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Synthesis of clay-CNTs nanocomposite

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Abstract

Nanocomposite of clay-carbon nanotubes (CNTs) is prepared by using carboxyl-modified multiwalled carbon nanotubes and amino-functionalized organophilic montmorillonite (clay). The nanocomposite is characterized by scanning electron microscopy to evaluate the morphology. The findings show uniform dispersion of CNTs.

Keywords: Carbon nanotubes, Montmorillonite, Carboxyl-modified multiwalled carbon nanotubes, Organo clay

Background

Carbon nanotubes (CNTs) were first discovered by Iijima in 1991 [1]. Since then, CNTs have been the focus of considerable research because of their physicochemical properties. The first observed CNTs were multiwalled carbon nanotubes (MWCNTs) (see Figure 1a), consisting of up to several tens of graphitic shells with adjacent shell separation of 0.34 nm, diameters of 1 nm, and large length/diameter ratio. MWCNTs can be considered as elongated fullerene [2]. A few months after Iijima's discovery, Ebbesen and Ajayan published their work on the bulk synthesis of MWCNTs by arcing graphite electrodes in inert atmospheres at optimum current and pressure conditions. However, it is necessary to note that the first images of CNTs were obtained by Oberlin et al. by pyrolysis of benzene and ferrocene at 1,000°C in the mid-1970s. In 1993, smaller-diameter, single-walled carbon nanotubes (SWCNTs) (see Figure 1b) were independently discovered by Iijima and Ichihashi and Bethune et al. using arc-discharge method and metal (iron and cobalt) as catalysts. CNTs have been termed 'materials of the twenty-first century' due to their unique properties such as functional mechanical, thermal, electrical, and optoelectronic properties which depend on the atomic arrangement (how the sheets of graphite are 'rolled'), the diameter and length of the tubes, the morphology, or nanostructure [3,4].

The adsorption-related applications of CNTs to solve environmental pollution problems have received considerable attention in recent years. CNTs are relatively new adsorbents and hold interesting positions in carbon-based adsorptive materials for many reasons [5].

The surface functional group density, rather than total surface area, becomes the primary determinant of inorganic pollutant adsorption capacity. The activation of CNTs plays an important role in enhancing the maximum adsorption capacity because of the modification in the surface morphology and surface functional groups. Activation of CNTs under oxidizing conditions with chemicals such as HNO₃, KMnO₄, H₂O₂, NaClO, H₂SO₄, KOH, and NaOH have been widely reported [6]. After activation, the metallic impurities, amorphous carbon, and catalyst support materials are removed, and the surface characteristics are altered due to the introduction of new functional groups as shown in Figure 2.

Nanotechnology is being used or considered in many applications targeted to provide cleaner and more efficient energy supplies and uses. While many of these applications may not affect energy transmission directly, each has the potential to reduce the need for the electricity, petroleum distillate fuel, or natural gas [7].

Clay minerals may be divided into four major groups, mainly in terms of the variation in the layered structure. The kaolinite group has three members, including kaolinite, dickite, and nacrite, each with a formula of Al₂Si₂O₅(OH)₄. The same formula indicates that the members of this group are polymorphs, meaning that they have same formula but different structures. Each member is composed of silicate sheets (Si₂O₅) bonded to aluminum oxide/hydroxide layers Al₂(OH)₄ the two types of layers are tightly bonded. These clays are used as fillers in ceramics, paint, rubber, paper, plastics and as plasticizer in molding sands. Montmorillonite, talc, pyrophyllite, saponite, and nontronite are a few members of the larger smectite clay group. The general formula for the chemical structure of this group is (Ca,Na,H)(Al,Mg,

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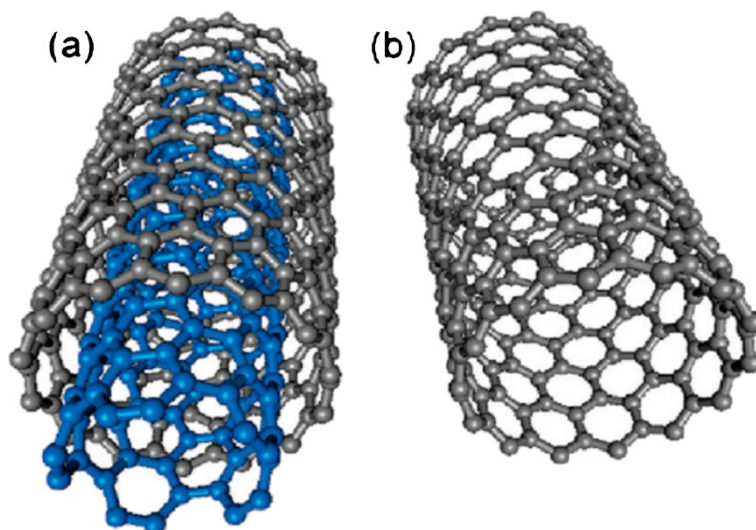


Figure 1 Structure presentations of (a) MWCNT and (b) SWCNT.

$\text{Fe,Zn)}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2\text{XH}_2\text{O}$. The important difference among the members of this group is seen in the chemical characteristics. The layer structure contains silicate layers sandwiching an aluminum oxide/hydroxide layer ($\text{Al}_2(\text{OH})_4$) [8].

One of the members, talc, has traditional presence in facial powder. 'Nanoclay' is the term generally used when referring to a clay mineral with a phyllosilicate or sheet structure with a thickness of the order of 1 nm and surfaces of perhaps 50 150 nm in one dimension. The mineral base can be natural or synthetic and is hydrophilic. The clay surfaces can be modified with specific methods to render them organophilic and therefore compatible with organic polymers adsorption of clay minerals can occur in two forms, selective and non-selective [9]. Selective sorption is also named as specific or non-exchangeable sorption, while non-selective sorption is named as exchangeable sorption.

In the process of non-selective adsorption, clay minerals adsorb ions through exchangeable cations and electrostatically bound counter ions in the diffusion layer which is formed because of the surface charge. Such ions are electrostatically bound to the surface and the surface charge is a factor controlling the sorption density. Selectively adsorbed ions are assumed to form inner sphere complexes with surface hydroxide sites that is, they are primarily bound to the surface of clay minerals by chemical bond. This bond is highly dependent upon the structure of the surface and its interaction with a specific ion and, hence, exhibits substantially different behavior from electrostatic bonding. In recent decades, clays such as montmorillonite, vermiculite, kaolinite, and mica were reported as inexpensive products in a large diversity of industrial processes, pharmaceutical industry, cosmetics, organic synthesis, and environmental remediation [10]. In this paper we have used

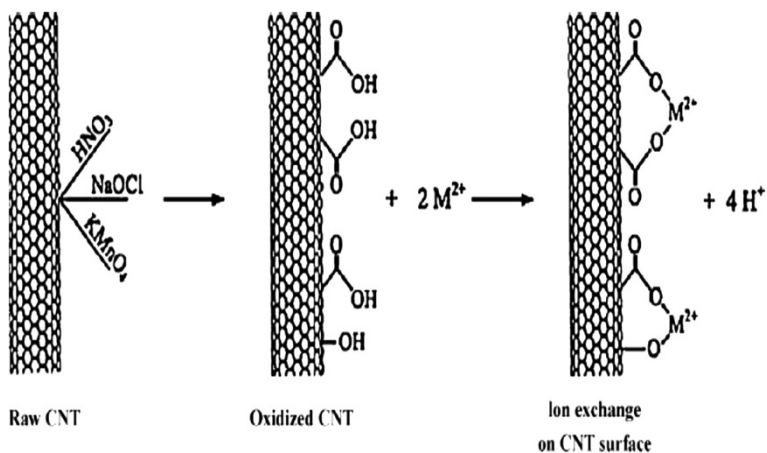


Figure 2 Schematic of the major mechanism for sorption of divalent metal ions onto CNT surfaces.

amino-functionalized clay and carboxyl-functionalized MWCNTs to synthesize the nanocomposite.

Results and discussion

The SEM analysis of nanocomposite

The failure surface of the MMT, OMMT, and clay-CNTs nanocomposite e film was observed via SEM. The SEM photographs were taken with a magnification 625,1,250, and $\times 2,500$ at room temperature. The study of the SEM images shows the differences between the MMT, OMMT, and clay-CNTs nanocomposite the reference sample (Figures 3, 4, and 5).

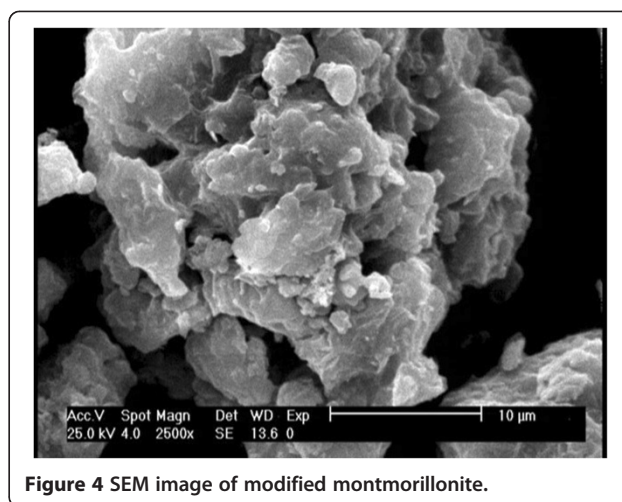
Conclusion

Because of a hydrophilic nature of the MMT, the organo-modification of the MMT is an important step in the preparation of MMT/HMDA composite. The organo-modification could change the hydrophilicity of Na-MMT to be more hydrophobic to generate a microchemical environment appropriate to the intercalation of MMT. Furthermore, the increase in the layer-to-layer spacing in the MMT is also desired. Primary aliphatic amines such as hexamethylenediamine and quaternary ammonium salts have been the most effective modifying reagents in the preparation of MMT/HMDA composite. Findings from the SEM images show that OMMT and clay-CNTs nanocomposite have uniform disperse and unique morphology. The clay-CNTs nanocomposite is favorable for many applications such as nanosponges for oil split remediation.

Methods

Materials

Montmorillonite (clay) was purchased from Fluka (Fluka Chemical Corporation, St. Gallen, Switzerland) and carboxyl-functionalized MWCNTs were purchased from China. In all experiment, double distilled water was used.



Synthesis of organic montmorillonite

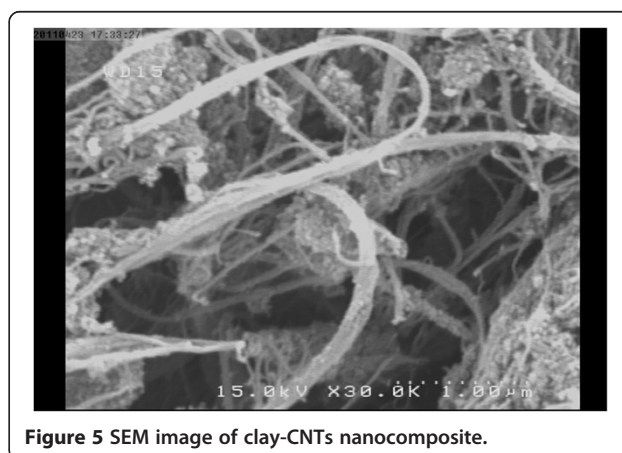
A 1.0 g of MMT was added in 40 mL of distilled water then mixed and heated to 80°C for 15.0 min. In a solution of 2.5 mM HCL, 0.04 g of hexamethylenediamine was added and mixed, and then the two abovementioned solutions were mixed together overnight at 80°C. The precipitate was removed by filtration and washed with distilled water, then dried in an oven at 60°C overnight.

Synthesis of clay-CNTs nanocomposite

A 0.1 g of the as-synthesized organoclay is mixed in 30 mL of DMF and sonicated for 40 min. Then 0.1 g of carboxyl-functionalized MWCNTs is added and heated to 90°C and refluxed for 24 h. The precipitate is washed with distilled water and dried in an oven.

Characterization

The as-synthesized nanocomposite has been characterized by scanning electron microscopy (SEM) using a XL-30 Philips model scanning electron microscope (Royal Philips Electronics, Amsterdam, The Netherlands).



Competing interest

The author declares no competing interest.

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