylcholine (MPC) utilized to adsorb BSA with the method of phase inversion [46]. 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 [47]. 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 ($p<0.05$). The vivo test results show that the modified HNTs possessed superior adsorb property than the unmodified ones for Zearalenone [48], 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 [49] in the industry. The modified HNTs were used as catalyst, due to their large special surface area, high-activity and luxuriant surface hydroxyl groups [50]. The HNTs could be modified and synthesized the catalyst composites [51].

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 [52]. 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 modified HNTs with the activation energy of 30.41 kJ·mol^{-1},enthalpy of 27.93 kJ·mol^{-1}, 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 catalyze system (HNTs-APTMS-Mo-SL) has been synthesized by APTMS grafted on the HNTs and self-assembly way [53]. The results revealed that the functionalized catalyst could be filtered and maintain high-activity to catalyze the alkene epoxidation. It is hardly loss catalytic activity even though repeated for at least eight times.The catalyst easily to converted 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.

4. Conclusion and future applications.

In this review, we focused on summarize the recent advance about modified HNTs. Key concerns, in field of nanoposites, catalysts, adsorbent and drug delivery system. Although the modified HNTs have obtained a lot of extraordinary achievement in various fields, such as 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 also the significant challenges needed to further research.

Conflict ofinterests

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

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