Review Article

Transport Behavior of Engineered Nanosized Photocatalytic Materials in Water

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Engineered nanoparticles (ENPs) possess unique properties and are employed in many sectors, and thus their release into environment remains. The potential risks of ENPs have been confirmed by an increasing number of studies that necessitate a better knowledge to the fate and transport of ENPs. One important application of ENP is photocatalysis for production of H_2 as energy and pollutant decomposition. Engineered photocatalytic nanoparticles (PCNPs) can also easily enter the environment with the rapid increase in its manufacture and use. This review focuses on the transport of PCNPs in water by addressing the important factors that determine the transport of PCNPs, such as particle size, pH value, ionic strength (IS), ionic valence, and organic matter. The transport of PCNPs in natural water systems and wastewater systems is also presented with an attempt to provide more abundant information. In addition, the state of the art of the detection technologies of PCNPs has been covered.

1. Introduction

Engineered nanoparticles (ENPs) with sizes at least in one dimension smaller than 100 nm have various unique properties, such as special optic, electric, thermotic, and magnetic properties [1]. They can be used for biomedical, pharmaceutical, catalytic, cosmetic, electronic, energy, environmental, and material applications and certainly have attracted intensive attention as one of the most promising technologies in the 21st century [2, 3]. Due to the existing and many potential applications of this technology, there has been a global increase in investment in nanotechnology research and development [4]. The market value for nanotechnology-related products in 2011–2015 is estimated to be more than USD 1 trillion per year [5]. It is particularly noted that owing to their excellent optical properties, a considerable portion of ENPs can be used as photocatalytic materials that can also be named as photocatalytic nanoparticles (PCNPs), which pose to play an important role in air purification, wastewater treatment, photocatalytic disinfection, photocatalytic degradation, dye-sensitized solar cells, and hydrogen generation [6–13].

The forecasted huge increase in the manufacture and use of ENPs results in their inevitable release into the environment. However, their unpredictable effects should not be ignored [14–19], and their adverse impacts on human health and ecology have been confirmed [5, 20–30]. Therefore, the fate and potential harmful effects of ENPs play an important role in evaluating the safety of ENPs in the environment [31]. To obtain detailed information on the above, a better understanding of the transport of ENPs is initially required. This review focuses on the transport behavior of PCNPs.

1.1. Transport Processes of the PCNPs. Each stage of the life cycle (production, transport and storage, use, and disposal) of PCNPs may lead to a potential exposure of human being [2, 3], once released into environment including air, water, and soil. The transport processes of PCNPs in the environment are depicted in Figure 1. Likewise, this transport behavior also occurs in aerosol, and the PCNPs are suspended in the air for a long period of time and then transport over a long distance by the aid of wind. They will then precipitate on the surface of water and be deposited on land by gravity. When the PCNPs enter the water, they may not only be stabilized or transported
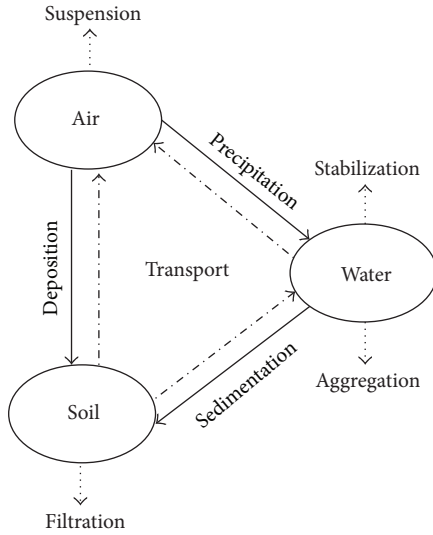
FIGURE 1: Transport processes of the PCNPs in the environment.

TABLE 1: Ingredients of the of photocatalyst matrix at the nanoscale.

Ingredients	Type	Examples
Catalyst bulk	Oxides	TiO_2 [32, 33], ZnO [34, 35], CeO_2 [36, 37] Fe_2O_3 [38–41], Fe_3O_4 [42] Goethite/Hematite [43]
	Sulfides	ZnS, PbS [44], HgS [45]
	Carbons	Fullerene [46–48]
Dopant	Metals	Pt, Au [49, 50], Ag [51, 52], Cu [53], Pd [54] Zero-valent iron (ZVI) [55]
	Oxides	NiO [56], MnO_2 [57, 58]
	Carbons	Carbon nanotubes (CNT) [59–64]
Support	Oxides	SiO_2 [65, 66], Al_2O_3 [67, 68]

TABLE 2: Analysis and characterization methods of PCNPs.

Type	Examples
Microscopy	TEM, SEM, AFM
Spectroscopy	UV-Vis, FTIR, AAS, Raman spectroscopy ICP-OES, fluorescence spectroscopy
Light scattering	DLS
Light diffraction	XRD
Computer technology	Molecular simulations

through the water flow but also can be aggregated and settled to sediments. The behavior in water highly depends on the physical and chemical properties of the PCNPs, as well as the conditions of water chemistry such as pH, ionic strength (IS), and content and property of dissolved organic matter (DOM). PCNPs may be blocked by soil particles and remain in the soil for a long period of time, or break through the soil matrix and reach groundwater. Among the environmental media, water is the connection between air and soil. Hence, the transport of PCNPs in water becomes the most crucial process. It is critically of importance in enhancing the knowledge on the environmental behaviors of PCNPs.

1.2. Types of the PCNPs. The matrix of photocatalyst embraces the catalyst buck, the support, and dopant as well. Each of the three ingredients shares its intrinsic role in the catalytic reactions, and in some cases a synergetic effect emerges. Interestingly, the three ingredients can be well fabricated at the scale of nanosize for an improved activity on the whole. Table 1 shows some common types of PCNPs, with each kind being different in morphology. They can be spherical, tubular, or irregularly shaped and may exist in fused, aggregated, or agglomerated forms. Obviously, the diversity in the physical structure may lead to differences as PCNPs transport in water.

1.3. Detection Technology of the PCNPs. Nowadays, the detection technology used for monitoring ENPs is being rapidly developed [69], and many analytical and characterization methods have been adopted to disclose the transport behavior of PCNPs in water (Table 2). The most popular approaches are microscopic methods such as transmission electron microscope (TEM) and scanning electron microscope (SEM), for the observation of the morphology. Light scattering technology such as dynamic light scattering (DLS) is employed to quantify the particle size. These measures can also be used to disclose the transport behavior of PCNPs in water. Using these methods, we can obtain intuitional

information about the morphology and size of PCNPs. X-ray diffraction (XRD) is another useful tool for studying PCNPs as it can show more abundant information on the solid surface. At the same time, atomic force microscope (AFM) and molecular simulation technology are used to study PCNPs in order to detect and predict the forces between nanoparticles in water and determine how they affect the transport of ENPs in such medium [70–74]. Spectroscopy instruments (e.g., ultraviolet-visible spectrophotometer [UV-Vis], atomic absorption spectrometer [AAS], and inductively coupled plasma optical emission spectrometer [ICP-OES]) are also commonly used to detect the change in the concentration of PCNPs in water [75–80]. Some other spectroscopy technologies (e.g., Raman spectroscopy, Fourier transform infrared spectroscopy [FTIR], and fluorescence spectroscopy) are very helpful in providing more details about PCNPs [81–84]. Although remarkable progress has been made, the development of analysis and characterization techniques for ENPs is still challenging [85]. For instance, the precise size of PCNPs in water is hard to be identified; only the average hydrodynamic radium or electron microscope picture can be used to evaluate the aggregation and stabilization of PCNPs in water. The detection techniques discussed above are offline which can only reveal the state of PCNPs in water after several minutes or hours, but some processes of PCNPs in water may be quickly, so they can hardly monitor the instantaneous state (about several milliseconds or less) of PCNPs in water. Generally, more sensitive and efficient techniques are in great need to shed a light onto the transport behavior of PCNPs in water. It is necessary to develop more online detection methods which can monitor the state of
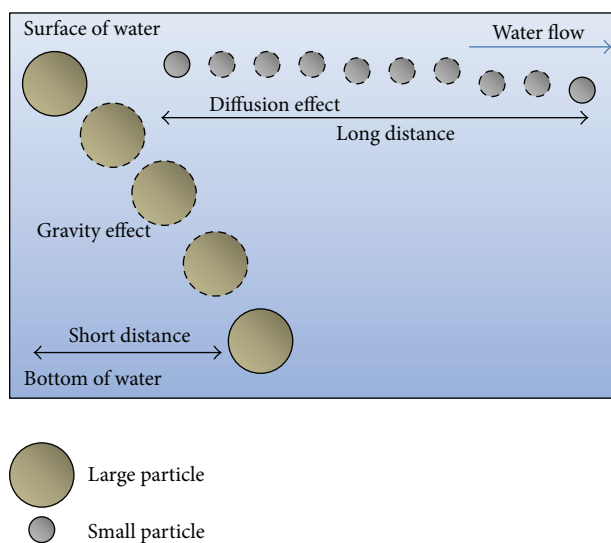
FIGURE 2: Different transport behaviors of PCNPs in different sizes.

TABLE 3: Reported size distribution of the selected ENPs as ingredients of photocatalyst matrix in water.

ENPs	Individual particle size (nm)	Hydrodynamic particle size (nm)	References
Ag	20–30	~100	Gao et al. [93]
Al	41	215 ± 99	Darlington et al. [94]
Cu	26.7 ± 7.1	94.5–447.1	Griffitt et al. [95]
NiO	10–20	750 ± 30	Zhang et al. [96]
CeO_2 (rods)	$(67 \pm 8) \times (8 \pm 1)$	231 ± 16	Keller et al. [76]
PbS	14.4 ± 1	240	Liu et al. [97]
TiO_2	15–27	90–290	Jiang et al. [98]
ZnO	13	36–413	Xie et al. [78]
SiO_2	14	205	Adams et al. [99]
Fe_2O_3	9.2	46.2	Baalousha et al. [100]
Fe_3O_4	<10	120	Illés and Tombácz [101]
Al_2O_3	60	763	Wang et al. [102]
ZnS	2.1	~12.5	Slaveykova et al. [103]

PCNPs in water at any time, and more combination methods which can analyze the physical properties of PCNPs and chemical conditions of water simultaneously are strongly recommended.

2. Factors Influencing the Transport Behavior of PCNPs in Water

2.1. Particle Size. The size of PCNPs not only affects the photocatalytic activity significantly but also plays an important role in defining their transport and fate in aquatic environments. Figure 2 shows the different transport behaviors of PCNPs in different sizes. PCNPs with relatively large size tend to settle quickly by the aid of gravity, and their transport will be greatly restricted. Meanwhile, PCNPs with smaller size pose to remain in the water for a long period of time through the diffusion effect and may transport over a long distance by water flow. Several studies have confirmed that as PCNPs are released into water, they may aggregate. Table 3 shows the reported size distribution of the selected PCNPs in water. It can be seen that the hydrodynamic particle size is much larger than the individual particle size in the dry phase. The aggregation reduces the overall specific surface area of the PCNPs and the interfacial free energy, and thus limiting the reactivity. In addition, some of the PCNPs are ultrasonicated before their hydrodynamic size is determined, indicating that aggregation is a common process for PCNPs in water and that ultrasonication can do little to completely break the aggregates in water.

The sunlight and UV irradiation can prevent PCNPs especially fullerene from aggregation due to surface oxygenation and hydroxylation through photochemical transformation in the presence of dissolved O_2 [86–88], so the size of PCNPs can remain stable [89–92].

In order to improve the photocatalytic activity and increase the light availability, the composite PCNPs that combine two or more PCNPs are synthesized extensively [32, 33, 36, 37, 49, 52]. The sizes of these composite PCNPs are different from the size of those original PCNPs, and it can conclude that they can exhibit dissimilar transport behaviors to the original PCNPs.

2.2. pH. pH is a major factor determining the zeta potential of colloids. Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The value of zeta potential can be related to the stability of colloidal dispersions. The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles in colloidal dispersions. For particles that are small enough, a high zeta potential will confer stability. This means that colloidal dispersions can resist aggregation. When the potential is low, attraction exceeds repulsion, and the dispersion will break, and flocculation takes place. Therefore, colloids with high zeta potential (negative or positive) are electrically stabilized, while colloids with low zeta potential tend to coagulate or flocculate.

The pH can significantly affect the zeta potential of colloids. A number of studies have proved that as the pH is at the point of zero charge (pH_{pzc}) or isoelectric point, the colloidal system of PCNPs exhibits the least stability, and the sedimentation or aggregation rate increases [76, 101, 104–106]. Figure 3 depicts the relationship of aggregation and repulsion of PCNPs in different pH. At the pH_{pzc}, the zeta potential is zero; the PCNPs can aggregate to become bigger particles due to the weak repulsion effect. As the pH continues to decrease until it becomes lower than the pH_{pzc}, the surface of PCNPs colloids is positively charged, and the PCNPs prefer to remain small because of the strong electrostatic repulsion. Similar situation happens when the pH continues to increase until it becomes above the pH_{pzc}, the surface of PCNPs colloids is negatively charged, and the size of PCNPs is also stable.

TABLE 4: Reported pH_{pzc} of selected PCNPs.

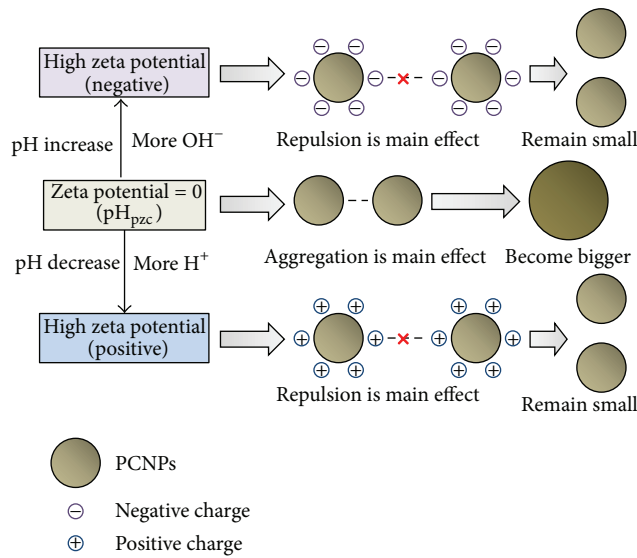| PCNPs	Particle size (nm)	pH_{pzc}	References
TiO_2	3.6, 8.1	1.8, 6.2	Guzmán et al. [105]
TiO_2	35	4.5	Fang et al. [107]
TiO_2	50 ± 5	5.9	Yang and Xing [108]
Hematite	12, 32, 65	7.8, 8.2, 8.8	He et al. [109]
Hematite	12.5, 29.4, 51.4, 66.5	7.5, 7.7, 7.9, 8.5	Zeng et al. [110]
Al_2O_3	60	7.9	Ghosh et al. [111]
MnO_2	50	2.4	Feitosa-Felizzola et al. [112]
CeO_2	157.4	>7.0	Necula et al. [113]
HgS	Unavailable	4.0	Ravichandran et al. [114]

FIGURE 3: The relationship of aggregation and repulsion of PCNPs in different pH.

Different sizes of the same kind of PCNPs or similar size of different kinds of PCNPs may display a distinct difference in pH_{pzc} (Table 4). Hence, at the same pH, different PCNPs have different surface charges. Keller et al. have reported that in the same simple solution with low IS and free of natural organic matter (NOM), TiO_2 nanoparticles are negatively charged, while ZnO nanoparticles are positively charged, and CeO_2 nanoparticles approach pH_{pzc} [76].

IS can affect the aggregation of PCNPs at their pH_{pzc}. French et al. have observed that at very low IS, the aggregation of TiO_2 is not remarkable as the pH comes close to pH_{pzc} [115].

When organic matters are present, they will coat the PCNPs and remarkably vary their surface properties, and thus served to reduce the charge of PCNPs and increase their size. As a result, the PCNPs become electrostatically or sterically stabilized, and the pH has little effect on the zeta potential of PCNPs [75, 116, 117]. PCNPs may be modified by organic matters in a specific pH value. The functional groups of PCNPs may be dissolved into solutions when the pH is changed. Therefore, this can affect the stabilization and aggregation of PCNPs [118–120].

The pH value can also influenced the hydroxyl radicals production rate of PCNPs significantly, which may affect both the photocatalytic behavior and transport behavior of PCNPs in water. Xiang et al. have characterized the hydroxyl radicals produced by various semiconductor photocatalysts and indicate that the acidic pH environment of the solutions is beneficial to enhancing the formation rate of hydroxyl radicals [121].

2.3. IS. IS is another important factor influencing the stabilization and aggregation of PCNPs. Many studies have revealed that an increase in IS compresses the electric double layer on the surface of PCNPs [75, 104, 116, 117, 119], thereby decreasing the electrostatic repulsion between two particles with the same charge. The energy barrier will then decrease, and the attachment probability becomes closer to unity [5, 122, 123].

The critical coagulation concentration (CCC), known as a threshold electrolyte concentration, represents the minimum amount of electrolyte needed to completely destabilize the suspension [124]. It provides a useful parameter of colloidal stability for PCNPs and hence can be used to predict the transport behavior in water [79].

The classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [125] describes the forces between charged surfaces interacting through a liquid medium. It combines the effects of the Van der Waals attraction with the electrostatic repulsion due to the so-called double layer of counterions. It is widely used as a model to predict the stabilization and aggregation of ENPs in water with electrolytes, and many extended models have been established based on the DLVO theory [126].

For spherical particles (e.g., TiO_2, ZnO, fullerene), an increase in IS induces aggregation, and the particles size grows much bigger [76, 115, 127] (Figure 4(a)). Some similar phenomena have been found in tubular particles (e.g., CNT), which become unstable and precipitate when IS increases [106]. When PCNPs are coated by charged macromolecules (e.g., citrate acid), they may become electrostatically stabilized. At low IS, PCNPs can still be stable due to charge neutralization, which must be broken only at high IS (Figure 4(b)). When PCNPs are coated by noncharged polymers (e.g., PVP), they will be highly sterically stabilized (Figure 4(c)). The lack of effect of IS on the aggregation of sterically stabilized PCNPs was also observed [116].

2.4. Ionic Valence. The Schulze-Hardy rule [128] states that the CCC, varying as the inverse sixth power of the counterion charge, plays a significant role in destabilizing the stability of colloidal [129]. According to this rule, multivalent and divalent ions may be more efficient in neutralizing the charge on the surface of PCNPs than monovalent ions. With respect to charge screening, compared with monovalent ions, multivalent and divalent ions have a higher charge density and can induce aggregation at lower IS through more efficient double-layer compression. Alkali metal cations (e.g., Na^+, K^+) and alkaline earth metal cations (e.g., Mg^{2+}, Ca^{2+}) are
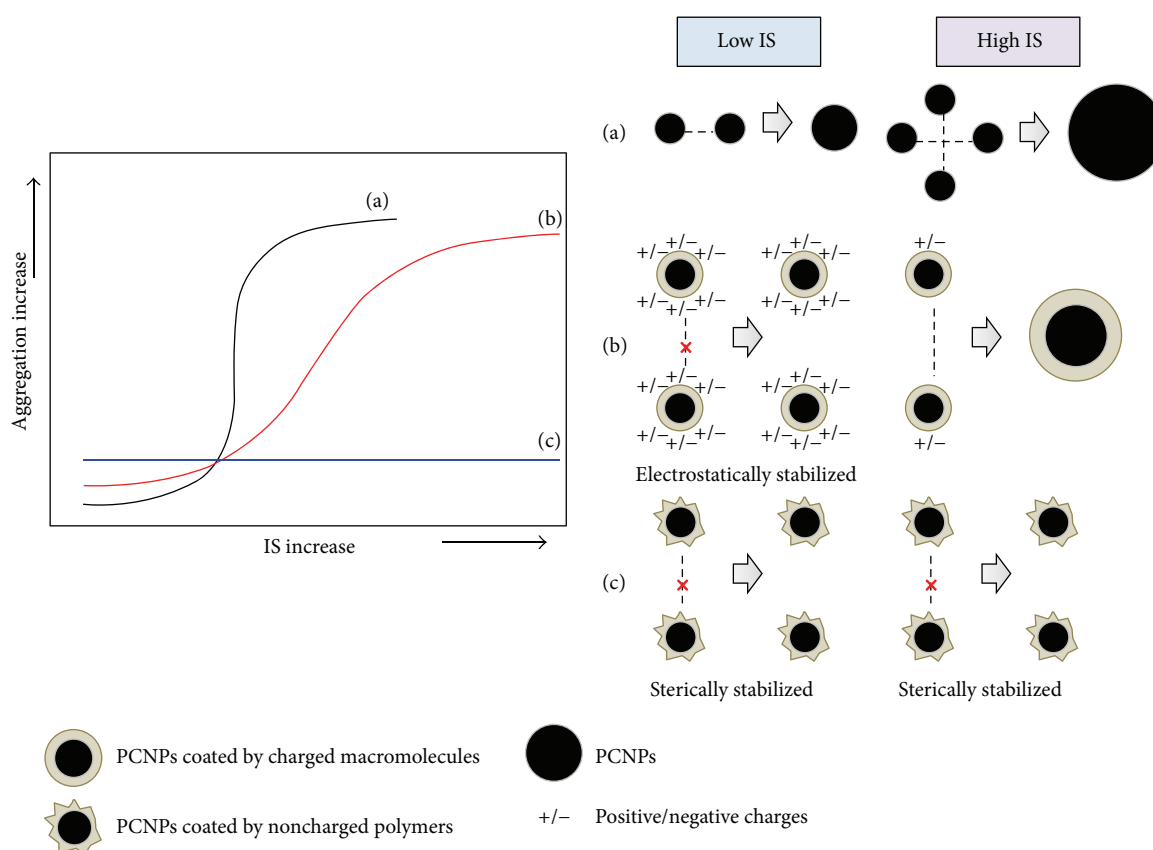
FIGURE 4: The different aggregation behaviors of PCNPs (a), PCNPs coated by charged macromolecules (b), and PCNPs coated by noncharged polymers (c) in low IS and high IS.

most commonly used as model monovalent and divalent cations because of their ubiquity in aquatic environment.

Many experimental results have evidenced that divalent cations are much more efficient in enhancing the aggregation of bare PCNPs in water [79, 115, 130]. When a negative-charged organic matter is coated on the surface of PCNPs, cations with different valence will affect the aggregation process of PCNPs through different ways. For monovalent cations, they will be attracted by the negative charge of the coated organic matter of PCNPs (Figure 5(a)). The aggregation process is controlled by electrostatic and Van der Waals interactions between the particles, which do not lead to enhanced aggregation. It is similar to the conventional particle-particle collision aggregation process. When the divalent cations are attracted by the negative charge of the coated organic matter of PCNPs, they (especially Ca^{2+}) can form complexly with the coated organic matter and bridge the PCNPs (Figure 5(b)). The aggregation process is controlled by sterical interaction, which can lead to notable aggregation. When coated by the noncharged organic matter, PCNPs will remain stable. Both monovalent and divalent cations cannot enhance the aggregation of PCNPs.

2.5. Organic Matter

2.5.1. NOM. As ubiquitous components of aquatic systems, NOM is known to greatly influence the aggregation and

stabilization of PCNPs by adsorbing to the particulate surface. It is considered to be a crucial factor affecting the transport of PCNPs in water and has been well investigated [79, 104, 131–133]. Suwannee River humic and fulvic acids (SRHA and SRFA, resp.), which can be obtained from the International Humic Substances Society (IHSS), are usually used as the standard models of NOM.

The chemical nature and structure of NOM serve to determine whether colloids will be stabilized or destabilized. Deonarine et al. have measured many parameters of NOM (e.g., aromatic carbon content, aliphatic carbon content, molecular weight, carbonyl and carboxyl content, etc.) that determine the relationship between the growth rate of ZnS-NOM particles and the specific NOM parameters [134]. They have found that an increase in the molecular weight of NOM leads to slower growth rate of ZnS-NOM particles. They have also revealed that aromatic carbon content shows the strongest linear relationship with the growth rate of ZnS-NOM particles, and a similar phenomenon is observed in multiwalled carbon nanotubes [119]. The factors which affect the aggregation behavior of PCNPs as NOM exists are presented in Table 5. Both high molecular weight and aromatic carbon content can reduce the aggregation of PCNPs. The former is attributed to the sterical repulsion, while the latter is due to the π-π interaction. With the addition of NOM, the negative surface charges of PCNPs increase significantly, and thus their propensity to aggregate

(a)

(b)

Coated organic matter M^+ Monovalent cation

PCNPs   Negative charge
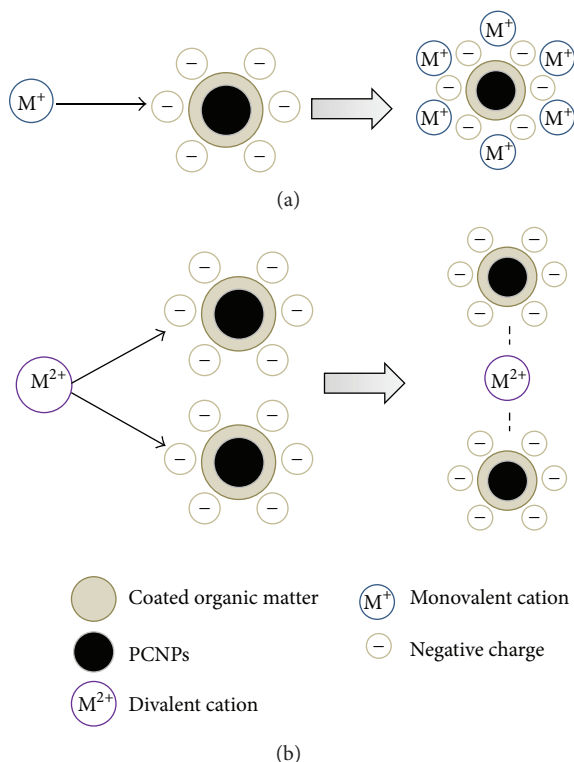
M^{2+} Divalent cation

FIGURE 5: Schematic diagrams for the mechanism of monovalent cations (a) and divalent cations (b) affecting the aggregation process of PCNPs coated by negative-charged organic matter.

TABLE 5: The factors affect the aggregation behavior of PCNPs as NOM exists.

	Factors	Cause
Reduce aggregation	High NOM molecular weight	Sterical repulsion
	High NOM aromatic carbon content	π-π interaction
Induce aggregation	High cation concentration	Charge neutralization
	Light irradiation	NOM degradation

Most polymers are commonly stable; hence, they may be used as a capping agent to improve the stability of PCNPs. Othman et al. use polyacrylic acid (PAA) and ammonium polymethacrylate (Darvan C) to disperse TiO_2 nanoparticles, and more dispersed and stabilized aqueous TiO_2 suspension is prepared successfully [144]. When they are coated on the surface of PCNPs, the latter can remain stable in water and may be stopped for further aggregation. This indicates that they can stay in water for a long period and is hard to be removed.

2.5.3. Biomacromolecules. Due to the potential harm of ENPs to human, animals, and plants, it is necessary to study the effect of biomacromolecules (e.g., polysaccharide, protein) on the transport of PCNPs in water. Saleh et al. have indicated that the presence of biomacromolecules significantly retards the aggregation rate of single-walled carbon nanotubes, and this is attributed to the sterical repulsion originating from the adsorbed macromolecular layer [145]. However, there is still lack of studies that focus on the effect of biomacromolecules, specifically on the transport of PCNPs.

3. Transport of PCNPs in Natural Water Systems

After PCNPs are released into the aquatic environment (e.g., rivers, lakes, seas, groundwater, stormwater, etc.), most of them have been shown to aggregate once they are hydrated, which results in the efficient removal of the small particles [146]. The formation of aggregates of PCNPs in natural water systems can be considered as physical processes, that is, Brownian diffusion, fluid motion, and settlement under gravity.

The aggregation and stabilization of PCNPs in natural water systems also depend on the above-discussed factors that influence the transport of PCNPs in water. The interactions between PCNPs or PCNPs and NOM play a crucial role in the transport of PCNPs in natural water systems. Mosley et al. have studied the forces between colloid particles in natural water system [70]. Under the conditions of low IS, the interparticle forces are dominated by electrostatic repulsion. However, at high IS, they are dominated by sterical repulsion forces, and electrostatic forces are largely absent. In addition, adhesive bridging between the surfaces of PCNPs

is reduced. On the other hand, the negative charges that NOM imparts to nanoparticles could be neutralized by cations (especially divalent cations). It has been proven that Ca^{2+} induces the aggregation of NOM-coated ENPs [135]. NOM may be degraded by PCNPs when light irradiates and leads to aggregation of PCNPs as well, and this will eminently affect the transport of PCNPs in water.

2.5.2. Surfactants and Polymers. Many approaches have been used to obtain the surfactant-stabilized suspensions of dispersed CNTs [136–139]. For nonionic surfactants, higher molecular weight may lead to better dispersion of ENPs [140–142]. Consequently, PCNPs can be well dispersed by surfactants, as they are generally insoluble in water. Hydrophobic interaction may play an important role in the stabilization of PCNPs suspensions for nonionic surfactants. The ability of nonionic surfactants to disperse PCNPs appears to be mostly dependent on the size of the hydrophilic group. Higher molecular weight suspends more PCNPs because of enhanced sterical stabilization with longer polymeric groups. For ionic surfactants, the addition of inorganic electrolyte can reduce the stabilization of suspensions of PCNPs. Bouchard et al. have indicated that CNTs dispersed by ionic surfactants are unstable in Ca^{2+} dominated systems at low surfactant concentrations and would likely aggregate and settle out of suspension [143].

by adsorbed NOM creates a strong energy barrier to the spontaneous disaggregation of colloid aggregates.

Most studies use laboratory-made water or artificial natural water instead of real natural water to study the aggregation and stabilization of PCNPs. Nevertheless, the results of such studies may probably assist in predicting the transport of PCNPs in real natural water systems. Keller et al. and Ottofuelling et al. have presented the aggregation and stabilization of metal oxide (MeO) nanoparticles in different natural water systems [76, 147]. They revealed that PCNPs in water systems with low IS and high NOM content (mesocosm freshwater) will remain stable, and the sedimentation rate of MeO nanoparticles is very slow. On the contrary, PCNPs in water systems with high IS and low NOM content (seawater) lead to a rapid sedimentation rate of MeO nanoparticles. This is consistent with the results of many studies that used laboratory-made water systems or artificial natural water systems. Obviously, natural water systems are complicated due to their diversity and randomicity, and it will be more complicated if photocatalytic reactions occur on the PCNPs in water. Therefore, the transport of PCNPs in natural water systems is influenced by the combined interactions of many factors. It is therefore a challenge to depict the detailed process of transport of PCNPs in natural water systems.

4. Transport of PCNPs in Wastewater Treatment Systems

There is a lack of knowledge regarding the transport of PCNPs in engineered systems, including wastewater treatment systems. The rapid increase in the production of PCNPs has created a demand for particle removal from industrial and communal wastewater streams. A common process wastewater treatment plants (WWTP) with advanced treatment includes the quite a few units. PCNPs involved within the wastewater will first be primarily treated. However, most PCNPs, except those surface-coated or functionalized, may still remain in the effluents because of their small size. Jarvie et al. have indicated that silica nanoparticles, which are surface-coated or functionalized, undergo rapid flocculation in wastewater and can be efficiently removed through primary treatment of WWTPs [148].

When PCNPs enter into an aeration tank, they will probably be absorbed on the activated sludge (AS). Recently, some PCNPs especially metal and metallic oxides nanoparticles are found in the AS [149–153]. Zou et al. establish an effective method to produce high-purity nano-SiO_2 by recovering silicon from sewage sludge [154]. Gómez-Rivera et al. have revealed that CeO_2 nanoparticles can be removed by the AS and suggest that it will be expected to provide extensive removal of CeO_2 nanoparticles [155]. Whereas, it is doubtful that AS treatment is the best way to remove the nanoparticles in WWTPs. Recently, only a few pieces of evidence have shown that some types of PCNPs decrease the activity of AS [156–158]. However, it can be deduced that PCNPs may be harmful to the microorganisms in the AS due to their potential toxicity. Some PCNPs can dissolve and release metal ion which can cause metal toxicity. Liu et al. and Mu et al. have found out that when the ZnO nanoparticles are absorbed on the AS, they will release Zn^{2+} which can exhibit great toxicity [159, 160]. Ag nanoparticles are excellent antimicrobial materials as we known; therefore when Ag^+ is released, it will probably enter the cells of microorganisms directly and inactivate cellular enzymes and DNA [149]. Because of the harmful impact of metal ions, some efforts are made to prevent the metal ion from dissolving by reassembling the nanoparticles into microspheres [161–165]. Due to their perfect photocatalytic property, PCNPs may also generate reactive oxygen species (ROS) which can kill the microorganisms by strong oxidation effect.

After secondary treatment, most of the PCNPs will be flocculated and removed from effluents. They may settle in finished biosolids after the solids handling process of WWTPs and can reenter the environment when the finished biosolids are used as fertilizers, incinerated, placed in landfills, or dumped in oceans [166]. After tertiary treatment, there is still a small proportion of PCNPs that remain in the treated effluent and enter the surface water environment, potentially disrupting numerous biological ecosystems.

5. Concluding Remarks

Increasing presence of PCNPs in the environment remains a challenge due to the rapid development of nanotechnology. It is essential to assess the potential risks of PCNPs that has been widely tested and employed as photocatalyst for environmental clean-up. Disclosure of the transport behavior of PCNPs in water is of particular importance for the prediction of associated environmental risk.

PCNPs could be intentionally or unintentionally discharged in each stage of the life cycle. They will then transport within the environment media. The transport of PCNPs in water poses as the most important process, and more studies should be conducted to explore such area. As PCNPs transport in water, they can aggregate and settle down or may be stabilized in water for a long period of time. The dramatic difference in the transport behaviors of PCNPs depends on several key factors that govern their stability and mobility as colloidal suspensions or their aggregation into larger particles and deposition in aquatic systems, such as particle size and water composition (e.g., pH, IS, ionic valence, and organic matters). However, only a few studies tackle the issue: which factor is predominant? Also, there is a lack of models that serve to predict the transport of PCNPs in water combining all the factors.

Most PCNPs will transport in natural water system once they are released into aquatic environment. The aggregation and stabilization of PCNPs in natural water systems highly depend on the water chemistry. Numerous studies have centered on the transport of PCNPs in laboratory-made or artificial water systems, which provide information on how to assess the transport behavior of PCNPs in real natural water system. However, there is still a lack of studies involving real natural water systems to determine the process of transport of PCNPs.

Wastewater treatment serves as an efficient process of preventing the release of PCNPs in water. Some studies have

indicated that most of the PCNPs can be removed through primary and secondary treatments and that only a little may still be left in water effluents after the tertiary treatment. The removed PCNPs may eventually become biosolids and return to the environment if the sludge is improperly disposed. Due to the potential toxicity of PCNPs to the microorganism of AS using conventional technology, more novel technologies should be put forward to solve such problem. During the actual process of transport, photocatalytic reaction of organic degradation under the illumination of sun light may occur, which serves to add complexity of the transport behavior, while this reaction may bring advantage by degrading more organic pollutants. Lack of relevant information in this issue requires the investigators to pay attention to this field.

Acknowledgment

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