Method of nanocarbon/montmorillonite powder extraction

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In this reported work, carbon/montmorillonite (C/MMT) nanometre particles and micrometre particles blended were extracted by the froth flotation method, extraction and density gradient centrifugation. X-ray diffraction, scanning electron microscopy, transmission electron microscopy and particle size analysis were employed to characterise the C/MMT extracted before and after. The results have shown that the froth flotation method cannot effectively collect C/MMT nanocomposites, and the extraction is not effective, whereas density gradient centrifugation can collect vari-size grained C/MMT nanocomposite particles. On using density gradient centrifugation, the thicknesses of C/MMT nanocomposite particles are <20 nm.

1. Introduction: Owing to tiny size, nanometre materials have unique electrical, magnetic, mechanical, thermal and other properties [1]. Montmorillonite (MMT) is a typical layered mineral. It is made to have particular characteristics such as good thixotropy [2], interlayer cation of interchangeability [3], adsorptivity [4] and thermal stability because of its special structure. At the moment, MMT is widely used for adsorbent metallurgy pellets, activated clay, drilling fluids [2], feed additive [5] and so on. However, these areas are areas of lower technology and create low added value. Preparation of nanometre MMT is has much scope for exploiting application fields, improving its application value and making high value-added products.

The key to MMT nanocrystallisation is to exfoliate the crystal into two-dimensional (2D) nanomaterials, which can be more stable [6]. At present, organic reagent intercalation is commonly used in the preparation of nanometre MMT [7], which is based on its interlayer ion interchangeability and its layers' extensible characteristics [8]. The nanometre MMTs prepared by intercalation are generally obtained through preparing polymer/MMT nanocomposites, in which exfoliated MMT nanometre power is hard to obtain [9]. There is a little research on the preparation of 2D MMT nanometre powder [10–13]. Previously, we have modified MMT by intercalation, carbonisation and airstream pulverisation, and produced 2D carbon/MMT (C/MMT) nanometre composite powder. This C/MMT nanometre composite powder consists of silicate nanosheets whose thickness is about 10 nm and the average diameter size is about 2 μm, and nanotubes whose diameter is 7–80 nm. The C/MMT nanometre composites possess some characteristics such as a high surface area and good surface activity, and could be widely used as a catalyst [14], hydrogen storage material and gas adsorption material or could be widely added to greases and oils. However, that particle is mixed with several layered particles and dozens of layered particles. Some refinement methods of carbon nanotubes, such as filtration [15], flotation [16, 17] and extraction [18] have been referred to. However, different size particles have different performance, which leads to uncertain performance of this C/MMT mixture. So its application would be restricted.

Aiming at the uncertain performance of mixed particles, the mixed superfine C/MMT particles were prepared by the method given by Zhang *et al.* [19] as raw material. This research lays a foundation for the study of C/MMT nanocomposites' properties and applications. With the purpose of obtaining pure nanometre C/MMT powder, the froth flotation method, extraction and density gradient centrifugation are applied in this Letter.

2. Experimental

2.1. Materials: The raw material Na-MMT (Kelamayi, Singkiang, China) was chosen by wet purifying. PVA (Beijing Chemical Co., Beijing, China) with a purity of 99% and a polymerisation degree of 1750 ± 50, was used as the carbon source. Cetyltrimethyl ammonium bromide (CTAB) (Xilong Chemical Co., Shantou, China) AR, sodium dodecyl benzene sulphonate (SDBS) (Xilong Chemical Co., Shantou, China) AR and Casein pass-100(OP10) (Xilong Chemical Co., Shantou, China) AR, were used to extract C/MMT nanometre composites.

2.2. Preparation of superfine C/MMT nanocomposites and extraction: The method of C/MMT preparation was based on the method given by Zhang [8].

Cationic surfactant (CTAB), anionic surfactant (SDBS) and non-ionic surfactant (OP-10) are used separately as the foaming agent. C/MMT nanometre particles and micrometre particles blended (C/MMT NB) were purified by the froth flotation method. C/MMT NB was mixed with CTAB, SDBS and OP-10 suspension to a 3 g:500 ml mixing ratio, respectively, to reach the critical micelle concentration. After stirring the mixed suspension under ultrasound for 2 h, it was left standing for 1 h, the foam samples were taken from CTAB (C/MMT-C-F), SDBS (C/MMT-S-F) and from OP-10 (C/MMT-O-F) and the suspension samples from CTAB (C/MMT-C-S), SDBS (C/MMT-S-S) and from OP-10 (C/MMT-O-S); the resulting suspension was centrifuged and then dried, grounded and the sample was screened through 200 mesh screens.

In the extraction method, 3 g of C/MMT NB powder was put into a 500 ml suspension mixed with dimethylbenzene and water (50%:50%). After stirring the mixed suspension under ultrasound for 2 h, and stewing for 2 h, was centrifuged the toluene liquid layer and the water layer separately, and dried, grounded and screened the sample through 200 mesh screens. C/MMT gained from water (C/MMT-W) and from the dimethylbenzene (C/MMT-D) was obtained.

In the density gradient centrifugation method, 3 g C/MMT NB powder was put into 500 ml of water and ultrasonic stirring was done for 2 h. The suspension was centrifuged at 2000 r/min, and the precipitation was C/MMT-2000, we then continued to centrifuge the 2000 r/min supernatant at 4000 r/min, and the precipitation

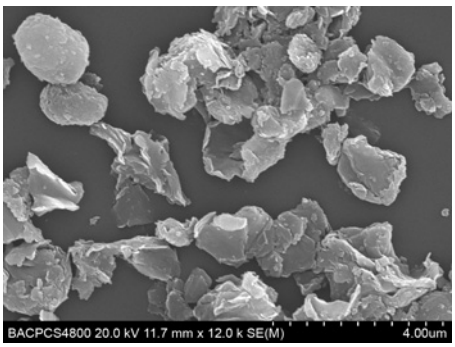

Figure 1 *SEM image of C/MMT NB*

was C/MMT-4000. Lastly, the 4000 r/min supernatant was centrifuged at 10 000 r/min. The precipitation was C/MMT-10 000, whereas the sample obtained from its supernatant was C/MMT-10 000-L. The sediment was then dried, crushed and sieved through the 200-mesh screen. Then samples were prepared.

2.3. Analysis and characterisation: X-ray powder diffraction (XRD) analysis was performed on a D/max-rA 12 kW diffraction at 40 kV and 100 mA using a Cu tube (Cu Ka target, $l = 0.154$ nm) at a scanning rate of 48 min^{-1}. The scanning electron microscopy (SEM) images were obtained using the HITACH S-4800 at 15 kV and 10 mA. The transmission electron microscopy (TEM) images were obtained using the JEOL JEM-2010 with 0.19 nm resolution, with a minimum beam spot of 1 nm and 0.14 nm lattice resolution. Grading analysis was performed with a Malven Zetasizer Nano ZS90. Its measurement range is 0.3–5.0 μm (diameter), measurement principle: dynamic light scattering. Surface morphologies of polyelectrolyte multilayers were characterised with atomic force microscopy (AFM, Dimension 3100) from Veeco, USA.

3. Results and discussion

3.1. Preparation of C/MMT NB: The SEM image of C/MMT NB is shown in Fig. 1. Most of the samples are exfoliated into C/MMT nanocomposite-shaped curly layers and others are non-exfoliated C/MMT composite-shaped particles and pieces.

The XRD pattern of C/MMT NB powder is shown in Fig. 2. The d_{001} basal spacing of the raw material C/MMT NB is 1.29 nm. The peak ($2\theta = 6.8°$) is relatively sharp, so there is a certain amount of non-exfoliated C/MMT composites.

3.2. Froth flotation method using CTAB: CTAB as a foaming agent, using the method in 2.2, C/MMT nanometre powder, was collected from C/MMT NB. The XRD patterns of C/MMT-C-F, C/MMT-C-S and C/MMT NB are shown in Fig. 3. The samples

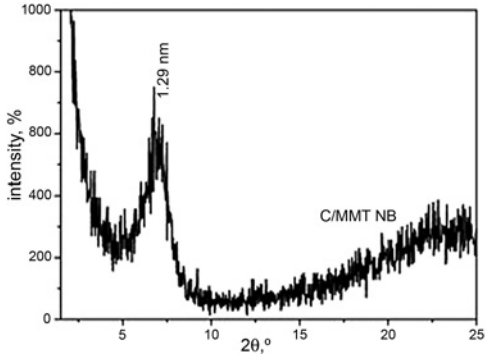

Figure 2 *XRD patterns of C/MMT NB*

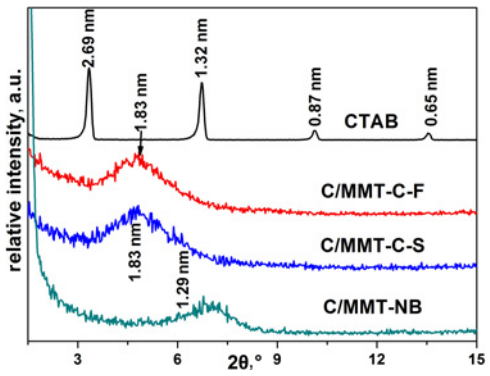

Figure 3 *XRD patterns of samples with CTAB as foaming agent*

of C/MMT-C-F and C/MMT-C-S have 1.83 nm basal spacing. These data indicate that C/MMT-C-F and C/MMT-C-S are modified by CTAB and their modification degrees are equal, but the two samples are mainly of a multilayered structure.

The size distribution of the samples C/MMT-C-F and C/MMT-NB is shown in Fig. 4. The grain size of the raw material C/MMT NB spreads from 100 to 700 nm, and its peak lies in 265 nm, whereas the size of C/MMT-C-F spreads from 200 to 475 nm, and its peak lies in 307 nm. The size distribution of C/MMT-C-F is not bigger than before, which indicates that this method can be used to extract a relatively smaller particle. At the same time, the smallest size of C/MMT-C-F is not as small as the smallest size of C/MMT NB, which may be as a result of CTAB coating on C/MMT. The results show that the froth flotation method with CTAB as the foaming agent can purify C/MMT NB to a certain extent. After using the froth flotation method with CTAB as the foaming agent, large particles are removed and their size distribution is around 307 nm. According to the XRD results, most of the C/MMT-C-F particles are multilayered.

3.3. Froth flotation method using OP-10: Using OP-10 as a foaming agent, and using the method in Section 2.2, C/MMT nanometre powders were collected from C/MMT NB. The XRD patterns are shown in Fig. 5. OP-10 is not a crystal, hence there is no peak in its XRD pattern. The XRD pattern of C/MMT-O-F has two peaks, whose interlamellar spacings are 4.74 and 1.86 nm, which indicates that there are two kinds of C/MMT in different modified degrees. The XRD pattern of C/MM-O-S has a similar peak, whose d_{001} is 1.77 nm, hence some of the C/MMT-O-F have a modification degree similar to the C/MMT-O-S. Meanwhile, XRD patterns of both samples have sharp peaks, which indicates that both the samples have a multilayer structure.

The size distribution of samples C/MMT-O-F and C/MMT NB is shown in Fig. 6. The grain size of the raw material C/MMT NB

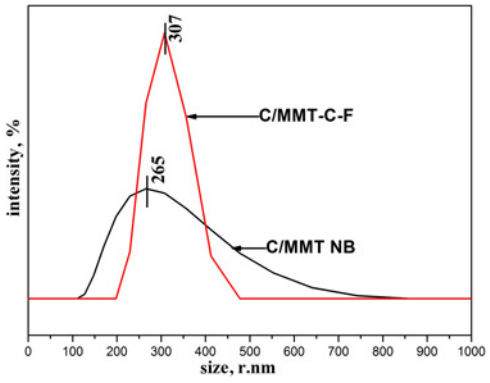

Figure 4 *Size distribution of samples C/MMT NB and C/MMT-C-F*

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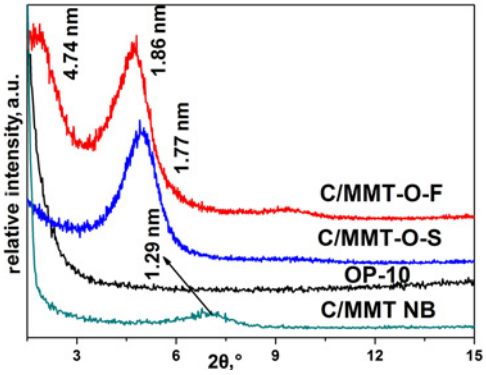

Figure 5 *XRD patterns of samples with OP-10 as foaming agent*

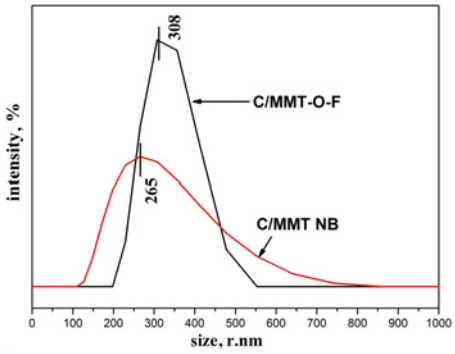

Figure 6 *Size distribution of samples before and after refined by OP-10*

spreads from 100 to700 nm and its peak lies in 265 nm, whereas that of the C/MMT-O-F spreads from 200 to 550 nm and its peak lies in 308 nm. Similar to the result with the sample refined by CTAB, the peak size distribution of C/MMT-O-F is a bit bigger than before. As a result of that bubbles rose in the water, not only small pieces rose with them, but also some big C/MMT fragments. Even this froth flotation method with OP-10 as the foaming agent cannot purify nanometre C/MMT composite powder totally. After using the froth flotation method with OP-10 as the foaming agent, large particles are removed and the size distribution of the particles is around 326 nm. According to the XRD results, most of C/MMT-O-F particles are also multilayered.

3.4. Froth flotation method using SDBS: Using the method in Section 2.2, and SDBS as the foaming agent, C/MMT nanometre powder was collected from C/MMT NB. The XRD patterns are

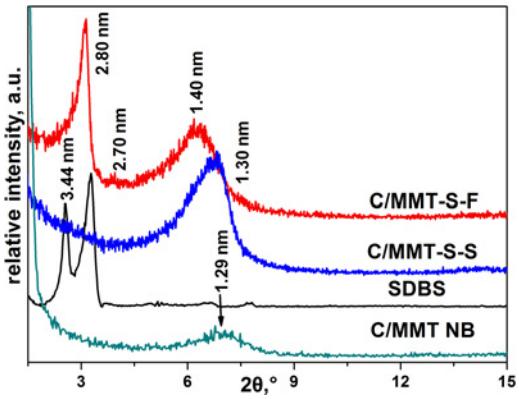

Figure 7 *XRD patterns of samples before and after refined by SDBS*

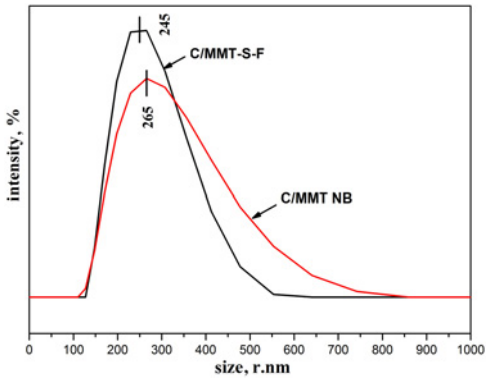

Figure 8 *Size distribution of samples before and after refined by SDBS*

shown in Fig. 7. The interlamellar spacing of C/MMT NB is 1.29 nm. The d_{001} value of SDBS is 3.44 and 2.70 nm. The d_{001} value of C/MMT-S-S is 1.30 nm, whereas the C/MMT-S-F has two peaks, which are 2.80 and 1.40 nm. The 2.80 nm peak indicates that some SDBS is intercalated into layers of C/MMT. As the anionic surfactant SDBS is charged negatively, which rejects the electronegative laminates of MMT, C/MMT powders are hard to be modified. As SDBS has a high concentration in the foam, some SDBS intercalated into the layers of MMT.

The size distribution of the C/MMT-S-F and C/MMT NB samples is shown in Fig. 8. The size of C/MMT-S-F spreads from 140 to 550 nm and the peak lies in 245 nm. The average size of C/MMT-S-F is 20 nm smaller than that of C/MMT NB. This froth flotation method with SDBS as the foaming agent can purify nanometre C/MMT powder to a lesser extent.

In general, even though the froth flotation method with SDBS as the foaming agent cannot extract monolayer C/MMT particles, it can purify nanometre C/MMT powder to a lesser extent, in which way the average of C/MMT-S-F is 20 nm smaller than that of C/MMT NB. There is a little improvement, whereas the effect is not obvious.

3.5. Extraction method: There were two samples purified from the water and dimethylbenzene mixture: C/MMT nanometre powder from the dimethylbenzene (C/MMT-D) and C/MMT powder from the water (C/MMT-W). C/MMT-D, C/MMT-W and C/MMT NB were tested by XRD. The XRD patterns are shown in Fig. 9. The d_{001} value of C/MMT-W is 1.32 nm, whereas the d_{001} value of C/MMT-D is 1.30 nm and the C/MMT NB is 1.29 nm. Viewed from the peak shape, the peaks of samples refined after extraction are both sharp. Both samples have a great number of multilayered C/MMT.

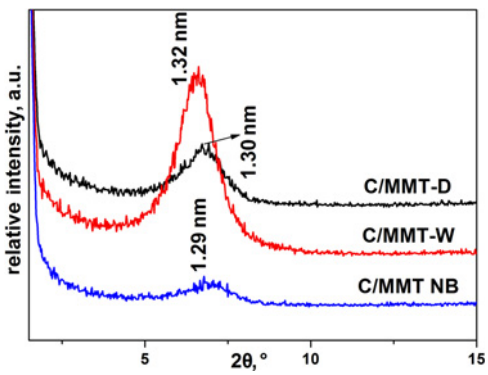

Figure 9 *XRD patterns of samples before and after refined by dimethylbenzene*

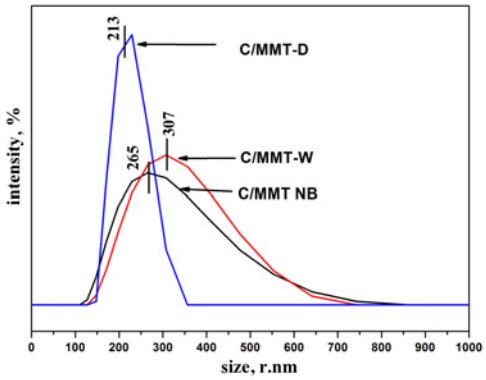

Figure 10 *Size distribution of samples before and after refined by dimethylbenzene*

The size distribution of C/MMT NB, C/MMT-W and C/MMT-D is shown in Fig. 10. The grain size of raw material C/MMT NB spreads from 100 to 700 nm and the peak lies in 265 nm, whereas the size of C/MMT-W spreads from 120 to 700 nm and the peak lies in 307 nm; the C/MMT-D's spreads from 150 to 350 nm and its peak lies in 215 nm. The size peak of C/MMT-D is about 50 nm smaller than that of C/MMT NB, whereas the size peak of C/MMT-W is a bit larger than the C/MMT NB. These data confirm that this extraction method has a relatively obvious effect on superfine C/MMT composite refinement.

C/MMT-D and C/MMT NB are detected by SEM. The SEM images are shown in Fig. 11. After extraction, monolayer C/MMT is more in dimethylbezene and C/MMT slices. These data confirm that this extraction method has some effects on C/MMT NB refinement.

In conclusion, the extraction method with dimethylbezene and water can extract monolayer C/MMT particles to some extent. It can purify nanometre C/MMT in dimethylbezene, and leaves bigger C/MMT particles in water. The average of C/MMT-D is 50 nm smaller than that of C/MMT NB.

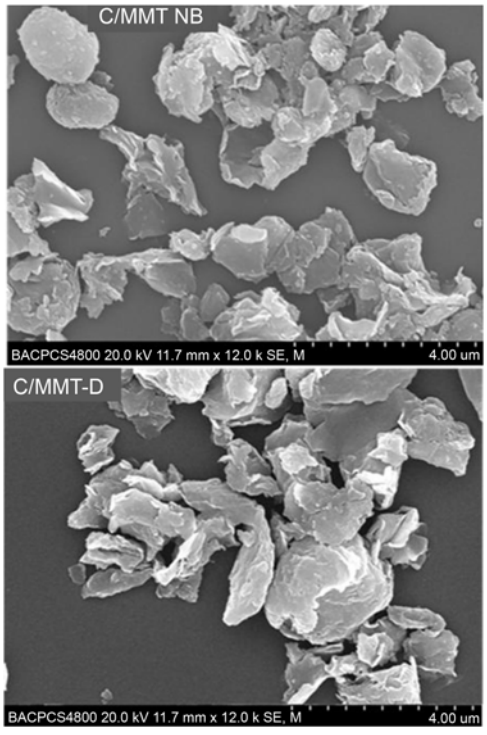

Figure 11 *SEM images of samples C/MMT NB and C/MMT-D*

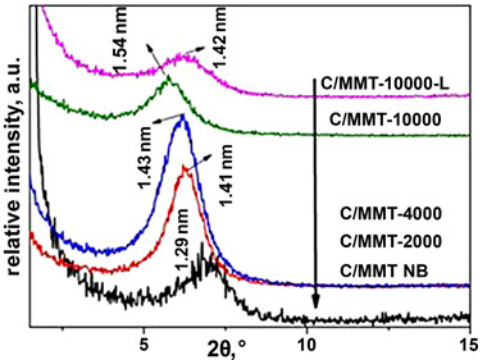

Figure 12 *XRD patterns of samples refined by gradient centrifugation*

3.6. Density gradient centrifugation: Four samples centrifuged separately at 2000 r/min (C/MMT-2000), 4000 r/min (C/MMT-4000), 10 000 r/min (C/MMT-10 000) and the supernatant of 10 000 r/min (C/MMT-10 000-L), which is centrifuged at 10 000 r/min and C/MMT NB were characterised by XRD. The XRD patterns are shown in Fig. 12. The d_{001} value of C/MMT NB is 1.29 nm, whereas the d_{001} value of the sample collected from a rotating speed from low to high C/MMT-2000, C/MMT-4000, C/MMT-10 000 and C/MMT-10 000-L is 1.41, 1.43, 1.54 and 1.42 nm, respectively. As the rotating speed gets higher, the d_{001} values of the samples became larger, except for the d_{001} values of C/MMT-10 000-L, which confirms that the gradient centrifugation has little influence on the structure of C/MMT. With the rotating speed going up, the XRD peak of the C/MMT sample becomes wider, which means the powder is disordered. So the gradient centrifugation method has an obvious effect on gathering powder in nanometres.

The size distribution of C/MMT NB samples, refined by gradient centrifugation, is shown in Fig. 13. The size of C/MMT NB spreads from 100 to 700 nm and the peak lies at 265 nm, C/MMT-2000 is from150 to 470 nm and peak at 268 nm, C/MMT-4000 is from 100 to 400 nm and peak at 198 nm, C/MMT-10 000 is from 50 to 300 nm and peak at 110 nm, and C/MMT-10 000-L is from 25 to 200 nm and peak at 71 nm. These data confirm that with rotating speed going up, smaller sized C/MMT samples are collected. After being centrifuged at 10 000 r/min, the C/MMT particle size has already reached 70 nm.

The TEM images of samples purified by gradient centrifugation and C/MMT NB are shown in Fig. 14. The Figure shows that as for the purification of slices, the MMT flake layer is purified with a thin edge. Compared with C/MMT NB, the 10 000 r/min centrifugal sample is thinner, the slice layer area is smaller and the edge of the curl was significantly bigger. The diameters of the nanosheets are about 10–500 nm. Accordingly, at a centrifugal rotational

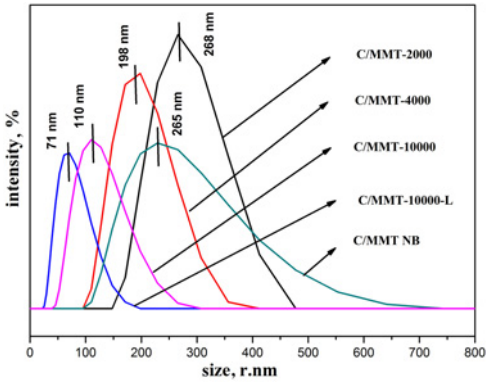

Figure 13 *Size distribution of samples refined by gradient centrifugation*

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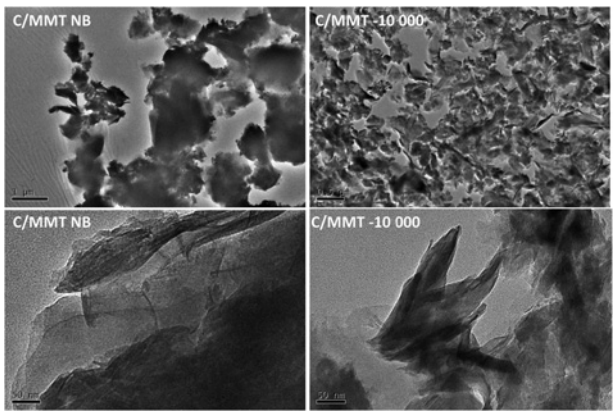

Figure 14 *TEM images of C/MMT NB and C/MMT-10 000 refined by gradient centrifugation*

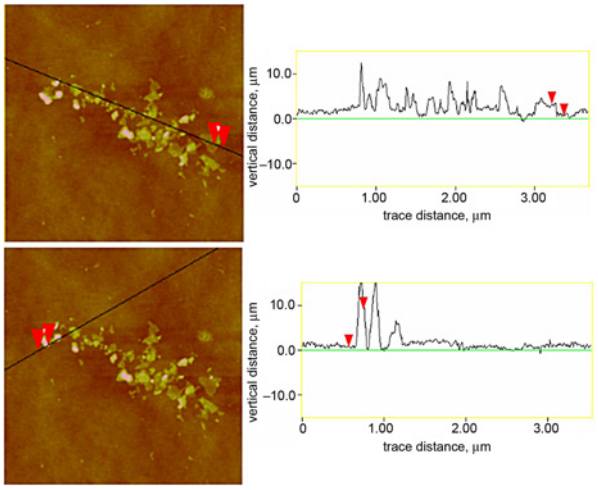

Figure 15 *AFM images of C/MMT-10 000*

speed of 10 000 r/min or higher, samples of nanofilms and nanoparticles are obtained.

The AFM data also supported the above discussion. Actually, the thickness of C/MMT-10 000-L was experimentally detected by AFM as exemplified by the typical image of nanosheet crystallites deposited on an Si wafer substrate. AFM observations also demonstrated that the thicknesses of C/MMT-10 000-L nanosheets are <20 nm as shown in Fig. 15. The AFM images indicate that the thicknesses of most MMT sheets are around 10 nm. Even the thickest particles are under 20 nm. Consequently, by means of gradient centrifugation, C/MMT has a smaller particle size and are more ordered than the above-mentioned two methods.

4. Conclusion: With C/MMT NB as the research object, from the structure and properties of C/MMT NB, combined with the purification method of carbon nanotubes, three methods of purification are proposed in the refinement of C/MMT. Through the froth flotation method, extraction and gradient centrifugation, and the three different methods of purification of C/MMT nanopowder, the results have shown that all three methods have a certain effect. Using the extraction method, the size of C/MMT-D is 50 nm smaller than the raw material C/MMT NB. Best of all, using the gradient centrifugation purification method, at the speed of 10 000 r/min, C/MMT can reach the nanometre, nanotablet diameter range is about 10–500 nm, and the thickness of nanotablet is about 30 nm. The thicknesses of nanosheets in a supernatant of 10 000 r/min are <20 nm and the diameters are <500 nm.

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