



## The role of humic acid in stabilizing fullerene (C<sub>60</sub>) suspensions

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**Abstract:** Natural organic matter (NOM) has a profound effect on the colloidal stability of discharged C<sub>60</sub> nanoparticles in the water environment, which influences the environmental behaviors and risks of C<sub>60</sub> and therefore merits more specific studies. This study investigates the effects of humic acid (HA), as a model NOM, on the aqueous stabilization of C<sub>60</sub> powder and the colloidal stability of a previously suspended C<sub>60</sub> suspension (aqu/nC<sub>60</sub>) with variations of pH values and ionic strengths. Our results reveal that HA could disperse C<sub>60</sub> powder in water to some degree, but was unable to stably suspend them. The aqu/nC<sub>60</sub> could remain stable at pH > 4 but was destabilized at lower pH values. However, the colloidal stability of aqu/nC<sub>60</sub> in the presence of HA was insensitive to pH 3–11, owing to the adsorption of HA onto nC<sub>60</sub> and the increased electrosteric repulsions among nC<sub>60</sub> aggregates. The colloidal stability of aqu/nC<sub>60</sub>, with and without HA, decreased as we increased the valence and concentration of the added cations. HA was found to mitigate the destabilization effect of Na<sup>+</sup> on the colloidal stability of aqu/nC<sub>60</sub> by increasing the critical coagulation concentration (CCC) of Na<sup>+</sup>, while HA lowered the CCCs of Ca<sup>2+</sup> and La<sup>3+</sup> probably by the bridging effect of nC<sub>60</sub> with HA aggregates formed through the intermolecular bridging of the HA macromolecules via cation complexation at high concentrations of cations with high valences.

**Key words:** Fullerene, Humic acid, Colloidal stability, Natural organic matter, Nanomaterial

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### 1 Introduction

Fullerene C<sub>60</sub> nanoparticles have triggered much attention by their unique physicochemical, electrical, and mechanical properties, which enable their numerous potential applications in electronics (Zhang *et al.*, 2013), biomedicine (Colvin, 2003; Nakamura and Isobe, 2003), cosmetics (Takada *et al.*, 2006), etc. C<sub>60</sub> is inevitably released into the aquatic environment

with its widespread production and usage (van Wezel *et al.*, 2011), and may thus threaten aquatic organisms and human health as well through food chains (Nel *et al.*, 2006; Oberdörster *et al.*, 2006; Britto *et al.*, 2012).

Once released into the water environment, the hydrophobic C<sub>60</sub> will be presented as aggregates (nC<sub>60</sub>). Ubiquitous natural organic matter (NOM), such as humic acid (HA), is likely to interact with the discharged nC<sub>60</sub> and influence the aggregation/dispersion behavior and ecotoxicity of nC<sub>60</sub> (Bhatt and Tripathi, 2011; Kim *et al.*, 2012). Therefore, it is essential to take into account the interactions between NOM and nC<sub>60</sub> when elucidating the behavior of nC<sub>60</sub> in natural water bodies.

Several studies have investigated the interaction between NOM and nC<sub>60</sub> and the effect of NOM on the aggregation/dispersion behavior of nC<sub>60</sub>. Xie *et al.* (2008) observed significant changes in the aggregate

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size and morphology of nC<sub>60</sub> with the addition of NOM. Li *et al.* (2009) revealed that NOM could effectively stabilize nC<sub>60</sub> in the aqueous phase and nC<sub>60</sub> nanoparticles may have been chemically modified under illumination. Mashayekhi *et al.* (2012) attributed the increased stability of nC<sub>60</sub> to the transformation of surface properties through the HA adsorption. The adsorption of HA can increase electrostatic and steric repulsions among nC<sub>60</sub> aggregates, and thus facilitate dispersion and stabilization of nC<sub>60</sub> in water (Chen and Elimelech, 2007; Mashayekhi *et al.*, 2012; Zhang *et al.*, 2013). Moreover, environmental conditions (e.g., water quality parameters) may have profound effects on the interaction between HA and nC<sub>60</sub> (Isaacson and Bouchard, 2010; Qu *et al.*, 2010; Yang *et al.*, 2013), which has not been well examined. Chen and Elimelech (2007) found that HA could increase the C<sub>60</sub> nanoparticle stability in NaCl or MgCl<sub>2</sub> electrolytes, but HA enhanced the aggregation at high concentrations of CaCl<sub>2</sub>. Therefore, water quality parameters, such as ionic strength and pH, are likely to have significant effects on the colloidal stability of C<sub>60</sub> in the presence of HA, which merit further investigations.

This work is aimed to study the capabilities of HA in dispersing and stabilizing C<sub>60</sub> powder in water and in maintaining the colloidal stability of nC<sub>60</sub> suspension (aqu/nC<sub>60</sub>) as affected by variations of pH and ionic strength. The changes of zeta potentials and hydrodynamic sizes of the C<sub>60</sub> powder and aqu/nC<sub>60</sub> under different pH values and the impact of ionic strength on the aggregation kinetics of the aqu/nC<sub>60</sub> in the absence and presence of HA were specifically examined.

## 2 Materials and methods

### 2.1 Preparation and characterization of HA

HA was purchased from Sigma-Aldrich. HA was purified before use and was characterized following the procedures detailed in Lin *et al.* (2012a; 2012b). HA of 500 mg was dissolved in 10 ml 1 mol/L NaOH solution, and adjusted to pH 7.0 using 1 mol/L HCl. The supernatant was obtained by centrifugation at 3000 r/min for 15 min, and then was diluted to 1 L using ultra-pure water and used as the stock HA solution (500 mg/L). NaN<sub>3</sub> (200 mg/L) was

added to prevent HA from microbial interference. The HA solution was scanned with an ultraviolet (UV) spectrophotometer (SHIMADZU, UV-2450, Japan).

### 2.2 Preparation and characterization of aqu/nC<sub>60</sub>

C<sub>60</sub> powder was purchased from Nanjing XFNANO Materials Tech Co., Ltd., China. The elemental contents were measured using an elemental analyzer (Vario ELIII, Germany). Aqueous suspension of C<sub>60</sub> was prepared following a solvent exchange procedure modified from previous works (Deguchi *et al.*, 2001; Chen and Elimelech, 2006; Kim *et al.*, 2010). C<sub>60</sub> powder (120 mg) was dispersed in 60 ml of high-performance liquid chromatography (HPLC)-grade toluene by stirring for several hours, forming a clear dark purple mixture. The mixture was then added into ultra-pure water at a volume ratio of 1:15, resulting in two distinct phases. The resultant mixture was sonicated with a sonifier cell disrupter (KBS-150, Kunshan, China) for more than 4 h, allowing for the evaporation of toluene. The stabilized C<sub>60</sub> suspension (aqu/nC<sub>60</sub>) was obtained by centrifugation at 2000 r/min for 15 min, and then stored at room temperature in the dark. The morphology and aggregate size of the aqu/nC<sub>60</sub> were examined with a transmission electron microscope (TEM; JEM-1230, JEOL, Japan). The hydrodynamic size and zeta potential were determined using a Zetasizer (Nano ZS90, Malvern Instruments, UK) at 25 °C (Tian *et al.*, 2010). The aqu/C<sub>60</sub> suspension was also scanned using the UV spectrophotometer.

### 2.3 Suspension experiment

A suspension experiment was performed to study the effect of HA on the aqueous stabilization of C<sub>60</sub> powder. C<sub>60</sub> powder (10 mg) was added into 20 ml of HA solutions (pH 7.0, 10 mg/L of NaCl) with initial HA concentrations of 0, 5, 10, 20, and 40 mg/L. The mixtures were sonicated (240 W, 40 KHz) for 1 h and were subsequently kept in a thermostat shaker (150 r/min, 25 °C) for 1 d. The zeta potential and hydrodynamic size of the samples were measured right after the shaking process with the Zetasizer at 25 °C. Each concentration was run in triplicate. The absorbance at 800 nm (UV800) was considered to be capable of quantifying the stabilized multi-walled carbon nanotubes (MWCNTs) (Lin *et al.*, 2010; 2012a). Similarly, UV800 of the C<sub>60</sub>

suspension was in a positive correlation with the concentration of suspended  $C_{60}$  determined by a total organic carbon (TOC) analyzer (SHIMADZU, TOC-VCPH, Japan), and the HA solution had no absorbance at 800 nm (Fig. 1). Therefore, the UV800 of the supernatant of the  $C_{60}$ -HA suspension after settling for 0–2 d was used to measure the stability of the  $nC_{60}$  suspensions in the presence of different concentrations of HA.

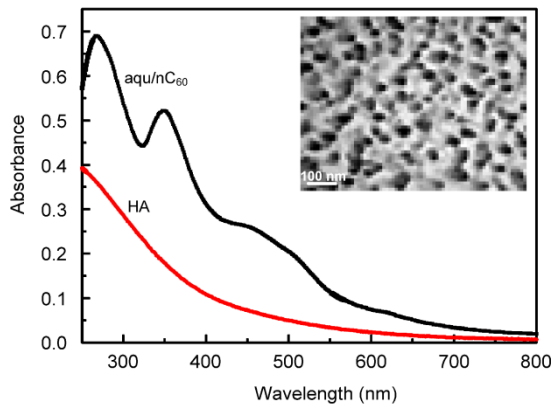


Fig. 1 TEM image of the  $aqu/nC_{60}$  and UV-vis absorbance spectra of the  $aqu/nC_{60}$  (8 mg/L) and HA (10 mg/L)

## 2.4 Effect of pH on stability of $aqu/nC_{60}$ with and without HA

The stock suspension of  $aqu/nC_{60}$  (10 ml) was added into 22-ml glass vials containing 10 ml of ultra-pure water or 20 mg/L HA with 20 mg/L NaCl. The pH values of the suspensions were then adjusted to 3.0–11.0 with several drops of 1 mol/L NaOH or HCl solutions. The mixtures were equilibrated (150 r/min) for 1 d, and then their zeta potentials, hydrodynamic sizes, and final pH values were measured. Each pH value was run in triplicate.

## 2.5 Aggregation kinetics of $aqu/nC_{60}$ with and without HA

Aggregation kinetics of the  $aqu/nC_{60}$  in the presence and absence of HA were investigated under various ionic strengths using a time-resolved dynamic light scattering (DLS) technique. A portion of the stock  $aqu/nC_{60}$  of pH 7.0 with or without 10 mg/L HA was added into a polystyrene measurement cell and the hydrodynamic sizes were recorded by the Zetasizer at an interval of 1 min for 30 min at 25 °C.

Various ionic strengths were obtained by mixing 0.5 ml of NaCl,  $CaCl_2$ , or  $LaCl_3$  solutions of different concentrations into the cells containing  $aqu/nC_{60}$  prior to the hydrodynamic size measurements. At the early stage of aggregation, the initial aggregation rate of the  $aqu/nC_{60}$  can be expressed as

$$\left( \frac{D_h(t)}{dt} \right)_{t \rightarrow 0} \propto k_{11} N_0, \quad (1)$$

where  $D_h(t)$  is the hydrodynamic size (nm) of  $nC_{60}$  at time  $t$ ,  $N_0$  is the initial particle concentration (mg/L), and  $k_{11}$  is the initial aggregation rate constant (Chen and Elimelech, 2006; Chen *et al.*, 2006). The initial rate of increase in  $D_h(t)$  is obtained by determining the initial slope up to the point where the hydrodynamic size reaches  $1.25D_h(0)$ .

The attachment efficiency ( $\alpha$ ) under different ionic strengths was calculated to quantify the aggregation kinetics of the  $aqu/nC_{60}$ :

$$\alpha = \frac{k_{11}}{(k_{11})_{\text{fast}}} = \frac{\frac{1}{N_0} \left( \frac{dD_h(t)}{dt} \right)_{t \rightarrow 0}}{\frac{1}{(N_0)_{\text{fast}}} \left( \frac{dD_h(t)}{dt} \right)_{t \rightarrow 0, \text{fast}}}, \quad (2)$$

where  $(k_{11})_{\text{fast}}$  refers to  $k_{11}$  in the diffusion controlled regime (Mashayekhi *et al.*, 2012).

## 3 Results and discussion

### 3.1 Characteristics of $aqu/nC_{60}$ and HA

Selected properties of the  $C_{60}$  powder and HA are listed in Table 1. The aggregate size of  $aqu/nC_{60}$  as determined using TEM was  $(34.8 \pm 5.9)$  nm (Fig. 1). The transparent yellow  $aqu/nC_{60}$  remained stable for several months during and after the experiments. The concentration of the stock  $aqu/nC_{60}$  was 8.0 mg C/L with the zeta potential of  $-40.8$  mV, hydrodynamic size of 172 nm, and pH value of 7.0. Fig. 1 shows the UV-vis absorbance spectrum of the  $aqu/nC_{60}$ . The  $aqu/nC_{60}$  had absorption peaks at 269 and 350 nm as well as a broad band between 410 and 550 nm, which were identified to be characteristics of  $nC_{60}$  suspension as previously reported (Hyung and Kim, 2009; Hwang and Li, 2010; Navarro *et al.*, 2013).

### 3.2 Effect of HA on aqueous stabilization of C<sub>60</sub>

Fig. 2 shows the changes of zeta potential, hydro-dynamic size, and UV800 of the C<sub>60</sub> powder sonicated in water against a concentration of HA. The zeta potentials of the C<sub>60</sub> powder in the presence of 0–40 mg/L HA were all lower than –50 mV, and the electronegativity initially increased with increasing the HA concentration and then leveled off at about –65 mV (Fig. 2a). The greater electronegativity of the C<sub>60</sub> powder in the presence of HA indicated a greater electrostatic repulsion among the C<sub>60</sub> particles, which was evidenced by the smaller hydrodynamic sizes in the HA solutions (Fig. 2a). The hydrodynamic size of the C<sub>60</sub> powder was (953±145) nm in the absence of HA, which however decreased to (516±31) nm in the presence of 40 mg/L HA, suggesting that HA could disperse the C<sub>60</sub> powder to some degree in water.

The increased electrostatic repulsion between C<sub>60</sub> aggregates accompanied by decreased hydrodynamic size with increasing HA concentrations led to the enhanced aqueous suspension of C<sub>60</sub> in the HA solutions, which was confirmed by the increased UV800 of the C<sub>60</sub> powder in the HA solutions. UV800 of the C<sub>60</sub>-HA suspension was positively correlated with the HA concentration after settling for 0–2 d, which was in accordance with the changes of zeta

potential and hydrodynamic size against the HA concentration (Fig. 2b). However, the UV800 of the C<sub>60</sub>-HA suspensions decreased with increasing settling time. After settling for 2 d, all of the C<sub>60</sub>-HA suspensions became transparent, suggesting the severe agglomeration and precipitation of the C<sub>60</sub> aggregates. The above result implies that after being discharged, the hydrophobic C<sub>60</sub> powder could hardly be dispersed and stabilized in the water environment even in the presence of HA.

### 3.3 Effect of pH on aqueous stability of aqu/nC<sub>60</sub> with and without HA

The stability of aqu/nC<sub>60</sub> in the absence and presence of HA was investigated under various pH values. Dramatic increases in electronegativity of the aqu/nC<sub>60</sub> with and without HA were observed as pH increased from 3 to 6, while the increases leveled off over pH 6 (Fig. 3). This suggests that the neutralization reaction between H<sup>+</sup> and the acidic surfaces of aqu/nC<sub>60</sub> occurred at low pH (Yang *et al.*, 2013), thereby reducing the electronegativity and electrostatic repulsion among the nC<sub>60</sub> aggregates and consequently causing the aggregation and destabilization of the aqu/nC<sub>60</sub> in the absence of HA. The aqu/nC<sub>60</sub> had a lower zeta potential in the presence of 10 mg/L HA, and the differences between the zeta potentials

Table 1 Selected properties of C<sub>60</sub> and HA

Material	Elemental content (%)				Ash (%)	Acidic site (mmol/g)		
	C	H	N	O		Total	–COOH	Phenolic –OH
C <sub>60</sub>	99.70	0.01						
HA	59.90	3.94	1.50	31.50	3.20	7.15	4.25	2.90

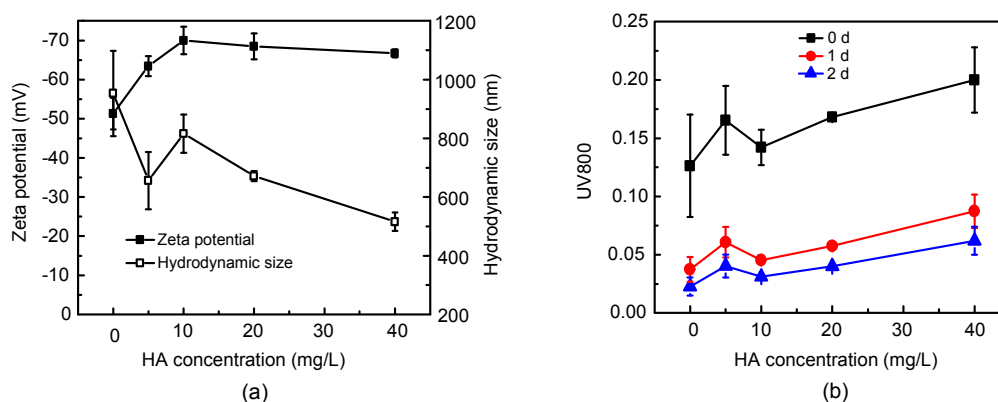
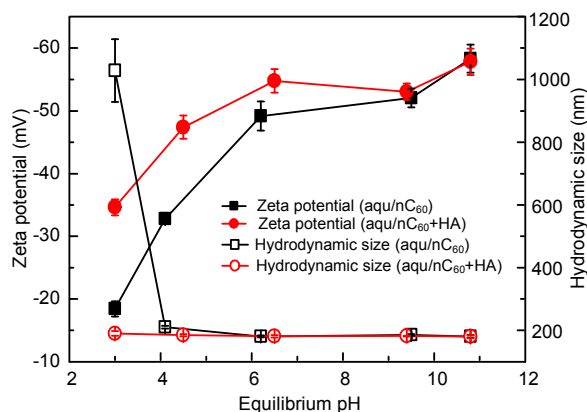


Fig. 2 Variations of zeta potential and hydrodynamic size (a) and UV-vis absorbance at 800 nm (UV800) (b) of C<sub>60</sub> powder sonicated in water after settling for 0–2 d with HA

Data are presented as mean±standard deviation, *n*=3

with and without HA became more significant under acidic conditions ( $\text{pH} < 6$ ). HA could be adsorbed by the  $\text{nC}_{60}$  aggregates (Mashayekhi *et al.*, 2012), and the dissociation of  $-\text{COOH}$  and phenolic  $-\text{OH}$  groups of the surface-bound HA (Table 1) could impart negative charges on the  $\text{nC}_{60}$  aggregates, causing the difference in the zeta potential of the  $\text{aqu/nC}_{60}$  with and without HA.



**Fig. 3** Variations of zeta potentials and hydrodynamic sizes of the  $\text{aqu/nC}_{60}$  with and without HA (10 mg/L)

The  $\text{aqu/nC}_{60}$  retained its hydrodynamic size of  $(186 \pm 10)$  nm at  $\text{pH} > 4$  with and without HA (Fig. 3). The hydrodynamic size of the  $\text{aqu/nC}_{60}$  in the absence of HA sharply increased to  $(1028 \pm 100)$  nm at  $\text{pH} = 3$ , whereas it remained largely unchanged in the presence of HA (Fig. 3). The differences in the hydrodynamic size of the  $\text{aqu/nC}_{60}$  with and without HA at  $\text{pH} = 3$  could be explained by the differences in the zeta potential. At  $\text{pH} = 3$ , the zeta potential of the  $\text{aqu/nC}_{60}$  increased to  $(-18 \pm 1)$  mV in the absence of HA while it remained lower than  $-30$  mV in the presence of HA (Fig. 3). Colloids with absolute zeta potential  $> 30$  mV are considered to have strong electrostatic repulsions and tend to remain dispersed, while with the absolute zeta potential lower than  $30$  mV, they are prone to aggregation and destabilization due to the weak electrostatic repulsions among them (Lin *et al.*, 2009; 2012a). The adsorbed HA could mitigate the neutralization reaction between  $\text{H}^+$  and the acidic surfaces of the  $\text{aqu/nC}_{60}$ , preventing the  $\text{nC}_{60}$  from aggregation, owing to the decreased electrostatic repulsion at low pH values. Moreover, the adsorbed HA could also enhance the aqueous stability of  $\text{aqu/nC}_{60}$  via the increased steric hindrance among the  $\text{nC}_{60}$  aggregates. From the above results, we can

see that the  $\text{aqu/nC}_{60}$  would remain stabilized in the water environment with broad pH values, but would be subject to aggregation and destabilization at extremely low pH values; the coexisting HA is likely to help to stabilize the  $\text{aqu/nC}_{60}$ , especially at low pH values.

### 3.4 Effect of ionic strength on aqueous stability of $\text{aqu/nC}_{60}$ with and without HA

#### 3.4.1 Aggregation kinetics of the $\text{aqu/nC}_{60}$ in the absence of HA

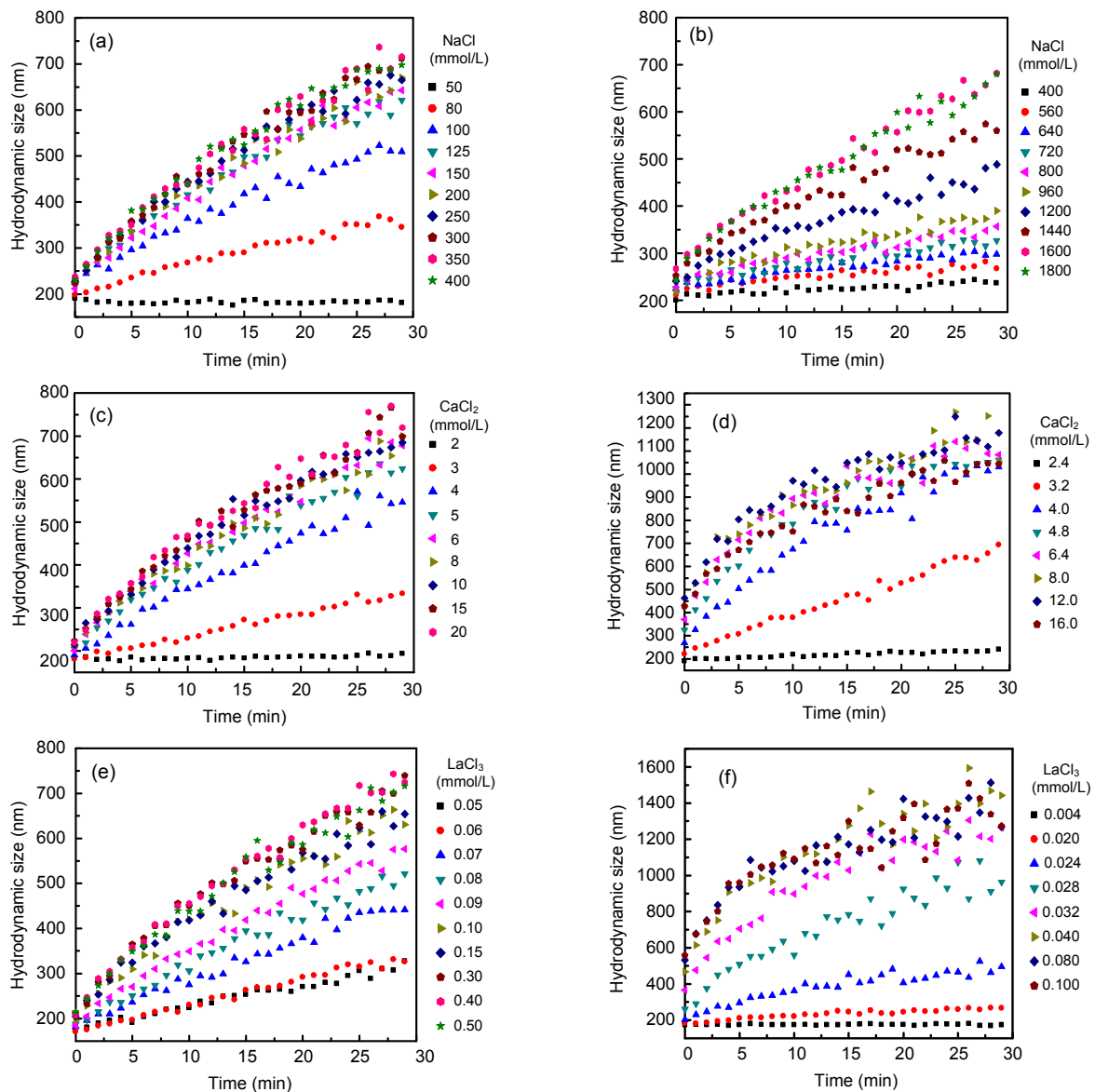
Aggregation of the  $\text{aqu/nC}_{60}$  occurred after the addition of various concentrations of the electrolytes as evidenced by the increase in its hydrodynamic size (Fig. 4). The cations at high concentrations immediately increased the aggregate size after their addition to the  $\text{aqu/nC}_{60}$ . Fig. 4a shows the increasing of the aggregation rate of the  $\text{aqu/nC}_{60}$  by increasing  $\text{Na}^+$  concentration from 50 to 400 mmol/L during 30 min. The hydrodynamic size remained constant when 50 mmol/L  $\text{Na}^+$  was added. But the aggregation rate markedly increased with the concentration of  $\text{Na}^+$  increasing from 50 to 150 mmol/L, and then remained steady with further addition of  $\text{Na}^+$ . The attachment efficiencies ( $\alpha$ ) of the  $\text{aqu/nC}_{60}$  at each  $\text{Na}^+$  concentration were calculated according to Eq. (2) (Fig. 5a). The increase in  $\text{Na}^+$  concentration could screen the surface charge of  $\text{nC}_{60}$ , reduce the electrostatic energy barrier, and subsequently lead to the fast aggregation in the reaction controlled regime where  $\alpha$  linearly increased with the increasing  $\text{Na}^+$  concentration. However, once the electrolyte concentration was beyond the critical coagulation concentration (CCC), the energy barrier was completely eliminated and the diffusion controlled aggregation began. Under the diffusion controlled regime,  $\alpha$  no longer responded to the increasing  $\text{Na}^+$  concentration. Based on the data in Fig. 5a, the CCC, the intersection of the reaction and diffusion controlled regimes, was determined to be 142 mmol/L for  $\text{Na}^+$ .

The DLS measurement was also applied to study the aggregation kinetics of  $\text{aqu/nC}_{60}$  in the presence of  $\text{Ca}^{2+}$  and  $\text{La}^{3+}$ . The increases in the hydrodynamic size with time were observed starting at 3 and 0.07 mmol/L of  $\text{Ca}^{2+}$  (Fig. 4c) and  $\text{La}^{2+}$  (Fig. 4e), respectively, revealing that much lower concentrations of the cations with higher valence were needed to destabilize the  $\text{aqu/nC}_{60}$ . This is because cations

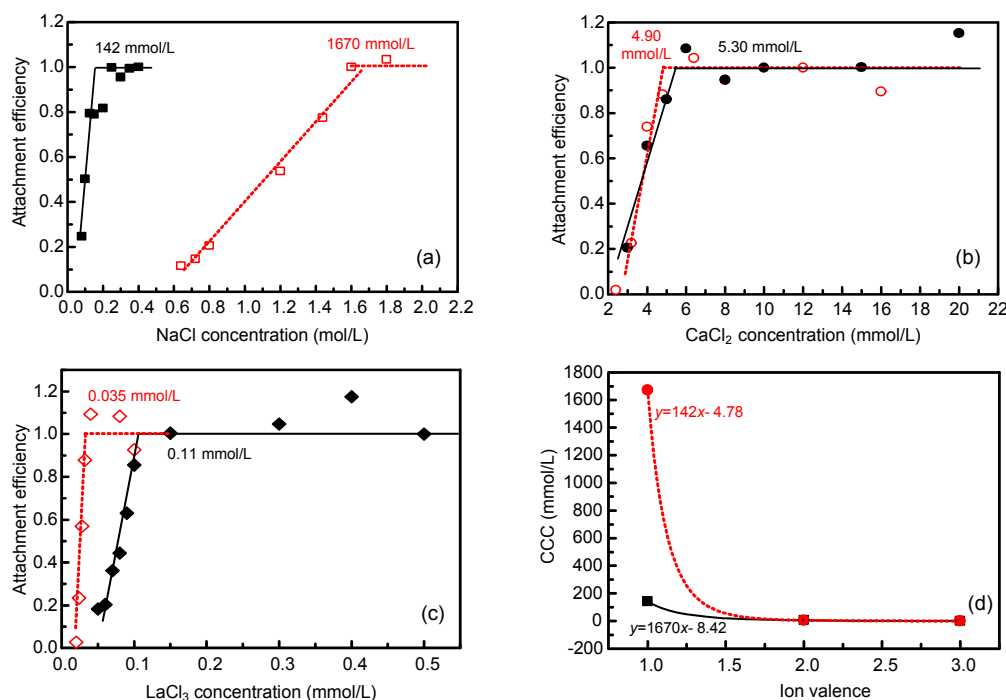
with higher valence have much higher capability of eliminating the energy barrier between the dispersed nanoparticles and thereby promoting the aggregation (Chen *et al.*, 2006). The increase in aggregation rate of the aqu/nC<sub>60</sub> leveled off (i.e.,  $\alpha=1$ ) with the concentrations of Ca<sup>2+</sup> and La<sup>3+</sup> over 5 and 0.1 mmol/L, respectively. Figs. 5b and 5c show variations of  $\alpha$  of the aqu/nC<sub>60</sub> with the concentrations of Ca<sup>2+</sup> and La<sup>3+</sup>, where their CCCs were calculated to be 5.30 and 0.110 mmol/L, respectively. The ratio of CCCs of the three electrolytes NaCl:CaCl<sub>2</sub>:AlCl<sub>3</sub> was 140:5.30:0.110 (i.e.,  $1^{-6}:2^{-6}:3^{-6}$ ) (Fig. 5d), which was

close to the ratio indicated by the Schulze-Hardy rule (i.e.,  $1^{-6}:2^{-6}:3^{-6}$ ) (Li and Huang, 2010).

Our CCC of NaCl is comparably higher than that determined by Chen and Elimelech (2006) for full-erene nanoparticles synthesized using the same technique (120 mmol/L). Their reported CCC of CaCl<sub>2</sub> was 4.8 mmol/L, which was close to our obtained result. It was noteworthy that the CCC values were quite similar, regardless of the 10 times higher suspension concentration which we employed, implying that the initial concentration of aqu/nC<sub>60</sub> may play an insignificant role in its aggregation.



**Fig. 4** Aggregation kinetics of the aqu/nC<sub>60</sub> at different concentrations of NaCl (a, b), CaCl<sub>2</sub> (c, d), and LaCl<sub>3</sub> (e, f) in the absence (a, c, e) and presence (b, d, f) of 10 mg/L HA



**Fig. 5** Attachment efficiencies of the aqu/nC<sub>60</sub> at different concentrations of NaCl (a), CaCl<sub>2</sub> (b), LaCl<sub>3</sub> (c), and the relationship between CCCs and cation valences (d) in the absence (solid lines) and presence (dash lines) of 10 mg/L HA

The CCCs of the electrolytes were marked in the figures

### 3.4.2 Aggregation of aqu/nC<sub>60</sub> in the presence of HA

The effects of HA on the aggregation rate of aqu/nC<sub>60</sub> at different concentrations of NaCl, CaCl<sub>2</sub>, and LaCl<sub>3</sub> are shown in Figs. 4b, 4d, and 4f, respectively. aqu/nC<sub>60</sub> started to aggregate with the hydrodynamic size increasing with time at Na<sup>+</sup> concentrations higher than 600 mmol/L and did not reach its maximum aggregation rate until 1670 mmol/L (CCC) of NaCl (Fig. 5a). Clearly, the presence of HA effectively prevented the aqu/nC<sub>60</sub> from homoaggregation and forming bigger aggregates as affected by NaCl. This was in accordance with the result of a previous study that NOM increased the stability of nC<sub>60</sub> suspension (Duncan *et al.*, 2008). It was supposed that the adsorption of NOM including HA on the nC<sub>60</sub> aggregates could increase electrosteric repulsions and thereby enhance stabilization of the nC<sub>60</sub> suspension (Chen and Elimelech, 2007). Environmental concentrations of Na<sup>+</sup> are generally much lower than 1670 mmol/L, therefore the Na<sup>+</sup> effect on the stability of aqu/nC<sub>60</sub> could be ignored in the presence of 10 mg/L HA.

The aggregation rate of aqu/nC<sub>60</sub> started to increase at 3.2 and 0.02 mmol/L of Ca<sup>2+</sup> (Fig. 4d) and La<sup>3+</sup> (Fig. 4f) and the increase leveled off at 4.80 and 0.032 mmol/L of Ca<sup>2+</sup> (Fig. 5b) and La<sup>3+</sup> (Fig. 5c), respectively. According to Figs. 5b and 5c, the calculated CCCs were 4.90 and 0.035 mmol/L of Ca<sup>2+</sup> and La<sup>3+</sup>, respectively, which were surprisingly lower than their respective CCCs in the absence of HA. The negative effect of HA on the stability of aqu/nC<sub>60</sub> as affected by Ca<sup>2+</sup> was also observed by Chen and Elimelech (2007). The accelerated aggregation in the presence HA was attributed to the bridging of nC<sub>60</sub> by the HA aggregates formed through the intermolecular bridging of HA macromolecules via cation complexation at high concentrations of cations with high valences (Chen and Elimelech, 2007). The ratio of CCCs of the three electrolytes NaCl:CaCl<sub>2</sub>:AlCl<sub>3</sub> in the presence of HA was 1670:4.90:0.035 (i.e., 1<sup>-8.42</sup>:2<sup>-8.42</sup>:3<sup>-8.42</sup>) (Fig. 5d), which was also largely comparable to the precipitation by the Schulze-Hardy rule (i.e., 1<sup>-6</sup>:2<sup>-6</sup>:3<sup>-6</sup>) (Li and Huang, 2010) but was different from the ratio in the absence of HA. This difference was owing to the different effects of the HA

on the colloidal stability of the aqu/nC<sub>60</sub> as affected by the three electrolytes as addressed above.

#### 4 Conclusions

The effects of HA on the aqueous stabilization of C<sub>60</sub> powder and on the colloidal stability of aqu/nC<sub>60</sub> as affected by variations of pH and ionic strength were studied. C<sub>60</sub> powder could be dispersed to some degree but hardly be stably suspended in the presence of HA. Low pH and high ionic strength would affect the colloidal stability of aqu/nC<sub>60</sub>. Big aggregates formed at pH<4, owing to the screening of surface charges of the aqu/nC<sub>60</sub> at such low pH. However, the colloidal stability of aqu/nC<sub>60</sub> in the presence of HA was insensitive to pH 3–11. It was supposed that HA could be adsorbed onto the surfaces of nC<sub>60</sub> and the surface-bound HA increased the surface electronegativity of the nC<sub>60</sub>, and thereby mitigated the aggregation through electrosteric repulsion at low pH values. Cation valence and concentration had a profound effect on the destabilization of the aqu/nC<sub>60</sub>. The CCCs of Na<sup>+</sup>, Ca<sup>2+</sup>, and La<sup>3+</sup> in the presence and absence of HA were exponentially decreased with the increase in cationic valence. The presence of HA could mitigate the impact of Na<sup>+</sup> on the colloidal stability of aqu/nC<sub>60</sub>, but enhanced the destabilization effect of Ca<sup>2+</sup> and La<sup>3+</sup> on the aqu/C<sub>60</sub>.

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## 中文摘要:

**本文题目:** 腐殖酸对富勒烯 C<sub>60</sub> 的悬浮作用

**The role of humic acid in stabilizing fullerene (C<sub>60</sub>) suspensions**

**研究目的:** 腐殖酸 (HA) 对富勒烯 (C<sub>60</sub>) 粉末的悬浮作用以及 pH、离子强度对 HA-C<sub>60</sub> 悬浮性能的影响。

**创新要点:** 研究水质条件对 C<sub>60</sub> 悬浮性能的影响。

**研究方法:** 测定 C<sub>60</sub> 粉末在 HA 溶液中的 zeta 电位, 水力学粒径和悬浮浓度; HA 存在下, C<sub>60</sub> 悬浮体系的 zeta 电位与水力学粒径随 pH 的变化及 C<sub>60</sub> 悬浮体系团聚动力学随离子强度的变化。

**重要结论:** HA 对 C<sub>60</sub> 粉末起到一定的分散作用, 但不能使其长时间稳定悬浮于水中。当 pH<4 时, C<sub>60</sub> 水悬液开始沉淀; 而当 HA 存在时, C<sub>60</sub> 水悬液在 pH 3-11 范围内都保持稳定, 这是由于 HA 吸附于 C<sub>60</sub> 表面, 通过静电排斥和空间位阻作用, 促进 C<sub>60</sub> 分散悬浮。C<sub>60</sub> 水悬液的稳定性随盐离子价位和浓度升高而降低。HA 会抑制 Na<sup>+</sup> 对 C<sub>60</sub> 水悬液的脱稳作用; 但高价离子 Ca<sup>2+</sup> 和 La<sup>3+</sup> 存在时, HA 与 C<sub>60</sub> 之间会发生桥联从而促进 C<sub>60</sub> 水悬液脱稳沉淀。

**关键词组:** 富勒烯; 腐殖酸; 胶体稳定性; 天然有机质; 纳米材料