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VERMICULITE NANOMATERIALS: STRUCTURE, PROPERTIES, AND POTENTIAL APPLICATIONS

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Abbreviations

MB	Methylene blue
MV	Methyl violet
CV	Crystal violet
NH4 ⁺ -N	Ammonium nitrogen
CTS-g-PAA/VMT	Chitosan-graft-poly(acrylic acid)/vermiculite
CTS-g-PAA/VMT	Chitosan-graft-poly(acrylic acid)/vermiculite
CTS-g-PAA/UVMT	Chitosan-graft-poly(acrylic acid)/unexpanded vermiculite
GG-g-PAA/RVMT	Guar gum-graft-poly(acrylic acid)/raw vermiculite
GG-g-PAA/Li ⁺ -VMT	Guar gum-graft-poly(acrylic acid)/Li ⁺ -exchanged vermiculite
GG-g-PAA/Na ⁺ -VMT	Guar gum-graft-poly(acrylic acid)/Na ⁺ -exchanged vermiculite
GG-g-PAA/K ⁺ -VMT	Guar gum- <i>graft</i> -poly(acrylic acid)/K ⁺ -exchanged vermiculite
GG-g-PAA/Ca ²⁺ -VMT	Guar gum-graft-poly(acrylic acid)/Ca ²⁺ -exchanged
	vermiculite
GG-g-PAA/Mg ²⁺ -VMT	Guar gum-graft-poly(acrylic acid)/Mg ²⁺ -exchanged
	vermiculite
GG-g-PAA/Al ³⁺ -VMT	Guar gum- <i>graft</i> -poly(acrylic acid)/Al ³⁺ -exchanged
	vermiculite
GG-g-PAA/OVMT	Guar gum-graft-poly(acrylic acid)/organo-vermiculite
GG-g-P(NaA-co-St)/VMT	Guar gum-graft-poly (sodium acrylate-co-styrene)/vermiculite
HEC-g-PAA/VMT	Hydroxyethyl cellulose-graft-poly(acrylic acid)/vermiculite
HEC-g-PAA/OVMT	Hydroxyethyl cellulose-graft-poly(acrylic acid)/
	organo-vermiculite
PAA/VMT	Poly(acrylic acid)/vermiculite
PAM/VMT	Polyacrylamide/vermiculite
Poly(SA)/CVMT	Poly(sodium acrylate)/crude vermiculite
Poly(SA)/EVMT	Poly(sodium acrylate)/exfoliated vermiculite
PKA-AM/UVMT	Expanded vermiculite/poly(potassium acrylate-acrylamide)
PAA-Am/EVMT	Poly(acrylate-co-acrylamide)/expanded vermiculite
AA/VMT	Acrylic acid/vermiculite
POBDS/VMT	Poly(4, 4-oxybis(benzene)disulfide)/vermiculite

9.1 Origin and Distribution of Vermiculite

A simple classification of clay minerals is available in literature, which classifies the clay minerals into three main groups: kaolinite group, illite group, and smectite-vermiculite group. Belonging to smectite-vermiculite groups, vermiculite is mostly formed by the removal of potassium from biotite, phlogopite, or muscovite [1]. It was discovered first by American H. Webb in a mine in Vinsted, Massachusetts, in 1824. It was named vermiculite in 1861, meaning "worm-like" in English due to its thermal expansion performance [2]. Natural vermiculite resources are mainly distributed in the United States, South Africa, Russia, China, Australia, and Zimbabwe. Among them, the reserves of vermiculite resources in China account for one-sixth of the world's total reserves, 95% of which are distributed in Xinjiang Province, China, with a prospective reserve of more than 100 million tons, which is a rare super-large deposit, ranking second in the world (the first being in South Africa).

9.2 Structure and Physic-Chemical Properties of Vermiculite

Vermiculite is a mica-type trioctahedral silicate clay mineral with 2:1 layered structure like the well-known montmorillonite. Each layer is composed of octahedrally coordinated cations, that is, Mg(II), Al(III), and Fe(II) sandwiched by tetrahedrally coordinated cations, that is, Si(IV) and Al(III). According to the AIPEA Nomenclature Committee [3], tetrahedral sheet is composed of continuous two-dimensional corner-sharing tetrahedra $[TO_4]^{4-}$ involving three basal oxygens and the apical oxygen. The structure formula of vermiculite is usually reported based on the structure unit (half unit-cell content). The general formula can be written as: $X_4(Y_{2-3})O_{10}(OH)_2M \bullet nH_2O$, where M is exchangeable cations, that is, Mg(II), Ca(II), Ba(II), Na(I), K(I) located in the interlayer spacing, used for compensating negative layer charge; Y is octahedral Mg(II), Fe(II) or Fe(III), Al(III), and X is tetrahedral Si, Al. Vermiculite has two configurations including trioctahedron and dioctahedrons, and its identification is based on the position of (060)reflection on their X-ray diffraction patterns. Dioctahedral vermiculites have an interlayer spacing value $d_{(060)}$ ranged from 0.149 nm to 0.150 nm, while trioctahedral vermiculites have an interlayer spacing $d_{(060)}$ ranged from 0.151 nm to 0.153 nm [4].

The chemical compositions of vermiculite are: SiO_2 37%–42%, Al_2O_3 9%–17%, Fe_2O_3 5%–18%, MgO 11%–23%, H_2O 5%–11%, and also contain trace amounts of Li, Cr, Ti, and Ni. The isomorphous substitution of Si(IV) by Al(III) leads to a net negative surface charge (>0.6 per formula unit). The negative structure charges can be compensated by interlayered exchangeable hydrated cations: Ca(II), Mg(II), Cu(II),



Fig. 9.1 Structure scheme of vermiculite. Reproduced with permission from K. Zhang, J. Xu, K.Y. Wang, L. Cheng, J. Wang, B. Liu, Preparation and characterization of chitosan nanocomposites with vermiculite of different modification, Polym. Degrad. Stab. 94(12) (2009) 2121–2127.

Na(I), and H(I). (Fig. 9.1) [5], resulting in vermiculite having a larger cation exchange capacity (CEC) (100-150 cmol/kg). The interlayer cations Mg(II) and minor amounts of Ca(II), Na(I), and K(I) bring vermiculite with hydration properties, hence vermiculite structures contain interlamellar water layers, which are subjected to the hydration and dehydration processes [6–8].

The interlayer spacing of vermiculite is dependent on the size of the cations and on the presence of interlaminar water, and the spacing may change with varying the type or hydration state of cations [9]. The hydration state of vermiculite was defined by the number of water layers in the interlayer space [10]. Vermiculite belongs to the monoclinic crystalline system, and the commonly accepted unit cell parameters are: $a^0 = 0.54$ nm, $b^0 = 0.93$ nm, $c^0 = 1.44$ nm, $\alpha = \gamma = 90^\circ$, $\beta = 97^\circ$; the unit cell belongs to $C_{2/c}$ space groups. Usually, when $c^0 = 1.481$ nm, the interlayer water molecule layer is intact; when $c^0 = 1.436$ nm, the interlayer water molecules are in double layer; when $c^0 = 1.159$ nm, the interlayer water molecules are in a single layer; when $c^0 = 0.902$ nm, vermiculite is completely dehydrated; after heating and dehydration at 500°C, vermiculite can be recovered by water absorption. However, if the process was carried out at 700°C, vermiculite cannot be recovered by water absorption [11, 12]. The degree of hydration state in the interlayer is related closely to the radius and charges of cations [13], which causes the difference in the interlayer spacing of different types of vermiculite. The basal spacing of Mg-vermiculite is declared to be 0.902 nm for zero-water layer, 1.150 nm for one-water layer, and 1.440 nm for two-water layer hydration state [14]. The vermiculite from Llano (Texas) has variable d values of the basal spacings [15]. The interlayer values $d=1.04-1.03\,\text{nm}$ are assigned to the interstratified one-zero

layer hydrate, and the value $d=1.28\,\mathrm{nm}$ is assigned as random interstratified phase of two-one layer hydrates. The hydrated states and interstratified phases in the vermiculites from Sta. Olalla (Spain), Paulistana (Brazil), Palabora (South Africa), and West China were described by Marcos et al. [16]. It is shown that the vermiculite from China is composed of alternating mica layers (d=1.02 nm, zero-water)layer hydration) with vermiculite layers (d=1.47 nm, double water layer hydration) and two-one layer hydration interstratification with d = 1.21 nm. The X-ray diffraction patterns of the South African vermiculite with high potassium content in the interlayer space $(K_{0.53})$ showed the value d = 1.45 nm corresponding to the vermiculite and additional peaks with d=2.52 nm, d=1.26 and d=1.205 nm, which resulted from a biotite-vermiculite mixed-layer mineral [17]. Reichenbach and Beyer [10] evaluated two superstructures formed by a regular 1:1 interstratification. One of them had a d=2.541 nm that proved to be a result of the altering layers with d = 1.376 nm and d = 1.165 nm. Another superstructure with the value d = 2.153 nm was assigned to the altering layers with d = 1.151 and d = 1.002 nm. These researches show that vermiculite possesses a semiordered structure when the transition from a layer to the next layer is obtained in two or more different ways. For semiordered stacks, the reciprocal space cannot be described by a set of hkl indexes but rather by modulated reciprocal hkl with the variable intensity along them [18].

Due to the special crystalline structure, vermiculite not only has the common properties of other clay minerals including cation exchange, adsorption, chemical stability, chargeability, large specific surface area, and active surface groups, vermiculite also exhibits several unique properties different from other clay minerals, such as expansion capability (maximum expansion to more than 30 times), electrical, thermal and sound insulation, fire resistance, and frost resistance [2, 19]. In addition, vermiculite could be easily modified with various acids, alkaline, metal ions, and organic modifiers, such as long chain quaternary ammonium, quaternary phosphonium salts, silane coupling agents, amino acids, or other organic molecules [20]. Therefore, vermiculite is proved to be an efficient, economical, and environmentally friendly raw material to fabricate adsorbents [21], water-saving material [22], carriers of catalyst [23, 24], reinforcing filler of polymer [25, 26], packing materials [27, 28], phase change and energy storage materials [29], gas barrier material [30], thermal insulator [31, 32], and so on.

9.3 Reducing the Size of Vermiculite

In order to meet the demonds of vermiculite as natural twodimensional nanomaterials in various areas, vermiculite usually needs various treatments to reduce the size or intercalate and exfoliate to form 2D nanolayer materials. The 2D nanolayer materials have excellent potential to be used in constructing various nanocomposites. Intercalation is a general term to describe the movement of atoms, ions, or molecules into a layered host structure, usually, for a swelling clay mineral. The resulting structure is an "intercalation structure" [33]. Exfoliation is a process to separate the layers of a host structure where units, either individual layers or stacking of several layers, are dispersed (freely oriented and independent) in a solvent or polymer matrix [34]. Currently, various physical methods (such as mechanical grinding, ultrasonication, and microwave treatment), chemical methods (such as acid, alkali, oxidation treatment, grafting, and intercalation) have been employed to reduce the size of vermiculite particles and fabricate intercalation or exfoliation structures. A series of research has been made to widely expand the application of vermiculite in various functional materials.

The mechanical treatments, such as grinding, ultrasonation, and extrusion, are common approaches to reducing the size of vermiculite. The specific surface area of the vermiculite obtained from Santa Olalla increased from $1 \text{ m}^2/\text{g}$ to $39 \text{ m}^2/\text{g}$ after grinding for 2 min and decreased to 20 m²/g after grinding for 10 min. The amorphous phase begins to be formed and the dehydroxylation temperature of vermiculite decreases after grinding treatment for over 10 min [35]. After milling in ball, jet, and vibrational mills, natural Mg-vermiculite (VB) from Brazil showed electrophoretic mobility (μ) in the range of 1.16 to $1.96 \times 10^{-4} \text{ m}^2/\text{Vs}$ and the ξ -potential in the range of -15.1 to -25.4 mV. The particles became small and particle size distribution became homogeneous [36]. High-power ultrasound is effective to reduce the size of vermiculite, not only along the basal planes but also in different directions [37]. The comparative study about grinding and sonication treatment indicates that the sonication treatment may reduce particle size with well remaining the plate-like morphology of the original vermiculite, while the long-time grinding process caused the loss of long-range order degree, crystallinity, and agglomeration of the particles [38]. The changes in the structure and properties of vermiculite caused by ultrasonication are also related to the crystalline charge of vermiculite. The high-charged vermiculite from Santa Olalla (0.88 p.f.u.) remained in the flake shape after sonication treatment, while the low-charge vermiculite from Ojén (0.47 p.f.u.) displayed scrolling of the flakes into tubes. The specific surface area increased from the $1 \text{ m}^2/\text{g}$ to $36 \text{ m}^2/\text{g}$ for high-charge vermiculite, and to 54 m²/g for low-charge vermiculites after sonication treatment [39]. The grinding of vermiculite in aqueous dispersion decreased the grain size from 2 to $3 \,\mathrm{mm}$ to $100 \,\mu\mathrm{m}$, and the ultrasonic milling at 20 kHz allowed the size of the grains to be decreased further (8µm) [40]. The micron-sized vermiculite can be easily prepared by sonication in Rosett reactor. The sonication promotes the dissolution of Na exchangeable cations through exfoliation and the exfoliation was improved by sonication at 90°C in water or at room

temperature in H_2O_2 . The highest quantity of submicrometric particle was obtained after sonication at 90°C in water [41]. The vermiculite with different size-fractions (0.1–0.2, 1–2, and $10-20\,\mu m$) was prepared using the sonication process, and it was found that the aspect ratios of particles are similar in all fractions. It was also observed that the finest particles tend to exhibit slightly more elongated surface morphologies than the coarser particles [42]. A pilot vermiculite exfoliation system was established by a process mineralogy, and the vermiculite expand quit rapidly when exposed to high-intensity electric fields as the degree of expansion was directly related to the applied electric field strength with a positive correlation. The microwave fields interact with the mineral to develop a pilot scale of microwave system based on the process for the exfoliation of vermiculite [43]. The chemical-mechanical treatment of vermiculite from State of Goiás, central-west Brazil by a high shear process in the presence of LiCl, NaCl, and HCl effectively reduces particle size and increases the swelling capability of vermiculite, and the effect of chemical additives is in the descending order of HCl>LiCl > NaCl [44]. The nanoscale vermiculite can be produced by a thermal treatment. Vermiculite was exfoliated as nano-layered vermiculite with low density after thermal treatment up to 900°C [45]. The alcohol and subsequent microwave irradiation could lead to the slight change of the structure of vermiculite and obtain purer vermiculite phase [46].

The chemical oxidation method is also a frequently used method to expand or exfoliate vermiculite efficiently. This process often utilizes an oxidizing agent, such as hydrogen peroxide or a synergistic acid treatment to expand vermiculite layers and then efficiently stripped them. A higher exfoliation rate was attained when hydrogen peroxide concentration exceeds 30%. Meanwhile, the maximum swelling values of 118fold were reached at 50% H_2O_2 concentration treated for 30 h [47]. The exfoliation mechanism was interpreted in terms of contents of crystal water, amounts of released cations and change of pH values of solutions. The hydrogen peroxide penetrated into the interlayer spaces and decomposed with generation of atomic oxygen, which subsequently disrupted the electrostatic equilibrium between the layers and the interlayer cations and thus led to delaminate of the layers. Similarly, Mgvermiculite was exfoliated after thermal, microwave and/or hydrogen peroxide treatments [48] or oxidized by the oxidation agent potassium persulfate $(K_2S_2O_8)$ which was chosen due to its stronger oxidation capability as compared to hydrogen peroxide [49]. However, the oxidation treatment of vermiculite with potassium persulfate solution led to an undesirable collapse of layered structure in comparison to treatment with hydrogen peroxide solution. The chemical oxidation treatment with H_2O_2 may be performed with the assistance of thermal shock and ultrasonic treatment to exfoliate vermiculite or reduce the size of vermiculite particles [50] since ultrasound treatment may generate cavity effect to promote the disassociation of particles and exfoliation of vermiculite [41]. It has been found that the treatment with 35 wt\% H_2O_2 in the assistance of ultrasound for only 1 h caused density of vermiculite to decrease from 1.026 g/cm^3 to about 0.23 g/cm^3 and produced small particles of vermiculite. This change can be attributed to the breaking of the particles by 20 kHz sonication that facilitated the formation of OH groups on the edges of the layers. The micron and submicron-sized vermiculite lamellar particles with nanometric thickness (<10 nm) can be obtained by ultrasonic treatments (<12h) of aqueous hydrogen peroxide with suspensions of the thermally exfoliated vermiculite [51]. In addition to sonication, microwaving promotes the exfoliation of vermiculite [52, 53]. The Goiás vermiculite was fully exfoliated after simultaneous treatment with 30%-50% H₂O₂ solution and microwave irradiation [54].

In fact, it is not necessary to fully exfoliate vermiculite before using it can be applied in various fields. Usually, vermiculite was modified or intercalated with organic modifiers or monomers first, and then nanocomposite can be formed by an intercalated or exfoliated structure developed during the preparation process. For the application of vermiculite in polymer composite, the key issue is to achieve an effective dispersion and exfoliation of the platelets into the polymer matrix to vield well-aligned and high-aspect ratio particles with mechanical reinforcement or a tortuous diffusion pathway to improve barrier properties [55]. Currently, two approaches have usually been employed to intercalate or exfoliate the layers of vermiculite: the first is the exfoliation/or intercalation by a mechanical shearing action; and the second is the in situ polymerization of organic monomers inside the layer space. Fig. 9.2 showed the schematic representation of the preparation processes of poly(4, 4'-oxybis(benzene)disulfide)/vermiculite nanocomposite [56]. In this process, the pristine vermiculite was first intercalated with octadecylammonium to expand the gallery spacing from 1.2 to 2.9 nm. Then the small molecular cyclo(4, 4'-oxybis(benzene)disulfide) oligomers (COBDS) with relatively lower melt viscosity were intercalated further into surfactant-intercalated vermiculite via the diffusion into galleries of vermiculite during the melting process. Upon heating the COBDS/ vermiculite nanocomposite precursor to 200°C, the ring-opening polymerization of COBDS occurred almost instantly. The nanocomposite with well-dispersed exfoliated vermiculite nanolayers inside was then obtained, as confirmed by XRD results that no characteristic reflection of vermiculite was observed in the XRD pattern of nanocomposite. Generally, the fabrication of polymer nanocomposite by a melt intercalation process depends greatly on the mobility of the matrix in terms of the polymer dynamics and diffusion in the confined environment of polymer/layered clay. The composite of double-organo-vermiculite (DOVerm) with polystyrene (PS) by an in situ polymerization process may reduce the size of vermiculite into nanoscale size (Fig. 9.3) [57].



Fig. 9.3 TEM images of (A) 1%DOVermPS, (B) 3%DOVermPS, (C) 5%DOVermPS and (D) 7%DOVermPS at different magnifications. Reproduced with permission from L. Wang, X. Wang, Z.Y. Chen, P.C. Ma, Effect of doubly organo-modified vermiculite on the properties of vermiculite/polystyrene nanocomposites, Appl. Clay Sci. 75–76 (2013) 74–81.

Fig. 9.4 Schematic drawing of modified vermiculite in three different ways. Reproduced with permission from K. Zhang, J. Xu, K.Y. Wang, L. Cheng, J. Wang, B. Liu, Preparation and characterization of chitosan nanocomposites with vermiculite of different modification, Polym. Degrad. Stab. 94(12) (2009) 2121–2127.

Fig. 9.4 illustrated the pretreatment and intercalation process of vermiculite. The diffraction peaks of vermiculite at 2θ =7.3° (d=1.2 nm) shifted to 2θ =8.1° (d=1.1 nm) after acid treatment, remained unchanged after the ion-exchange treatment with Na⁺. It shifted to 2θ =8.1° (d=3.7 nm) after treatment with cetyltrimethylammonium bromide. As the change of gallery spacing depends on the packing density and alkyl chain length, the increase of gallery spacing (d value) confirmed the successful intercalation by cetyltrimethylammonium bromide into the interlayer space. The surfactantsintercalated vermiculite can also be intercalated by other polymer chains, and the well-dispersed nanolayers of vermiculite were formed in the polymer matrix [5].

9.4 Modification of Vermiculite

9.4.1 Acid Activation

The acid leaching process of vermiculite may create more structure defects, which allows more functionalizing agent (such as 3-mercaptopropyl) trimethoxysilane (MPTS) to be anchored on it. The increase of total acidity of the synthesized H-vermiculite-SO₃H material led to an increase in the reaction test velocity, which can further widen its applications in adsorption or catalysis [58, 59]. The splitting of vermiculite particles has five stages (Fig. 9.5), and the splitting degree depends on the content of Al in the octahedral sheet [60]. The exchange of the interlayer cations with H⁺ ions and the stepwise reduction of the

Fig. 9.5 Dissolution- and delamination-model of the swellable vermiculite by acid activation. Reproduced with permission from A. Steudel, L.F. Batenburg, H.R. Fischer, P.G. Weidler, K. Emmerich, Alteration of swelling clay minerals by acid activation, Appl. Clay Sci. 44 (2009) 105–115. octahedral sheet were observed in this process. Splitting of the particles proceeded along the interlayer spaces and OH-groups of the octahedra (edge attack). The remaining tetrahedral sheets of the swelling clay minerals are connected by H^+ as well as residual interlayer cations and residual octahedral fragments. Generation of solid acidity is found to be dependent on the substitution degree of Al in the original tetrahedral sheets. Besides, the acid activation efficiency is also closely re-

lated to the type of clay minerals and this finding was confirmed by the comparative study about the acid treatment of four different 2:1 clay minerals under various degrees of Al substitution in the tetrahedral sheets with different concentrations of H_2SO_4 solution [61]. The solid acidity and SiO_2 content of clay minerals increased obviously after acid treatment, as confirmed by the analysis of weak acid site at about 200°C and strong acid site at about 250–300°C in the NH₃-TPD spectra. The results also showed that the solid acidity of vermiculite is better than phlogopite and montmorillonite, but poorer than saponite.

The acid activation efficiency of vermiculite can be improved by means of mechanical pretreatment, treatment with different acids, or the introduction of oxidants such as H_2O_2 . The fine grinding of the mineral before acid activation may cause fragmentation of the mineral. Several changes in its structure occurred: edges of the flocks became frayed; the surface cracked; cation exchange capacity (CEC) and specific surface area increased. Most of the iron in oligonuclear and bulk form was removed, so that less acid is required to achieve a good activation effect. The environmental impact of acid activation was minimized [62]. The grinding-associated acid activation could create more adsorption sites and thus enhance the adsorption capability of vermiculite. The vermiculite first treated with nitric acid and then with citric acid have maximum adsorption capacities of $100.8 \pm 0.8 \text{ mg/g}$ and $150 \pm 4 \text{ mg/g}$ for Astrazon Red and methylene blue, respectively, in column experiments, are all better than the adsorption capacity of raw vermiculite [63]. Egypt vermiculite was chemically activated by leaching with 0.5 mol/L HCl solutions or by treatment with 30% H₂O₂ solutions [64]. This leaching process of vermiculite with HCl solution results in partial transformation of its ordered layer structure into delaminated structure, while its treatment with H₂O₂ solution results in high separation and fragmentation of the layers with no structure change. The expansibility factors of raw and acid-activated vermiculite were determined to be 2.5 and 14.83, respectively, for samples activated by HCl and H_2O_2 .

The removal of metal cations in the octahedral sheets of vermiculite by a moderate acid leaching process facilitates the increase of the content of SiO₂ to different levels. Therefore, acid leaching usually has been used to produce silica nanosheets from natural vermiculite. The resultant twodimensional porous silicate materials by acid leaching of vermiculite have high surface area and excellent pore size, which can provide novel options for the application in functional material fields. The silica nanosheet was \sim 5.5 nm thick with a surface area of 505 m²/g, and has an average pore size of 1.8 nm as well as a pore volume of $0.406 \text{ cm}^3/\text{g}$ [65]. The selective leaching of vermiculite usually has been employed to produce high surface area silica. The acid leaching of vermiculite with 2 mol/L HCl solution at 80°C for 2 h produced a maximum value of surface area $(672 \text{ m}^2/\text{g})$ with total pore volume of 0.44 mL/g due to keeping of high concentration of micropores in the present vermiculite after leaching [17]. At the same time, the acid concentration and leaching time have a great influence on the porous properties of silica [65, 66]. For example, the acid-activation of vermiculite with 2mol/L HCl solution for 12h gave a maximum specific surface area of 764 m^2/g and zeta potential of $-38.9 \,mV$. The active groups (Si-OH groups) were also formed on the surface of silica nanosheets, which enabled it to be used as capable catalyst supports, adsorbents, and morphology-controlling reagents of nanomaterials.

9.4.2 Organification Modifications

9.4.2.1 Modification by Surfactants

Since vermiculite has negative surface charges and exchangeable cations, it is expected that organic molecules such as surfactants would expand its layers to make it easy to be intercalated or exfoliated, or alter the hydrophilic vermiculite to a hydrophobic one. The intercalation of vermiculite with different cationic or anionic surfactants has been comparatively studied [67]. It has been demonstrated that cationic surfactants covered the surface of the vermiculite with a second layer, but the expansion of the clay mineral layer was more limited compared to the anionic surfactant; the anionic surfactant produced electrostatic interaction with the positively charged edges of vermiculite, and thus fully expanded the layer structure of the vermiculite (Fig. 9.6). Moreover, the increase of interlayer spacing of vermiculite is dependent on the chain length of each surfactant.

Various aspects of intercalation of vermiculite with cationic surfactants have been widely concerned [68, 69]. The adsorption mechanism of Na-form of Kovdor vermiculite for trimethyloctylammonium (TMOA), decyltrimethylammonium (DTMA), and dodecyltrimethylammonium (DDTMA) cations from premicellar aqueous solutions of their bromides was studied [70]. The nonselective exchange of

TMOA cations with sodium ions occurs preferentially at the external surface of vermiculite. The adsorption of DTMA occurs by a mixed mechanism: some cations substitute the exchangeable Na⁺ ions in the vermiculite, while the others are sorbed in the form of salt. The DDTMA cations interact with the vermiculite by an ion-exchange mechanism with almost complete displacement of the Na⁺ ions from the exchange complex of the mineral. The intercalation of vermiculite with 16-19 wt% of cetyltrimethylammonium ions leads to an increase in the d_{001} space from 1.15 nm to 1.22–1.24 nm for the pure vermiculite [71]. The combination of thermal energy and mechanical energy may drive the cationic surfactants into the interlayer space of layers and thus carries out the cation exchange reaction [72]. The cetyl-trimethylammonium (CTA⁺)-intercalated Na⁺-exchanged vermiculite (Na-VMT) prepared by hot solution method (OVMT (H)) and a novel ball milling method (OVMT (M)) showed remarkably large interlayer spaces, in which alkyl chains-built paraffin-type bilayer arrangements nearly perpendicular to silicate layers. The interlayer distance of the OVMT (M) (4.283 nm) was larger than that of the OVMT (H) (4.052 nm), showing that the tilting angle of alkyl chains in the former was larger than that in the latter. Moreover, the interlayer spacing is related to the concentration of surfactants [73]. The basal spacing of vermiculite increased after being modified with surfactant (hexadecyltrimethyl ammonium bromide, HDTMAB), but the intercalation by surfactant into the interlayer space of vermiculite is not homogeneous. At low HDTMAB concentration, only part of the interlayer spaces of vermiculite was intercalated by surfactants; with the increase of surfactant concentration, more and more interlayer spaces were intercalated, reaching a "saturation" state at last (Fig. 9.7) [73]. However, vermiculite does not have an obvious protection effect on

Fig. 9.7 Structure and interlayer spacing of different amounts of HDTMAB intercalated vermiculite. Reproduced with permission from X. Su, L. Ma, J. Wei, R. Zhu, Structure and thermal stability of organo-vermiculite, Appl. Clay Sci. 132 (2016) 261–266.

the thermal stability of surfactants in the interlayer space due to the high value of interlayer height.

There are two notes regarding the modification of vermiculites that worth pointing out. Firstly, the modification of vermiculites with surfactants extends the interlayer space of the vermiculite and increases the interactions of vermiculite and polyvinylbutyral (PVB), leading to the increase of the elastic modulus of PVB. Secondly, vermiculite modified with anionic surfactant resulted in a better exfoliation and improved the mechanical and thermal properties compared with modification of vermiculite with cationic surfactant in PVB nanocomposites [74].

Gemini surfactants are a class of amphiphilic molecules containing two head groups and two aliphatic chains and they have recently attracted attention for modification of clay minerals [75, 76]. Gemini surfactants have been claimed to have many advantages compared to the conventional surfactants, such as low critical micellar concentration, better wetting, foaming, higher efficiency in reducing the oil/water interfacial tension and antibacterial activities [77]. The homoionic-vermiculites were modified with Gemini surfactant 1, 2-bis (hexadecyldimethylammonio) ethane dibromide (16-2-16), which filled the interlayer gap of vermiculite (Fig. 9.8) [78].

The comparative study of organo-vermiculite, organomontmorillonite, and organo-silica nanosheets functionalized by an ether-spacer-containing Gemini surfactant revealed that the Gemini surfactants in vermiculite (Vt), montmorillonite (Mt), and silica nanosheets (SiNSs) showed different arrangements [79] and the adsorption capacity of organo-vermiculite (298 mg/g) for Congo red is better than that of organomontmorillonite (154 mg/g) and organo-silica nanosheets (64 mg/g). In comparison with other Gemini surfactant-modified clay minerals, the Gemini surfactant-modified vermiculite (G-VER) exhibited the highest

Fig. 9.8 Intercalation by Gemini surfactant (16-2-16) into interlayer spacing of vermiculite. Reproduced with permission from W. Zang, M. Gao, T. Shen, F. Ding, J. Wang, Facile modification of homoionic-vermiculites by a gemini surfactant: comparative adsorption exemplified by methyl orange, Colloids Surf. A Physicochem. Eng. Asp. 533 (2017) 99–108.

removal rate (100%) against *C. marina* at the G-VER (21.1% Gemini) dosage of 6.5 mg/L and maintained good stability in sea water [80].

9.4.2.2 Modification With Silane

The loading of guest organic molecules onto some layered clay minerals that established an inorganic nanolayer through a surface grafting processes leads to formation of new organo-functionalized compounds. The acid-activated vermiculite was in turn modified by silane coupling agent, acrylamide (by a polymerization reaction), and grafted by triethylene tetramine to form an amine-functionalized adsorbent, which has the adsorption capacity of 219.4 mg/g for Pb(II) [81]. After the surface or interlayer modification, the vermiculite has a good compatibility with the polymer matrix and can be exfoliated in the polymer matrix or intercalated by polymer chains to form a polymer nanocomposite via a mechanical shearing and melt blending process. The vermiculite can be modified by organic cation intercalation (oleyl bis(2-hydroxyethyl) methyl ammonium) and silane grafting (glycidoxypropyl trimethoxy silane). Combination of silane grafting and alkylammonium cation intercalation obtains organo-vermiculite [82]. It has been proved that the exfoliation of vermiculite predominantly occurred in the nanocomposites containing 2.0 wt% of vermiculite; whereas intercalated structures together with exfoliated vermiculite were observed with high contents of organo-vermiculite. The double organification modification of the vermiculite resulted in a higher level of exfoliation, due to enhanced interactions between the end groups of the poly(l-lactic acid) and the organo-vermiculite containing the epoxy groups [82]. The vermiculite/polystyrene nanocomposites were prepared by dispersing a doubly organo-modified

Fig. 9.9 Schematic representation of the processes of preparing the DOVerm and the Verm/PS nanocomposites based on the DOVerm. (A) Verm. (B) Na⁺-Verm. (C) OVerm. (D) DOVerm. (E) Verm/PS nanocomposites. Reproduced with permission from L. Wang, X. Wang, Z.Y. Chen, P.C. Ma, Effect of doubly organo-modified vermiculite on the properties of vermiculite/ polystyrene nanocomposites, Appl. Clay Sci. 75–76 (2013) 74–81.

vermiculite (DOVerm) in polystyrene (PS) via in situ polymerization (mass/mass ratios of DOVerm/PS being 1/99, 3/97, 5/95, and 7/93). The morphology of Verm/PS nanocomposites evolved in three stages as the content of DOVerm decreased in the nanocomposites: intercalation at high filler content, intermediate state of intercalation to exfoliation, and exfoliation of vermiculite in PS matrix with low filler content (Fig. 9.9) [57]. The nanocomposites filled with 1 and 7 mass% of DOVerm exhibited more pronounced effects on the properties of vermiculite. At the same time, the double organo-modification clearly enhanced the ultimate properties of the vermiculite/ polystyrene nanocomposites [82].

9.4.2.3 Modification With Organic Monomers

Surfactants-intercalated vermiculite showed moderate hydrophobic properties and relatively larger interlayer spacing. Therefore, it is possible to be intercalated by organic monomer molecules further, and thus to prepare a new polymer nanocomposite with the intercalation or exfoliation structure of vermiculite by in situ polymerization of monomers in the interlayer space [83, 84]. It has been proved that the constraint effect of exfoliated vermiculite layers on polylactide chains is beneficial to the tensile strength, increased storage and loss modulus, tensile strength, and glass transition temperature [85]. Octadecylamine was intercalated into natural Mg-vermiculite (VER) by a low-temperature melting process [86]. At the lowest concentration (molar ratio of vermiculite: octadecylamine=2:1), the distorted octadecylamine molecules in the interlayer displayed a two-layer

arrangement; however, the octadecylamine molecules exhibited a different octadecylamine chain-disorder and interlayer-space saturation under increased concentration of octadecylamine molecules and treatment time. The interlayer octadecylamine molecules were hence inclined to the vermiculite basal plane with an inclination angle for two-layer arrangements ranging from 76 to 95 degrees, and correspondingly, the basal spacings varied from 5.2 to 5.8nm (for vermiculite: octadecylamine=1:2 and 1:6, respectively) [86]. The aminotriazole molecules can be intercalated into Mg-vermiculite at pH 4 with loading amount of 167meq/100g (almost 20% greater than the CEC of vermiculite), and the basal spacing was stabilized at 1.368 nm after 5 weeks of treatment with aminotriazole [87]. Part of the aminotriazole is exchanged with Mg²⁺ cations, and the rest is adsorbed in the form of molecules by coordination to the Mg²⁺ cations that remain in the interlayer. 4-vinylpyridine was intercalated into the vermiculite by the ion exchange reaction of 4-vinylpyridine in the gallery of copper(II) ion-exchanged vermiculite [88]. The in situ redox polymerization of 4-vinylpyridine produced a new poly(4-vinylpyridine)-intercalated vermiculite polymer nanocomposite material with the polymer content of ~18-19 mass%. The intercalated structure was confirmed by the increase in gallery spacing by 0.47nm. The exfoliated polypropylene-vermiculite nanocomposites can be prepared by melt blending of maleic anhydride-delaminated vermiculite with polypropylene, and it was noted that the moduli of nanocomposites tend to increase with increasing polypropylene-vermiculite content. The tensile strength of composite containing 8wt% vermiculite is higher than that of polyamide 6 [89]. By contrast, the in situ intercalative polymerization of monomers in the layer spaces of vermiculite makes it easier to exfoliate vermiculite or form an intercalated nanocomposite than the conventional physical processing method.

9.4.3 Ion-Exchange Modification

In addition to organic cations or molecules, inorganic polymers are also commonly used in intercalated vermiculite to improve their properties and thus their application. Vermiculite was modified with NaCl, CaCl₂, and MgCl₂ by an ion-exchange process. The $d_{(002)}$ reflection spacings of Na-vermiculite, Ca-vermiculite, and Mg-vermiculite corresponding to different salt solution modifications are 1.223, 1.474, and 1.448 nm, respectively. The as-obtained vermiculite modified by NaCl solution can lower the temperature where expansion begins, whereas the vermiculites modified by CaCl₂ and MgCl₂ solutions have a high expansion ratio. It was revealed that electrostatic attraction force between interlayer cations and interlayer water molecules are the key factors affecting the expansion ratio of vermiculite [90].

Replacing the exchangeable interlayer ions in Palabora vermiculite with magnesium, aluminum, or iron (III) ions does not affect the exfoliation onset temperature $(456 \pm 11^{\circ}\text{C})$. However, cointercalation of vermiculite with minor amounts of urea lowers the exfoliation onset temperature to $209 \pm 35^{\circ}\text{C}$. This significant decrease is attributed to the low thermal stability of urea, which releases ammonia and water as blowing agents [91]. Polyhydroxy iron cations were intercalated into vermiculite to increase the interlayer spacing, and then the removal capacity of vermiculite was enhanced to 93% for Se(IV) in $1.0 \,\mu$ mol/L solution (250 mL) after 5 min of contact time with 625 mg of adsorbent by an adsorption process, with the adsorption capacity of $47 \pm 5 \,\mu$ mol/g ($3.7 \pm 0.4 \,\text{mg/g}$) ($R^2 = 0.97$) [92].

9.5 Applications of Vermiculite

To sum up above discussion, vermiculite has a special twodimensional layer structure, cation exchange capacity, active surface group, thermal stability, thermal expansion properties, and eco-friendly advantages. Therefore, it has been substantially employed in the fields of adsorption, cultivation substrate in agriculture, catalyst carrier, thermal resistance material, friction material, and many other related industries. With the development of nanoscience and nanotechnology, the application of vermiculite as a natural two-dimensional nanomaterial for fabricating functional materials has received more and more attention, and its potential fields of application have also evolved from traditional agricultural, environmental, and carrier applications to energy, biomedicine, special protection materials, antibacterial, polymer composite materials, and other areas that demand its special properties. This section focuses on the research progress of the application of vermiculite materials as functional materials in various areas.

9.5.1 Adsorption

9.5.1.1 Adsorption of Heavy Metal lons

Vermiculite has a large specific surface area, a surface negative charge, and a high cation exchange capacity, which grants it excellent adsorption ability toward heavy metal ions [2, 93–96]. In recent years, researchers have evaluated the adsorption properties of natural vermiculite minerals from various countries and regions for different heavy metal ions. The natural vermiculite from the Askos area (northern Greece) has the adsorption capacities of 32.68 mg/g for Cu(II) and 37.85 mg/g for Ni(II) (initial concentration, 250 mg/L; pH 5.1 for Cu(II) and 4.85 for Ni(II); adsorbent dosage 1 g/L), and the adsorption process is pH-dependent [97]. The raw vermiculite had the adsorption capacity of 73 mg/g for Ag(I) and 117 mg/g for Cu(II), and the adsorption

process is spontaneous and endothermic [98]. The major mechanism of adsorption of metal ions (e.g., Ni(II)) onto vermiculite is as follows: alkali cations enter the interlayer of vermiculite and cause the collapse of the vermiculite interlayer to various extents due to the different ionic radii and hydrated energies [99]. The total adsorption capacity of vermiculite with respect to different metal ions was found to decrease in the following order: Mn > Ni > Zn > Cd > Cu > Pb, and the adsorption capacities decreased with decreasing pH and increasing ionic strength [100]. The formation of stable metal ions-ligand complexes in solution hinders the adsorption of the metal ions on vermiculite, and the metal adsorption increases in the order of $Cu^{2+} < Ni^{2+} < Zn^{2+}$ $\leq Pb^{2+} < Cd^{2+} < Mn^{2+}$ in the presence of ligands [100]. The total adsorption capacity of vermiculite increases in the following order: Mn^{2+} (26.78 mg/g) > Ni²⁺ (25.33 mg/g) > Zn²⁺ (23.4 mg/g) > Cd²⁺ $(37.71 \text{ mg/g}) > Cu^{2+}$ $(20.61 \text{ mg/g}) > Pb^{2+}$ (64.1 mg/g). Mechanisms including cation exchange at the planar sites, the inner-sphere complexes through SiO- and AlO- groups at the vermiculite particle edges are the main contributors to the adsorption [100]. The interaction of vermiculite with urea metal complexes $\{[Cr(Urea)_{6}]^{3+}$ and $[Al(Urea)_{6}]^{3+}$ was studied [101], and it was found that the vermiculite treated with $[Al(Urea)_6]^{3+}$ exhibited a complete adsorption of the complex at room temperature, while the vermiculite treated with $[Cr(Urea)_6]^{3+}$ only showed a partial exchange. In addition, vermiculite was also a low-cost and eco-friendly adsorbent for removal of rare metals such as Cs(I), Sr(II), Eu(III), and Am(III) from aqueous solutions to manage radioactive liquid wastes, and the tested removal rate was in the desending order: Cs(I)- Sr(II) (both about 95%) > Am(III) (about 90%) > Eu(III) (about 80%) [102]. The dynamic adsorption behavior of vermiculite for Cu(II) and Zn(II) in binary system was evaluated, and the optimum flow rate was obtained at 7 ml/min. Zn(II) was better removed than Cu(II) in binary dynamic system [103]. After adsorption, the adsorbed metal ions such as Cs⁺ and Ce³⁺ can be desorbed by exchange with Mg^{2+} ions [104], ammonium ions [105], or sea water by a hydrothermal process [106].

The moderate mechanical treatment, acid treatment, alkaline treatment, organification, nanocomposite and intercalation modification of vermiculite have been proved to be effective to improve the adsorption capacity of vermiculite toward heavy metal ions. In contrast to raw vermiculite, the grinded vermiculite shows an increase of 19% of the maximum adsorption of Mn^{2+} . Ultrasonic milling of vermiculite in aqueous dispersion at 20 kHz allows the increase of adsorption capacity by 31%. The sonication of the vermiculite dispersed in 35% hydrogen peroxide allowed it to obtain a maximum adsorption uptake of 36.77 mg/g (30% of increase compared to raw vermiculite) because the mechanical treatment reduced the size of particles and increased the surface

active sites in the edge layer [40]. The mechanochemical treatment of vermiculite using a vibration mill led to a reduction in the particle size and a significant increase in the surface area, surface hydroxyl (silanol, magnesiol, and aluminol) groups, and amorphous silica phase, which gave a dramatic improvement in the lead(II) adsorption capacity [107]. The vermiculite modified with acid, base, and combined acid/base treatment had good adsorption capacity for Cu²⁺, and the vermiculite treated by alkaline was a good adsorbent for metal ions and also an effective adsorbent for dyes [108]. The acid-activated and oxidation-treated Egypt vermiculite by leaching with 0.5 mol/L HCl solution or treating with 30% H₂O₂ solution showed higher adsorption capacity for heavy metal ions than raw vermiculite, and the removal efficiency of peroxide-activated vermiculite was higher than that of the acid-activated vermiculite for both cadmium and leadions [64]. Grafting of β-Cyclodextrin onto KH560-modified vermiculite enhanced its adsorption capacities to 2.246 mg/g for Cr(VI) and 0.918 mg/g for phenol [109]. Modification of vermiculite by coating chitosan onto vermiculite (without intercalation) and then crosslinking with epichlorohydrin produced a new adsorbent with improved adsorption capacities of 58.48 mg/g and 166.67 mg/g for Cd(II) and Pb(II), respectively, as the -NH₂ groups of chitosan have relatively stronger electrostatic attraction and chelation interaction with metal ions [110]. The chitosanmodified vermiculite (C-mVMT) has good adsorption properties for As(III) ions with the maximum adsorption capacity of 34.9 and 72.2 mg/g for raw vermiculite and C-mVMT sorbents, respectively, while exhibiting decent reusability performance [111]. Ultrasound assistance may promote the intercalation of vermiculite with chitosan and partial exfoliation of layers, which provided vermiculite a high adsorption capacity for Cd(II) ions from aqueous solution [112]. The Na⁺-exchanged vermiculite (Na-VT) modified with the thiols-containing modifiers including l-cysteine (CYS-VT), cysteamine hydrochloride (CTA-VT), and (3-mercaptopropyl) trimethoxysilane (3-MPS-VT) have the adsorption capacities of 83 ± 30 , 57 ± 4 , 21 ± 2 and $18 \pm 1 \mu \text{mol/g}$ (n=3) for CTA-VT, CYS-VT, 3-MPS-VT, and Na-VT, respectively, due to the strong binding of Hg(II) to the incorporated thiols [113]. The grafting of dimercaprol (BAL), containing thiol and hydroxyl groups, onto the natural vermiculite produced an adsorbent for Hg(II), with the maximum adsorption capacity of 8.57 mg/g for BAL-Vm. It was revealed that the adsorption of Hg(II) on the adsorbent mainly depend on the ion exchange, electrostatic attraction, and chemical complexing action [114]. The adsorption capability of vermiculites regarding to Hg(II) ions was improved significantly by functionalization with mercaptoethylamine (MPTMS) and mercaptopropyltrimethoxysilane (MEA). The adsorption capacities were in the order of MPTMS-vermiculite > MEA-vermiculite > Vermiculite (286.29, 176.33, and 99.95 µg/g, respectively) [115].

Loading of oxides or other inorganic components onto vermiculite is also exceedingly effective to improve its adsorption for heavy metal ions. The hierarchical MgAl-layered double hydroxide (MgAl-LDH)/ vermiculite (VMT) composite exhibits higher sorption-regeneration performance for Cr(VI) than traditional MgAl-LDH, as the specific surface area and transfer channel are significantly improved due to its porous 3D framework [116]. The iron oxide-vermiculite displayed better synergism effect on the competitive adsorption of Ni(II) and Cu(II) than raw vermiculite, with the maximum adsorption capacities of 53.1 and 59.7 mg/g for Cu(II) in single and binary systems and 94.6 and 101.3 mg/g for Ni(II) in single and binary systems, respectively [117].

The magnetic vermiculite adsorbent with superparamagnetic property and higher specific surface areas $(52.6 \text{ cm}^2/\text{g})$ which was prepared by introducing Fe₃O₄ component, showed fast adsorption rate and high adsorption capacity of 70.4 mg/g (as contrasted to only 37.0 mg/g for raw vermiculite). The magnetic vermiculite can be easily and fleetly separated using a magnet after adsorption [118]. The manganese oxide-modified vermiculite (Mn-MV) showed the maximum adsorption capacity of 69.2 mg/g for Ag(I) (as contrasted to only 46.2 mg/g for raw vermiculite), and 95% of the Ag(I) ions adsorbed was desorbed successfully from the sorbent surface by using 10 mL 0.5 mol/L HCl solution. This provides evidence that the adsorbent can be reused for at least for another 10 adsorption-desorption cycles [119]. The adsorption energy was calculated to be 9.6 kJ/mol, and the adsorption process is feasible, spontaneous, and exothermic. The chemical ion exchange and the increase of adsorption surface (about 10 times higher than raw vermiculite) after modification provides major contribution to the improved adsorption capability. The $ZrO(OH)_2$ nanoparticles sized between 5–20 nm were loaded on the vermiculite to prepare a reusable vermiculite-based hydrated zirconium oxide (ZrO(OH)₂/VMT) nanocomposite, which displayed a high adsorption capacity of 90.21 mg/g for Ni(II) and can be used for Ni(II) removal from electroplating wastewater [120].

In addition to the adsorption of heavy metal ions in solution, the vermiculite materials were also capable for the immobilization of heavy metals in soil. It has been proved that the addition of vermiculite significantly reduces the uptake amounts of metal pollutants (i.e., Al, Cd, Cu, Cr, Fe, La, Mn, Ni, Pb, Sc, Ti, V, Y, Zn, and Zr) by plants. This finding provides evidence that this clay is qualified to be used in amendment treatments of metal-contaminated soils [121].

9.5.1.2 Adsorption of Dyes

The special cation exchange capability, interlayer spacing, porous structure, and active surface groups of vermiculite enable it to form stronger affinities with dye molecules and thus capture them from a

water solution. The raw vermiculite, raw expanded vermiculite, and expanded vermiculite showed different adsorption capacities for C. I. Basic Red 9 dye of 6.016×10^{-5} , 6.890×10^{-5} , and 7.66×10^{-5} mol/g [122]. In comparison with clinoptilolite, vermiculite removes dye more effectively at a faster rate. Nearly 91% of dye was removed at 10 mg/L initial dye concentration with the adsorbent concentrations above 5.0 g/L [123]. The adsorption of vermiculite for dyes was also influenced by the molecular structure of dyes [124]. For example, the dye crystal violet has the same ionic charge (+1) with methylene blue, but its triangular molecular structure is different from the linear molecular structure of methylene blue. The maximum adsorption capacity of methylene blue on vermiculite at 25°C decreased from 0.076 to 0.053 mmol/g. The initial concentration (C_0) increased from 0.3 to 0.5 mmol/L. The adsorption isotherm does not obey the Langmuir model, but the adsorption of CV on vermiculite showed a typical Langmuir isotherm with a R^2 of 0.99 at 25°C. This is because the linear structure of the methylene blue molecule can cause the "adsorbateadsorbate" steric effect more easily as compared to crystal violet [124].

The modification of vermiculite with different physical or chemical approaches proved to be helpful to improve the adsorption properties. The fine grinding-assisted acid activation treatment with 1 mol/L HNO₃ solution may enhance the meso- and microporosity, thus lead to an increase in the total volume of pores, and then may increase the adsorption capacity of vermiculite for Astrazon Red from 55 ± 7 to $136 \pm 7 \text{ mg/g}$. Such treatment can result in higher adsorption capacity at a given acid concentration compared to the rough ground material [62]. Additional treatment of acid-activated vermiculite with NaOH solution results in an obvious increase of adsorption capacity in contrast to the increase of the samples modified with only acid (first step of activation) with respect to raw material. The adsorption capacity of modified vermiculite, based on column studies, increased from 48 ± 2 to $203 \pm 4 \text{ mg/g}$ for methylene blue and from 51 ± 1 to $127 \pm 2 \text{ mg/g}$ for Astrazon Red dye. The adsorbents worked efficiently in seven adsorption-regeneration cycles [125].

The moderate organification modification of vermiculite may improve its hydrophobic properties and adsorption capacity toward anionic dyes such as congo red [79], and the organovermiculite showed the best adsorption capacity of 298 mg/g, which is much better than that of organo-montmorillonite (154 mg/g) and organo-silica nanosheets (64 mg/g). The order of adsorption capacities is consistent with the sequences of the layer charge and the hydrophobicity of particles is characterized by Lipophilic to Hydrophilic Ratio (LHR). The adsorption process is endothermic and spontaneous, which further proved the importance of hydrophobic interaction of CR adsorption with organo-clays (Fig. 9.10).

Fig. 9.10 The proposed structure of surfactant-modified vermiculite (BDEE-Vt), montmorillonite (BDEE-Mt), and silica nanosheets (BDEE-SiNSs), and the adsorption process for Congo red. Reproduced with permission from F. Ding, M. Gao, T. Shen, H. Zeng, Y. Xiang, Comparative study of organo-vermiculite, organo-montmorillonite and organo-silica nanosheets functionalized by an ether-spacer-containing gemini surfactant: congo red adsorption and wettability, Chem. Eng. J. 349 (2018) 388–396.

The homoionic-vermiculites modified with Gemini surfactant 1, 2-bis (hexadecyldimethylammonio) ethane dibromide (16-2-16) (Fig. 9.8) exhibited higher removal efficiencies toward Methyl Orange and in the order of organovermiculite-Li>organovermiculite-Na> organovermiculite- K > organovermiculite [78]. The adsorption processes of organovermiculite toward Methyl Orange all fitted well with pseudo-second-order, Freundlich isotherm and endothermic processes in nature. Therefore, not only do these findings bring new lights to the high-efficiency and cost-effective adsorbent, especially organovermiculite-Li and organovermiculite-Na, they also provide theoretical guidance for the modification of vermiculite with gemini surfactant to fabricate high-efficiency adsorbents [78]. In addition, other organic molecules such as ethylenediamine-modified vermiculite with the ethylenediamine dosage of 0.2 mol/L which behaved as a good sorbent for anionic dye, displayed good adsorption capacity of 11.02 mg/g for Remazol Brilliant Blue RN [126].

The vermiculite can be compounded with inorganic adsorbent as well to improve its adsorption properties and applicability. A new hybrid vermiculite-hydrotalcite-like layered double hydroxide (LDH) was prepared by a sustainable strategy, which presented good adsorption capacities of 238 ± 3 , 111 ± 2 , 44 ± 1 and 70 ± 1 mg/g for Congo red, Reactive Red 184, Astrazon Red, and Cu²⁺, respectively, and a strong synergic effect on adsorption was observed in the hybrid materials [127]. By virtue of the higher stability and better safety, the inorganicinorganic hybrid adsorbents would attract much more attention in the field of environmental remediation.

9.5.1.3 Adsorption of Pharmaceuticals or Antibiotics

In recent years, the abuse of antibiotics has caused a serious environmental crisis. Therefore, the removal of pharmaceuticals or antibiotics from polluted waterneed to acquire more attention. Vermiculite has decent cation exchange capacity and surface active sites and is able to also be modified easily to alter the surface charge, hydrophilicity, and surface groups. As a result, vermiculite has been considered as one of the most efficient adsorbent for removal of pharmaceuticals or antibiotics as more attention are drawn to this area. The phosphatidylcholine-intercalated vermiculite (PC-VER) was prepared for the removal of oxytetracycline (OTC) and ciprofloxacin (CIP) from aqueous solution [128]. The maximum adsorption capacities of the PC-VER adsorbent for the antibiotics are 66.40 mg/g for OTC and 93.72 mg/g for CIP [128]. The electrostatic attraction, surface complexation, hydrogen bonding, and hydrophobic interaction are the main contributors to the improvement of adsorption capacity (Fig. 9.11). The vermiculite intercalated by inorganic Fe(III) polymers with different [OH⁻]:[Fe(III)] ratios was proved to be an efficient adsorbent for pharmaceuticals or antibiotic molecules [129]. In comparison to the potassium-saturated vermiculite, the inorganic Fe(III) polymers-intercalated vermiculite displayed better adsorption capability of atrazine and its metabolites deethylatrazine, deisopropylatrazine, and hydroxyatrazine (ATOH) from their aqueous solution. Almost 80% of atrazine and deisopropylatrazine were removed at the lowest initial concentrations [129]. The base-treated, raw, and expanded vermiculites showed lower maximum adsorption capacities of 6.3 ± 0.5 , 5.8 ± 0.7 , 3.9 ± 0.2 mg/g, respectively, as compared to the acid/basetreated material $(33 \pm 4 \text{ mg/g})$ for the removal of venlafaxine [130]. The cetyltrimethylammonium ions-intercalated vermiculite may remove the hazardous hormone molecule ethinylestradiol more effectively than raw vermiculite, and showed a high adsorption capacity of 6.5-9.3 mg/g [71]. The hydrophobic cavities formed by the C18 chains of the cetyltrimethylammonium molecules in the vermiculite interlayer space are responsible for the sorption of ethinylestradiol molecules. Tri et al. [131] revealed that the adsorption of chloramphenicol onto the surface of vermiculite is a strong chemisorption process, and was characterized by the adsorption energy of -106.5 kcal mol⁻¹ at the most stable configuration. Stability of configurations was contributed mainly by Mg...O/Cl attractive electrostatic interactions and C/OH...O hydrogen bonds, which confirmed vermiculite is a solid material that can be potentially used for adsorption and subsequent removal of this type of antibiotic drugs.

The adsorption capacity of exfoliated vermiculite to gemfibrozil, mefenamic acid, and naproxen was evaluated in lab-scale batch assays. The vermiculite adsorbents are able to remove these pharmaceuticals from an aqueous medium with high adsorption capacities. It was predicted by quantum chemistry calculations that the forms of binding of the three kinds of molecules to the vermiculite surface should be

Fig. 9.11 Schematic illustration of the mechanism for the adsorption of OTC and CIP onto VER and PC-VER. Reproduced with permission from S. Liu, P. Wu, L. Yu, L. Li, B. Gong, N. Zhu, Z. Dang, C. Yang, Preparation and characterization of organo-vermiculite based on phosphatidylcholine and adsorption of two typical antibiotics, Appl. Clay Sci. 137 (2017) 160–167.

essentially identical. However, the adsorption isotherm of naproxen differs substantially from that of the other two's. The linear forms of naproxen impose limits at lower concentrations to the removal efficiencies of these pharmaceuticals by vermiculite [132].

9.5.1.4 Adsorption of Other Organic Molecules

Beside the dyes or antibiotics covered previously, the vermiculite-based adsorbents are able to adsorb other organic molecules such as benzoic acid and Di-(2-ethylhexyl) phthalate. To achieve good equilibrium adsoption capacity of benzoic acid, adsorbent was

prepared by grinding natural vermiculite in a laboratory vibratory disk mill and the surfactant modification of ground vermiculite was carried out by cetyltrimethylammonium bromide [133]. The cetyltrimethylammonium bromide may improve the adsorptive characteristics of ground vermiculite for benzoic acid more as compared to cetylpyridinium bromide, both at the optimum conditions: adsorbent dosage of 0.5 g/50 mL, initial pH of 3.5, and contact time of about 140 min [134]. Theoretical study by a mathematical model was carried out to figure out the adsorption behavior of modified vermiculite for benzoic acid, and provided consistent results with the experiments where the effective diffusivity of benzoic acid was estimated as $0.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. At the same time, grinding treatment enhanced the ion exchange ability of natural vermiculite. The pseudo-second-order model provided a close correlation of the kinetic data and the equilibrium data were well described by the Langmuir and Temkin equations. Thermodynamically, it was concluded that the process is endothermic and spontaneous [135]. The adsorption study of Di-(2-ethylhexyl) phthalate onto vermiculite indicated that Di-(2-ethylhexyl) phthalate molecules were adsorbed on the surface of vermiculite in a monolayer and the acting force was mainly from hydrophobic interactions. The process of DEHP adsorption to vermiculite was strongly pH-dependent, and extreme acidity (pH 3) inhibited adsorption. The adsorption process was exothermic and spontaneous [136].

The magnetic fluorinated vermiculite by cationic fluorinated surfactant can selectively and rapidly adsorb perfluorooctanesulfonate (PFOS) from model fire-fighting foam wastewater. In this experiment, its maximum adsorption capacity was shown to be 1127 mg/g (2.26 mmol/g), and the hybrid adsorbent with C–F chains in the interlayer space still keep the hydrophobic fluorinated interlayer structure. Moreover, the loaded Fe₃O₄ nanoparticles enable the adsorbent to be separated by a magnet (Fig. 9.12) [137]. The desorption percentages of PFOS reached a level of nearly 100%, except for the first elution. Meanwhile, the removal of PFOS dropped from 68.9% to 61.8% after the first regeneration and remained relatively steady in the subsequent 4 cycles. These results give rise to the possibility of applying vermiculite for PFOS removal from real wastewater.

9.5.1.5 Adsorption of Ammonium and Phosphates

Ammonia and phosphates have adverse impacts on the ecosystem, especially water environment due to their aquatic biota toxicity, conduciveness to eutrophication, and oxygen-consuming nature in nitrification processes. Both ammonia molecules (NH_3) and ammonium ions (NH_4^+) that exist in aqueous phase are harmful to the eco-system and human health. So, the removal of ammonium is vital and high standard is set (<5mgN/L in China) for wastewater discharge. Vermiculite is a common layered silicate clay mineral that has excellent adsorption and

Fig. 9.12 The adsorption mechanism and removal efficiency of the hydrophobic vermiculite for perfluorooctanesulfonate. Reproduced with permission from Z. Du, S. Deng, S. Zhang, W. Wang, B. Wang, J. Huang, Y. Wang, G. Yu, B. Xing, Selective and fast adsorption of perfluorooctanesulfonate from wastewater by magnetic fluorinated vermiculite, Environ. Sci. Technol. 51(14) (2017) 8027–8035.

ion-exchange properties and has thus been used for removal of ammonium or phosphate pollutants from wastewater. Chinese vermiculite (from Heibei Province, China) with the particle-size ranged from 0.025-0.075 mm has the adsorption capacity of 18 mg/g for ammonium in lowconcentration solution after 3h of adsorption at the optimal adsorption pH (in the range of 6–7) and temperature (at 60°C) [138]. It has been revealed that the mechanism for ammonium uptake from low-concentration solutions was cation exchange. Simulated groundwater containing NH₄⁺ and humic acid was treated by vermiculite and palygorskite in a column, and it was found that the NH₄⁺ removal efficiencies were significantly different among the three column settings; NH₄⁺ was mainly adsorbed on the vermiculite layer [139]. The presence of organic acids or metal ions significantly decreased the adsorption of NH_4^+ by vermiculite adsorbents. The influence of organic acids on adsorption capacity followed the order of citric acid > malic acid > oxalic acid; meanwhile, the influence of metal ions on decreasing the adsorption of NH₄⁺ toward the ion exchange selectivity were in the orders of Mg>Ca \geq K>Na and Mg>>Ca>Na>K, respectively [140]. The adsorption of NH₄⁺ by vermiculite adsorbents showed the total recovery rate of adsorbed NH_4^+ of 94.6% [140].

The ammonia removal as well as the current efficiency during electrolysis was studied using a vermiculite-packed electrochemical reactor under continuous mode. The adsorption of ammonia by vermiculite and electrolytic desorption of ammonia existed simultaneously in the reactor, leading to 89% removal of initial 30 mgN/L ammonia and current efficiency of 25% under the condition of 2.0A, 6.0min hydraulic retention time with 300 mgCl/L chloride as the catalyst [141]. The treatment results of secondary effluent indicated that 29.9 mgN/L ammonia can be reduced to 4.6 mgN/L with 72% removal of total nitrogen and a current efficiency of 23%, which was 2% less than synthetic wastewater due to the reducing components in the real wastewater [141]. The vermiculitederived adsorbents can also be used to remove phosphate from aqueous solution. The vermiculite treated by algal biomass was converted to SiO₂biochar nanocomposites by a pyrolysis process, gaining ability to better remove phosphate from aqueous solution than the unmodified biochar, due to the SiO₂ particles on the carbon surface that served as sorption sites through electrostatic interactions [142]. In addition, SiO₂-biochar nanocomposites could be effectively regenerated by NaOH solution. The floating adsorbents with EV/glycerol ratio of 1/4 were made from exfoliated vermiculite (EV) at calcinations temperature of 380°C, which showed the specific surface area of 58.6 m²/g, carbon content of 62.2%, and the highest Langmuir sorption capacity of phosphate (714.3 mg/kg) [143]. Due to the strong affinity of La with phosphate, the La(OH)₃-modified exfoliated vermiculites were used to remove phosphates with a maximum adsorption capacity of 79.6 mg P/g at 25°C. 97.9% of final adsorption capacity was reached the synthetic wastewater in 10 min [144]. Its adsorption was pH-dependent and little affected by competitive ions, and the spent adsorbent could be regenerated and reused for phosphate adsorption.

9.5.1.6 Adsorption of Oils or Organic Solvents

The in situ carbonization of organic matters which were then attached on the surface or intercalated in the interlayer spacing of vermiculite is an emerging method to modify the surface properties of vermiculite. The "sponge-like" carbon nanostructures-modified vermiculite was produced by a chemical vapor deposition process from ethanol in the presence of Fe/Mo catalysts at 600, 700, 800, and 900°C. It was proved that the FeMo catalyst promoted 2%-3% growth of carbon nanofibers on the expanded vermiculite surface, and the absorption of the product for soybean, diesel, and engine oil increased by around 500% with the introduction of only 2%-3% carbon species by ethanol/CVD process [145]. The sponge-like exfoliated vermiculite/ carbon nanotube (CNT) hybrids with different CNT contents (from 11.4% to 94.8%) were prepared by intercalating aligned CNT arrays into natural vermiculite layers. The oil adsorption capacities was found out to be 26.7 g/g for diesel oil at the CNT content 91.0%, due to significant amount of pores produced by intercalated growth of aligned CNT [146]. The intercalation by organic molecules such as glycerol into expanded vermiculite which were then treated by carbonization produced a highly efficient absorbent to remove spilled oils in water (i.e., diesel, soybean, and engine oil spilled on water). Oil removal efficiency was enhanced by 600% in contrast to expanded vermiculite [147]. The expanded vermiculite (EV) was impregnated with glycerol (Gly) at EV/ Gly ratios of 1/2, and treated at 700°C to form carbon-covered vermiculite whose optimal adsorption capacity was 5.4 g/g for soybeans [148].

9.5.1.7 Adsorption of Other Substance

Emission of CO_2 is considered as one of the major causes for the greenhouse effect. In order to prevent any adverse effects that could potentially be caused by greenhouse gases, especially CO_2 , new technologies for CO_2 capture, storage, and utilization are highly demanded [149]. The Li₄SiO₄-based high-temperature CO_2 sorbent was prepared directly from the expanded vermiculite, which displayed much improved CO_2 sorption/desorption cycling stability (Fig. 9.13) [150]. After adsorption, the CO_2 concentration decreased substantially from 100 to 20 vol%. The CO_2 sorption capacity of Li₄SiO₄-(EXVMT)-4 only slightly decreased from 19.4 to 18.6 wt%, but the capacity for Li₄SiO₄ synthesized from pure SiO₂ decreased significantly from 22.0 to 11.3 wt% after 10 time cycles. Therefore, the VMT-derived Li₄SiO₄-based high-temperature CO_2 sorbent is especially promising for practical application.

Boron is a vital element for plants, animals, and humans, but extensive damage to the environment and wide-ranging health problems are caused by diverse boron applications. Adsorption is thus crutial where boron-selective adsorbents were employed to treat solutions with minimal concentration of boron [151]. The micron-grade natural vermiculite modified by grafting of a specific boron complexant (i.e., *N*-methyl-D-glucamine: NMDG) bared a high adsorption capacity of 0.04 mmol/g for boron at low initial concentrations of the aqueous solutions ([B] \approx 5 mg/L) [152]. The micron-grade vermiculite from Palabora (South Africa) modified by thermal shock (700°C), chemical exfoliation (80°C in the presence of H₂O₂), and ultrasonic treatments (20 kHz, H₂O or H₂O₂) showed an increase in adsorption of boron from

0.015 mmol/g for raw vermiculite to 0.151 mmol/g for modified one, resulting from the change of particle morphology, the reduction of particle size, and a modification of the surface (pH of the vermiculites and number of OH surface groups by titrations) [50].

9.5.2 Catalysis

Catalyst supports have critical effects on catalyst performance. Clay mineral matrices and metal oxides are of current interest because of their high thermal stability, large surface area, excellent adsorption abilities and decent catalytic properties. The activated vermiculite can be directly used as a catalyst due to its active Lwis acid or base sites [153]. However, the activity of raw vermiculite is limited. In order to solve this issue, vermiculite has usually been used as a support to fabricate various composite catalysts used in gas phase, liquid phase, or solic phase reactions, for catalysis degradation of pollutants in the environment, and catalysis synthesis and conversion of chemicals.

9.5.2.1 Catalysis for Environmental Protection

The energy band gap (Eg) of vermiculite is less than 4 eV, so it is possible to behave as semiconductor materials and act as photoactive materials in the presence of UV radiation. The simultaneous degradation of sulfamethoxazole (SMX) and trimethoprim (TMP) by UV and solar-light radiation was achieved using vermiculite as a photocatalyst. The reaction rate constant for SMX and TMP degradation in UV radiation was increased by 11.4 and 46.4 times, respectively, when 10 mg of vermiculite were added to the UV system due to the higher percentage of doping ions in the vermiculite (Fig. 9.14) [154]. The photo-degradation of a low-concentration $(100 \mu g/L)$ mixture of trimethoprim (TMP), sulfamethoxazole (SMX), carbamazepine (CBZ), and diclofenac (DCF) was achieved by a solar-advanced oxidation process using vermiculite as photoactive catalyst [155]. At the optimal dose of vermiculite of 0.2 g/L, the photodegradation efficiency using vermiculite as catalyst decreased in the following order: DCF>SMX>TMP>CBZ. The degradation rate constants for the four materials increased by 9.05, 18.9, 2.08, and 23 times, respectively, by adding H_2O_2 ($[H_2O_2] = 200 \text{ mg/L}$), with the DOC (dissolved organic carbon) removal percentage of 48%. The percentage removal of DCF and SMX using vermiculite as a catalyst was similar to that of TiO_2 [155]. The cerium oxide (CeO₂) nanoparticles (size 8.5 ± 0.5 nm)loaded vermiculite composite catalyst showed the specific surface area of $62 \text{ m}^2/\text{g}$, the micropore volume of $0.3928 \text{ cm}^3/\text{g}$, average pore diameter of 58.5 nm, and more active photocatalysis properties than commercial catalyst Evonik P25, which can decompose N₂O under UV irradiation with the conversion efficiency of 53.3% at the CeO₂ loading

Fig. 9.14 A schematic illustration for the catalysis degradation of organic pollutants by photocatalysis reaction process under sunlight by using a vermiculite-based catalyst. Reproduced with permission from J.I. Martínez-Costa, J. Rivera-Utrilla, R. Leyva-Ramos, M. Sánchez-Polo, I. Velo-Gala, Individual and simultaneous degradation of antibiotics sulfamethoxazole and trimethoprim by UV and solar radiation in aqueous solution using bentonite and vermiculite as photocatalysts, Appl. Clay Sci. 160 (2018) 217–225.

amount of 36 wt% [156]. In addition to the gas-phase reaction, the floating vermiculite/TiO₂ (20 wt%) catalyst prepared by impregnation of Ti(OCH(CH₃)₂)₄ on exfoliated vermiculite (EV) followed by hydrolysis with HCl/H₂O vapor and calcination exhibited good photocatalysis activity for the photocatalytic degradation of dye pollutant in an aqueous solution [157].

Due to the excellent thermal stability, vermiculite was considered as a potential supporter to fabricate composite catalysts with decent activity to eliminate nitrogen oxides. The acid-activated vermiculites could be used as selective catalysts for the DeNO_x process (4NO + $4NH_3 + O_2 = 4N_2 + 6H_2O$), and the vermiculite activated with nitric acid (0.8 M) at 95°C for 24 h achieved the best catalytic activity. The highest NO conversion was reached for acid-activated vermiculite (V24) at 500-550°C. At even higher temperatures, the effectiveness of the DeNOx process was limited by the side reaction of ammonia oxidation [158]. Nevertheless, vermiculite treated with HNO₃, HCl, and H₂SO₄ solutions is still highly-efficient catalysts for high-temperature decomposition of N₂O to N₂ and O₂, especially the HNO₃-treated vermiculite may achieve the 100% of N₂O conversion at about 900°C when it is used as the catalyst [159]. However, the performance of the catalysts can be further enhanced. Vermiculites intercalated with alumina pillars and modified with transition metals (Cu, Fe) was proved to be better catalysts for the selective reduction of NO in the presence of

ammonia (DeNO_x process) in comparison with acid-treated vermiculite [160]. It was also found out that the Cu-containing catalyst was more active at lower temperatures than the pillared clays modified with iron; and transition metals-modified alumina-pillared vermiculites were deemed to be active, selective, and stable catalysts of the DeNOx process [160]. The porous clay heterostructures (PCH) based on vermiculite have better catalytic activity for selective reduction of NO with ammonia than PCHs based on montmorillonite and saponite because vermiculite has relatively higher content of iron and titanium [161]. The catalytic activity of PCH can be enhanced further by the deposition of transition metals (Cu, Fe) on it, and the PCH-Sap-Fe catalyst was able to convert more than 90% of NO with the high selectivity to nitrogen in the temperature range of 350–500°C [161]. The efficient selective catalytic reduction of NO_x by ammonia (NH_3 -SCR) was achieved using the $MnO_x/vermiculite$ (VMT) and $MnO_x-Fe_2O_3/VMT$ as catalysts [162]. The MnO_x-Fe₂O₃/VMT (mainly composed of MnO₂ and Fe_2O_3) catalysts provided an excellent NO conversion rate of 96.5% at 200°C with a gas hourly space velocity (GHSV) of $30,000 \text{ h}^{-1}$ and an NO concentration of 500 ppm. The corresponding MnO_x-Fe₂O₃/VMT monolithic honeycomb catalysts (MHCs) achieved excellent SCR activity at low temperatures, with a NO conversion greater than 98.6% at 150°C and a GHSV of 4000 h⁻¹. In particular, the MnO_x-Fe₂O₃/VMT MHCs provided a good SCR activity at room temperature (20°C), with a NO conversion of 62.2% (GHSV = 1000 h^{-1}) [162].

Fenton catalysts have been widely applied for the decontamination of organic pollutants in polluted water due to their high activity and decent degradation efficiency. After the grinding treatment of vermiculite, iron in the form of Fe^{2+} (30%) and Fe^{3+} (70%) was exposed on the surface. Treated vermiculite gained high efficiency to activate H₂O₂ to oxidize organic molecules in water in a Fenton-like reaction at pH near 7 for the oxidation of hormone ethinylestradiol and model textile dye indigo carmine, and it is noticed that no significant leaching of iron ions took place during this process [163]. The iron-pillared vermiculite (Fe-VT) is a novel heterogeneous photo-Fenton catalyst, which was prepared by intercalating the hydroxy-Fe with low polymerization degree into the silicate layers of vermiculite [164]. The Fenton reaction using Fe-VT as catalyst may achieve 98.7% decoloration and 54.4% TOC removal for the brilliant orange X-GN solution (100 mg/L dye solution; pH 3; 30°C; 3.92 mM H_2O_2 ; 0.5 g/L Fe-VT dosage) under 75 min UV irradiation, and the decoloration efficiency was higher than 90% after the catalyst Fe-VT was reused for three cycles [164]. The vermiculite (VMT)-supported zero-valent iron (nZVI) and nZVI doped with palladium (abbreviated as Fe-VMT and Pd/Fe-VMT, respectively) as a catalyst may achieve the dechlorination of 2,4-dichlorophenol [165]. The Fe⁰-vermiculite (Fe-Ver-C-H₂) composite as catalysts can degrade bisphenol A (BPA)

by a photo-Fenton reaction, and the synergistic effect between iron core (Fe⁰) and iron oxide shell (Fe₃O₄) is beneficial to improve catalytic performance at the optimal condition: pH of 5, dosage of 0.2 g/L, and H₂O₂ concentration of 20 mM [166].

9.5.2.2 Catalysis for Synthesis and Conversion

Clay minerals and their composites are commonly used to catalyze various types of organic (i.e., Michael addition, allylation, alkylation, acylation, rearrangement/isomerization) or inorganic (i.e., growth of crystal or nanomaterials) synthesis reactions and chemical conversion reactions, and the reaction medium is involved with gas, liquid, or solic phase reaction. The vermiculite-based catalysts are a very effective catalyst for CO methanation [167]. The expanded multilayered vermiculite (VMT)/NiO composite prepared by a microwave irradiationassisted synthesis route exhibited a high CO conversion rate of 99.6%, CH₄ selectivity of 93.8%), and turnover frequency of 5.88×10^{-4} s⁻¹, at a temperature of 400°C, a gas hourly space velocity of 12,000 h⁻¹, a synthesis gas flow rate of 65 mLmin⁻¹ and a pressure of 1.5 MPa. The Nisupported plasma-treated vermiculite possesses high catalytic activity at a very low Ni loading (0.5 wt%), and a CO conversion of 93.5% and a turnover frequency (TOF) of 0.8537 s⁻¹, at a temperature of 450°C, a gas hourly space velocity of $6000 \,\mathrm{mLg}^{-1} \,\mathrm{h}^{-1}$, a synthesis gas flow rate of 65 mL/min, and a pressure of 1.5 MPa [168]. The modified-vermiculite supported Ni (loading amount of 12%) catalysts exhibited decent catalytic activity and stability, with a little decrease of methane conversion of 5.1% during 53h of reaction. Higher stability of the catalyst may be attributed to its interlayer structure, and active metal sintering appears to be the main reason for the deactivation of Ni-based catalysts [23]. For liquid phase reaction, the palladium/vermiculite nanocomposite catalyst with loading of 1 wt% palladium was tested for its catalytic activity toward selective hydrogenation reactions involving some α,β -unsaturated carbonyl compounds using a pulse reactor, which was found to be pretty selective toward the desired product of unsaturated alcohols [169]. The CuO-promoted natural vermiculite may be considered as promising catalysts for total oxidation of ethanol, which was proved to be the best of the studied clay catalysts with the highest activity and good selectivity. The selectivity toward CO2 was over 99% for vermiculite/Ag(3%) and vermiculite/Cu(3%); selectivity was over 97% for vermiculite/Cu (1%) and vermiculite/Ag (1%), respectively [170]. The expanded multilayered vermiculite (EML-VMT) is used as the catalyst support for the acetylene hydrochlorination, and the high acetylene conversion of 97.3%, a vinyl chloride selectivity of 100% and a turnover frequency (TOF) value of 8.83×10^{-3} s⁻¹ at a temperature of 140°C, an acetylene gas hourly space velocity (GHSV) of 108 h⁻¹, and a feed volume ratio $V(HCl)/V(C_2H_2)$ of 1.15 were achieved by mixing/

loading HgCl₂ and carbon on the surface of EML-VMT, and the composite catalyst is very stable [171].

The vermiculite with surface activity may catalyze the nuclearation or growth of new nanomaterials. The carbon nanotubes (CNT) and nanofibers with a "sponge structure" can be synthesized on the surface of expanded vermiculite/FeMo by a CH₄-chemical vapor deposition (CVD) method. The absorption capability of the composite to different oils (soy bean, engine, diesel) remarkably increased about 600%. This gives promising results that confirms the possibility for vermiculite composites to be used in environmental remediation, especially in oil spilled on waters [172]. The short-aligned carbon nanotubes (CNTs) were intercalated grown among vermiculite layers from ethylene through a simple fluidized bed chemical vapor deposition (CVD) process. This process included a synthesizing duration of 1-5 min at 650°C, and the yield of 0.22g/gcat was attained for a 5-min growth of obtained CNTs. The length of obtained CNTs were of 0.5~1.5 µm and the mean outer and inner diameter of CNTs were 6.7 and 3.7 nm, respectively. In addition, the Fe/Mo/vermiculite catalyst induced the growth of short-aligned CNTs which are of good alignment and small diameter with a length of around 1 µm. The mean outer and inner diameter of the CNTs are found to be 6.7 and 3.7 nm, respectively [173].

In the area of catalysis conversion, the addition of vermiculite to the food waste extends the thermophilic phase, speeds up the organic matter loss, and reduces the NH₃ emissions as well as electrical conductivity values where the amount of nitrogen loss through NH₃ emissions at a decreases by 26.39% [174]. The CdS quantum dot/vermiculite (CdS/VMT) nanocomposites with 5% of vermiculite exhibits the best hydrogen evolution rate of 92 µmol h⁻¹ under visible light irradiation ($\lambda \ge 420$ nm) and the highest apparent quantum efficiency of 17.7% at 420 nm because vermiculite can cause efficient separation of the photogenerated charge and carriers. As a result, the visible light photocatalytic hydrogen production activity of the photocatalyst can be enhanced through the process [175].

9.5.3 Fillers of Polymer Materials

Use of nano-sized filler particles to form polymer composites has attracted much attention in recent years because of their potential performance advantages that could create new technological opportunities. Potential benefits include increased mechanical strength, decreased gas permeability, superior flame-resistance, and even enhanced transparency when dispersed nanoclay plates inhibit polymer crystallization [176, 177]. The hydrophilic clay minerals are commonly treated with organic ammonium cations with long alkyl chains to improve the compatibility between the silicate layers and the polymer matrix. The methods used to prepare the preparation of clay-polymer nanocomposites include solvent intercalation, in situ polymerization, and melt-compounding [178–181]. Both solvent intercalation and in situ intercalative polymerization allow polymer chains to enter into the galleries of silicate clays; and melt blending is more attractive as the nanocomposites can be processed by conventional processing methods such as extrusion and injection molding. The influences of the addition of various types of clays on nonisothermal crystallization process of thermoplastics have been studied intensively. Poly(4-vinylpyridine)/ vermiculite nanocomposite with ~18-19 mass% of organic component was synthesized by the intercalative redox polymerization of 4-vinylpyridine in the gallery of copper(II) ion-exchanged vermiculite, and the incorporation of vermiculite also enhanced the thermal stability (The initial decomposition temperature increased by $\sim 300^{\circ}$ C.) of the nanocomposite [88]. The polylactide (PLA)/vermiculite nanocomposites prepared by in situ intercalative polymerization of L,L-lactide (LLA) in the presence of organomodified vermiculite (VMT) showed increased storage and loss modulus and glass transition temperature (from 26.3 to 34.4°C after introducing 3 wt% vermiculite) as compared to the neat PLA [85]. The tensile strength and the elongation at break at 23°C of PLA/VMT-3 is about 2.0 and 3.1 times higher than that of pure PLA, respectively. The poly(*p*-dioxanone) (PPDO)/vermiculite (VMT) nanocomposites with exfoliated structure were prepared by in situ intercalative polymerization of *p*-dioxanone (PDO) in the presence of organo-modified vermiculite (OVMT) with the aid of ultrasonic action [26]. The incorporation of 1 wt% OVMT enhanced the tensile strength by 47% and the elongation at break by 108% since the nanoscale OVMT platelets restricted the motion of PPDO segments. The introduction of 3 wt% OVMT clearly improved thermal stability of the nanocomposites. The polyurethane foam/unmodified vermiculite nanocomposite was prepared by dispersing vermiculite either in polyol or isocyanate before blending, followed by conducting foaming and polymerization reactions with vermiculite as a catalyst [182]. When 2.3 wt% of vermiculite was dispersed in the isocyanate, the vermiculite is partially exfoliated in the polymer matrix. The compressive strength and modulus normalized to a density of 40 kg/m³ and are 40% and 34% higher than the foam without vermiculite, respectively. On the other hand, the thermal conductivity is found to be 10% lower than the foam without vermiculite [182]. The vermiculite was modified with tertiary amine catalytic sites and long alkyl chains by Qian et al. to form an organo-vermiculite (Q50-VMT), which could be used to prepare polyurethane-vermiculite nanocomposites via an industrially friendly in situ intercalative polymerization method (Fig. 9.15). At the Q50-VMT loading amount of 5.3 wt%, the tensile modulus at 25°C increased by 390% and the CO_2 permeability decreased by 40%, which evidently shows their potential in coating and adhesive applications [183]. Qian et al. [25] also prepared vermiculite-reinforced polyurethane nanocomposites and found that the vermiculite platelets were extensively intercalated or exfoliated. The incorporation of 5.3 wt% of vermiculite increased the tensile modulus by >270% and enhanced the tensile strength by >60%, and reduced the N₂ permeability by about 30%. The cyclo(4,4'-oxybis(benzene)disulfide) (COBDS) oligomers can

be intercalated into cetyltrimethyl ammonium bromide exchanged vermiculite, and in situ ring-opening reaction of cyclic oligomers leads to the formation of an exfoliated poly(4,4'-oxybis(benzene)disulfide) (POBDS)/vermiculite (VMT) nanocomposite [184]. The vermiculite was exfoliated well to form vermiculite nanolayers with thickness of 2-5 nm, and length of 200 nm when the addition amount of vermiculite is 5 wt%, which lead to the enhancement of the maximum weight-loss temperature from ~414 to ~434°C.

The in situ melt intercalation has also been frequently used to prepare the polymers/vermiculite nanocomposites. Exfoliated poly(4, 4'-oxybis(benzene)disulfide)/vermiculite (POBDS/VMT) nanocomposites synthesized via in situ melt intercalation by cyclo(4, 4'-oxybis(benzene) disulfide) oligomers (COBDS) into ctadecylammonium-exchanged VMT (organo-VMT) showed high storage modulus and increased glass transition temperature (from 68.5 to 73.5C°) even at a minimal addition amount of VMT [56]. Epoxy resin/vermiculite (VMT) nanocomposites were prepared by in situ melt intercalation of bisphenol-A epoxy resin into amino-modified vermiculite catalyzed by N, N-dimethyldecan-1amine oxide to accelerate the curing of epoxy [185]. Resultant nanocomposite showed decent mechanical properties and thermal stability. The incorporation of organo-vermiculite into poly (l-lactic acid) increased the crystallization enthalpies, reduced the glass transition and cold crystallization temperatures, and improved the mechanical properties of the poly (l-lactic acid) polymer [82]. Direct melt compounding of polymer with vermiculite may also form polymer nanocomposite containing exfoliated or intercalated vermiculite. Tjong et al. [186] prepared an exfoliated polyethylene (PE)-layered vermiculite (VMT) nanocomposite via direct melt compounding in a twin-screw extruder followed by injection molding using maleic anhydride modified vermiculite as starting material. The maleic anhydride plays two roles in the process. One is as the intercalation agent for vermiculite and the second is as a compatibilizer for PE and vermiculite phases. The tensile strength increased by about 25.35%, and the storage modulus increased by 50% after incorporating 4wt% vermiculite into polyethylene. Meanwhile, the glass-transition temperature of polyethylene/vermiculite nanocomposites was also increased. Due to the **Fig. 9.15** Schematic illustration for the dispersion of catalystmodified vermiculite in polyol and the in situ intercalative polymerization process to form polyurethane/vermiculite nanocomposite. Reproduced with permission from Y. Qian, W. Liu, Y.T. Park, C.I. Lindsay, R. Camargo, C.W. Macosko, A. Stein, Modification with tertiary amine catalysts improves vermiculite dispersion in polyurethane via in situ intercalative polymerization, Polymer 53(22) (2012) 5060–5068. excellent thermal stability and barrier performance of vermiculite, it can be incorporated into polyamide 11 by an exfoliation reaction to improve its fire-retarding and mechanical (Young's modulus and the elongation at break) performance [187]. In addition to the method mentioned above, the solid-state shear compounding (S3C) method using pan-mill equipment has also been proved to be an effective one to prepare polymer/ vermiculite nanocomposite [188].

The vermiculite and modified vermiculite have been proved to be a reliable reinforcing agent or nanofiller for rubber. The acid-treated vermiculite (DVMT) was mixed with maleic anhydride (MA) and styrene-butadiene rubber (SBR) to obtain SBR/DVMT/MA nanocomposites, which was then subjected to gamma irradiation at different doses from 25 to 150 kGy. By comparison, the incorporation of DVMT and MA improved the physico-chemical and thermal properties of the SBR/vermiculite nanocomposite when the contents of both DVMT and MA were 10 parts per hundred of rubber (phr) and at an irradiation dose of 100 kGy [189]. The gamma irradiated ethylene propylene diene monomer rubber (EPDM)/vermiculite clay (VMT)/maleic anhydride (MA) nanocomposites with VMT contents from 2.5 to 10 phr by direct melt compounding in an internal mixer. The maximum improvement was achieved when the content of DVMT clay was 5 phr and the irradiation dose of 50kGy was applied [190]. The incorporation of organo-vermiculite (OVMT) (modified with cetyltrimethylammonium bromide) into natural rubber (NR) with the loading amount of 15 phr through a melt process in a HAAKE mixer improved the tensile strength and the elongation at break to 28.4 MPa and 623.2%, respectively. The modulus, tear strength, and hardness (Shore A) of the nanocomposites also increased by 300% with the increase of the OVMT loading [191]. In addition, the storage modulus and the glass transition temperature of the nanocomposites were increased after incorporation of OVMT, which indicates that the organo-vermiculite is a potential nanofiller to fabricate rubber nanocomposite.

It has been proved that the brick wall nanostructure of vermiculite may produce an extremely tortuous path for oxygen molecules, so the application of vermiculite for its impressive barrier behavior becomes more prominent to the researchers, and thus the application of vermiculite in the area of polymer film material has acquired much more attention in recent years. Poly(ethylene terephthalate) (PET) film with the thickness of 130 μ m was coated with 1–3 μ m thick homogeneous layers of vermiculite/chitosan (with 0–50 wt% of vermiculite) to form a new composite film [192]. It was found that the coating of a 2.40 μ m thick chitosan/vermiculite (50 wt%) layer improved the barrier improvement factor (BIF) to 100 in helium, and the oxygen transmission rate decreases from 0.36 to 0.016 cm³/m²•day with addition

of 40 wt% of vermiculite onto chitosan layers. The commercially available polyvinyl alcohol (PVA)/vermiculite nanocomposite coating films and linear low-density polyethylene film were modified with a waterborne vermiculite coating. This lead to a sharp increase of oxygen permeability at a relative humidity rate above 60% and an enhancement of the stability of the film in 3% acetic acid solution [193]. In addition to the coating of vermiculite on film, direct incorporation of organically modified vermiculite into epoxy nanocomposites by an intergallery polymerization and solution-casting approach produced new composite with excellent resistance to oxygen and water vapor permeation [194]. For the aspect of separation film, the incorporating of thermoexfoliated vermiculite (VMT) into poly(ether sulfone) (PES) ultrafiltration membranes (MMMs) greatly improved the flux and antifouling properties of mixed matrix membranes, which displayed a higher flux compared to control PES membrane without incorporating VMT (Fig. 9.16) [195]. PES-VMT (10%) film had the highest flux of $476.4 L/(m^2 h)$ (LMH) before fouling, and the highest flux of 210.7 LMH after usage for three cycles. In addition, the rejection rate of the PES-VMT(15%) film to bovine serum albumin (BSA) sample was >77%, lower than that of the PES-VMT(10%) (>84%), which suggested a better antibiofouling resistance of the nanocomposite film.

Fig. 9.16 Schematic illustration of the PES/thermoexfoliated vermiculite nanocomposite film and its biofouling alleviation. Reproduced with permission from Y. Orooji, F. Liang, A. Razmjou, S. Li, M.R. Mofid, Q. Liu, K.C. Guan, Z.K. Liu, W. Jin, Excellent biofouling alleviation of thermoexfoliated vermiculite blended poly (ether sulfone) ultrafiltration membrane, ACS Appl. Mater. Interfaces 9(35) (2017) 30024–30034.

9.5.4 Thermal Insulators

Heat-insulating materials are a common and essential type of materials in many industrial areas whose applications are significant and wide-ranged [196]. Vermiculite expands to become a highly efficient heat-insulating material when heated to above 300°C. Low-bulk density, low-heat conductivity, relatively high melting point, chemical inertness, endurance, and environmental safety endow vermiculite with great potential for an ideal thermal insulator. The heat insulators based on expanded vermiculite can be used as replacements for lightweight chamotte components and fibrous heat insulators in thermal power units with the hot-wall temperature below 1150°C [31]. The vermiculite-derived thermal insulator reduces inefficient heat losses, and hence decreases the total fuel consumption by 10–15 times in continuous furnaces and by more than 45% in batch furnaces [197].

After vermiculite was added into polyurethane (PU) foam, the thermal insulation properties of PU foam were simultaneously improved, and smaller vermiculites in PU foam displayed better thermal-insulating properties. The thermal conductivity decreases to 0.054 W/mK after the addition of 5 wt% vermiculites with diameter of 0.71-2.00 mm and foaming at 50 kg/m^3 [198]. The incorporation of 5 or 25 wt% of vermiculite into an industrial plaster matrix composed of dihydrate, calcium sulfate hydrates, and calcium carbonate may decrease the thermal conductivity of the matrix from $0.50 \text{ Wm}^{-1} \text{ K}^{-1}$ to $0.45 \text{ and } 0.23 \text{ Wm}^{-1} \text{ K}^{-1}$ for volume pore fractions at 47%, 51%, and 74% respectively [199]. Therefore, the composite made from vermiculite and plaster matrix can be used as an effective thermal insulators and also used for fire passive protection in building construction.

9.5.5 Friction and Lubrication

Fly ash-based fiber-reinforced hybrid phenolic composites filled with vermiculite were fabricated. During this fabrication process, addition of vermiculite contributed to reduce the maximum disc temperature rise, which enhanced the frictional amplitude, that is, μ_{max} - μ_{min} . Addition of vermiculite has also caused an increase in the postbraking onset of degradation temperature of the surface composition as compared to the prebraking composition [200]. The addition of organized expanded vermiculite (OEVMT) into phenolic resin (PF) by a melt intercalation process increased the thermal decomposition temperature of PF from 433.9 to 482.6°C in air atmosphere, and the brake pad based on PF/OEVMT had more stable friction coefficient, high temperature wear-resistance, and lower wear rate than that of the brake pad based on PF [201]. The vermiculite was used as a friction modifier of brake to prepare PI-matrix materials by the heat-press molding method. The friction coefficient increases with increasing the vermiculite content at low-friction speeds (between 20-40 km/h). At high friction speeds (between 60 and 120 km/h), the friction coefficient increases at first when vermiculite content is below 10 wt% and then decreases with further increase of vermiculite content [202].

As an oil additive, the modified vermiculite with polyphenylsiloxane leads to a sharp decrease in the wear rate in the second (formation of a coating, 60 min) and third (tribotests, 180 min) stages. The decrease of wear rate is due to the formation of the metal-siloxane coating on friction surfaces and the modified vermiculite also demonstrates better performance than polytetrafluoroethylene [203].

9.5.6 Biological and Biomedicine

Bio-related polymeric nanocomposites can be classified into naturalbased materials, such as natural polymers and clay minerals, and synthetic polymers such as poly(lactic acid). These composites can be used as drug delivery carrier and antibacterial materials. Clay minerals have been proposed to be valuable materials for modulating drug delivery. Therefore, these materials become common in pharmaceutical production either as inorganic carriers or active agents. The pH-sensitive-chitosan-g-poly (acrylic acid)/vermiculite/sodium alginate composite hydrogel bead which showed good loading and controlled release properties for diclofenac sodium (DS) in stimulated gastric fluids (pH 2.1) and intestinal fluids (pH 6.8) was prepared. It was found that the incorporation of vermiculite into the hydrogel beads can slow down the release rate of the drugs and thus help to improve the burst-release effect of the drugs [204].

Incorporation of several antibacterial organic or inorganic compounds into vermiculite clay minerals can be potentially used to fabricate emerging materials for antibacterial applications. The chlorhexidine acetate intercalated vermiculite with 33.7 mass-% of chlorhexidine acetate demonstrates decent antibacterial activity, which has inhibition zones of 16.7 and 14.5 mm on *Escherichia coli* and Staphylococci aureus, respectively [205]. The antibacterial chlorhexidine/vermiculite with the chlorhexidine contents of 209-231.6 mg/g is extremely stable with a high antibacterial activity and the minimum inhibitory concentration (MIC) of 3.33 (%; w/v) for Staphylococcus aureus (exposition 30h) [206]. Superior antibacterial activity of vermiculite/chlorhexidine nanocomposites was also confirmed by Holešová et al. [207]. Moreover, vermiculite proved to be harmless for tissues and cells by an in vivo toxicological analysis experiment. Therefore, vermiculite/chlorhexidine composites can be used as an antibacterial component to prepare carmellose mucoadhesive oral films for treatment of oral infections [208]. In addition to the loading of organic drugs on vermiculite, inorganic antibacterial components were also loaded on vermiculite to form a composite antibacterial material. Vermiculite-supported copper nanoparticles with a broad range of sizes from 1 to 400 nm were recognized to be new antibacterial materials that possessed stronger antibacterial activity against *Staphylococcus aureus* at 37°C with an inhibition zone of about 30 mm in diameter (as compared to the control sample which had no inhibition zone.) [209]. The zinc oxide-nanoparticles/vermiculite with excellent antibacterial activity were used as a filler to prepare Polyethylene (PE) nanocomposites with the contents of fillers to be 3, 6, 10, and 15 wt%. The nanocomposites also showed long-term antibacterial effects, as confirmed by the decreasing number of surviving bacterial colony forming units (CFU) with the increase in time of exposure [210].

9.5.7 Electrical Conductors

Conducting electroactive polymers remain a subject with intense investigation from research groups worldwide. The surface active sites and interlayer structure of vermiculite gives it possibility to be modified via intercalation by monomers and polymerization reaction to form new composite [211]. Vermiculite is an inactive inorganic host without redox character but with large surface area and strong absorptive capacity, so the composite of vermiculite with polypyrrole [212] and polyaniline [213] are potential as electrical conducting materials with extensive applications. The conductive polypyrrole can be intercalated into the interlayers of expanded vermiculite to produce the nanocomposite with high conductivity by a synchronous polymerization of pyrrole and intercalation of pyrrole reaction in aqueous solution. The composite has a competent conductivity of 67 S cm⁻¹ and outstanding environmental stability [214]. The self-assembled monolayer polypyrrole was coated on expanded vermiculite (VMT) by a chemical grafting reaction, and the resultant composites possess high electrical conductivity (50 S cm⁻¹, at vermiculite content of 9.35%) at room temperature, and the conductivity is weakly temperature dependent [215]. The polyaniline/vermiculite clay nanocomposites with similar structure to polypyrrole/vermiculite were also prepared by in situ chemical oxidative grafting polymerization [216]. The electrical conductivity of 3.9×10^{-3} S cm⁻¹ was obtained for polyaniline/ vermiculite clay nanocomposites, at the polyaniline content of 142.7 wt%. Just like polypyrrole/vermiculite nanocomposite, polyaniline/vermiculite nanocomposite also possesses superior thermal stability, making it a potential semiconductor material to be applied in electrochemical fields.

9.5.8 Ceramics and Building Materials

Strong or resistant ceramic composites have wide-ranging applications in various areas such as construction industry where they are ideal candidates for building materials. The vermiculite-ceramics composite was fabricated from 35 mass% vermiculite, 30 mass% SiO₂, 10 mass% Al₂O₃, and 25 mass% cellulose fibers. It was tested and noticed that the thermal conductivity (0.81 W/m K) and compressive strength (39 MPa) of the composite measured perpendicular to the pressing direction are

higher than those (0.52W/mK and 28MPa, respectively) measured parallel to the pressing direction, and the anisotropy in both thermal conductivity and compressive strength was confirmed to be attributed to the microstructural anisotropy [217]. Increased usage of vermiculite in cement fiber concrete composites reduced the consumption of Portland cement and simultaneously increased the flame retardant properties [218]. Vermiculite was incorporated with Class G Portland Cement at a proportions of 5%, 7%, and 9%. This process helped to improve compressive strength values of the cement up to 10 MPa. The use of vermiculite as an extender for oil well cement slurries also allowed for more stable slurries with high water/cement ratio and low densities (12.5 lb/Gal) [219]. The cement mortars contained expanded vermiculite as partial sand replacement at constitution levels of 30% and 60%. The expanded vermiculite led to reduction of the unit weight and compressive strength loss, and improvement of the flow diameter and the heat resistance and thermal stability of the mortars [220].

As a common inorganic modifier, the introduction of organoexpanded vermiculite into bitumen with a semiexfoliated state clearly improved the aging resistance of bitumen. The mass change rate, viscosity aging index (at 60°C) of bitumen decreased from 0.66% to 0.49%, and from 982% to 609%, respectively. The retained penetration of bitumen and the retained ductility (at 15°C) increased from 43% to 49% and from 5% to 12%, respectively [221]. The organized expanded vermiculite (OEVMT) has good compatibility with other nanoparticles such as zinc oxide to modify thermal oxidation and photo-oxidation aging resistance capability of bitumens [222].

9.5.9 Superabsorbent Composites

Superabsorbent is a new type of functional polymer material with special three-dimensional network structure, excellent water absorption, and water retention capability [223]. Since the first superabsorbent material has been reported by the US Department of Agriculture [224], the research and development of superabsorbent materials have come into noice globally. The researched products were made industrially available and are now widely applied in many industries. Common examples include disposable diapers, agriculture, food packaging, artificial snow, biomedicines, healthcare, and agriculture applications [225]. With the global warming crisis, drought originating from regional vegetation damage and lack of water caused serious desertification. Therefore, the development of new types of water-saving superabsorbent materials with high level of water absorption and retention, salt tolerance, low production cost, and environmentally friendly properties become one of the most important tasks at hand. In order to improve the water absorbency, salt-resistance properties, and environmental friendliness of superabsorbent materials, various approaches

have been employed. Among all the approaches, the combination of synthetic polymers (i.e., poly(acrylic acid), poly(acrylamide)), natural polymers (i.e., starch, cellulose, and chitosan) with inorganic clay minerals to form organic-inorganic superabsorbent composite has become an ideal strategy. It has been proved that the clay minerals can improve the network structure, water absorbency, salt-resistant properties, as well as gel strength [226–228]. In addition, the addition of economical inorganic clay minerals can also reduce the production cost.

As a silicate clay mineral with surface reaction activity, vermiculite and modified vermiculite have also been used as the inorganic components to prepare superabsorbent composites. Zheng et al. [229] reported poly(acrylic acid)/unexpanded vermiculite (PAA/UVMT) superabsorbent composites made through free-radical polymerization reaction, and the equilibrium water absorbency increased with increasing UVMT content. The concentration of 20 wt% clay gave the best absorption (1232 g/g in distilled water and 89 g/g in 0.9 wt% NaCl). It was also found that at a higher ionic strength $(>1 \times 10^{-3} \text{ M})$, the water absorbency in monovalent cationic solutions was higher than those in multivalent cationic solutions. At the same ionic strength $(>1 \times 10^{-3} M)$, the effect of three anionic salt solutions on the swelling has the following order: NaCl < Na₂SO₄< Na₃PO₄. Wang et al. [230] reported about guar gum-g-poly(sodium acrylate)/organo-vermiculite (GG-g-PNaA/CTA⁺-VMT) superabsorbent, and found that Organo-VMT improved the gel strength of the nanocomposite as compared to VMT. The maximum storage modulus of the nanocomposite reached 658 Pa $(\gamma = 0.5\%, \omega = 100 \text{ rad/s})$. The water absorbency of the superabsorbent nanocomposite containing 5 mass% CTA+-VMT is 575 g/g at the CTA content of 4.03 mass%. Wang et al. [22] also prepared GG-g-PNaA/ Mⁿ⁺-VMT superabsorbent nanocomposites based on natural GG and cationic exchanged vermiculite $(M^{n+}-VMT)$ (Fig. 9.17), and found that the nanocomposites improved the water absorption where the extent of improvement is in the following order: VMT < Li⁺-VMT < Na⁺- $VMT < K^+ - VMT < Ca^{2+} - VMT < Mg^{2+} - VMT < Al^{3+} - VMT$. Compared with VMT, Mⁿ⁺-VMT improved the water absorption more significantly, and the divalent (Ca²⁺ and Mg²⁺) or trivalent cation (Al³⁺)-exchanged VMT enhanced the water absorption to a higher degree than the monovalent ones (Li⁺, Na⁺, and K⁺). Zhang et al. [231] compared the effect of different types of clay minerals on the performance of the as-prepared poly(acrylamide)/clay superabsorbent composites. It was found that the superabsorbent composites incorporated with 10wt% of various kinds of clays were all endowed with equilibrium water absorbency of more than 1300 g/g, and the vermiculite-based superabsorbent composite exhibited the highest water absorbency in CaCl₂ and FeCl₃ aqueous solution, respectively. The water absorbency of the superabsorbent composite is related to the dispersion state of vermiculite in polymer matrix. When the content of vermiculite is less than or equal

Fig. 9.17 Proposed mechanisms for the formation of the superabsorbent nanocomposite network. Reproduced with permission from W.B. Wang, N.H. Zhai, A.Q. Wang, Preparation and swelling characteristics of a superabsorbent nanocomposite based on natural guar gum and cation-modified vermiculite, J. Appl. Polym. Sci. 119(6) (2011) 3675–3686.

to 10%, the water absorbency of the superabsorbent composite prepared by adding the exfoliated vermiculite is higher than that of the untreated vermiculite; when the vermiculite content is about 20%, the water absorbency of superabsorbent composite prepared by exfoliated vermiculite is smaller than that of untreated vermiculite [232].

The introduction of a moderate amount of hydrophobic monomer into the hydrophilic superabsorbent network can effectively inhibit the entanglement of the polymer chain and minimize weakening of the hydrogenbond interaction between the hydrophilic groups, thereby improving the regularity of the water absorption network and enhancing the absorption ability of water molecules. Shi et al. [233] proved that the inclusion of 24.3 mmol/L of styrene into guar gum-*g*-poly(sodium acrylate)/ vermiculite (10wt%) may improve significantly the water absorbency from 387 to 562 g/g, which are all higher than that of guar gum-*g*-poly (sodium acrylate) (358 g/g), suggesting that the hydrophobic monomers may generate synergism effect to improve the water absorbency.

As water-saving and water-retention materials for agroforestry applications, it has been expected that the materials can also release slowly substances with special functions such as fertilizers or pesticides. Among the numerous organic-inorgranic superabsorbent polymers, superabsorbent containing fertilizer is one of the most important families. Yuan et al. [234] reported poly(acrylic acid-co-acrylamide)/ sodium carboxymethyl cellulose/vermiculite (VMT) superabsorbent composites prepared by a frontal polymerization (FP) method, finding that the introduction of urea not only endows the superabsorbent polymer with functions of slow-release of urea, but also increases their water absorbency by 17.4% as compared to the original superabsorbent. The study about effects of slow-release fertilizer on tall fescue seeds germination and growth indicated that the germination rate and vigor index of tall fescue seeds applying with a slow-release fertilizer with 10% urea increased germination by 17.5% and 80.2%, respectively. In comparison with the control group, the slow release time of urea was also made to be more than 30 days in soil.

The research on superabsorbent composites has made great progress in recent years. The water absorbency of different synthetic polymers-based and natural polymers-based superabsorbent composites containing vermiculite components from various research groups was summarized comprehensively, and the comparison results are listed in Table 9.1.

9.5.10 Three-Dimensional (3D) Network Adsorbent

Three-dimensional (3D) network adsorbents have better adsorption capacity and faster adsorption rate than the conventional adsorbents, as the large number of functional groups in the network gives rise to high absorbing capacities of the adsorbent. The special 3D polymer network may also slightly expand to reduce resistance of the mass transfer during the adsorption process [240]. The type and number of functional groups in the 3D network could be controlled by altering the types of monomers or the parameters of polymerization. 3D network adsorbents can be classified into three main types: synthetic polymer 3D network adsorbents, natural polymer 3D network adsorbents, and composite 3D network adsorbents. Synthetic polymer 3D network adsorbents are usually prepared by the copolymerization of hydrophilic monomers (i.e., acrylic acid, acrylamide, and acrylonitrile); natural polymer 3D network adsorbents are mainly prepared by grafting hydrophilic monomers onto natural polysaccharides, and the composite 3D network adsorbents are

Table 9.1 Comparison of the Water Absorbency (W.A.)of Different Superabsorbent Composites in DifferentSwelling Medium (S.M.)

Superabsorbent	Clay Content (%)	S.M.	W.A. (g/g)	References
GG-g-PAA/RVMT	5	Distilled water	496	[22]
GG-g-PAA/Li ⁺ -VMT	5	Distilled water	532	[22]
GG-g-PAA/Na ⁺ -VMT	5	Distilled water	535	[22]
GG-g-PAA/K ⁺ -VMT	5	Distilled water	566	[22]
GG-g-PAA/Ca ²⁺ -VMT	5	Distilled water	563	[22]
GG-g-PAA/Mg ²⁺ -VMT	5	Distilled water	578	[22]
GG-g-PAA/AI ³⁺ -VMT	5	Distilled water	586	[22]
GG-g-PAA/AI ³⁺ -VMT	5	0.9 wt% NaCl solution	61	[22]
PAA/VMT	20	Distilled water and	1232	[229]
PAA/VMT	20	0.9 wt% NaCl solution	89	[229]
GG-g-PAA/OVMT	5	Distilled water	575	[230]
PAM/VMT	5	Distilled water	1873	[231]
PAM/VMT	10	Distilled water	1689	[231]
PAM/VMT	20	Distilled water	1228	[231]
PAM/VMT	30	Distilled water	1143	[231]
PAM/VMT	40	Distilled water	1030	[231]
Poly(SA)/CVMT	20	Distilled water	667	[232]
Poly(SA)/EVMT	20	Distilled water	527	[232]
poly(SA)/CVMT	10	Distilled water	449	[232]
Poly(SA)/EVMT	10	Distilled water	536	[232]
Poly(SA)/CVMT	1	Distilled water	363	[232]
Poly(SA)/EVMT	1	Distilled water	371	[232]
GG-g-P(NaA-co-St)/	5	Distilled water	311	[233]
VMT				
GG-g-P(NaA-co-St)/	10	Distilled water	562	[233]
VMT				
GG- <i>g</i> -P(NaA- <i>co</i> -St)/	20	Distilled water	356	[233]
VMT				
PAA-Am/EVMT	50	Distiled water	850	[235]
CTS-g-PAA/VMT	5	Distilled water	223.3	[236]
CTS-g-PAA/VMT	5	0.9% NaCl solution	51	[236]
CTS-g-PAA/UVMT	5	Distilled water	247.8	[237]
CTS-g-PAA/UVMT	5	0.9 wt% NaCl solution	54.2	[237]
HEC-g-PAA/VMT	10	Distilled water	575	[238]
HEC-g-PAA/O-VMT	10	Distilled water	682	[238]
PKA-AM/UVMT	30	Distilled water	1048	[239]

often prepared by incorporating inorganic components (i.e., silica, clay minerals) into the organic superabsorbent polymers.

Common preparation methods of 3D network adsorbents mainly include solution polymerization [241-243], suspension polymerization [244], dispersion polymerization [245], emulsion polymerization [246], glow-discharge-electrolysis plasma polymerization [247], and surface-initiated redox radical polymerization [248, 249]. Among them, aqueous solution polymerization was one of the most frequently used approaches due to the simplicity and environmental friendliness of this process as compared to others. However, conventional aqueous solution polymerization can only obtain a bulk gel product, which is difficult to dry (due to the high energy consumption requested), and the gel product needs to be prilled for further use [250]. Suspension polymerization, on the other hand, can obtain granular product, but this process requires large amounts of organic solvents or surfactants, which may create environmental pollution [251]. Wang's groups first synthesized granular 3D network adsorbents using aqueous solution polymerization in the presence of cationic polymer chitosan [252]. The granular products are easy to be dried and can be used directly in practice without further treatments such as prilling [243]. The formation mechanism of the granular product is mainly the electrostatic assembly between positively charged chitosan and the negatively charged acrylic acid, as well as the associated grafting and crosslinking reaction. The $-NH_2$ groups of chitosan can be protonated by the H⁺ from acrylic acid, leading to generation of electrostatic interaction with the COO^{-} groups to form $-NH_{3}^{+}$...OOC pairs. During the initiation stage of the polymerization, the acrylic acid monomers could be grafted onto chitosan backbone to form grafted poly(acrylic acid) chains, which may entangle with the chitosan macromolecular chains to form large amounts of insoluble particles. In the presence of crosslinking agent, the grafted chains can be crosslinked to form a network structure, and these particles may aggregate with each other to form a granular product (Fig. 9.18) [253]. Other positively charged polymer, such as polyvinylpyrrolidone, also has the similar effects to chitosan to promote the formation of granular products from its aqueous solution [254].

In the presence of vermiculite, the granular product is also easy to be formed. Vermiculite is negatively charged and may interact with positively charged chitosan. Therefore, vermiculite can act as an inorganic crosslinking point to facilitate the formation of granules [255]. The main adsorption mechanism of NH₄-N onto the chitosan-*g*-poly(acrylic acid)/ unexpanded vermiculite (CTS-*g*-PAA/UVMT) is due to the electrostatic attraction between positively charged NH₄-N and negatively charged – COO⁻ groups. Water molecules penetrate quickly into the composite hydrogel and dissociate –COOH groups to –COO⁻ groups, resulting in a dimensional increase of polymeric networks because of the strong

Fig. 9.18 Scheme illustrating the bulk gel product and the granular product. Reproduced with permission from W.B. Wang, D.J. Huang, Y.R. Kang, A.Q. Wang, One-step in-situ fabrication of a granular semi-IPN hydrogel based on chitosan and gelatin for fast and efficient adsorption of Cu2+ ion, Colloids Surf. B 106 (2013) 51–59.

repulsion between negative charges on carboxylate groups Subsequently, this allows more NH_4 -N ions to be diffused into and trapped within the polymeric networks under the influence of the ionic interaction (Fig. 9.19). The electrostatic attraction and network trapping are also responsible for the adsorption of cationic dye onto chitosan-g-poly(acrylic acid)/vermiculite adsorbent [256]. Lu et al. [257] prepared a poly(acrylic acid)/vermiculite hydrogel initiated by glow-discharge-electrolysis plasma, and the hydrogel displayed the maximum adsorption capacities of 2575.2 and 2674.0 mg/g for CV and MB, respectively.

Fig. 9.19 Model scheme for the adsorption of NH₄-N onto CTS-*g*-PAA/UVMT. Reproduced with permission from Y. Zheng, Y. Xie, A. Wang, Rapid and wide pH-independent ammonium-nitrogen removal using a composite hydrogel with three-dimensional networks, Chem. Eng. J. 179 (2012) 90–98.

Table 9.2 Comparison of Adsorption Capacities (AC)
of Different 3D Network Composite Adsorbents

Adsorbents	Clay Content (%)	Adsorbates	Initial Conc. (mg/L)	AC (mg/g)	References
CTS-g-PAA/UVMT	40	NH4 ⁺ -N	100	21.7	[255]
CIS-g-PAA/VIVII	10	()/ MB	1000	1612.32	[256]
AA/VMT	3	MB	70 110	2674.0	[257]

After decades of development, research on different classes of three-dimensional network adsorbents have been matured (Table 9.2). These advanced 3D network adsorbents present excellent adsorption properties for different types of pollutants, and have proven their unique value in wastewater treatment and environmental remediation application.

9.5.11 Energy Storage Materials

9.5.11.1 Electrochemical Energy Storage

Lithium-sulfur batteries are one of the most promising battery systems due to their high theoretical energy density. However, the dissolution and diffusion of polysulfides may induce parasitic reactions with lithium metal anodes, which can lead to compromization of the safety of lithium-sulfur batteries. The emerging lamellar separator reassembled with exfoliated vermiculites has proved to be effective in Li–S batteries for both cathode and anode [258]. This is resultant from the separator structure formed by 2D vermiculite flakes. The structure holds interstitial spaces which allow selective transportation of ions, and the negatively charged 2D exfoliated vermiculite sheets can repel the polysulfide anions by electrostatic interaction (Fig. 9.20A). The interspace of the vermiculite flakes allows the enrichment of positively charged lithium ions through an ion-exchanging process (Fig. 9.20B) to form a permselective Li-ion transfer channels. The formation of permselective Li-ion transfer channels help to effectively avoid the shuttle effect in working Li-S batteries. In other words, vermiculite separators are capable of regulating the polysulfide ion transportation by electrostatic repulsion and steric hindrance. At the same time, they do not hinder the transportation of Li⁺ ions with smaller ion radii. Moreover, vermiculite flakes have high rigidity with the microscale

Fig. 9.20 (A) Schematic of exfoliated vermiculite separator in lithium-sulfur battery, which can effectively repel the polysulfide anions and mitigate the "shuttle effect." (B) The structure of vermiculite sheets with enriched interlayer lithium cations as transfer channels. Reproduced with permission from R. Xu, Y.Z. Sun, Y.F. Wang, J.Q. Huang, Q. Zhang, Two-dimensional vermiculite separator for lithium sulfur batteries, Chin. Chem. Lett. 28, (2017) 2235–2238.

Young's modulus of 175 GPa, which is sufficient to suppress the growth of Li dendrite because of mechanical resistance and to suppress the lithium dendrite penetration to grant high-safety of the rechargeable batteries. Thus, the vermiculite separator allows more stable electrochemical cycles with Coulombic efficiency above 90% and a low-capacity decay rate.

The natural vermiculite can be converted to porous Si nanosheet by the acidification and magnesiothermic reduction process, and the porous Si product can be subsequently used as scalable and economical anode material for fabricating lithium-ion batteries [259]. Meanwhile, the porous Si nanosheet could also accommodate volume change effectively, hence exhibits a reversible capacity of 900 mAh g⁻¹ at 0.1 A g⁻¹ and high-capacity retention.

9.5.11.2 Phase Change Materials

Phase change materials (PCMs) can be incorporated with building materials to obtain a novel form-stable composite PCM with outstanding energy storage performance in latent heat thermal energy storage (LHTES) systems. Expanded vermiculite is a capable natural encapsulation material for medium-temperature heat storage. The hydrated and/dehydrated inorganic salts are an appropriate energy-storage medium that is compatible with the air temperature provided by conventional transpired solar collectors (at <70°C). The porous vermiculite was used as a carrier to combine $CaCl_2$ with LiNO₃ to form a salt in matrix (SIM). The peak reactor temperature rose to only by 14°C with a reduction in temperature output from this initial peak over a

duration of 60 h. This increase in the peak reactor temperature has many implications for reactor design and the operation procedure of any practical building scale installation [260]. The combination of expanded vermiculite with medium-temperature PCMs such as LiNO₃, NaNO₃, and KNO₃ led to formation of a composite material with the maximum encapsulation mass fractions of 84.6, 85.7, and 87.0 wt%, the thermal conductivity of 0.51, 0.44, and 0.33 W/(mK) for LiNO₃expanded vermiculite, NaNO₃-expanded vermiculite, and KNO₃expanded vermiculite, respectively. The phase change temperatures of the composite materials are between 243.1°C and 325.1°C, and latent heats are between 83.1 and 295.4 J/g [261]. The Na₂HPO₄·12H₂Oalumina/expanded vermiculite composite phase change materials (NEAfs-CPCMs) exhibited large encapsulation mass fractions at above 59.7 wt%, heat storage capacity (melting process: 97-151 J/g; solidification process: 60–89 J/g) and NE5.3 thermal conductivity of 0.418 W/ (mK), and supercooling degree of 1.4°C, because the large specific surface area of EVM could provide nucleation sites for crystallization of PCMs [262]. In another experiment, Mg(OH)₂/vermiculite composite phase change materials for storage and transformation of heat in a temperature range of 250-350°C were prepared. The incorporation of vermiculite reduced the size of Mg(OH)₂ and increased the decomposition temperature of hydroxide by 50°C in comparison with bulk hydroxide, and the maximal heat storage capacity of the composite with the hydroxide content of 67.4 mass% is 540 kJ per kg, which is larger than the heat of melting for promising PCMs [263].

Combination of vermiculite with organic components may also produce high-quality phase change composites. The capric-myristic acid eutectic mixture could be obtained by 20wt% into pores of the vermiculite without seepage of melted PCM from the composite; therefore, this mixture was described as form-stable composite phase change material with decent thermal reliability and chemical stability even when it was subjected to 3000 melting/freezing cycling. Thermal conductivity of the form-stable capric-myristic acid/vermiculite composite phase change material was increased by about 85% with introduction of 2wt% expanded graphite (EG) into the composite [264]. The polyethylene glycol (PEG)-enwrapped silicon carbide nanowires (SiC NWs) network/expanded vermiculite form-stable composite phase change materials (PSE fs-CPCMs) had excellent chemical compatibility as well as thermal stability and reliability. These additional traits of the composite help PEG to minimize form instability during phase transition and to improve the slow heat transfer rate of PEG. The composite phase change material exhibited a thermal conductivity of of 0.53 W/mK (8.8 times higher than PEG) and the maximum adsorption ratio of PEG as high as 73.12 wt% [265].

In recent years, the form-stable phase change materials based on expanded vermiculite have been developed and evaluated as credible candidates for thermal energy storage materials. Common examples of the form-stable phase change materials include the following: paraffin/expanded vermiculite composite [266, 267], sodium nitrate-expanded vermiculite [268], LiCl-vermiculite [269], vermiculite/SrBr₂ composite [270], stearic acid/modified expanded vermiculite composite [271], vermiculite/calcium hydroxide [272], $[Na_2SO_4 \cdot 10H_2O - Na_2CO_3 \cdot 10H_2O (1:1)]/vermiculite [273], polyeth$ ylene glycol/vermiculite [274, 275], polyethylene glycol/expanded vermiculite composite [276], capric-palmitic-stearic acid/expanded vermiculite [277], polyethylene glycol-carbon nanotubes/expanded vermiculite [278], capric-stearic acid/modified expanded vermiculite [279], stearic acid/modified expanded vermiculite [280], fatty acid eutectics/expanded vermiculite [281], lauric-myristic-stearic acid/ Al₂O₃-loaded expanded vermiculite [282], LiCl/vermiculite [283].

9.5.12 Others

Cations such as Li⁺, whose hydration energy is higher than the energy of the vermiculite-cation attraction, can initiate water-assisted swelling of the layers. This process can lead to reassembling of the flakes in the damaged sites to self-repair. Additionally, the air dried vermiculite membranes exhibit an interesting self-healable humidity dependent conductivity. Therefore, Li⁺-vermiculite was used to prepare highly responsive bilayer membranes by assembling clay flakes with different charge-balancing cations and to fuse them with lamellar membranes of other 2D materials, such as graphene oxide and vanadium pentoxide [284]. Vermiculite can also be a gamma-ray shielding material. This application was firstly studied by Gülbicim et al. [285]. The photon total mass attenuation coefficients μ_m , the half value layer, the tenth value layer, and the mean free path values have been experimentally determined for the photon energies at 0.244, 0.262, 0.342, 0.600, 0.778, 1.173, 1.332, 1.408, and 1.728 MeV. From the results, vermiculite was proved to possess excellent shielding characteristics for gamma radistion, which gives vermiculite the possibility to be qualified for a shielding material for gamma radiation.

9.6 Suggestions and Future Prospects

This chapter focuses on the structural features, properties, surface modification, intercalation/exfoliation, structure regulation, nanocomposites, and functional applications of vermiculite. Vermiculite has large specific surface area, ion exchange capacity, and surface activity. It has thus been widely applied in numerous fields, such as agriculture, the chemical industry, and environmental protection. In recent years, mineral materials have received more and more attention and research on vermiculite and its related materials have also made considerable progress. Various physical and chemical ways to reduce the size of vermiculite particles were also established and matured. The reduction of size of vermiculite leads to the improvement of specific surface area, ion exchange capacity, surface active groups, and surface hydrophilic/hydrophobic characteristics, which subsequently enables vermiculite to be used in both hydrophilic or hydrophobic environments or respective substrates. Therefore, the field of application of vermiculite has also grown exceedingly from traditional fields to emerging fields such as energy and biomedicine materials. Despite of the great progresses in vermiculite-related research so far, there are still many issues in the theoretical and applied research. One of which would be not taking full advantages of vermiculite as nanomaterials. Currently, there are several areas where more attention needs to be drawn, of which some more important ones are presented as follows:

- (i) Devising eco-friendly and economical exfoliation and intercalation method of vermiculite. It has been confirmed by researches that the performance of the obtained composite material derived from vermiculite is highly dependent on the intercalation or exfoliation degree of vermiculite Ususlly, intercalation or exfoliation methods of vermiculite include solution intercalation and melt intercalation or exfoliation. However, complete exfoliation of vermiculite into a single nanosheet still remains a major challenge. Therefore, a viable solution that is eco-friendly needs to be proposed to solve the issue and improve the exfoliation efficiency of vermiculite.
- (ii) Developing an artificial synthesis technology of vermiculite. The isomorphism phenomenon usually occurred during the formation of vermiculite, leading to the existence of variable ions in the crystalline structure of vermiculite. These ions in the crystal structure restricted the application of vermiculite in many areas such as anticorrosion, plastic, barrier materials, and radiation-protection materials. Such special application requires vermiculite materials to be used without impurity ions, so artificial synthesis of vermiculite becomes a crucial subject. Researchers may need to conduct basic research prospectively on full synthesis or semisynthesis of vermiculite, laying foundation for large-scale industrial applications in the future.
- (iii) Developing new functional materials by utilizing the sizelimitation feature of the interlayer domain of vermiculite. Vermiculite has nano-scale inter-layer domains and ion-exchange properties. After intercalation with different ions, the inter-layer domains can change in the nanometer range. That is, these

interlayer domains can be used to synthesize nanoparticles of various sizes. For example, the nanoscale interlayer domain of vermiculite can be used to synthesize vermiculite/graphene nanocomposites that can be potentially applied on a large scale to energy storage-related industries or as catalysis materials.

- (iv) Developing a comprehensive utilization technology of different grades of vermiculite. Among natural vermiculite minerals, low-grade minerals occupies a large proportion. Since great difficulties lies in the separation and purification process of pure vermiculite due to lack of economical and effective ways of processing, through research is still needed for complete conversion and utilization of these low-grade vermiculite minerals. In particular, research is needed on the dissolution-recombination behaviors of metal ions in vermiculite under different conditions and the structure-activity relationship of how the properties of vermiculite change after octahedral ions are dissolved needs to be further studied.
- (v) Preparation of single crystal silicon material using vermiculite. Vermiculite has a two-dimensional nanoscale layer with stable silicon skeleton. It can thus be directly converted into single crystal silicon via a high-temperature reduction approach. The single crystal silicon products are known to have wide-ranged applications in solar energy, battery, and catalysis.
- (vi) Further extension of application of vermiculite to more fields. For instance, better temperature-resistant materials and radiation-protection materials are supposed to be obtained by combining expanded vermiculite with graphite and other materials. Such products are expected to have broad application prospects in the nuclear industry. Vermiculite is a safe, nontoxic, natural nanomaterial and can thus be used to prepare antibacterial materials, toxin adsorption materials, medical materials, materials for animal breeding and other biochemical materials where its nontoxic characteristic is desired. In addition, there are definitely many fields of application where vermiculite and its related materials may have potential but still remain to be exploited. To explore all the possibilities and find out other potential applications of vermiculite remain an important subject for researchers in this area.

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