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Limitation and challenge faced to the researches on environmental risk of nanotechnology

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Abstract

Nanotechnology is a new booming science, which has leaped huge significant achievements for only short dozens of years, and created so much wealth for human beings. Their usages on environmental security have been ignored by public, however, multiples of evidences have been demonstrated nano-materials would perform different influence upon a variety of organism. Here, this article concerns that situations and challenges to separate or detect the nano-particles contained in the products or the environment. Meanwhile, a case was presented to introduce an available approach to prepare the nano-colloid (nano-TiO₂) for environmental risks research. Therefore, it's necessary for the relevance authorities to formulate effective or available detections upon nano-materials. And the key point should be focused on the normalization of nano-materials control and the establishments on environmental risk assessment upon nano-materials, which will finally promote the developments on the fields of nanotechnology.

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1. Introduction

Nanotechnology has been regarded as an industrial revolution in next scientific period, which has caused significantly revolutionary change in the whole global scope areas, such as scientific, industrial and agricultural[1]. Their applications have been covered from medical imaging or pharmacology to industrial or commercial products. With increasingly successful manufacture of new innovative nano-materials (NMs) and their related industrial production or application, their environmental risk has become another new upward burgeoning issue in researches of EHS (Environment Health & Safety). Those advanced, fantastic properties of both physical and chemical have been extended for a wide

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application prospect for NMs, like the medical diagnose, catalysis, pollution control and even cosmetics. According to the statistics data of the related departments, it's predicted that the annual production values from global nano-technology would outweigh one billion dollar in 2020[2], which would provide a greatly significant economic benefit for society[3]. In this review, we shortly generalize some methods to determinate nano-material, the limitation and the challenge in the process of researches. Meanwhile, we propose an available method to prepare the colloid to be used in the researches on the environmental risk of nano-TiO₂. Moreover, some suggestions are provided for current researches situation.

2. Exposure of Nano-Materials in the Environments

Presently, accompanying with big amount of nano-products being exposed to environment, their problems of environmental safety have been considered as a necessity for the research. Nano-materials would be inevitably touched with humans and organisms when being discharged into environmental mediums. Many striking facts could be cited to highlight their dangerousness, such as the discoveries of nano-particles being discharged, removed and transferred into water, soil, air and even some animals.

However, there are still no fully comprehensive systems could be established the assessments for potential effects of pollution between toxicity and nano-particles in the environment. As lacking of quantitative analytical methods to trace those related nano-particles, additionally, the concentrations of the nano-particles be exposed in environmental mediums are still ambiguous. It's noteworthy that some prominent achievements have been reaped by a series of researches and obtained some certain of results and conclusions for those researches on environmental risk of nano-particles. *Tang et al*[4] had expounded nano-particles might cause various reactions in the macro-interfacial processes when entering into the mediums of environment, and finally exerting water pollution. *Biswas et al*[5] had reviewed the "life history of nano-particles" and stated tracking information ranged from their potential use to eventual fate in environment. Recently, some researchers have reported the detection of nano-particles in virtually and demonstrated a distribution near ubiquity, which could be discovered in the water domains areas, including the atmospheric water, groundwater, oceans, surface waters, and drinking water[6-9].

Fig. 1 shows predicted nano-material concentrations (U.S.) in sediment and sludge treated soil for nano-TiO₂ in mg/kg (left side axis) and for nano-ZnO, nano-Ag, CNTs, and fullerene in µg/kg for the period 2001-2012[10]. Gottschalk et al [10] has established simulated models to predict and calculate probabilistic concentration of (TiO₂, ZnO, Ag and carbon nano-tubes) nano-particles that exposed to the sediments, sludge and soil in the environment for the U.S., Europe and Switzerland. The concentrations in sediments (U.S.) will presumably rise between 2008 and 2012 from 0.2 to 0.6 mg/kg, from 1.8 to 5.7µg/kg, from 0.7 to 2.2µg/kg, and from 0.2 to 0.5µg/kg, for nano-TiO₂, nano-ZnO, nano-Ag and CNT, respectively. While the concentrations that contained in sludge-treated soil will increase from 0.1 to 0.5 mg/kg, from 6.8 to 22.3µg/kg, from 2.3 to 7.4µg/kg, and from 0.1 to 0.4µg/kg, for nano-TiO₂, nano-ZnO, nano-Ag, and CNT, respectively.

The increasing use of nano-materials in our life or the customer productions has inevitably caused the accumulation exposure of the nano-particles into the environment, yet the fate of these particles may greatly depend on their environmental mediums, physical or chemical property. Various types of nanoparticles and related concentration values are given in Table 1[11-13], which presents the distribution of the nanoparticles. The predicted data is also in agreement with the range of predicted models results (shown in Fig. 1). The results obtained from predicted models and hypotheses also present an enlightenment to establish some related estimations for the evolution of the products that contain nano-materials in the worldwide market. Unfortunately, there are still no fully sophisticated systems or assessments towards the pollutants like nanoparticles, especially in those developing countries [14].

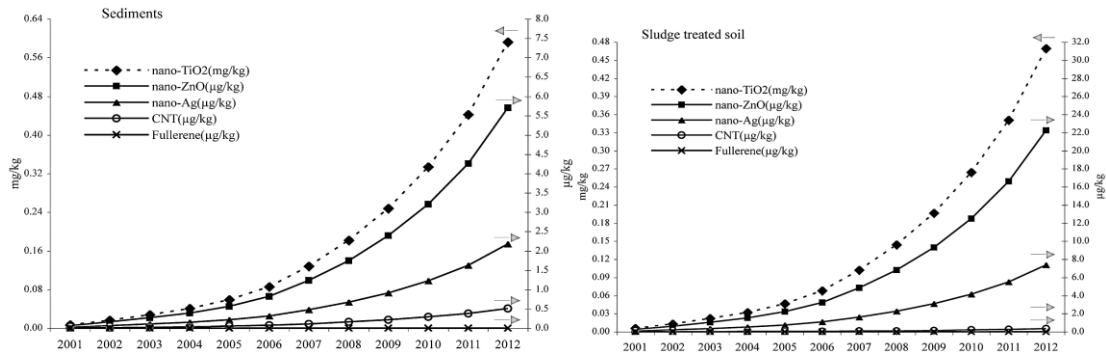


Fig. 1. Predicted nano-material concentrations (U.S.) in sediment and sludge treated soil [10].

Table 1. Predicted model concentrations of selected nano-materials in water, soil and air [11-13].

Nanoparticles	Water(µg/kg)	Soil(µg/kg)	Air(µg/m ³)
<i>Inorganic</i>			
Ag	0.010–0.03	0.02–0.43	0.0017–0.0014
Al ₂ O ₃	0.0002	0.01	–
Au	0.14	5.99	–
CeO ₂	<0.0001	<0.01	–
Hydroxyapatite	10.1	422	–
SiO ₂	0.0007	0.03	–
TiO ₂	0.7–24.5	0.4–10.30	0.0015–0.042
ZnO	76	3194	–
<i>Organic</i>			
Carbon Nanotubes	0.0005–0.0008	0.001–0.02	0.0015–0.0023
Fullerenes	0.31	13.1	–
Latex	103	4307	–
Organo-silica	0.0005	0.02	–

3. Research on Environment Risk of Nano-materials

Nowadays, one of big challenges need to face to is the fate of these nano-particles existed in the environment (in liquid, gaseous, or solid phase) as well as the separation from mediums which is mainly determined by their aggregation or stability[15-17]. Because of the disturbance from pH value, the existence of natural organic matter, ionic strength and even other characteristic in the aqueous medium, the phenomenon could hardly to be stated[18-20]. On the other hand, the physicochemical property, especially superficial area of these particles may greatly influence their transformation and bioavailability during spreading into environment. Due to their diffusing and transforming were different from their primary fate, and aggregation could be performed then precipitation may be arisen.

Toxicological function is affected by the particle size, compounds, or aggregation of these nanoparticles. Currently, some literatures have pointed there had been negative influence upon the aquatic organisms with the emergence of nanoparticles in aqueous condition or at aqueous interface [21-24].

The reaction between nano-materials and organisms is one of complicated processes. We could hardly define which nano-material is poisonous without any fully persuasive evidences. And there are also many complicated or comprehensive factors that need to be taken into consideration when conducting toxicology experiments. Firstly, bio-toxication posed by those harmful substances in high level might hardly support same function in low level ones. Previously, many literature and researchers had reported silver nanoparticles would cause negative effect yet performed bactericidal property [25-28]. Additionally, the morphology is another related problem for those so-called pollutants, which is concerned with the risks and jeopardizing to organisms when these nanoparticles were discharged into the mediums. So, the risk assessment for the nano-materials in the environment is far from an easy task and need to take full considerations according to many complicated conditions or affected parameters. We should not simply expand the results or conclusions that obtained from laboratories to the real life. Therefore, it's essential for people to realize the achievements or results obtained from the scientific research stages or fields are not the final conclusions anymore.

4. Methods of Characterization and Analyses

The size of nanoparticles and their fates are greatly affected by analysis technique at present and the composition of the basic element in optimal condition. As the determination of these nano-materials is still limited by their structure, size and matrix, we just could hardly separate them throughout the whole environment compartment. Although some engineering nano-materials have been detected in some certain conditions, there are still great number of opportunities in the fields of detection and determination for those commercial or engineering nano-materials. For example, it is possible to occur to significantly environmental transportation onto these nanoparticles under the condition of oxidation, photo-degradation and biodegradation; and due to their role of carriers with the small size and strong specific surface, they may cause potential environmental impact. Table 2 summarizes the most methods currently available for the separation and segregation of metallic nanoparticles. In despites of that the improvements on the analytical methods, there are still remained a great number of challenge. And remained choices towards the target and the analyses may diverse and could be tailored based on the analytical objectives.

Table 2. Common methods for separation and segregation of metallic nano-particles[13].

Method	Mechanism	Size range	Complementary technique
Filtration	Size fractionation	Down to 1 kDa	
Micro-filtration	Size-exclusion membrane	100 nm–1 μ m	SEM
Nano-filtration	Size-exclusion membrane	0.5–1 nm	TEM, AFM
Cross-flow ultrafiltration (CFUC)	Size-exclusion membrane	1 nm –1 μ m	TEM, ICP-MS
Dialysis	Size-exclusion membrane	0.5–100 nm	TEM, SEM
Size-exclusion Chromatography (SEC)	Packed porous beads as stationary phase	0.5 –10 nm	ICP-MS ICP-OES
Ultracentrifugation (UC)	Acceleration up to 10 ⁶ g	100 Da –10 GDa	SET, TEM, EDS, RF,ICP-MS, ICP-OES
Field-flow fractionation (FFF)	Physical separation on an open tube based on applied field	1 nm –1 μ m	ICP-MS, ICP-OES
Electrophoretic mobility (EM)	Charge-size distribution along a gradient	3 nm –1 μ m	ICP-MS, ICP-OES

5. Problems and Challenges

Nevertheless, the existing data and evidences that we obtained currently just can be illustrated comparatively little information about what kind of natural conditions that these environmental nano-particles could be formed, how long they would persist, or even their interaction with contaminants would affect the overall environmental quality somewhat.

Those traditional research methods undertake the systems of ultrapure water with adding certain amount of commercial nano-particles by sonication treatment. For the particles in these systems, those once considered as remain in nano-size can no longer be regard in as such, and consequently, may hardly be kept for a high stability.

The dissolution of the natural organic matter will influence the stability of these particles in the aqueous environment. Those stabilizers or modifiers could control the stability of nano-colloid to prevent particles aggregating together. The emergence of these stabilizers or modifiers could modify Brownian movement of these particles and then adjust the electric double layer of the colloid. Because of these stabilizers or modifiers, however, it would cause threaten or disturbance to the security, validity or accuracy of final results. Moreover, the parameters such as pH value, ionic strength, temperature, sediment and aggregation, concentration polarization of filter membrane or filtration may also affect our availability of tested colloid, especially the long-term exposure experiments[13]. So, how or what kind of dispersant, stabilizer or modifiers to choose will be one of principal challenges.

In previous researches on the risk of nano-materials in the environment, the simulation researches were established only according to added amounts of commercial nano-materials. Actually, the results by this method have ignored one point about the status or the property of these nanoparticles might not been kept as in the nanoscale yet, or the true concentration of particles (keep in the nanoscale) that has been dispersed into the dissolved mediums was still ambiguous as well. So, those physical, chemical or even biological methods should be searched for being applied on the fields of nano-science. Besides, the millipore filtration (aims to the particles range from 0.1 to 10 μm), ultrafiltration (25 μm below) and nanofiltration (500 nm below) have been widely used as one universal method for the predissociation, which has simplified the pretreatment towards those engineering or commercial nano-materials[29].

In order to guarantee the authentic validity of dispersed or dissolved concentration of nanoparticles in the fields of toxicology exposure research, the optimized dispersed methods should be established. But the most principal point must guarantee the emergence of added chemical reagents would not influence experiments, and particles in the mediums should be stabilized in nanoscale. Furthermore, those Biological stabilizers have been available ones to be applied, such as FBS (Fetal Bovine Serum), BSA (Bovine Serum Albumin) and some others. Unfortunately, the cost and the payment are so expensive to pay for the engineering or the researches. Their application may be more reasonable if they had easy acquiring, high-stabilizing or low payments when considering these situations. *Zhang et al*[30] had developed a practical method to prepare stable colloid with 100% FBS which could be kept for at least 120 h. However, the components contained were various and complicated so that it could be limited only in the biological researches due to its multiples of interferential factors.

This article introduced an available method by comparing with 3 kinds of common dispersants (SHMP, CTAB and PASS) in the commercial fields. The agglomerate commercial TiO_2 nanoparticles (10mg, 10-20 nm, purchased from company of *WanJingxin*, Hangzhou, China) were dispersed into 100mL of ultrapure water with adding SHMP (Sodium Hexametaphosphate, 0.1g), PAAS (Sodium Polyacrylate, 0.5g) or CTAB (Hexadecane Three Methyl Brominated Ammonium, 0.2g), respectively. Meanwhile, the intensity energy of ultrasonication (360W) onto nanoparticles dispersing in the solutions was undertaken at a frequency of 40 kHz for 15 minute at room temperature. The characterization of dispersed commercial TiO_2 nanoparticles was estimated by using TEM (Transmission Electron Microscope)

analysis (shown in Fig. 3) and Zetasizer Nano (shown in Fig. 2 and Table 2). The measurement was tested for the time interval per 4 days and executed 3 times totally.

Fig. 2 shows that nano-TiO₂ is dispersed in the ultrapure water without any dispersant, the average size of commercial nano-TiO₂ agglomerates is approximately 700 nm, then tended to agglomeration with various time, and was nearly 5300 nm after 8 days. While the average size with organic polymer dispersant one (PASS) was reflected even worse effect than the ones with the inorganic ones (SHMP or CTAB) as well, and the size was approximately 2450 nm at least. The average size with SHMP (198 nm) one reflected better than the one with CTAB (227 nm) after 8 days. It was finally indicated that nano-TiO₂ aggregates were irreversible dispersed to primary size (10-20) nm in suspension, but real dispersed effect of colloids was needed to be analyzed by TEM. The letter of A, B or C in Fig. 3 refers to the dispersed system of nano-TiO₂ with PAAS, CTAB or SHMP, respectively. In this study, the dispersed effect of these particles performs the best with SHMP, then CTAB follows, and PAAS shows the worst.

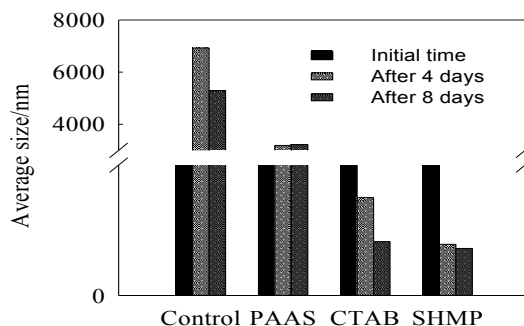


Fig. 2. The dispersion effect of commercial TiO₂ with different dispersants.

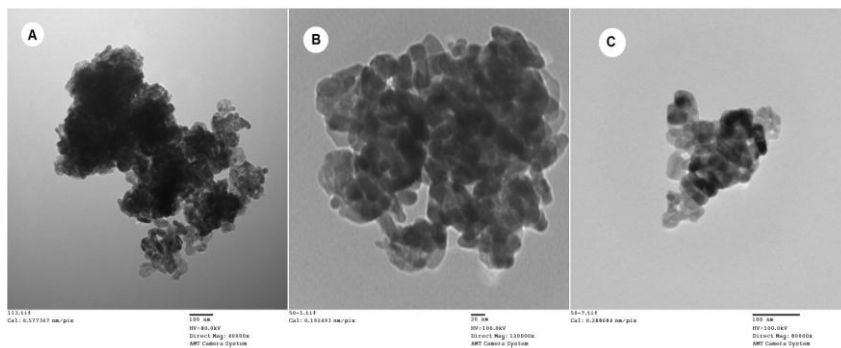


Fig. 3. The characterization of nano-TiO₂ under TEM.

The Zeta-potential of colloid varied with the impact of the dispersants and turned to be higher (except for PASS ones, shown in Table 3) after stabilizing for a longer time. Because parts of hydrolyzed molecular chains of Sodium Polyacrylate were intertwined with particles, and bridging effect was performed, then even stronger Van Der Waals' force would be performed. Because the negative charge performed in the surface charge, the repulsive force between TiO₂ nano-particles and the anionic dispersant of SHMP performed stronger than the cationic dispersant of CTAB. Then Zeta-potential performed higher with SHMP hence.

Table 3. The Zeta-Potential of nano-colloid with different dispersant.

Dispersant	Initial time	After 4 days	After 8 days
Control	-19.1±5.4	-37.1±4.1	-41.1±2.3
PAAS	-89.6±3.5	-76.4±3.4	-60±2.9
CTAB	30.6±4.4	33.3±6.9	38.2±4.2
SHMP	-52.5±5.9	-52.1±5.1	-55.6±7.8

Combined with 2 parameters (the average size and Zeta-potential,) it's much proper to prefer SHMP in the research. Consequently, the real concentration of colloid was detected by ICP-OES. The results indicated that actual concentration of colloid in triplicates samples after stabilizing for 8 days was $11.2 \pm 2.9 \text{ mg} \cdot \text{L}^{-1}$, the average size $187.8 \pm 18 \text{ nm}$ and Zeta-Potential was $-57.3 \pm 7.6 \text{ mV}$, respectively. Totally, it should be noted that the advantage of SHMP, such as green, inexpensive, environmental and nontoxic or convenient should be taken into consideration on the accounts of choosing to the proper dispersant, modifiers or stabilizers.

6. Conclusions

With advantages of nano-materials, the industries or the products from nano-materials have been covered in many fields, and exhibited a thriving trend in a rapid growth of novel nanotechnology. Due to the interference associated with uncertainty caused by nano-materials, it will be far more difficult for the detection or the monitoring survey. Therefore, the approaches should be improved in the fields of characterization, the detection to the particles morphology and the trace methods to the fate of nanoparticles. Furthermore, the more convenient, environmental and low-pay approaches should be also involved regarding to biological or chemical reagents, such as stabilizers, dispersants or the masking agents, to be used for dispersing or preparing the colloids for the cytotoxicity assays or the environmental risk researches. Finally, more adequate available control and managements should be employed to promote the risk assessment of nano-materials in environment, and more rigid, effective regulations, standards or legislations on the accounts of nano-materials would be normalized by the governments or the relevant authorities in the products of nano-materials in commercial market and industrial products.

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