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COMPARISON OF ULTRASOUND TREATMENT WITH MECHANICAL SHEARING FOR MONTMORILLONITE EXFOLIATION IN AQUEOUS SOLUTIONS

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ABSTRACT

The exfoliated nanosheet of montmorillonite (MMT) mineral is a superior material applied in many fields especially in strengthening biodegradable polymers. The exfoliation with ultrasound treatment has been studied in this work compared with mechanical shearing through the measurements of laser size analysis, centrifugal classification and AFM. The results have shown that ultrasound treatment allowed a lower energy consumption and higher production in MMT exfoliation than the shearing method. The exfoliated nanosheets were about 1 nm in thickness, indicating that single layer of MMT has been produced.

Keywords: Montmorillonite, Exfoliation, Ultrasound treatment, Shearing, Nanosheet, Single layer.

Contribution/ Originality

The paper's primary contribution is finding that the ultrasound treatment was superior to mechanical shearing for the exfoliation of MMT. As a superior material, the exfoliated single layer can be applied in many fields especially in strengthening biodegradable polymers.

1. INTRODUCTION

Montmorillonite (MMT) is a valuable layered silicate mineral which has wide applications, such as, biodegradable polymers-enhancer, ion-exchanger, adsorbent, catalyst, catalyst support, decoloring agent, and so on [1-4]. The unite layer of MMT is 2:1 type, which implicates that the MMT nanosheets may have the better mechanical/heat stability properties, barrier properties and gas absorbability than graphene nanosheets. Thus the exfoliated nanosheets of MMT may become a promising nano material in the fields of hydrogen accumulators, catalyst and other

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potential fields [5]. Particularly, in traditional polymer industry, the environmental problems and petroleum consumption were raised. The application of biodegradable polymers has received extensive attention over the last two decades [6]. The natural biodegradable materials show poor mechanical, barrier and thermal characteristics. The layered MMT films are the necessary filling materials to improve the quality of biodegradable polymers [7, 8]. The exfoliated nanosheets can be fully dispersed into the polymer matrix. The phase homogeneity of exfoliated nanosheets is higher than the intercalated MMT. So the exfoliated nanocomposites exhibite a batter performances than the intercalated nanocomposites [9, 10], for example, the higher Young's moduli [11], larger elongation at break [12], and better thermal stability [13].

However, it is not easy to achieve complete exfoliated MMT nanosheet in polymer. The majority of the polymer nanocomposites were the intercalated nanostructure [14]. Nie, et al. [15] obtained intercalated structure by stirring method. Zhang, et al. [16] found that the anionic surfactants can be entered into the interlayer space of Ca-MMT by means of ultrasound, but the single layer of exfoliated layer was not obtained. Chivrac, et al. [17] indicated that the intercalated and exfoliated morphologies were obtained simultaneously, but the cost raised by the cationic starch consuming. Wang, et al. [18] obtained the exfoliated MMT layers by the method of hydrothermal reaction. The thickness of the layers was 20nm. Aouada, et al. [19] considered that the homogenous and transparent MMT nanocomposites were possibly obtained by means of the combination of the intercalation from solution and melt-processing preparation methods. But the exfoliated single layers were difficult to achieve. The main reason may be that the force between the interlayers was so strong that the MMT was very difficult to achieve exfoliation [20].

In liquid, the ultrasound wave can generate the cavitation event. Numbers of micro bubbles were created by the pressure fluctuations and collapse adiabatically in short time scale [21]. The cavitation can penetrated into the interlayers of the MMT particles and then trigger the explosion. Then the MMT layers were exfoliated into nanosheets by the cavitation effect. On the other aspect, the shearing effect in the liquid can generate the turbulent flow. The MMT particles also can be exfoliated by the turbulent flow and the rolling impeller.

In this work, the exfoliation of MMT by means of ultrasound was investigated compared with the shearing method. Both the laser size analysis and Stokes size analysis were used to evaluate the exfoliation processes. Moreover, the morphology of the exfoliated nanosheets was characterized by AFM and laser size analysis.

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2. EXPERIMENTAL

2.1. Materials

Na-MMT was obtained from Chifeng Ningcheng MMT Co. (Inner Mongolia, China). The swelling capacity of the prepared MMT was 93 mL/g. The XRD pattern of the MMT was shown in Fig. 1. The diffraction peaks in the pattern belong to MMT. It was indicated that the MMT sample was pure. Analytical NaCl was purchased from Aladdin Chemical Co. The deionized water was used in all experiments.

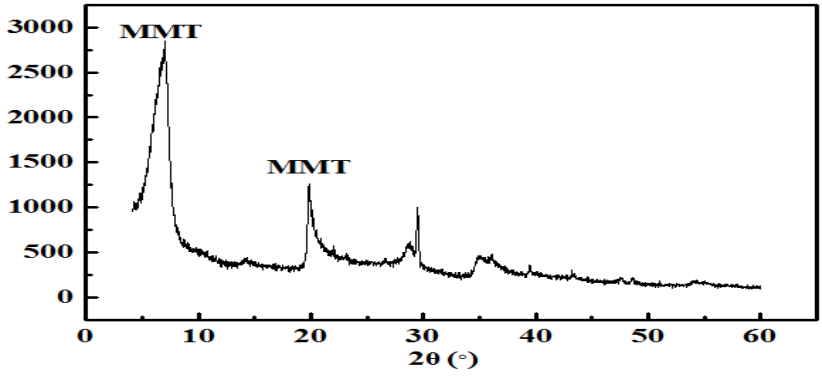

Fig-1. XRD pattern of MMT.

2.2. Purification of MMT Sample

A certain amount of Na-MMT was immersed in deionized water. The mass ratio of MMT/water was 0.03. The suspension was dispersed by mechanical stirring for 6 h. The shearing strength was 450 rev/min. After that, the suspension was purified by the centrifugal method to remove the sedimentation component. The centrifugal time was 1min. The rotation speed was 800rev/min. In order to obtain a saturated charged Na-MMT, the raw MMT was dispersed in 1 M NaCl solution for 12 h by shaker. Then the MMT was washed twice by water: the solid and liquid of the suspension was separated by centrifugation at the speed of 4800rev/min for 1h. The supernatants were then decanted out. After that, the sediments were immersed into the same amount of water. Then the suspension was dispersed by the mechanical stirring at the speed of 450 rev/min for 12 h.

2.3. Exfoliation of MMT

Two different exfoliation methods were compared in this investigation, including ultrasound and shearing. The ultrasound exfoliation experiment was performed on a VERNON HILLS ILLINOIS CP505 ultrasound dispersion instrument. Each subsections were exfoliated in the different ultrasound strengths and ultrasound time respectively. FLUKO FA25 high speed mixer

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was used to study the shearing exfoliation. The prepared MMT suspensions were devided into several 140 mL subsections. Each subsections were exfoliated in the different stirring strengths and stirring time respectively. The exfoliated samples were analyzed by the laser size analysis, the Stokes size analysis and the three-dimensional topographic detection respectively.

2.4. Measurements

A BRUKER D8 ADVANCE X-ray diffractometer (XRD) was used to mineralogically characterize the MMT sample at a voltage of 40 kV and a current of 30 mA with Cu K radiation (λ= 0.15418 nm). The swelling capacity was determined according to the standard of DZG93-06 [22].

Both the laser particle size and the Stokes particle size were analyzed. The optical size was determined by MALVERN MASTERSIZER APA 2000 laser particle size analyzer. The Stokes size was measured by centrifugal classification. The sample was centrifuged by using THERMO FISHER SORVALL ST16 centrifuge at different speed. Both the supernatants and the sediments at different centrifugeal speed were filtered and dried at 60℃ in blast oven which was used to calculate the percentage of the undersize. The rotation speed of the centrifugal was determined by the following expression [23, 24]:

$$N = \sqrt{\frac{63.0\times10^{8} n \log(R/S)}{tD^{2}\Delta S}} \qquad (1)$$

where N is the rotation speed (rev/min); n is the viscosity of the fluid (0.00748 poise at 25 °C); R is the distance from the deposit surface to the axe of rotor (5.5 cm); S is the distance from the suspension surface to the axe of rotor (2.5 cm); t is the centrifugation time (2 min); D is the maximum diameter of the particles in the supernatant (μm); ΔS is the specific gravity difference of the particles and the liquid.

The three-dimensional topographic image was scanned by BRUKER MULTIMODE 8 atomic force microscope. The sample preparation was as follow: 3 mL suspension was diluted in 250 mL deionized water. After that, the diluted suspension was dropped on the mica plate. The mica plate was drying 1 day to obtain the AFM sample.

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3. RESULTS AND DISCUSSION

3.1. Optical Particle Size of Exfoliated MMT

The cumulative undersize size of exfoliated MMT particles by ultrasound treatment at various strengths and treating time were shown in Fig. 2 and Fig. 3, respectively. It can be seen from Fig. 2, the particle size decreased greatly with the ultrasound strengths increased. In addition, it can be noted that in Fig. 3, the particle size decreased significantly with the increment of the ultrasound time. It is indicated that the exfoliation can be achieved by the ultrasound method. Even though the sample was treated at the ultrasound strength of 100W for 4min, the exfoliation effect also occurred. It means that the ultrasound method was an effective method to obtain the exfoliated MMT layers.

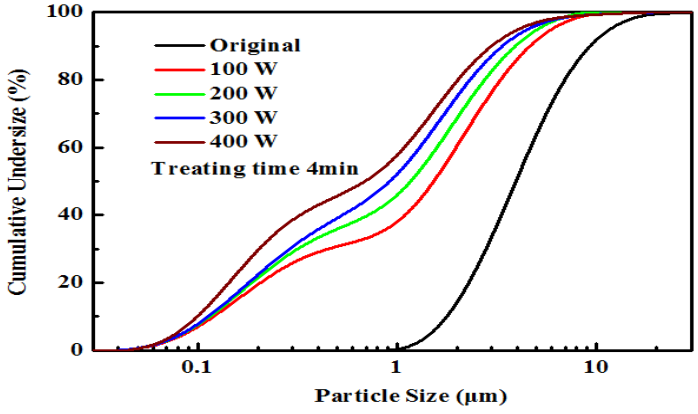

Fig-2. Particle size distribution of exfoliated MMT particles prepared by ultrasound treatment with various strengths.

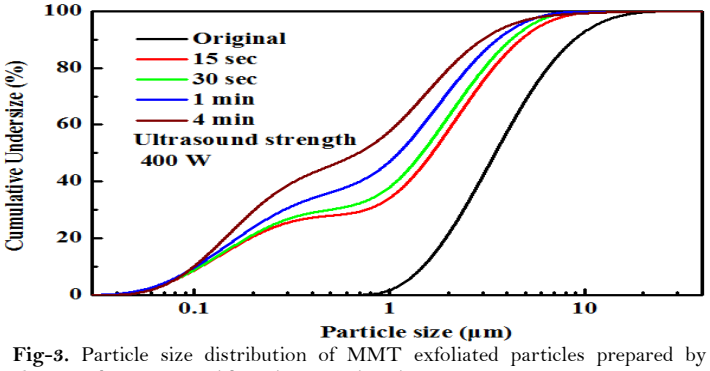

Fig-3. Particle size distribution of MMT exfoliated particles prepared by ultrasound treatment with various treating time

The Particle size distribution of MMT particles prepared by mechanical shearing at various stirring strengths and time were shown in Fig. 4 and 5, respectively. In Fig. 4, as the shearing strengths raised, the particle size was greatly dropped. In Fig. 5, the particle size was greatly

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dropped with the increment of the shearing time, which indicats that the exfoliation also can be achieved by shearing method.

The D50 of the MMT sample treated by ultrasound was 1.2 μm at the ultrasound strength of 400 W for 1min. Compared to the D50 of shearing method was 2.0 μm by mechanical shearing at the strength of 27000 rev/min for 1min. In this case, the particle size of ultrasound method was smaller than that of the shearing method. The energy consumption of the ultrasound method was 2400 J in the conditions of 400 W, 1 min. When the shearing strength was 27000 rev/min, the input power of the electric motor was 500 W. The energy consumption of the shearing was 3000 J in the conditions of 27000 rev/min, 1 min. The energy consumption of ultrasound method was lower than that of the shearing method. So, the ultrasound method was recommended in the exfoliation process of the MMT mineral.

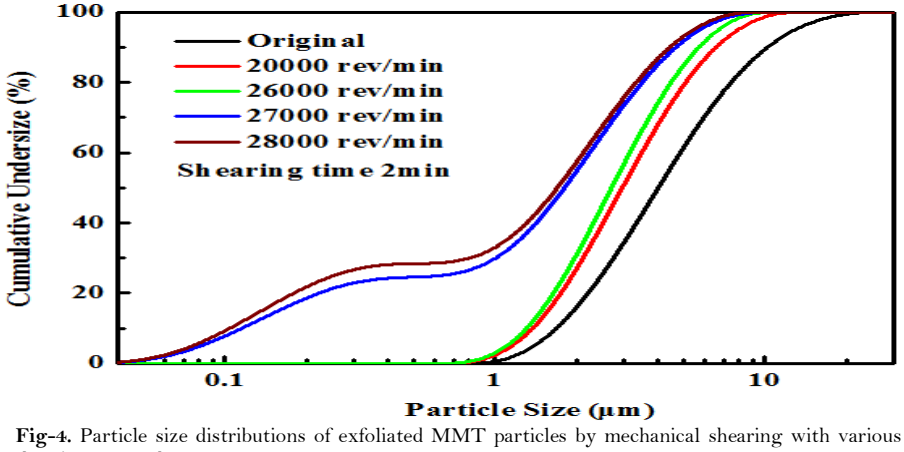

Fig-4. Particle size distributions of exfoliated MMT particles by mechanical shearing with various shearing strengths

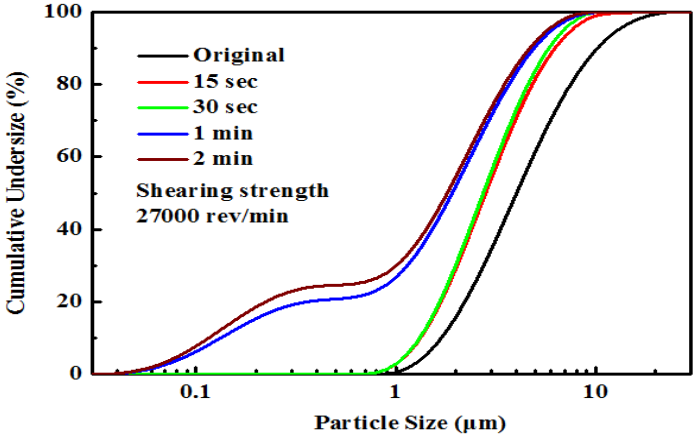

Fig-5. Particle size distributions of exfoliated MMT particles by mechanical shearing with various shearing time

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3.2. Stokes Size of Exfoliated MMT Particles

Compared with the original particles, the exfoliated particles were diminished both in the width and thickness dimension remarkably. So the exfoliation effect can be detected by the laser size analysis. But the laser size was not the true geometrical size of the platelet [25]. Compared the Fig. 6 and the Fig. 2, the Stokes diameter of MMT was smaller than the laser size diameter. The diffraction of the random orientation platelet average length was longer than the geometric average length. The equivalent diameters were larger than the Stokes diameters. The Stokes diameter detection was more closed to the geometric diameter. So the Stokes particle size experiment was arranged.

The Stokes undersize curves in different ultrasound strengths and time are showed in Fig. 6 and Fig. 7 respectively. The separation size was ranged from 0.2 μm to 1.2 μm. In Fig. 6, with the ultrasound strength increased, the particle size was greatly decreased. For example, when the separation size was 0.2 μm, the percentage of fine fractions were increased from 43.18% to 61.09% as the strength increased from 0 W to 400 W. In Fig. 7, the particle size was significantly decreased as the ultrasound time increased. It was reconfirmed that the MMT can be exfoliated by ultrasound.

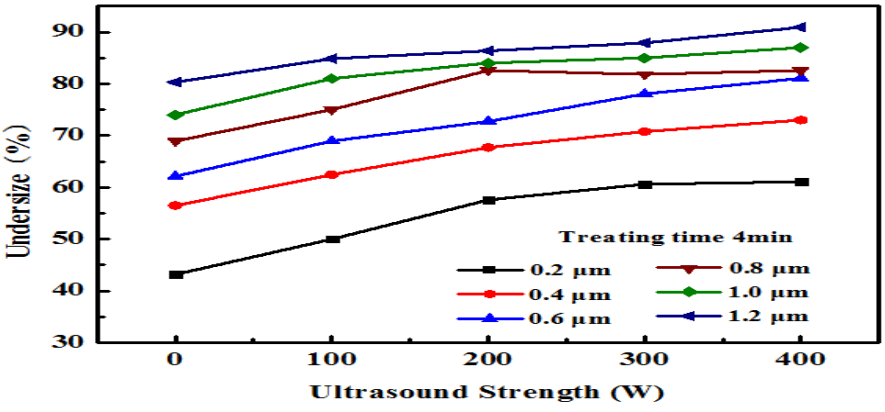

Fig-6. The percentage of the Stokes undersize as the separation size range from 0.2 μm to 1.2 μm with various ultrasound strengths

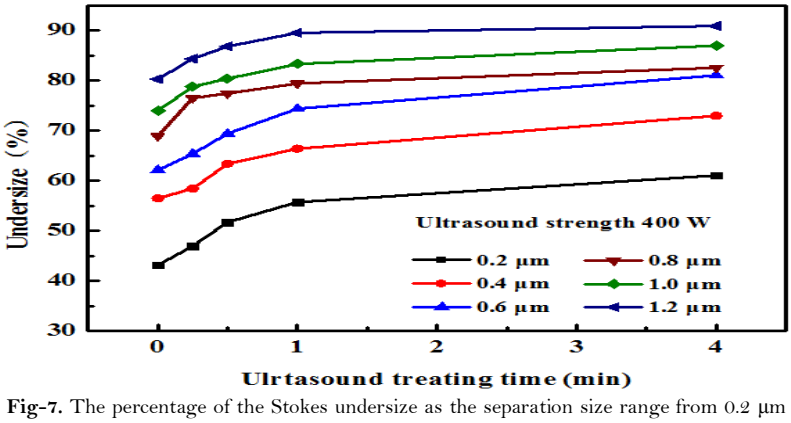

Fig-7. The percentage of the Stokes undersize as the separation size range from 0.2 μm to 1.2 μm with various ultrasound time

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Fig. 8 and Fig. 9 showed the Stokes undersize curves in different shearing strengths and time respectively. The separation size was ranged from 0.2 μm to 1.2 μm. In Fig. 8, as the ultrasound strengths increased, the particle size was decreased. For example, when the separation size was 0.2 μm, with the shearing strength increased from 0 to 27000 rev/min, the percentage of undersize was increased from 43.18% to 57.87%. Fig. 9 showed the percentage of undersize was raised as the increasing of the shearing time. It was reconfirmed that the MMT can be exfoliated by shearing.

The D50 of the MMT sample treated by ultrasound was 1.2 μm at the ultrasound strength of 400 W for 1min. the D50 of shearing method was 2.0 μm by mechanical shearing at the strength of 27000 rev/min for 1min. The Stokes particle size result also indicated that a lower particle size can be achieved by ultrasound method. So, the ultrasound method was superior to the shearing method in MMT exfoliation.

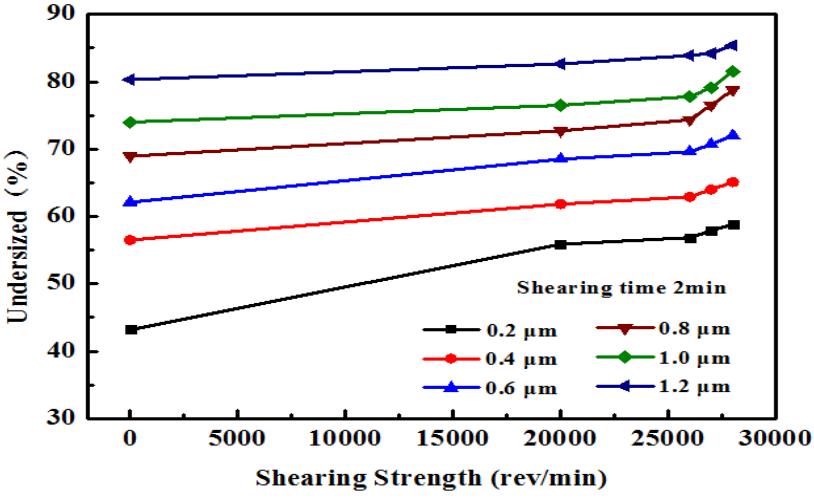

Fig-8. The percentage of the Stokes undersize as the separation size range from 0.2 μm to 1.2 μm with various shearing strengths

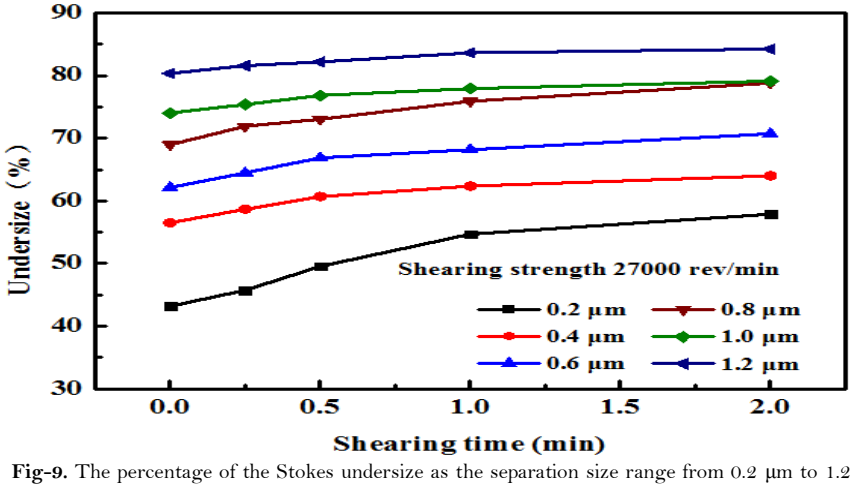

Fig-9. The percentage of the Stokes undersize as the separation size range from 0.2 μm to 1.2 μm with various shearing time

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3.3. Morphology Analysis

Fig. 10 was AFM image of the MMT nanosheets exfoliated by the ultrasound method MMT sample treated by ultrasound at the ultrasound strength of 400W for 4min which showed that the thicknesses of the exfoliated MMT particles were all around 1 nm. Bergaya, et al. [26] has summarized that the single-layer of MMT was nearly 1 nm. It is means that the exfoliated MMT particles were almost single-layer. Therefore, the single-layer nanosheets of MMT could be obtained by ultrasound method.

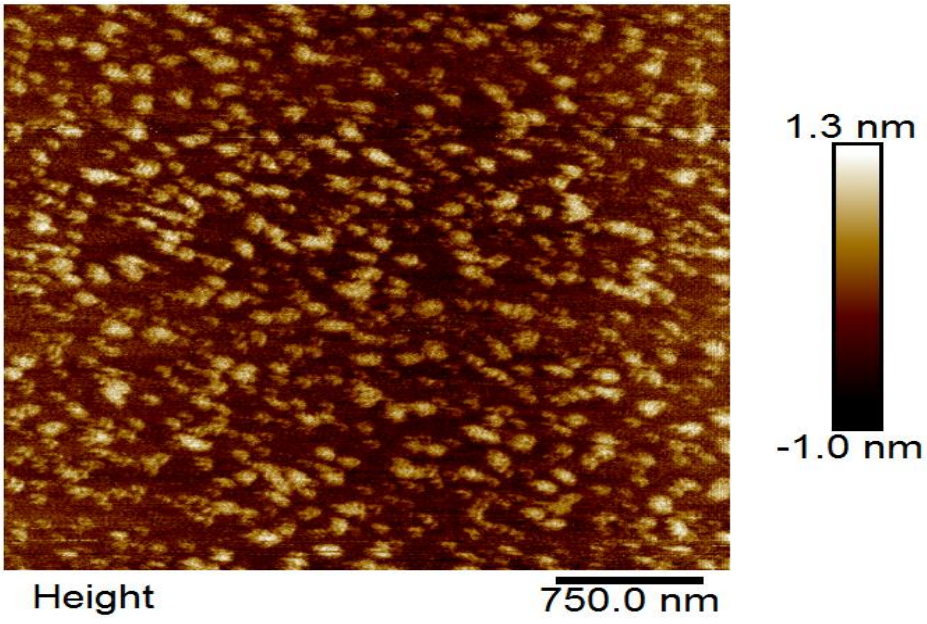

Fig-10. AFM image of the exfoliated nanosheets with the ultrasound treatment condition of 4min, 400 W

Considering the AFM images can not statistically represent the scale of the particles, the volume distribution of the laser particle size in different exfoliation conditions was used as a support (see Fig. 11). It was shown that there have the particle peaks on the fine particle size range which were all appeared in the size of 180 nm. It means that although the percentage of the fine particles were different between the different exfoliation conditions, the scale of the exfoliated particles was uniform.

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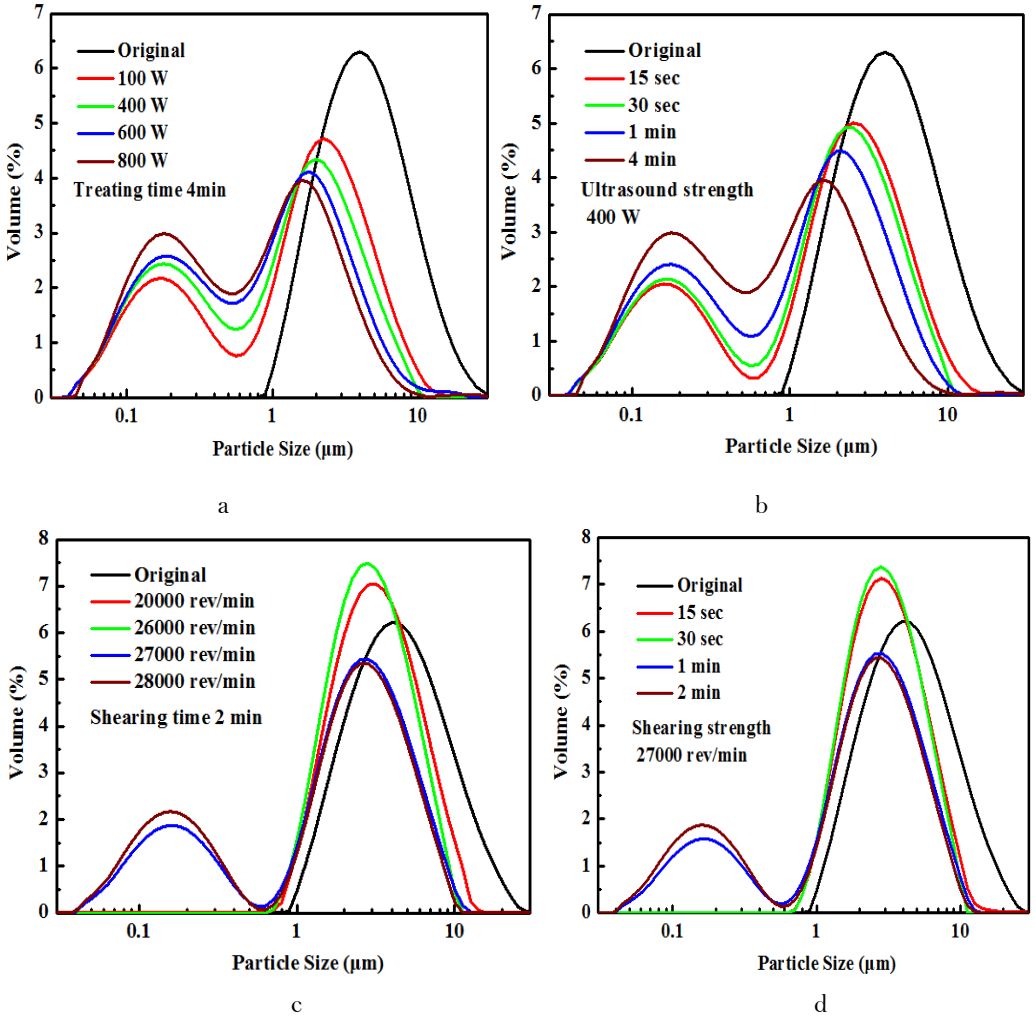

Fig-11. Particle size distribution of exfoliated MMT. (a) with various ultrasound strengths. (b) with various ultrasound treating time; (c) with various shearing strengths; (d) with various shearing time

According to the AFM detection, the single layers of MMT were produced. It means that the limitation of exfoliation was approached. The ratio of the strength toward thickness direction to width direction of single layer was nearly a constant value [26]. So the width of the MMT should also be approached to the minimum value in case of the thickness was approached the minimum value. This was the reason why the fine particles peaks of the laser particle size curves were all located in the 180 nm. AFM result also proved that the width of the nanosheets were around 180 nm (Fig. 10). So the ratio of the thickness to the width of the exfoliated nanosheet was approximately equals to 1:180. Additionally, the ratio of the strength toward thickness direction to width direction of single layer was also approximately equals to 1:180.

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4. CONCLUSIONS

(1) The experiment results have shown that the ultrasound treatment was superior to mechanical shearing for the exfoliation of MMT, allowing higher fine particle production and lower energy consumption.

(2) The exfoliated MMT nanosheets were about 1 nm in thickness, indicating that single layer of MMT has been produced.

5. ACKNOWLEDGMENTS

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