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## Dispersion performance of nanoparticles in water

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**Abstract:** Engineering Nanoparticles (ENPs)' superior characteristics of adsorption depends on their dispersion in the medium. In this study, multi-walled carbon nanotubes (nonmetal), iron nanoparticles and silver nanoparticles (metallic simple substance), and Nano-TiO<sub>2</sub>, Nano-Fe<sub>2</sub>O<sub>3</sub> and Nano-ZnO (metal oxide) were selected and respectively added into pure water and aqueous solution with 1% Sodium dodecyl benzene sulfonate (SDBS) surfactant. The dispersion effects were compared by leaving the solutions standing at room temperature under ultrasound. The results show that the dispersion of iron nanoparticles is the lowest among the six ENPs, and that of multi-walled carbon nanotubes (MWCTS) is the highest. Adding anionic surfactants (SDBS) can obviously improve the dispersion performance of ENPs. The concentration of solution decreases by only 5% in 10 days after adding 1% SDBS for ultrasonic dispersion.

**Keywords:** Nanoparticles; Dispersion; Sodium dodecyl benzene sulfonate (SDBS)

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## Introduction

Traditionally, the powders or materials with their particle size in the range of 0.1~100 nm are called nanomaterials (ZHANG Li-de, 2001). Engineering Nanoparticles (ENPs) refer to the nano-scale particles manufactured by various physical and chemical methods. Due to the small size effect, quantum size effect and surface effect on the scale of 1~100 nm, ENPs have excellent adsorption properties and can be widely used in environmental pollution remediation technology (MAO Da-heng *et al.* 2013; Ghoreishi *et al.* 2010). However, this characteristic of ENPs also leads to the lack of adjacent donor atom on their surface, thus making them highly active. The activity results in the agglomeration of ENPs and makes ENPs lose part of their adsorption performance. Therefore,

whether the adsorption properties of ENPs can be fully developed depends to a great extent on their dispersion pattern (uniform or agglomerate) in the medium (YAN Xiao-san, 2019). The dispersion process of ENPs in the medium can be divided into three steps: (1) wetting the ENPs in the medium; (2) breaking larger aggregates into smaller pieces through external forces; (3) stabilizing the dispersed particles to ensure the dispersion stability of the particles in the liquid phase and preventing them from reaggregating. According to different dispersion principles, the dispersion methods can be divided into physical dispersion (mechanical method) and chemical dispersion (surface modification method). Mechanical method refers to the use of equipment to increase the dispersion stability of ENPs in solvents, mainly including mechanical stirring method, ultrasonic dispersion method and high-energy treatment method. The surface modification method refers to the method

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of reducing the interfacial tension and increasing the steric repulsion force of particles by adding stabilizers such as polymer or surfactant into the system.

Previous studies (BU Lu-xia, 2019; WU Bo *et al.* 2019; YANG Heng *et al.* 2017; MAO Sheng-chun *et al.* 2009; YANG Chun-xia and ZHAO Wen-bin, 2018; LI Yue-fang, 2019; YANG Shi-zhao *et al.* 2020; WANG Jing-wen *et al.* 2018; YUAN Ming *et al.* 2018) mainly focused on the selection of dispersion conditions for specific nanoparticles, and the research on the dispersion properties of different nanoparticles is rarely involved. This study selects six kinds of nanomaterials that have been widely used in environmental remediation, chemical industry, electronics and other industries. They are multi-walled carbon nanotubes (nonmetal), iron nanoparticles and silver nanoparticles (metallic simple substance), and Nano-TiO<sub>2</sub>, Nano-Fe<sub>2</sub>O<sub>3</sub> and Nano-ZnO (metal oxide). The study explores the effect of ultrasonic dispersion and the dispersion effect of ultrasonic dispersion after adding surfactants, and screen out the form of ENPs with the best suspension effect, which provides a certain reference for the subsequent selection of appropriate ENPs for practical applications in many fields.

## 1 Experimental materials and methods

### 1.1 Materials and instruments

The six types of ENPs are: Ag, Fe, ZnO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MWCTs (multi-walled carbon nanotubes, particle size 40~60 nm). The above ENPs are provided by Shijiazhuang Gaokai District Nano Products Co., Ltd. The following materials and equipment have also been used in this study: Sodium dodecyl benzene sulfonate (SDBS, Shanghai, AR), KBS-150 ultrasonic cell crusher (Kunshan, Jiangsu), ultraviolet-visible spectrophotometer (Shimadzu UV2500), TGL-16M centrifuge (Changsha).

### 1.2 Method

#### 1.2.1 Drawing the standard curves of ENPs

Weigh 0.010 g of silver nanoparticles and pour them into 100 g of deionized water to make a 100 ppm solution. Use the KBS-150 ultrasonic

cell crusher to sonicate for 10 s at 100 W, then stop for 10 s. This is one cycle, and the ultrasonic cell crusher needs to work for 360 cycles. After sonication, prepare the solution with a colorimetric tube into 20 ppm, 40 ppm, 60 ppm, 80 ppm aqueous solution of Ag, and use the ultraviolet-visible spectrophotometer (Shimadzu UV2500) to scan 0 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm, 100 ppm solution at 200~800 nm for the absorbance of the band, and make the relationship curve of different concentration and absorbance. The relationship curve between the peak concentration and the absorbance is selected, and the relationship equation with the correlation coefficient >0.99 is used as the standard curve equation of silver nanoparticles.

In the same way, the standard curve equations of MWCTs, Nano-Fe, Nano-ZnO, Nano-TiO<sub>2</sub>, and Nano-Fe<sub>2</sub>O<sub>3</sub> were made.

#### 1.2.2 Dispersion experiment of ENPs in deionized water

Weigh 0.010 g of silver nanoparticles and pour them into 100 g of deionized water to make a 100 ppm solution. Use the KBS-150 ultrasonic cell crusher to sonicate for 10 s at 100 W, then stop for 10 s. This is one cycle, and the ultrasonic cell crusher needs to work for 360 cycles. At the end of the ultrasound, the solution was left standing at room temperature. Take a certain amount of the solution and use the ultraviolet-visible spectrophotometer (UV2500) to measure the absorbance of Nano-Ag when the standing time is 0 min, 2 min, 5 min, 10 min, 15 min, 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 240 min, 300 min, 360 min and 420 min. Then the absorbance is converted to concentration according to the standard curves made in 1.2.1.

In the same way, the dispersion effect of MWCTs, Nano-Fe, Nano-ZnO, Nano-TiO<sub>2</sub>, Nano-Fe<sub>2</sub>O<sub>3</sub> in water is measured. Draw a curve of concentration versus time.

#### 1.2.3 Dispersion experiment of ENPs in aqueous solution with 1% SDBS surfactant

Weigh 0.10 g SDBS surfactant and 0.010 g of silver nanoparticles, then pour them into 100 g of deionized water to make 100 ppm solution. Use the KBS-150 ultrasonic cell crusher to sonicate for 10 s at 100 W, then stop for 10 s. This is one

cycle, and the ultrasonic cell crusher needs to work for 360 cycles. At the end of the ultrasound, the solution was left standing at room temperature. Take a certain amount of the solution and use the ultraviolet-visible spectrophotometer (UV2500) to measure the absorbance of Nano-Ag when the standing time is 0 min, 2 min, 5 min, 10 min, 15 min, 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 240 min, 300 min, 360 min and 420 min. Then the absorbance is converted to concentration according to the standard curve made in 1.2.1.

In the same way, the dispersion effect of MWCTs, Nano-Fe, Nano-ZnO, Nano-TiO<sub>2</sub>, Nano-Fe<sub>2</sub>O<sub>3</sub> in SDBS aqueous solution is measured. Draw a curve of concentration versus time.

#### 1.2.4 Determination of long-term dispersion effect of Nano ZnO and MWCTs

Weigh 0.010 g of Nano-ZnO and MWCTs and pour them respectively into 100 g of aqueous solution with 1% SDBS surfactant to make a 100 ppm solution. Use KBS-150 ultrasonic cell crusher to sonicate for 10 s at 100 W, then stop for 10 s. This is one cycle, and the ultrasonic cell crusher needs to work for 360 cycles. After sonication, the solution was left standing at room temperature, and a certain amount of the standing solution was taken every day to measure the absorbance of Nano-ZnO and MWCTs with an ultraviolet-visible spectrophotometer (UV2500). Then the absorbance is converted to concentration according to the standard curve made in 1.2.1. Draw a curve of concentration versus time.

## 2 Results and discussion

### 2.1 Study on the dispersion effect of ENPs in water

When ENPs are put into water, most of them will agglomerate and sink to the bottom of the water quickly. The physical dispersion technology can make the ENPs fully and uniformly dispersed in water. Ultrasonic dispersion (HU Xin-hua and ZI Jian, 2002) is one of the most widely used method in ENPs dispersion. The principle (XIA He-sheng *et al.* 2003) is to form microbubbles in the liquid by the cavitation of ultrasonic waves. The rapid formation and sudden rupture of microbubbles produces a strong vibration wave, forming a short-term high-energy microenvironment. The nano interaction energy between ENPs can be greatly weakened by using this high energy. SUN Jing *et al.* (1999) studied the effect of ultrasonic time on the particle size distribution of nanomaterials. The average size of the particles decreased by more than half under the condition of 4 min ultrasonic and 50% duty cycle. MO Jian-qiang and MO Guo-qiang (2015) studied the dispersion of silica (20~40 nm) by ultrasonic frequency, and explored the ultrasonic frequency (40 kHz) and power density (1.8 W/cm<sup>2</sup>) for the best dispersion effect of silica. In this experiment, an ultrasonic cell crusher was selected to measure the absorbance curve of ENPs in pure water for two hours under 50% duty cycle. The experimental results are shown in Fig. 1.

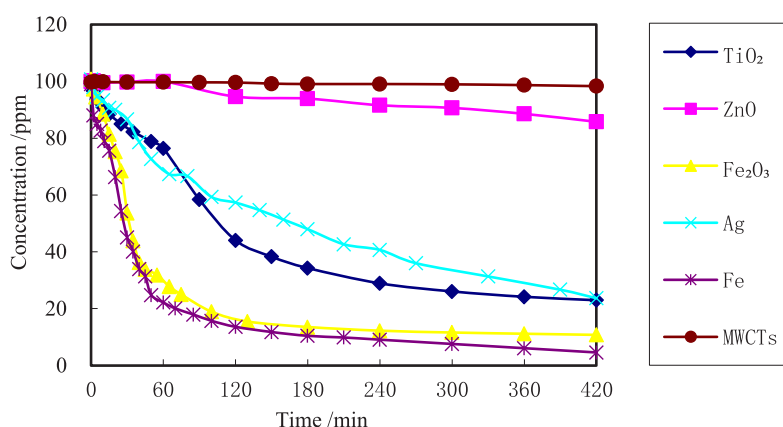


Fig. 1 Dispersion effect of six kinds of nanoparticles in the water

It can be seen from Fig. 1 that the concentration change curve of multi-walled carbon nanotubes

(MWCTs) is a straight line approximately parallel to the X-axis, and its concentration basically does

not change within 420 minutes, indicating that despite the ultrasonic effect of the cell crusher, MWCTs particles can still maintain strong uniform dispersion in water after standing for 420 min. The concentration of ZnO only decreases by 14% within 420 min, indicating that the dispersion performance of ZnO in water is relatively stable. The other four kinds of nanoparticles have obvious changes in concentration in water. In 420 min, the concentration is reduced by 80% to more than 90%, and the Nano-Fe has completely agglomerated together.

The correlation coefficient ( $R^2$ ) was used to measure the fitting degree. From Table 1, it can be seen that the logarithmic equation has the highest fitting degree. This is because the local high temperature generated by ultrasonic cavitation can greatly weaken the nano-interaction energy between ENPs (WANG Bu-xuan, 2007), which

makes the ENPs aggregates broken into smaller particles suspended and dispersed in water. After ultrasonic treatment, with the decrease of the particle size and the increase of the surface area, part of the mechanical energy of the dispersed nanoparticles will be transferred to the newly increased surface, resulting in the increase of the surface energy of the powder. In the thermodynamics the increase of surface energy is unstable and ENPs begin to agglomerate. The large particles quickly settle to the bottom of the water after agglomeration, which reduces the concentration of the solution. In the later stage, due to the reduction of suspended particles in the solution, the probability of collision between particles is reduced, which weakens the agglomeration effect, leading to a process of rapid decrease in concentration at first and then slow decrease.

**Table 1** Fitting equations and their correlation coefficients ( $R^2$ ) of adsorption rate curve

Correlation coefficient ( $R^2$ )	Nano-Fe	Nano-Ag	Nano-Fe <sub>2</sub> O <sub>3</sub>	Nano-TiO <sub>2</sub>
Linear equation	0.528 6	0.899 4	0.522 2	0.847 3
Exponential equation	0.815 3	0.981 7	0.729 5	0.923 7
Logarithmic equation	0.913 9	0.902 6	0.902 1	0.867 4
Power exponent equation	0.926 9	0.801 7	0.913 3	0.807 5

## 2.2 Dispersion effect of ENPs in SDBS aqueous solution

When a stabilizer such as a surfactant is added to the system, the interfacial tension can be reduced, the steric repulsion force can be increased, and the wettability and stability of ENPs can be improved and modified to achieve the uniform dispersion. Among them, anionic surfactants are more efficient than nonionic surfactants to enhance the dispersion effect. It may be because the anionic surfactants adsorbed on the surface of ENPs change the distribution of surface electric charge of ENPs and stabilize the steric hindrance. QIAO Yin-po *et al.* (2007) used sodium dodecyl sulfate (SDS) to modify the surface of Nano-TiO<sub>2</sub> through hydrolysis. The wettability of the modified Nano-TiO<sub>2</sub> was 5 times that of unmodified Nano-TiO<sub>2</sub>, which significantly enhanced the suspension stability. ZHANG Ying *et al.* (2006) used aluminum hydroxide and sodium dodecyl benzene sulfonate (SDBS) to coat and modify the surface of

Nano-SiO<sub>2</sub>. After modification, the agglomeration of Nano-SiO<sub>2</sub> powder was reduced, and the surface structure and dispersion of nano-SiO<sub>2</sub> were improved. In addition, in the study of Bu Lu-xia (2019), it was found that the addition of SDBS had a significant impact on the dispersion performance of MWCTs. When the concentration of SDBS was 1.2 mmol·L<sup>-1</sup>, the dispersion performance of MWCTs was the best. In this experiment, 0.1% SDBS was added to modify the solution, and the absorbance of ENPs in SDBS aqueous solution was measured with time after sonicating with the ultrasonic cell crusher under 50% duty cycle for two hours. The experimental results are shown in Fig. 2.

It can be seen from Fig. 2 that the concentration of Nano-ZnO and MWCTs after adding the surfactant SDBS is basically unchanged after 420 min. However, the concentration of Nano-ZnO in pure water was reduced by 14% with the same standing time, which shows that SDBS improved the dispersion performance of ENPs.



The concentration of Nano-TiO<sub>2</sub> decreased by less than 8% after 420 minutes, which further proved the effectiveness of surfactant addition. The other three kinds of ENPs had gradually agglomerated

to the bottom of the container when they were left for 420 minutes. The concentration decreases are shown in Fig. 3. Moreover, the concentration of ENPs decreased rapidly first and then slowly.

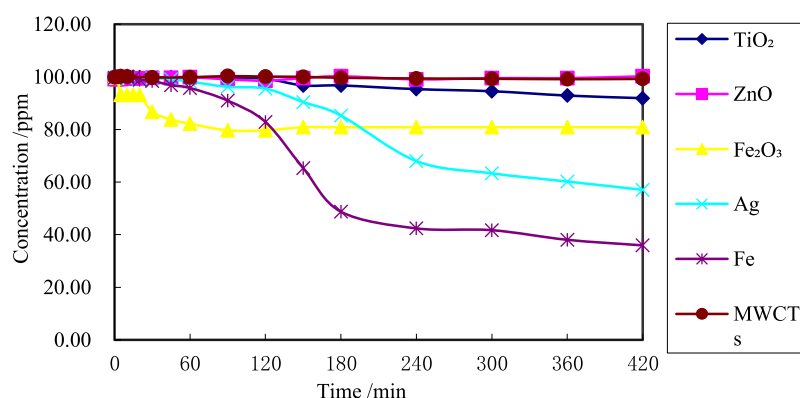


Fig. 2 Dispersion effect of nanoparticles in the SDBS solution

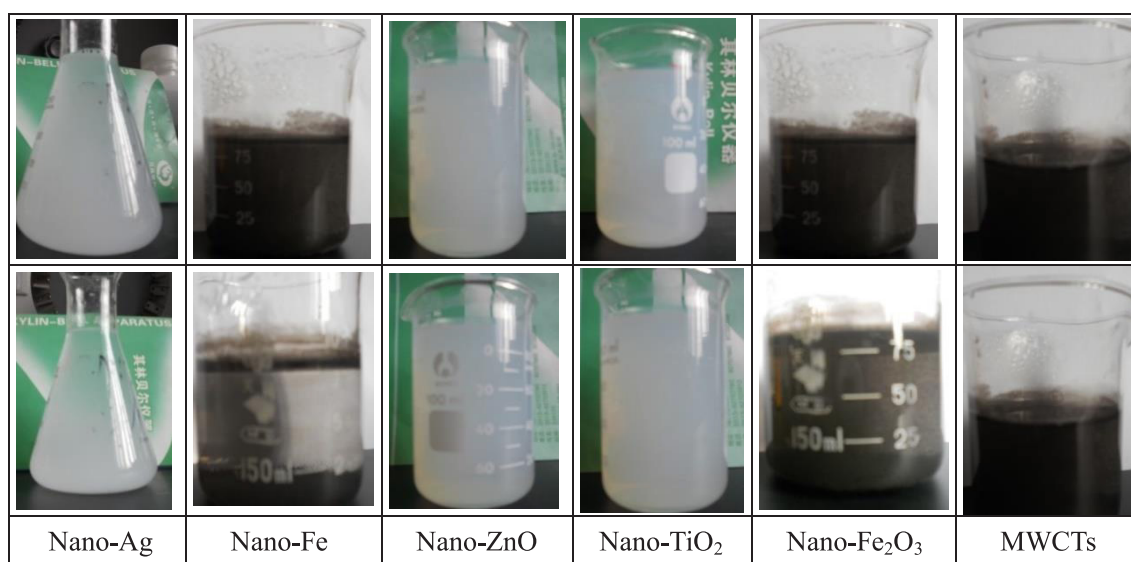


Fig. 3 The change of nanoparticles in the SDBS solution

This is because the surface energy of ENPs is relatively high (GONG Xiao-yi *et al.* 2016), and when the surfactants (SDBS) was added, they were effectively encapsulated on the surface of nan-oarticles through the mechanical action of ultrasonic dispersion. It makes the particles repel each other (XU Peng, 2018), so as to achieve the purpose of dispersion. The dispersion of nanoparticles is often a combination of physical dispersion and chemical dispersion (LIU Jing-fu *et al.* 2010). If an appropriate amount of dispersant is added during the ultrasonic dispersion process, the dispersion effect will be significantly improved. This is because it is difficult to prevent the re-agglomeration of nanoparticles after sonication with only the cavitation effect of ultrasonic waves

(Bystrzejewski *et al.* 2010). After adding the dispersant, it can prevent the particles from agglomerating again. At the same time, the ultrasonic effect is beneficial to the coating of the dispersant on the surface of the nanoparticles.

### 2.3 A comparison of long-term dispersion performance

In view of the fact that the concentration of Nano-ZnO and MWCTs after the addition of the surfactant SDBS basically did not change during the reaction time of 420 min, the project team designed a 10 day long-term suspension performance experiment for these two ENPs. The experimental results are shown in Fig. 4.

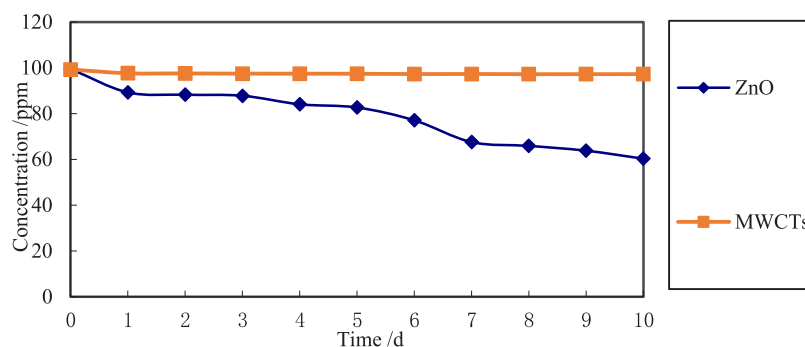


Fig. 4 Comparison of dispersion effect between Nano-Zn and MWCTs

It can be seen from Fig. 4 that the concentration of MWCTs remained stable during the 10 days, and the concentration change was only 5%. It shows that MWCTs have excellent dispersion properties, and can fully exert the small size effect of nanoparticles. They are also cost-effective, which is more affordable than other metals and oxides. It can be applied to recyclable chemical catalysts, surfactants, electronic devices, optical materials and medical materials (GAO Pei-yu *et al.* 2015; Mohannad and Daniel, 2017; ZHENG Guo-dong *et al.* 2015; SHANG Hong-zhou *et al.* 2017; HAN Jin-quan *et al.* 2018; GE Chao-qun *et al.* 2018). However, the concentration of Nano-ZnO decreased by 40% in the reaction time of 10 days, indicating that it is impossible to achieve long-term stable dispersion performance only by adding surfactants and ultrasonic pulverization.

### 3 Conclusions

The following conclusions can be drawn from this study:

(1) There are many factors that affect the dispersion of nanoparticles, including the surface characteristics of nanoparticles, particle properties, particle shape and size, dispersant and other factors. The six ENPs selected in this experiment have some common properties while each of them has their own properties. The addition of surfactants does not affect its suspension ability. The worst dispersion performance of these six ENPs is Nano-Fe, and the best is multi-walled carbon nanotubes (MWCTs). At the same time, a general trend of the concentration change of ENPs suspension solution is that it first decreases rapidly and then gradually slows down, and finally tends to stabilize. From the above experiment,

it can be concluded that among the six kinds of nanoparticles selected in this experiment, Nano-Fe and Nano-Ag have the worst dispersion performance under the same particle size and dispersant concentration, followed by Nano-Fe<sub>2</sub>O<sub>3</sub>, Nano-TiO<sub>2</sub> and Nano-ZnO, and nonmetal MWCTs have the best dispersion performance.

(2) The addition of anionic surfactant (SDBS) can significantly improve the dispersion performance of ENPs. After adding 1% SDBS surfactant, the solution concentration of the six ENPs changed from 10%~90% to 1%~60% with the same standing time after sonication in water. The dispersion stability of each ENPs is improved.

(3) After MWCTs were dispersed by adding dispersant and using the ultrasonic dispersion method, the solution concentration changed only 5% after standing for 10 days. This shows that MWCTs have excellent dispersing properties and are cost-effective. They are more affordable than other nano-scale metals and oxides. They can give full play to the small size effects of nanoparticles and can be applied to chemical catalysts, surfactants, electronic devices, optical materials and medical materials.

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