Nano-Structures & Nano-Objects 39 (2024) 101230

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

journal homepage: www.elsevier.com/locate/nanoso

A comprehensive review of varied applications of modified halloysite nanocomposites

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ARTICLE INFO

Keywords:
Nanomaterial
Clay material
HNT
Nanocomposite
Fabrication
HNT applications

ABSTRACT

The recent past has evidenced the technological development in the evolution of nanoscience, with a key role of naturally occurring nanomaterials. Halloysite Nanotubes (HNTs) are 1D dioctahedral 1:1 kaolin-derived clay minerals, with $Al_2Si_2O_5(OH)_4.nH_2O$ as their chemical formula. The dual functionality of the HNT multiwalled nanotube due to siloxane, aluminol, and silanol groups on the outer surface (negative charge) and aluminol groups on the inner surface (positive charge) makes it unique and pertinent for varied applications. Owning to this charge distribution, several advantages accompanied by feasible modes of synthesis have led to an escalation in the applications of halloysite heterostructure in material science. Various modification strategies and applications have been reported in the last decade with an emphasis on facilitating analytes for the benefit of mankind. Key techniques like hydrothermal, electrospinning/electrostatic fiber spinning, polymerization and co-polymerization, ultrasonication, magnetic stirring, and other hyphenated methods are well exploited for fabricating HNT composites. Innumerable applications, in domains like catalysis, sensing, drug delivery, environmental applications, flame retardants, etc. have been implemented and have paved the way for future research. Thus, the present review articulates the varied fabrication approaches of HNT- nanocomposite and their applications, providing a blueprint for young researchers.

1. Introduction

Nanotechnology is the branch of science in which at least one of the dimensions of the material, (known as nanomaterial) lies in the range of 0.1–100 nm. Such materials follow quantum laws and exhibit significantly different characteristics from their large-scale counterparts. With a high surface-to-area ratio, nanomaterials can be used as per the need and requirement. Thus, facilitating the use of the right substance in the right quantity in the right place at the right time.

Kaolin clay, a natural fine-grained nanomaterial, predominantly exists as layered arrangements of aluminosilicates and is formed by the chemical weathering of different silicate minerals. In order to design new functional materials, these naturally occurring minerals, particularly Halloysite Nanotubes (HNTs) are attracting substantial interest in the material science community [49]. In 1826, M. Berthier coined the term "halloysite", named after Omalius d'Halloy who found this mineral in Angleur. HNTs are 1D dioctahedral 1:1 kaolin mineral with the chemical formula $Al_2Si_2O_5(OH)_4.nH_2O$ [48]· These inorganic moieties are naturally formed by weathering numerous igneous and non-igneous rocks, found in ample amounts in wet subtropical and tropical. Their low cost, availability in ample amounts, biocompatibility, non-toxic nature, and excellent thermal and mechanical properties make them a preferable and suitable mineral for broad-scale applications [28,29]. HNTs have rich internal/external surface properties in terms of chemical

Abbreviations: HNT, Halloysite Nanotube; CNT, Carbon Nanotube; GO, Graphene Oxide; PDA, Polydopamine; PEO, Polyethylene oxide; APP, Ammonium Polyphosphate; GOx, Glucose Oxidase; PPY, Polypyrrole; MIP, Molecularly Imprinted Polymer; PVDF, Polyvinylidene Fluoride.

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https://doi.org/10.1016/j.nanoso.2024.101230
Received 22 April 2024; Received in revised form 1 June 2024; Accepted 5 June 2024

composition and surface charge which facilitates their chemical modification to develop multi-functional materials. Moreover, the high specific surface area, size, chemical, and thermal stability of HNTs, make them an inexpensive substitute for Carbon Nanotubes CNTs [61]. Given their earth-abundance, HNTs are exploited as raw materials and have unveiled new frontiers in multidisciplinary research fields (Fig. 1).

The review compiles the recent advanced applications of HNT composites from various domains and gives a holistic comparison between the most feasible and widely used fabrication technique. This would ultimately open doors for new researchers to effortlessly adopt an appropriate modification process.

2. Structure and morphology of HNTs

Although halloysites possess similar chemical compositions, the structural arrangement of different layers makes them unique in terms of morphology and physicochemical characteristics. HNTs are multi-walled kaoline minerals, comprising 10–15 bilayers with an interlayer spacing of 7 Å (dehydrated HNT), 10 Å (hydrated HNT), and density of 2.53 gcm^{-3}. The molecular formula of halloysite ($Al_2Si_2O_5(OH)_4 \cdot nH_2O$) is like kaolinite except for the presence of water molecules in the interlayer spacing [38]. Based on the presence or absence of interlayer water molecules, 'n' the HNTs are classified into hydrated and dehydrated forms. Hydrated HNTs contain two water molecules in the interlayer space which upon heating at 30–110 °C loses interlayer water molecules, resulting in the formation of dehydrated halloysite. HNTs structure arises from the amalgamation of SiO_4 tetrahedral sheets at the corners and AlO_6 octahedral layers at the edges. This arrangement thus enables them to undergo hydrogen bonding, cation exchange, and covalent modifications.

The morphology of the mineral depends upon two main factors; geological and crystallization conditions [20]. Halloysite is the only known kaolin clay mineral that exists in the nanotubular form [53]. In nature, halloysites display crumpled lamella, cylindrical disk, fiber, lath, scroll, prismatic, rolled, crinkly, walnut-meat, platy, or tabular morphological forms. The tubular geometry is the most dominant form in the nanometre range [39]. Individual HNTs have a length of 0.2–1.5 μm, an outer diameter of 40–70 nm, and an inner diameter of 10–30 nm, respectively [43]. Their outer surface comprises of siloxane (Si-O-Si) groups, while the inner surface contains a gibbsite–like arrangement of aluminol (Al-OH) groups, and the edges contain Si-OH groups [48]. In the layered form, Si-O groups are present at the external surface and Al-OH groups at the internal surface (Fig. 2). This type of distinct atomic arrangement leads to a unique charge distribution across the inner and outer surface of HNTs within 3–8 pH range [38]. Thus, HNT's nanotubular geometry, size, and dual surface charge make them unique.

3. Applications of fabricated HNT-based composites

HNTs are multi-walled kaolin clays with contrasting surface charges. The outer surface consists of siloxane groups, with aluminol (Al-OH) and silanol (Si-OH), which possess a negative charge, and contribute a negative zeta potential. While the inner surface consists of aluminol groups, possesses a positive charge, and contributes a positive zeta potential. Due to the positively charged lumen, there arises a charge disparity, leading to the possibility of modification via Van der Waals forces, hydrogen bonding, electrostatic, and covalent interactions [74]. The surface chemistry of HNTs thus allows their interfacial framework to become accessible for guest molecules. Nanotubes have a high specific surface area making them the perfect base material to boost reactant diffusion and increase the overall reaction rates [74]. As per the requirement of the application, the efficiency of the material can be enhanced by its selective surface modification [90]. Selective surface modification often leads to the enhancement of required properties, which can be observed in their effect on the interfacial characteristics by the changes in the ζ potential, morphologies, and other physicochemical

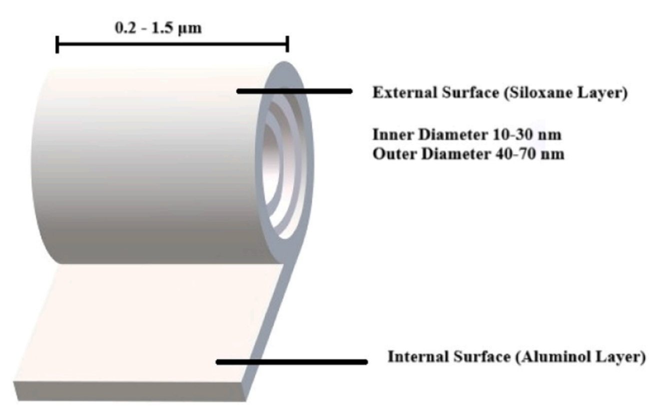

Fig. 2. Morphology of single HNT [8].

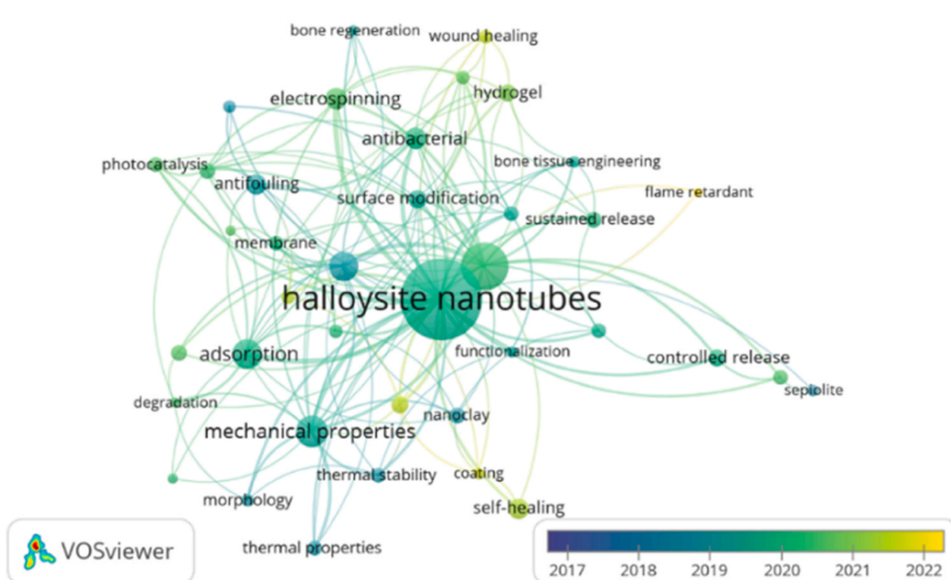

Fig. 1. Co-occurrence mapping of publications related to Halloysite Nanotubes (minimum number of occurrence 5).

properties [96]. Table 1 enlists different strategies including surfactant modification, etching, polymer modification, coupling agent modification, intercalation modification, surface coating modification, free radical modification, etc. for the selective modification of the inner lumen and the outer surface of HNTs. The nanotubes' programmable surface chemistry makes it possible to modify their interaction with a variety of guest molecules.

Thus, depending on the targeted application, HNTs can be subjected to various kinds of surface modifications. Fig. 3 depicts the effective surface modifiers for HNTs.

In material science, researchers introduced physical modes of composite formation [48] making a diverse form of conjugates/hybrids such as; films, scaffolds, emulsions, gels, electrospun fibres, ionic liquids, etc. [9,46]. HNTs have been generally used for catalytic, energy storage, electrical, magnetic, optical, thermal, and sensing applications [28,29]. The lumen of HNTs has been exploited for loading and controlled release of several biologically active molecules. The non-toxic and biocompatible nature makes halloysite a suitable drug carrier [48]. HNTs have also gained considerable attention as an immobilization matrix for biosensing applications [28,29]. Dyes are colour-imparting chemical moieties that are found abundantly in daily usage. These dyes when left unprocessed turn out to have toxic effects on living organisms. HNTs have been known to show superior efficiency in their extraction from environmental samples, thereby preventing the adverse effects of dye pollution. The fascinating nanotubular geometry is useful to entrap flammable volatile compounds. Thus, widely employed for manufacturing flame retardants, chemicals that retard the growth of fire. Fig. 4 represents the schematic representation of modification strategies for HNTs.

In general, the hydrothermal method of synthesis uses inorganic chemicals and water as a solvent. Whereas, the electrospinning method uses electric fields to obtain different forms of ultrafine polymeric fibers of nano-range. The method of polymerisation and co-polymerization synthesizes chain or branched three-dimensional structures. The dispersion technique utilizes a rotating magnetic field and the ultrasonication method homogenizes using ultrasonic waves.

3.1. Hydrothermal method

The hydrothermal method refers to the synthesis of inorganic materials in a closed reaction system above the ambient pressure and temperature conditions (up to 600 °C) [92]. With water as an economical solvent, the reaction system attains high temperature and pressure within a short time (S. [24]). HNTs can withstand such a high-temperature range, so they can be employed for hydrothermal synthetic routes. The hydrothermal approach modifies the reaction parameters (temperature, pressure, pH, and reaction time) to precisely control the HNTs' length, diameter, and wall thickness. This process can yield HNTs with consistent size and shape, imparting consistency for specific applications. The closed hydrothermal system minimizes contamination, leading to high-purity HNTs. Nano-sized water oxidizing catalysts have been fabricated by incorporating MnO onto the HNT surface [54]. The decomposition of MnO_4^- with HNT under a hydrothermal environment aided the formation of MnO_2. Wu et al. [87] synthesized a halloysite/carbon catalyst utilizing cellulose as a carbon precursor for the removal of phenol from wastewater. Cellulose got carbonized and developed a carbon coating onto the HNT surface. The composite upon surface activation with $ZnCl_2$ exhibited a high phenol adsorption rate (increased by 49-fold) as compared to unmodified clay. In another study, hydroxyapatite@halloysite nanotubes (HAP@HNTs) were fabricated by this method under magnetic stirring for bone regeneration displaying cytocompatibility [103]. High temperature and pressure conditions facilitated the formation of seed-like single-crystal HAP nanoparticles on the HNT surface (Fig. 5).

The removal of Bisphenol A was carried out by CuO/HNTs [98], and dehydrogenation of formic acid was facilitated by PdAu/NH_2-HNTs

Table 1
Selective surface modification of HNTs [74,90,96].

Modification Category	Interaction/ Description	Example of Surface Modifier	
		Inner surface	Outer surface
Acid etching	Etching the alumina sheets on the inner surface of the HNTs lumen	H_2SO_4, HCl	-
Alkali etching	Etching the Siloxane and silanol groups on the outer surface of the HNT, causing thinning of the walls of HNT, and increasing the density of hydroxyl groups on the surface	-	NaOH
Nanomaterial	Deposition of nanoparticles on the nanotube's surface either through on-the-spot reduction of the precursor salt solution or through the adsorption of already prepared nanoparticles	Ag NPs, Cu-Ni NPs, Carbon nanodot	Ru NPs, Co_3O_4 NPs, Fe_3O_4 NPs TiO_2 NPs, Ag NPs, ZnO NPs, Au NPs
Polymer and Biopolymer	Promoting the polymerization of a monomer on HNTs surface	PDA, PMMA, PEO	PEDOT, PEI, PANI, Pectin, DNA, Chitosan,
Surfactant	Adsorbed selectively at the internal or external surface via electrostatic interactions	PCF5H, PCF7H, PCF8H	ATAB, HDTMS, SDS, HDTMA
Biomolecules or Compounds of Biological Origin	Functionalizing the surface through adsorption experiments and loading biomolecules into the inner lumen	Curcumin	Tannic Acid
Organosilane	Introduces amine groups for the modification of the inner lumen	APTES	APTES, AEAPTMS, MPTS
Coupling Agent Modification	Grafted silane coupling agent onto the surface through physical or chemical bonding	-	Polyamide 6, PEN
Intercalation Modification	Small molecules reacting via the hydroxyl groups	-	PPA, PA
Surface Coating Modification	Surface of HNTs is coated with a layer of polymer or inorganic material through electrostatic adsorption	-	Chitosan, Alginate
Free Radical Modification	Hydroxyl groups on the surface of HNTs react with monomers on the inner or outer surface.	PMMA	PMMA, PS
Alkyl phosphate	Self-assembling on some metallic oxide surfaces	-	Octadecylphosphonic acid, Styrene, (P(S-co-MAPC1(OH)2))
Ionic liquid	Functionalize the tubes inner surfaces through the	HEMIC	-

(continued on next page)

Table 1 (*continued*)

Modification Category	Interaction/ Description	Example of Surface Modifier	
		Inner surface	Outer surface
	condensation reaction between the aluminol and alcohol to yield stable Al−O−C bonds		
Arylboronic acid	Arylboronic acid can rapidly react with diols via dehydration condensation;	-	1-pyrenylboronic acid
Electrostatic lumen coating	Utilizes the difference in electric potentials	-	Lipase, NaL, DeTAB, Perfluorinated anionic surfactants
Click chemistry	Copper catalyzed reaction of an azide (−N3) with an alkyne (−C≡H) to form a triazole ring	-	Polyfluorenes with terminal alkyne groups

H_2SO_4: Sulphuric acid; HCl: Hydrochloric acid; NaOH: Sodium hydroxide; Ag NPs: Silver nanoparticles; Cu-Ni NPs: Copper Nickel nanoparticles; Ru NPs: Ruthenium nanoparticles; Co_3O_4 NPs: Cobalt oxide nanoparticles; Fe_3O_4 NPs: Iron oxide nanoparticles; TiO_2 NPs: Titanium dioxide nanoparticles; ZnO NPs: Zinc oxide nanoparticles; Au NPs: Gold nanoparticles; PDA: Polydopamine; PMMA: Polymethyl methacrylate; PEO: Polyethylene oxide; PEDOT: Poly(3,4-ethylenedioxythiophene); PEI: Polyethylenimine; PANI: Polyaniline; DNA: Deoxyribonucleic acid; PCF5H: Perfluoropentanoic acid; PCF7H: Perfluoroheptanoic acid; PCF8H: Perfluorooctanoic acid; ATAB: Alkyltrimethyl ammonium bromide; HDTMS: Hexadecyltrimethoxysilane; SDS: Sodium Dodecyl Sulfate; HDTMA: hexadecyltrimethylammonium bromide; APTES: 3-aminopropyltriethoxysilane; AEAPTMS: 3-(2-aminoethylamino)propyltrimethoxysilane; MPTS: 3-Mercaptopropyltrimethoxysilane; APPH: 3-amino-phenoxy-phthalonitrile; PA6: polyamide 6; PEN: Poly (arylene ether nitrile); PPA: phenylphosphonic acid; PA: potassium acetate PMMA: polymethyl methacrylate; PS: polystyrene; $(P(S\text{-co-}MAPC1(OH)_2))$: (methacryloyloxy)methyl phosphonic acid; HEMIC: 1-(2-hydroxyethyl)-3-methylimidazolium; NaL: Sodium laurate; DeTAB: decyltrimethylammonium bromide

fabricated by Co-impregnation method [71]. Pd@CeO_2(P@C) were synthesised using a one-pot alkaline carbonization hydrothermal method for the photodegradation of unburnt hydrocarbons, carbon monoxide, and nitrogen oxides [84]. Dysprosium vanadate (DyV) and HNTs had been fabricated (DyV/HNTs) by hydrothermal method for the determination of dimetridazole [42].

3.2. Electrospinning/ Electrostatic fiber spinning

Electrostatic fiber spinning is an efficient and flexible way to assemble different forms (hollow, porous, and core-shell) of ultrafine nano-range polymeric fibers. The thickness and surface roughness of nanofibers can be modulated by using varying amounts of polymer. This technique is one of the most preferred routes for HNT composite synthesis because of its consistency, recyclability fabrication of a wide variety of fibers with enhanced mechanical properties, high aspect ratio, and low cost. The HNTs can be uniformly dispersed in the polymer solution either by sonication or by mechanical stirring. The mechanical strength and toughness of polymer nanofibers are considerably increased by adding HNTs. Several chemical groups can be added to functionalize HNTs, thereby imparting additional properties, such as enhanced thermal stability, antimicrobial activity, or controlled drug release. The process of electrospinning ensures that HNTs are uniformly dispersed throughout the polymer matrix, resulting in consistent characteristics across the entire composite material. Magnetic Fe_3O_4 nanoparticles were synthesized via the co-precipitation method. They were uniformly integrated with HNTs and polyethylene oxide/ chitosan composites (PEO/CS) through electrospinning for fabricating (HNT/Fe_3O_4/PEO/CS). This unique conjunction showed synergistic adsorption capacity resulting in the removal of heavy metal ions [46]. A novel, chemically and thermally stable HNT-inserted graphene-oxide- polydopamine/poly (arylene ether nitrile) (GO-PDA/PEN) nanofibrous hybrid was introduced [95]. The PEN nanofibrous layer was obtained by electrospinning and hot-pressing (Fig. 6). Single-layered GO, intercalated with porous HNTs provided flexibility, thickness, and development of nano-micro scale water channels which facilitated the separation of oil-water emulsions.

Silane-modified HNTs were blended with polyethylene oxide (PEO)/ polycaprolactone (PCL) and curcumin (Cur) to develop a curcumin release system against carcinoma cells, MCF-7 (human breast) cell lines [5]. HNT loaded with diclofenac sodium salt was incorporated with soy protein isolate/hydroxyethyl cellulose nanofibers. These were found to be biocompatible, antibacterial, and exhibited in-vitro release behavior [75]. HNT/TiO_2 and HNT/ZnO composites were synthesized for HNT-embedded photocatalytic nanofibers with antibacterial properties using the electrospinning method [26]. In another study, Abid et al. [1] combined electrospinning of halloysite with nitriding to produce N-HNT-TiO_2 composite nanofibers which were used for acetaminophen photodegradation However, electrospinning has certain limitations like difficulty in making large-volume scaffolds and the use of toxic solvents in biomedical applications [19].

3.3. Polymerization and co-polymerization

Polymerization is a chemical process in which monomeric units combine to produce chainlike or branched three-dimensional structures [78]. Co-polymerization is the method of polymerizing different monomers. This method is beneficial as HNTs have high mechanical strength, thermostability, and reusability.

Enhancing HNTs' compatibility and interfacial adhesion with the polymer matrix can be achieved by functionalizing them with coupling agents or other surface modifiers. To achieve the necessary polymer characteristics and homogenous nanocomposite formation, factors like temperature, initiator concentration, and reaction time control are crucial. To achieve valuable characteristics, it is essential to attain a homogeneous dispersion of HNTs in the monomer or polymer matrix. Improved dispersion can be attained through surface functionalization, mechanical stirring, and ultrasonication. In the inverse suspension polymerization technique, mechanical agitation to manufacture polymer spheres was employed to fabricate a halloysite/poly (sodium acrylate-acrylamide) composite by Dong et al. [18]. Herein, HNTs prevented the intertwining of polymeric chain grafts and thereby caused a decrease in hydrogen bonding among –COOH functionalities of acrylate-acrylamide. This increased the overall specific surface area of the composite to enhance the humidity control property. Similarly, another research group [66] introduced an HNT-based ternary composite for catalytic applications. These HNTs were modified with 3-(trimethoxysilyl) propyl methacrylate by the polymerization and then conjugated with cyclodextrin. It was reported to have excellent catalytic activity to carry out ligand and Cu-free Sonogashira and Heck coupling reactions. Chen et al. fabricated multifunctional self-healing coatings to enhance the blockade properties of water-born epoxy coating against corrosive ions [9]. Polydopamine (PDA) coating was applied on the surface of benzotriazole-loaded HNTs (PBH) through the self-polymerization of dopamine monomers. PBH hybrids were conjugated with GO via π-π* interactions between PDA and GO as depicted in Fig. 7. GO enhanced the shielding performance against corrosive ions whereas benzotriazole released from the HNT lumen improved the healing property.

Another binary composite comprising HNT polymerized with pyrrole (PPy/HNT) was fabricated and the composites showed enhanced flame-retardant properties, moisture retainment, conductive, and adsorption capacity [22]. In-situ polymerization improved the thermal resistance of polypyrrole with HNT particle distribution in the polymeric matrix. A

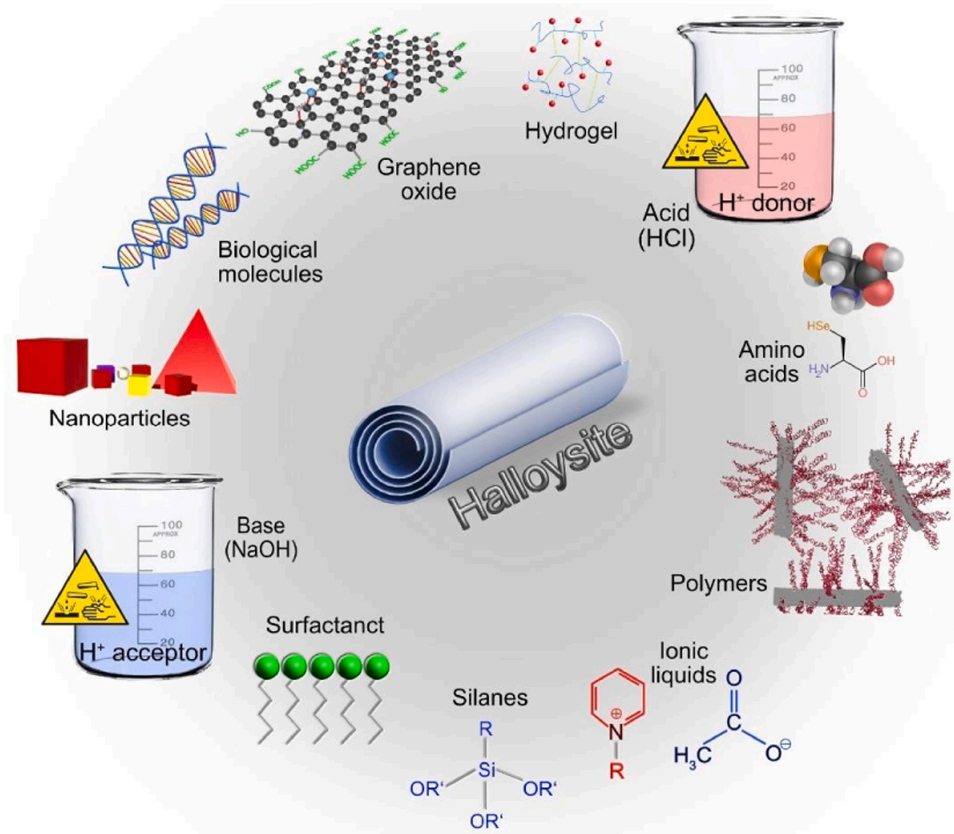

Fig. 3. Effective surface modifiers for HNTs.

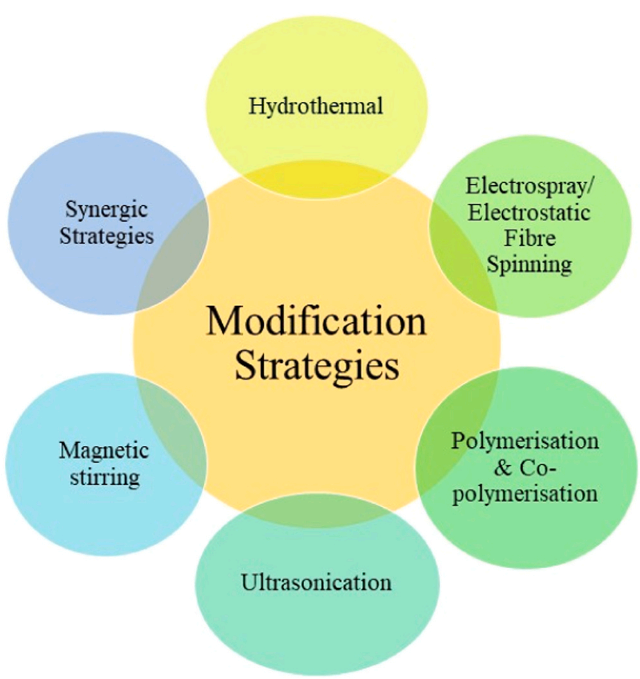

Fig. 4. Schematic representation of modification strategies for HNTs.

sensitive, simple, and cost-effective electrochemical sensor has been developed using an in situ polymerized HNT/PPY. HNT/PPY offered many reactive sites for ibuprofen molecules. These electron-rich centers proliferated the electron transfer rate, showing a higher electrocatalytic response towards the oxidation of ibuprofen as compared to the unmodified electrode [41]. A novel nanocarrier with positive effects on cancer therapy was developed. This PAA and CMC hydrogel with HNT (PAA/CMC/HNT/CUR) was developed and used for Curcumin (CUR) delivery by encapsulation in a water-in-oil-in-water nanoemulsion. Its in-vitro release study proved its pH-responsivity [58]. Adsorption of Acid Violet 90 (AV90) dye was facilitated by an adsorbent, composed of chitosan, boron nitride, and HNT. The composite was synthesized using a simple dropping method in a suitable precipitation bath. The adsorption kinetics were examined by Pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models [30].

3.4. Ultrasonication

Ultrasonication is a process wherein a large particle is broken into smaller uniform fragments using ultrasonic waves. It is a widely used homogenization technique for a variety of matrices and breaking up agglomerates for several applications. This process is essential not only for distributing HNTs uniformly but also for enhancing their compatibility with other materials. This better surface modification and material compatibility result from the high-energy environment created by ultrasonication, between HNTs and functionalizing agents. Ultrasonication is one of the most used fabrication methods as it can be easily scaled up for larger batches, making it suitable for an industrial setup. It was used for the synthesis of chlorantraniliprole HNT emulsion. This HNT-based pesticide formulation had foliar adhesion, enhanced rain erosion resistance, and insecticidal effect [11]. Similarly, sunflower oil was reinforced with HNT as a lubricant additive [4]. Chitosan biopolymer with HNT was synthesized using magnetic stirring followed by brief ultrasonication. These were hydrophobically modified at the oil-water interface as complementary pairs for stabilizing oil droplets of Louisiana sweet crude [55]. In another study P, N-decorated HNTs were synthesized with enhanced polyamide 6/aluminum diethyl phosphinate

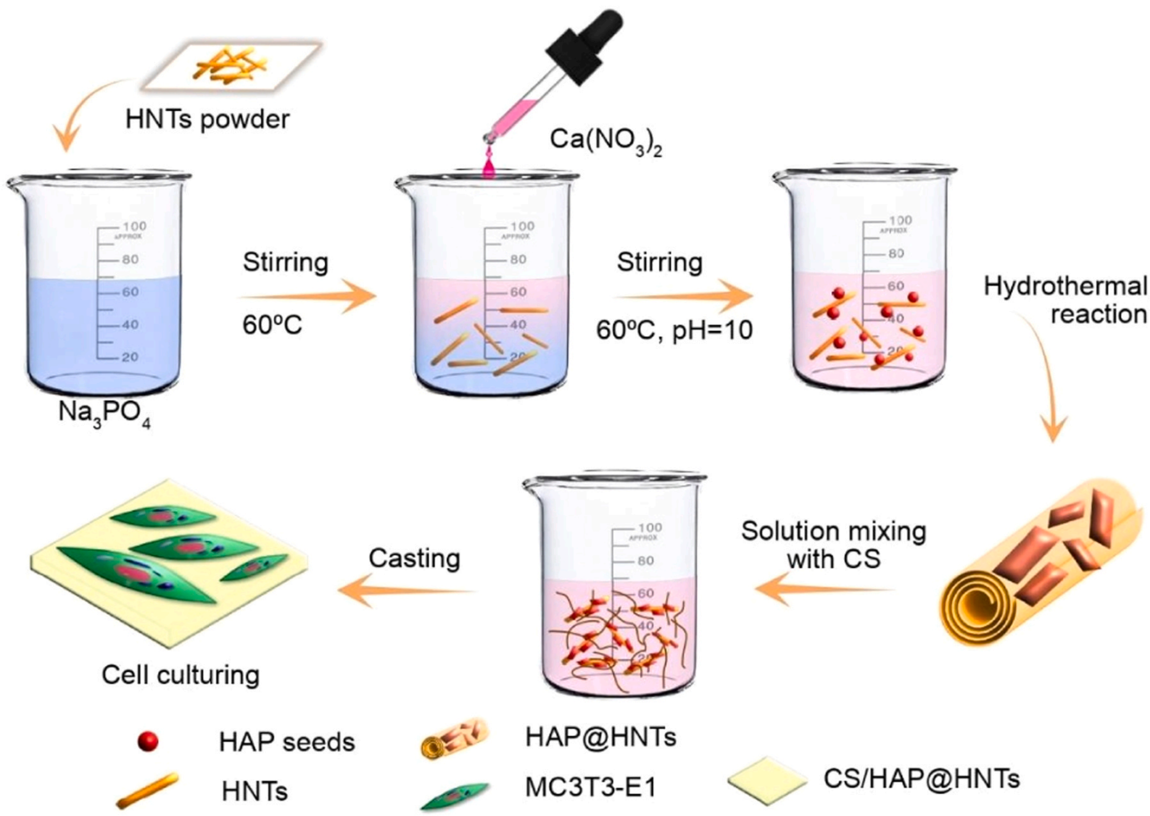

Fig. 5. Hydrothermal growth of HAP crystals on the surface of HNTs [103].

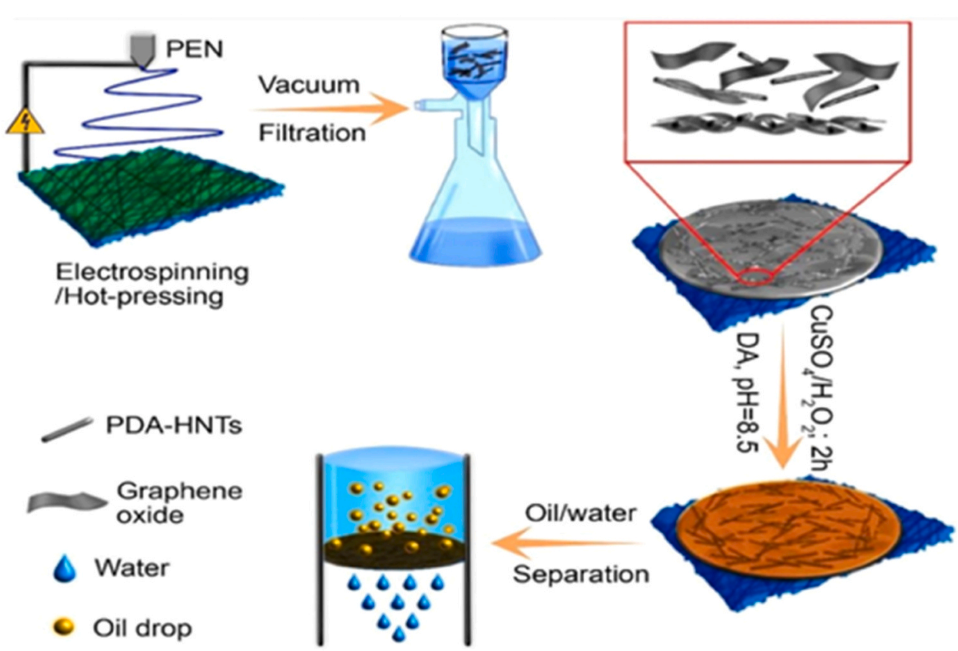

Fig. 6. Fabrication of HNT-inserted graphene oxide-polydopamine/poly (arylene ether nitrile) membranes for oil-water filtration [95].

which were then used as flame retardants [33]. A solid polymer electrolyte membrane of PEO-20 % $LiCF_3SO_3$-HNT has been fabricated for potential solid electrolyte materials [57]. The use of HNT resulted in improved electrochemical stability, flame retardance, and dimensional stability. Another group had functionalized HNTs endowing epoxy resin with simultaneously enhanced flame retardancy and mechanical properties by ultrasonication method [3]. Results with enhanced flame retardancy were obtained by the transfer of heat and smoke by the synergistic effect of Mxene@HNT on Rigid polyurethane foam (RPUF) with dual hydrogel (DH). The composite, RPUF/Mxene@HNT/DH was prepared using a layer-by-layer coating approach [81]. Bare tungsten trioxide (WO_3) and Ag/WO_3/HNT composite catalysts were synthesized using ultrasonication. Ag/WO_3/HNT photocatalysts were found to have excellent stability, recyclability, and significant photocatalytic

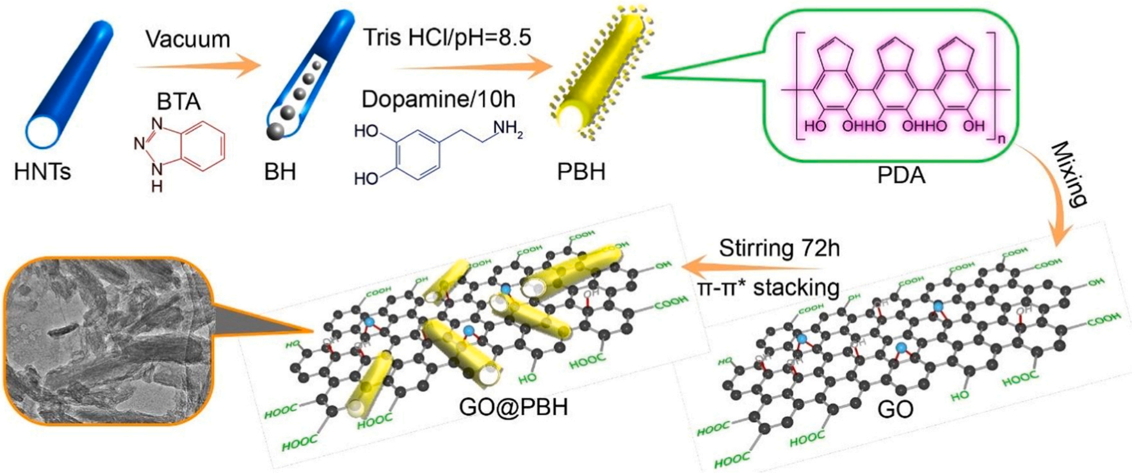

Fig. 7. Synthesis of GO@PBH composites [9].

performance with 96 % degradation for MB[44]. Green synthesis of 20 % loading, bimetallic CuO-NiO-HNT composites using ultrasonication. The composite exhibited higher removal efficiency of pollutants (congo red and tetracycline), good stability, and reusability even after 5 cycles [59].

3.5. Magnetic stirring

Magnetic stirring is a dispersion technique utilizing a rotating magnetic field, immersed in the given solution. Although magnetic stirring might not be as strong as ultrasonication in dissolving agglomerates, it works well in preserving a homogenous solution and promoting reactions related to surface modification. For HNTs to disperse and functionalize efficiently, stirring parameters and reaction conditions must be carefully controlled. HNTs possess great thermal stability which enables them to act as a heat barrier against thermal degradation. This improvement is also due to the synergism by the barrier effect and trapping of volatile analytes in its lumen [77]. Experiments on thermal degradation and fire resistance of epoxy coatings comprising HNTs and expandable graphite, with the help of an amine hardener were studied. A low concentration of filler component was useful to improve the thermal stability of completely cured epoxy/HNTs samples [76]. The role of the HNTs as thermal stability modifiers was significantly demonstrated. A high thermal stability was obtained by the addition of HNTs to PA6–NBR. The samples were synthesized by a melt-mixing process at 230°C and 80 rpm for 6 min. Further, the increased HNT content in the system also increased the resistance against decomposition [56].

Halloysite nanotube composites like CS/HNT and PA/HNT, were formed by the stirring method and were applied for fire protection of bamboo fiber/polypropylene composites [36]. In another study, HNTs were magnetically stirred and modified with 9,10-dihydro-9-oxa-10--phosphaphenanthrene-10-oxide (DOPO). Thus formed DOPO-HNT was used to control the temperature in the building [14]. Another biobased core-shell flame retardant, APP@CS@HNT was synthesized by mechanically stirring ammonium polyphosphate (APP) and HNTs [83].

3.6. Other methods

HNTs possess a good affinity for covalent linkage, H-bonding, and supramolecular interactions. This makes it possible for them to undergo a combination of methods for synthesizing adequate nanocomposites. Hyphenated methods often involve the integration of various processes to modify and incorporate HNTs into different materials more effectively. HNT composites fabricated using hyphenated techniques along with their corresponding applications have been discussed ahead. One of the most widely used hyphenated techniques for synthesizing nanocomposites is magnetic stirring and ultrasonication. The ability of ultrasonication to disperse large amounts of energy and the ability of magnetic stirring to offer continuous mixing are two advantages of combining the two methods. Similarly, by combining the dispersing power of ultrasonication with the heat and pressure conditions of hydrothermal treatment, it is possible to improve the functionalization and dispersion of HNTs. HNT/sodium alkanoate was synthesized using a selective modification of the inner cavity with weight loss, and hydrogenated surfactants (sodium undecanoate, sodium dodecanoate) with different tail lengths. These were then used as inorganic micelles for encapsulating hydrocarbons and aromatic oils [7]. The nanocomposite of surface-functionalized HNTs and silver nanoparticles provides good support for the electrical wiring and efficient immobilization of the redox enzyme glucose oxidase (GOx). The glassy carbon electrode (GCE) was used to deposit the GOx immobilized HNT/AgNPs, which were then used for the bioelectrocatalyzed electrochemical detection of glucose. Compared to composite electrodes made without surface functionalization, the GOx-modified composite electrodes exhibit glucose sensitivity as high as 5.1 $AmM^{-1}cm^{2}$ [45]. Another study employed a GCE modified with HNT extensively loaded with palladium nanoparticles for non-enzymatic glucose sensing. The current response of the palladium nanoparticles (Pd NPs)-HNT modified electrode towards glucose covered two linear regions (0.5 μM - 2.0 mM and 2.0 mM - 15.0 mM) and the detection limit was 0.43 μM [86]. Polysiloxane-modified HNTs were coated with a superhydrophobic coating using a spraying technique. Tetraethoxysilane and n-hexadecyltriethoxylsilane were treated with HNTs as silane impacted the coating's transparency, shape, and superhydrophobicity. HNT coatings were found to have excellent oil/-water separation and self-cleaning capabilities [23]. A sensor made up of tubular HNTs-PDA-Au nanocomposites, identified hydrazine in the range of 0.75 $molL^{-1}$ - 2.8 $molL^{-1}$, with a sensitivity of 171.7 A ($mmolL^{-1}cm^{2}$) and a detection limit of 0.25 $molL^{-1}$ (S/N = 3) [99]. Wu et al. fabricated g-C_3N_4/TiO_2/HNT photocatalysts via a combination of sol-gel and calcination techniques [85]. The catalytic performance of the prepared composite was augmented by calcining it with graphitic carbon nitride. Combining both techniques enhanced photoelectric and photocatalytic properties by improving the electronic charge transfer across g-C_3N_4/TiO_2/HNT heterojunction and assisted in the separation of photogenerated electron-hole pairs. He et al. followed thermal spraying, a simple procedure in which material components are thermally applied on a varied range of substrates to manufacture effective drug delivery, anti-corrosion, and heat-resistant coatings. This method was used to synthesize doxorubicin-loaded HNT coatings for capturing and killing tumor cells (MCF-7) [32]. The layer-by-layer (LBL) process, in which different layers of materials are deposited employing oppositely charged electrostatic interactions to synthesize thin films was reported [63]. Bioactive LBL films based on beta-lactamase (BlaP) loaded and poly(ethylene-imine) (PEI) stabilized HNTs were designed. HNT-Zein-based pH-responsive biocomposite for phenytoin-controlled release was fabricated in an aqueous medium via the LBL method [94]. In another research, the two forms of halloysite nanotubes, powder HNTs, and granular forms having abundant potential for the removal of phosphate from agricultural runoff were analyzed. The granular form exhibited 94.7 % efficiency whereas the powdered form exhibited 79.5 % efficiency [67]. Massaro et al. loaded the external surface and lumen with doxorubicin and curcumin derivatives via covalent and supramolecular linkage, respectively. The π- π linkage promoted sustained drug delivery as this framework showed successful cytotoxic results against breast cancer cell lines (MDA-MB-231 and SUM-149) and myeloid leukemia cell lines (HL60R and HL60) [50]. For all-in-one detection of aromatic amines and nitrofuran in real samples, $CoFe_2O_4$@HNTs/AuNPs substrate was developed for a rapid and efficient magnetic solid-phase extraction (MSPE) and surface-enhanced Raman scattering (SERS) [97].

A simplified and innovative scheme to construct an HNT-based electrochromic device was proposed [64]. The external layer of HNTs was hydroxylated to facilitate ion exchange with intrinsic acetate ions in the metallic-supramolecular polymer i.e., polyFe through electrostatic interactions along an ion-exchange scheme (Fig. 8).

Doxorubicin and derivatives of curcumin were loaded concurrently on both surfaces of HNT. The multifunctional systems, based on their physicochemical and biological properties were evaluated on different cancer cell lines [50]. 5-fluorouracil was loaded onto HNTs for targeted drug delivery using a subcritical gas antisolvent process and subcritical CO_2 resulted in high drug loading (43 %) [31]. Polyvinylidene fluoride (PVDF) was used for the preparation of the electrospun nanofiber adsorptive membranes incorporating TiO_2-HNT nanoparticles as adsorbents. A maximum of 31.2 mg/g of arsenic adsorption was achieved using a TiO_2-HNT to PVDF ratio of 0.5 w/w [2]. HNTs were rationally integrated with coumarin moieties. The nanocomposite was prepared by treating amino-functionalized HNTs with 7-hydroxy-4-methyl-2-oxo-2 H-chromene-8-carbaldehyde. The Zn^{2+}-sensitive chemosensor thus prepared, displayed a weak fluorescence signal. However, a remarkable "turn-on" behavior was observed upon exposure to Zn^{2+} ions of a concentration as low as 1×10^{-6} M [73]. In another process, phosphazene-loaded HNTs (HNT@PPCP) were used as bifunctional nanohybrid fillers for PEO-Based solid polymer [93]. These have been widely used due to their enhanced ionic conductivity, improved fire safety, low voltage polarization, and broad electrochemical windows. Investigated is the deposition of Pd nanoparticles from various Pd precursors and solvents onto HNT [52]. These catalysts were characterised using low-temperature N_2 adsorption, transmission electron microscopy, and zeta potential measurement. PVDF coating, modified by well-dispersed MEA-ATO@HNT was prepared using coprecipitation. Its photocatalytic properties demonstrated that the addition of HNTs speeds up electron transport and encourages the breakdown of Rhodamine B [62]. The additional applications of fabricated HNT-based composites are summarized in Table 2.

4. Conclusion

Halloysites are non-toxic, tubular, amenable to large-scale production, and highly biocompatible wonder material. Their association with various dopants makes them an interesting support system with better physicochemical characteristics, decreased particle agglomeration, and enhanced efficiency. With strong capabilities and potential in different fields, this review provides insights into the multicomponent nanosystem created using HNTs. Owing to their unique surface functionalities, these nanotubes have been employed in hydrothermal, electrospinning, polymerization, ultrasonication, magnetic stirring, and other functionalization strategies. It is thus required to envisage the structure-property relationship on HNT-based composites to understand the implications which are the determining factors for applications of this wondrous clay material. The existing literature illustrated that the hyphenation of synthesis methods is the most feasible fabrication technique for diverse applications of halloysite composites as the nanomaterial's performance can be modulated by choosing the right combination of approaches. Synergic methods of synthesis facilitate distinct properties, exhibiting unique characteristics and enabling a more effective and uniform dispersion into the given matrix. Furthermore, several chemical modifiers can be impregnated onto the HNT surfaces to produce robust materials for various applications and their large-scale production. The long-term stability and mathematical modelling for catalyst optimization must be considered before scaling up. Among the numerous clay minerals, HNTs have thus emerged as a remarkable material with cutting-edge nano-systems that might be successfully used in real-world industrial applications. In the scientific domain, HNTs are surprising researchers with their unique features and leading towards the creation of intelligent nano-systems with programmable features and a greener impact than current ones.

CRediT authorship contribution statement

Swati Gupta: Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Gurpreet Kaur:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **S.K. Mehta:** Writing – review & editing, Validation, Supervision, Project administration. **Evgeniya Sheremet:** Software, Data curation. **Raul D Rodriguez:**

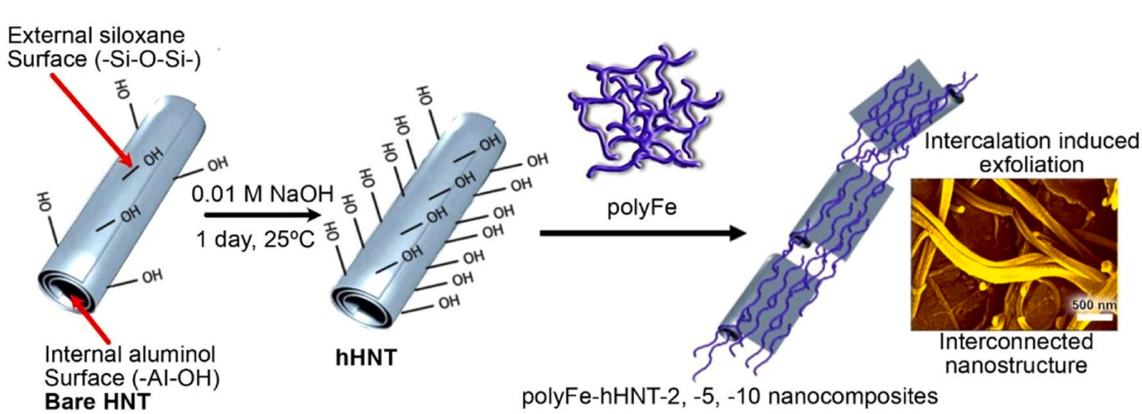

Fig. 8. Synthesis of polyFe-hHNT composites [64].

Table 2
Applications of fabricated HNT composites using synergic strategies.

Composite	Mode of synthesis	Application	Reference
Highly controllable imprinted-polymer nanoshell	Ultrasonication and magnetic stirring	Selective recognition and rapid adsorption of tetracycline	[15]
Ferrocene carboxylic acid primed HNT	Modified glassy carbon electrode using ultrasonication	Simultaneous voltammetry detection of dopamine and uric acid from pharmaceutical products and urine samples	[51]
HNTs@PPy-Pd	Ultrasonication and magnetic stirring	An immunosensor to detect PSA quantitatively with Pd NPs acting as the signal amplifier	[90]
Hal-NH_2 nanomaterial	Ultrasonication and magnetic stirring	Enhanced removal of lead (II) ions from aqueous solutions	[6]
Molecularly Imprinted Polymer (MIP) based on magnetic HNTs	Ultrasonication and magnetic stirring	Norfloxacin extraction from samples using a Quality by Design (QbD) approach using computer-aided design	[25]
Ag/HNT/MoS_2	One-step hydrothermal method	Electrochemical sensing for efficient nitrite sensing	[27]
Ni $(OH)_2$@g-C_3N_4/halloysite nanocomposite	Chemical modification	Nanocomposite photocatalyst for efficient photocatalytic hydrogen generation	[35]
Hal-IM-AM	Click reaction, co-polymerization	A desirable cross-linking agent to construct hydrogels	[101]
Modified HNTs and polyacrylic latex with a soft core-reactive shell	Grafting method	High-performance nanocomposite coatings	[91]
Expanded graphite- mixed clay sponge- 1-Hexadecylamine (EG-MCS-HAD), C(carbonised)-EG-MCS-HDA phase change composites	Polymerization, impregnation	Thermal energy storage by enhanced light-thermal conversion efficiency of mixed clay base phase change composites	[80]
Hollow imprinted HNT materials	Etching technique	Adsorbents for extracting Zearalenone from grain samples	[82]
HNTs/poly(ethylene glycol) methyl ether methacrylate-diacrylate-fluorescein (PEGMA-Fl)	Surface-initiated light-induced RAFT polymerization	Composites show high water dispersibility, strong fluorescence, and low toxicity and have potential for biomedical applications	[10]
Porous MIP using HNT as a template	Ultrasonication, polymerization, etching	Chloramphenicol, an antibiotic found in aquatic environments, was selectively identified, and eliminated	[47]
$MnCo_2S_4$/HNT	Chemical synthesis and stirring	Composites for advanced battery-like supercapacitor application by designed nanoflakes anchored nanotubes	[70]
Manganese oxides-halloysite/carbon composite	One-step carbonization activation, impregnation method	Catalytic performance of composites for the selective catalytic reduction of NO with NH_3	[88]
Copper-metal nanoclusters-HNT (CuNCs@HNT)	Chemical: one-step synthesis, post-synthesis	Catalytic performance of composites on contrasting azo dyes	[17]
Fe_3O_4–HNT	synthesized from iron salt precursors using maize leaf extracts as reducing and capping agents	Adsorbent in water treatment technologies	[21]
Ag/HNT/PVA sponge	Mechanical foaming	Reduction of waste 4-nitrophenol to useful 4-aminophenol	[13]
Acid-Etched HNT	Acid etching	A superior carrier for ciprofloxacin with 25 % higher antibacterial properties than non-etched composites	[60]
AuNPs-HNT composites	wet chemical method	Catalytic degradation of phenothiazine dyes	[69]
HNT/epoxy composite	Ultrasonication, compression, and degassing	Uniform distribution and reflecting interfaces of HNT's epoxy generated during the curing process	[72]
Bi/$BaSnO_3$@HNTs	Precipitation-photoreduction	The degradation of methylene blue under visible light	[12]
$CoMn_2O_4$ spinel oxide halloysite (40-CMO/HNT)	Co-precipitation and calcination	Degradation of pharmaceuticals in water bodies	[89]
Co–CHNTs	Impregnation-chemical reduction-calcination	Efficient degradation of sulfamethoxazole antibiotics	[34]
Polyethylene glycol (PEG)/HNT	Vacuum impregnation	Thermal behavior and flame-retardant performance of phase change material microcapsules	[40]
HNT/CS hydrogel solution & CS/ HNT/ g-C_3N_4	Ultrasonication, calcination	Chitosan/halloysite/graphitic-carbon nitride nano vehicle for targeted delivery of quercetin	[65]
PEI/PVP/HNT composite	Magnetic stirring	Polyetherimide membranes for treating oil-in-water contaminants	[68]
Ag-Cu bimetallic nanoclusters on HNTs	Ultrasonication and magnetic stirring	Ag-Cu NCs/HNT-b composite was used to study the antibacterial properties	[37]
$MnCo_2O_4$@HNTs	Co-precipitation and low-temperature calcination	Degardation of many antibiotic pollutants such as ornidazole	[102]
Cefixime-HNT	Ultrasonication and magnetic stirring	Good antibacterial properties and low cytotoxicity which can be used for biomedical application	[79]
PVDF–PDA–DETA@PVP@HNT nanofiber membrane	Polymerization and Ultrasonication	High efficiency oil–water emulsion separation	[16]
HNT-CDP (cresyl diphenyl phosphate)	Ultrasonication and magnetic stirring	Outstanding flame retardancy is mainly due to the synergistic effect between HNT and CDP	[100]

Software, Data curation. **Varnika Prakash:** Project administration, Investigation, Formal analysis. **Shweta Sharma:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

The authors acknowledge the financial support from UGC-DAE CSR through a Collaborative Research Scheme (CRS) project number CRS/2021–22/01/385.

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