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HIGHLIGHT

Application of imogolite clay nanotubes in organic–inorganic nanohybrid materials

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The unique one dimensional structure and the positively charged external surface are the driving forces for imogolite clay nanotubes emerging as one of the most promising nano building blocks for various hybrid materials. This paper reviews the utility of imogolite in organic–inorganic nanohybrids, including polymer–imogolite nanocomposites and imogolite based hybrid hydrogels. Several effective approaches for dispersing imogolite down to small-sized bundles or even individual nanotubes in polymer matrices, including both hydrophobic and hydrophilic polymers, are introduced. The application of imogolite for the direct gel formation of biomolecules is also introduced.

Through the combination of several components at the molecular level, the

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fabrication of nanohybrids is one of the most effective approaches for producing new materials with advanced properties that were usually unavailable in the past. Organic–inorganic nanohybrids formed by dispersing inorganic nanostructures in organic matrices are attracting a great deal of research interest; the complementation and/or synergy of the rigid inorganic and the soft (sometimes functional as well) organic ingredients are capable of affording the resultant nanohybrids with novel features.¹ Well dispersed inorganics in the nanohybrids are generally used as reinforcing fillers that provide high

strength or stability for the organics. Since the invention of polymer–clay nanocomposites by Toyota in 1984,² extensive worldwide research on organic–inorganic nanohybrids has been conducted and several products, such as nylon–clay³ and rubber–silica,⁴ are already used in the fields of the packaging industry, sporting goods, and automobiles.⁵ Discovery or synthesis of new nanomaterials, such as carbon nanotubes and graphene, have been providing diverse candidate nanofillers for the construction of nanohybrids, and carbon nanotubes even made a boom for



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nano hybrid preparation;⁶ under such a background, clays survive the rapid advance in material science and still keep their vitality due to the versatile characteristics of an attractive structure, tunable surface chemistry, and “green” features (easily available and biocompatible) that is in high demand for releasing several of the severe global issues from the environment to climate.

In addition to commonly used lamellar structures, such as laponite, kaolinite and montmorillonite, clays can also form tubular structures, which are garnering research interest due to their unique one dimensional structure, high porosity, and large surface area. Halloysite and imogolite compose two of the known tubular clays. They are naturally occurring and are both composed of aluminosilicate. Halloysite, $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O})$ with a length of 500–1000 nm, diameter of ca. 50 nm, and lumen of 15 nm is mined from abundant mineral deposits.⁷ The dimensions of imogolite $(\text{Al}_2\text{SiO}_3(\text{OH})_4)$ are considerably smaller than those of halloysite. It has a length of approximately 100 nm, internal diameter of about 1 nm, and external diameter of about 2 nm,⁸ therefore, it can provide much more surface area than halloysite under the same volume. Imogolite presents a SiOH-functionalized interior and AlOH-functionalized exterior (Fig. 1), thus it can be positively charged in acidic conditions. Typical applications of imogolite involve its use as a gel former,⁹ for gas storage,¹⁰ as a coagulant and thickener,¹¹ and as a nanofiller for

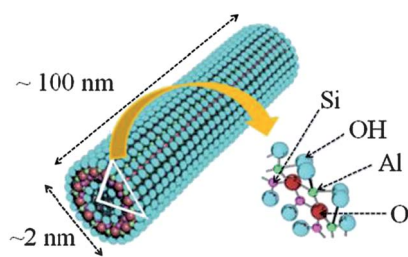


Fig. 1 A schematic representation of the structure of an imogolite nanotube.

polymers.¹² Natural imogolite was first discovered (in 1962) in certain volcanic soil deposits in Japan,¹³ then in many other volcanic and podsol soils throughout the world. However, mining is not an economic way to supply imogolite, because the concentration of natural imogolite is very low. As an alternative, this nanomaterial can also be obtained by chemical synthesis under mild conditions.¹⁴ Recent progress in synthetic protocols has resulted in several promising methods for producing imogolite (or imogolite-like) nanotubes in large quantities.¹⁵ These efforts may potentially stimulate new interest in imogolite research and open up possibilities for large-scale applications.

The applications of imogolite as a one dimensional building block for nano-devices¹⁶ and nanohybrids^{9a,9c,12a,b,12d,17} have been demonstrated previously. This paper reviews the utility of imogolite for the fabrication of organic–inorganic nanohybrids, including polymer–imogolite nanocomposites and imogolite hybrid hydrogels. The direct mixing of

imogolite with organic polymers is not a suitable way to prepare the nanocomposites, because imogolite nanotubes are likely to form bundles due to their rigid structure and high surface energy, and the bundles may form further larger bundles or random aggregates. Several effective approaches for dispersing imogolite down to small-sized bundles or even individual nanotubes in polymer matrices are introduced.

Imogolite–polymer nanocomposites by the *in situ* synthesis of polymer in an imogolite solution

Imogolite nanotubes exhibit very strong tube–tube interactions through their external AlOH groups, thus from the aspects of both kinetics and thermodynamics, they are very difficult to disperse in hydrophobic polymers. One feasible approach for dispersing imogolite into such materials is to reduce their tube–tube interactions by modification with organic compounds.¹⁸ However, the relief in the enthalpic problem alone is still not enough to make a stable dispersion, because the rigid nanostructures are usually entropically incompatible with linear polymer chains due to “depletion demixing”.¹⁹ On the other hand, the depletion demixing can be suppressed by grafting polymer chains onto the nanostructure’s surface, thereby, stable mixtures of nanostructures and polymers can be achieved.²⁰ According to the above consideration, we prepared a poly(methyl



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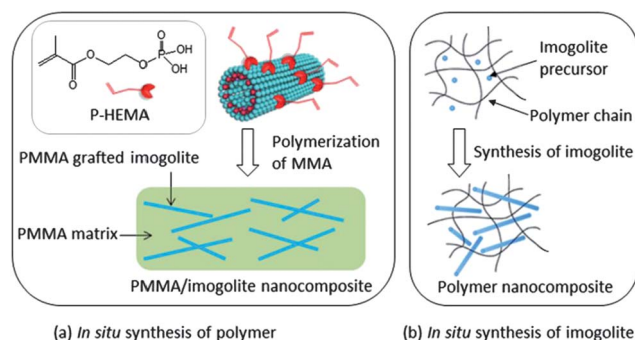


Fig. 2 Schematic illustration of polymer–imogolite nanocomposites prepared by *in situ* synthesis of polymer in an imogolite solution (a) and *in situ* synthesis of imogolite in a polymer solution (b).

methacrylate) (PMMA)–imogolite nanocomposite by free radical polymerization of methyl methacrylate (MMA) in the presence of imogolite modified by phosphonic acid with a polymerizable methacrylate group (Fig. 2 (a)).^{12a} During the polymerization of MMA, several growing PMMA chains can be grafted to the inorganic surface by reaction with the methacrylate groups immobilized on the imogolite surface. Moreover, the grafted polymers have molecular weights comparable to that of the free polymers, because of the same kinetic condition. This is very important for an athermal mixture to get a thermodynamically stable dispersion, which requires the molecular weight of the grafted polymer chains to be at least as large as that of the matrix polymer.^{20,21}

In our case, 2-acidphosphoxyethyl methacrylate (P-HEMA) was used for imogolite surface modification. The modification process was carried out in a weakly acidic aqueous solution, since imogolite prefers to adequately disperse in such conditions. A free radical polymerization using 2,2'-azodiisobutyronitrile (AIBN) as the initiator was employed for the *in situ* MMA polymerization. The resultant PMMA–imogolite nanocomposite was as transparent as the pure PMMA product; this is attributed to the excellent dispersion of imogolite. As a contrast, a PMMA–imogolite blend prepared by directly mixing PMMA with unmodified imogolite appears translucent. Fig. 3 compares the transparency of PMMA, PMMA–imogolite nanocomposite, and PMMA–imogolite blend films. In addition, the mechanical properties of the PMMA–imogolite nanocomposite were also significantly improved with respect to the pure PMMA

and PMMA–imogolite blend. For example, the dynamic storage modulus of the PMMA–imogolite nanocomposite was approximately 1.5 times as high as that of pure PMMA in all temperature ranges, the tensile modulus and ultimate strength of the PMMA–imogolite nanocomposite were approximately 1.4 times as high as those of the pure PMMA, and the elongation of the nanocomposite was 4 times as high as that of the PMMA–imogolite blend. All of these excellent performances of the nanocomposite are attributed to the fine dispersion of imogolite in the polymer matrix and the good affinity between the PMMA matrix and the PMMA grafted imogolite.

Imogolite–polymer nanocomposites by the *in situ* synthesis of imogolite in a polymer solution

From the aspect of thermodynamics, there is still a possibility for the unmodified imogolite to homogeneously and

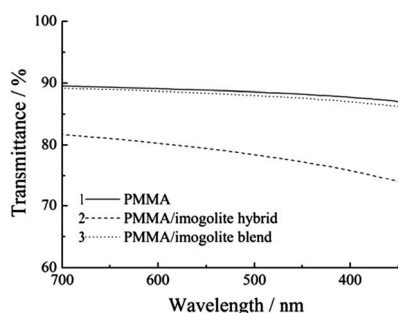


Fig. 3 Light transmittance of PMMA, PMMA–imogolite nanocomposite, and PMMA–imogolite blend films in the visible light region. Imogolite content was 1.0 wt %. Reproduced from ref. 12a. Copyright 2005 Elsevier B.V.

stably disperse in a polymer matrix, if the polymer can form favorable enthalpic interactions with the bare imogolite surface. Specific interactions between imogolite and several polymers, such as poly(vinyl alcohol) (PVA)²² and poly(acrylic acid) (PAA),^{16a} through hydrogen bonding and/or ionic interactions have been revealed. However, on the other hand, an unsuitable preparation method might make such a possibility unapproachable. Unlike the soft polymer chains, rigid imogolite has very poor mobility, thus it can be anticipated that the simple mixing of hydrophilic polymers with imogolite is not a suitable approach for achieving a good dispersion. Light transmittance and haze studies revealed that the PVA–imogolite blend prepared by directly mixing PVA with freeze-dried imogolite in water presented a low transmittance and high haze value,^{12b} indicating the poor dispersion state of the imogolite nanotubes.

In order to overcome the above kinetic problems for imogolite dispersion, we introduced a novel method for PVA–imogolite nanocomposite preparation: *in situ* synthesis of imogolite nanotubes in a PVA aqueous solution (Fig. 2 (b)).^{12b} The imogolite precursor was prepared beforehand, and mixed with a PVA aqueous solution. The mixture was heated at 369 K for 4 days. After cooling, the mixed solution of imogolite and PVA was precipitated from ethanol, then filtered and rinsed with water and ethanol, thus the PVA–imogolite nanocomposites were obtained. The successful synthesis of imogolite in a PVA solution was confirmed by Fourier transform infrared (FT-IR) spectroscopy and wide angle X-ray diffraction (WAXD) measurements. The synthesized imogolite nanotubes were quite homogeneously dispersed in the PVA matrix in a wide range of imogolite contents, as confirmed by atomic force microscopy (AFM) observations (Fig. 4), and the nanocomposite films appeared very transparent with a light transmittance close to the pure PVA film (Fig. 5). Imogolite nanotubes can be stabilized by both static repulsion, caused by the positive charges on the imogolite's surface, and the potentially adsorbed PVA chains in the synthetic solution. The adsorbed PVA chains play a crucial role in preventing imogolite aggregation during

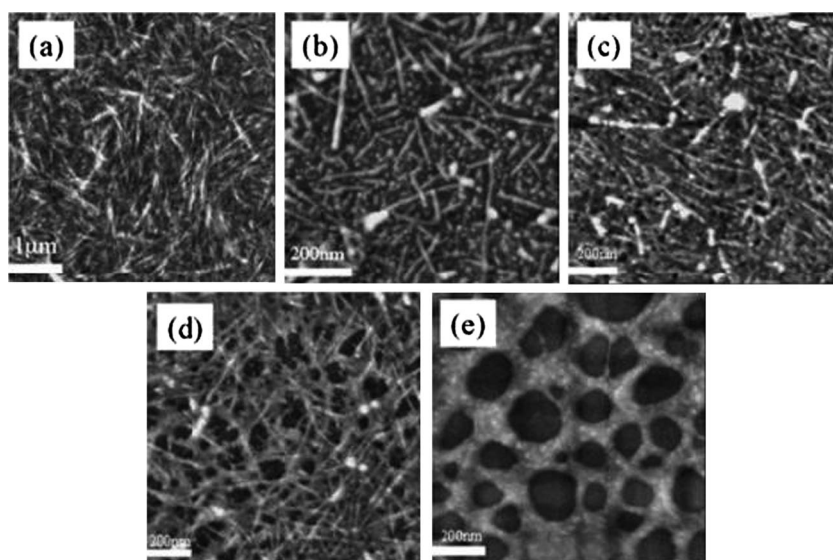


Fig. 4 AFM height images of *in situ* synthesized PVA–imogolite nanocomposites. Imogolite : PVA (w/w) = 1 : 1 (a), 1 : 5 (b), 1 : 10 (c), 1 : 20 (d), and 1 : 50 (e). Reproduced from ref. 12b. Copyright 2005 Royal Society of Chemistry.



Fig. 5 The transparency of the *in situ* synthesized nanocomposite (upper) and blend (lower) films with imogolite : PVA = 1 : 20. The thickness of the films is *ca.* 100 μm. Reproduced from ref. 12b. Copyright 2005 Royal Society of Chemistry.

the precipitation for nanocomposite recovery. Moreover, the dispersion of imogolite in PVA is a thermodynamically stable state, since no macroscopic phase separation occurs during water evaporation in a solvent cast process for the nanocomposite film preparation. The excellent thermal and mechanical properties of the PVA–imogolite nanocomposites involve the significantly improved heat distortion temperature and storage modulus; for example, the storage modulus and heat distortion

temperature increased from 4.2 to 6.6 GPa and 374 to 402 K, respectively, at 20% imogolite content. These transparent imogolite–polymer nanohybrids can potentially be used in optical devices.

Imogolite–polymer ternary nanocomposites *via* surface-initiated radical polymerization

In addition to the binary polymer–imogolite nanocomposites as mentioned above, we also prepared a ternary imogolite nanocomposite, in which two different polymers are used: one is grafted on the imogolite surface, and the other is employed as a polymer matrix.^{12d} Compared with the binary ones, ternary nanocomposites have the advantage of a tunable interface depending on the interactions between the grafted and the matrix polymers. A strong interface can be expected if the two polymers involved exhibit specific interactions. Moreover, in such an enthalpy controlled system, the molecular weight of the grafted polymer chains does not necessarily need to be larger than that of the matrix polymer, which is required in an entropy controlled nanocomposite.²⁰ In our study, a surface-initiated atom transfer radical polymerization (SI-ATRP) is employed for the preparation of an imogolite ternary nanocomposite, in which PMMA and

poly(vinyl chloride) (PVC) are used as the grafted and matrix polymers, respectively.^{12d}

To realize the polymerization of MMA on the surface of the imogolite nanotubes, we synthesized a water-soluble and surface-attachable ATRP initiator, the ammonium salt of 8-(2-bromo-2-methylpropanoyloxy) octyl phosphate [BMPO- $\text{PO}_4(\text{NH}_4)_2$].²³ This initiator can readily chemisorb to the imogolite surface from an aqueous solution. The subsequent SI-ATRP was carried out under mild conditions by using a new ATRP technique, activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP).²⁴ Fig. 6 presents the preparation procedure for PMMA grafted imogolite nanotubes (PMMA-g-imogolite). The obtained PMMA grafted imogolite nanotubes are likely to disperse in various organic solvents and the dispersions show perfect Tyndall effect. A PVC–PMMA-g-imogolite nanocomposite was prepared by mixing PVC and PMMA-g-imogolite in solvent. The successful dispersion was confirmed by differential scanning calorimetry (DSC) measurement and transmission electron microscopic (TEM) observation. Further characterizations of the microstructures of this nanocomposite reveal that the interfacial adhesion between the PMMA-g-imogolite and the PVC matrix may be weak or strong with respect to the cohesive energy of the matrix, depending on the environmental temperatures. At low temperature (for example in liquid nitrogen or at room temperature), the interfacial adhesion between the PMMA-g-imogolite and the matrix is weaker, while at high temperatures (such as 90 °C), it is stronger than the cohesive energy of the PVC matrix. In accordance with the interfacial performance, the nanohybrid shows inferior tensile performance at room temperature; whereas, it shows superior tensile performance at 90 °C, compared with the pristine PVC under the same conditions. Such temperature dependences of the interfacial features contribute to a better understanding of the different reinforcement effects of nanofillers in various polymer nanocomposites, and it strongly confirms the importance of a strong interface for an excellent polymer nanocomposite.

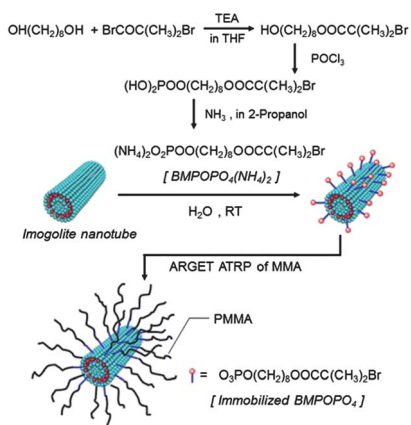


Fig. 6 Schematic representation for the preparation of PMMA grafted imogolite nanotubes. Reproduced from ref. 23. Copyright 2011 Royal Society of Chemistry.

Imogolite–biomolecule hybrid hydrogels

Due to the high polarity of the charged surface, clay minerals can also be used as building blocks for hydrogels. The soft consistency of hydrogels minimizes the frictional irritation of the surrounding cells and tissue, therefore, they are suitable for biomedical applications that require contact with living tissue. The properties of gels can be significantly enhanced by the incorporation of inorganic systems, such as clays, into the gels. Several hydrogels formed by the hybridization of synthetic polymers with clay nanosheets have been reported.²⁵ However, there are few reports on hydrogels produced by directly mixing clays with biomolecules. This is because most of the biomolecules are negatively charged, thus they are repulsive with commonly used clays. On the contrary, imogolite nanotubes are positively charged and are readily dispersed in water in acidic conditions, thus, they have a potential utility in the direct gel formation of various biomolecules. More interestingly, the biomolecules do not necessarily need to have a binder structure,^{25b} because imogolite itself can gelate under certain conditions, such as at high concentrations or high pH.

The first imogolite hybrid hydrogel formed by immobilizing an enzyme (we used pepsin) onto imogolite nanotubes was reported by our group in 2006 (Fig. 7).^{9a} Pepsin is negatively charged in acidic conditions, and also has

a phosphoric group, thus it can adsorb onto the imogolite surface by both electrostatic adhesion and the specific affinity between the AlOH groups of imogolite and the phosphonic groups of pepsin. By incubating the mixture of imogolite and pepsin in water under shaking, an imogolite–pepsin hybrid hydrogel was prepared. Due to the extremely large surface areas of the imogolite nanotubes, the immobilization amount of pepsin was as high as 1.8 mg per 1 mg of imogolite. Fluorescence microscopy observations indicated that the pepsin was evenly dispersed in the gel. Compared with the free one, the pepsin immobilized on this hydrogel can be easily recovered from the reaction system, and can be used repeatedly.

Very recently, we mixed imogolite with DNA and prepared an imogolite–DNA hybrid hydrogel.^{9c} DNA is a very important biomolecule containing life information, and has also been studied for disease therapy. Free DNA is rapidly degraded in the environment, while DNA bound onto solid particles appears to be resistant to degradation.²⁶ Therefore, an imogolite–DNA hydrogel may have the potential to act as a reservoir for DNA storage and even control its release. The driving force for this hydrogel formation is attributed to the strong interaction between the phosphate groups on the outside of the DNA double helix and the aluminol groups on the imogolite surface. The maximum DNA content in the hydrogel can reach as high as 3 mg DNA per 1 mg of imogolite under an optimal DNA–imogolite feed ratio. Release experiments of DNA out of this hydrogel suggest a very slow release rate even under severe conditions, such as high pH and high ion (NaCl) concentrations (Fig. 8), indicating that DNA could be effectively

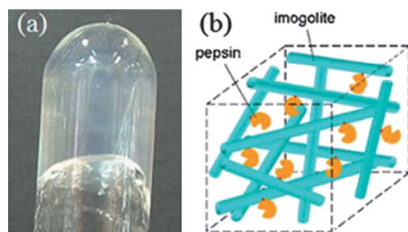


Fig. 7 Photograph (a) and schematic representation (b) of the (imogolite–pepsin) hybrid hydrogel. Reproduced from ref. 9a. Copyright 2006. The Chemical Society of Japan.

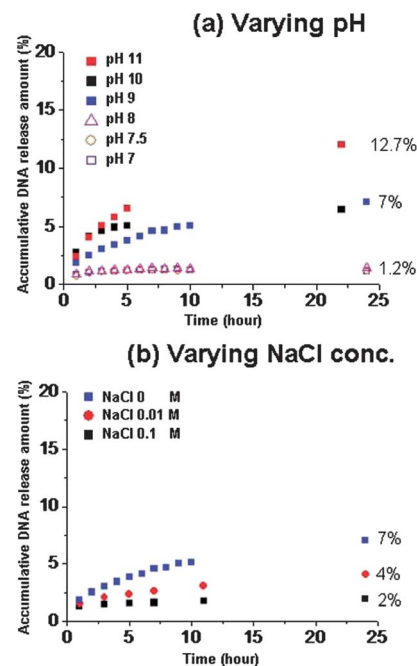


Fig. 8 The release of DNA from imogolite–DNA hybrid hydrogels; by (a) varying pH 7–11 (at 37 °C) and (b) varying the NaCl concentration (at pH 9, 37 °C). Adapted from ref. 9c. Copyright 2012. American Chemical Society.

protected by hybridization with imogolite.

Conclusions

The unique one dimensional structure and the positively charged external surface are the driving forces for imogolite clay nanotubes emerging as one of the most promising building blocks for various organic–inorganic nanohybrids. We introduced three approaches for dispersing imogolite nanotubes into synthetic matrices, including both hydrophobic and hydrophilic polymers, to prepare binary or ternary nanocomposites. Due to the good dispersion and the transparency feature of imogolite itself, transparent polymer–imogolite nanocomposites were successfully prepared. Mechanical properties of the original polymers were improved by the interaction with imogolite. Moreover, the capability of imogolite for the gel formation of biomolecules was demonstrated by fabricating imogolite-based enzyme and DNA hybrid hydrogels. The amount of biomolecules in the hybrid hydrogels can be very high, because of the extremely large surface areas of the

imogolite nanotubes and the strong interactions between the biomolecules and the imogolite surface. Imogolite is a “green nanomaterial”, although natural imogolite is not sufficient for real utility, the advances in imogolite synthesis do not require toxic raw materials or aggressive solvents, especially new methods for large quantity production, making this nanomaterial easily available. The applications of imogolite in organic–inorganic nanohybrid materials are of course not limited to reinforcing several polymers or stabilizing several biomolecules. Novel applications of imogolite are still under development, for example, high proton conductivity due to the AlOH^{2+} external groups may make imogolite an excellent additive for proton exchange membranes that can even be used under very high temperatures.

Acknowledgements

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