



# Characterization of surface hydrophobicity of engineered nanoparticles

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## ABSTRACT

The surface chemistry of nanoparticles, including their hydrophobicity, is a key determinant of their fate, transport and toxicity. Engineered NPs often have surface coatings that control the surface chemistry of NPs and may dominate the effects of the nanoparticle core. Suitable characterization methods for surface hydrophobicity at the nano-scale are needed. Three types of methods, surface adsorption, affinity coefficient and contact angle, were investigated in this study with seven carbon and metal based NPs with and without coatings. The adsorption of hydrophobic molecules, Rose Bengal dye and naphthalene, on NPs was used as one measure of hydrophobicity and was compared with the relative affinity of NPs for octanol or water phases, analogous to the determination of octanol–water partition coefficients for organic molecules. The sessile drop method was adapted for measuring contact angle of a thin film of NPs. Results for these three methods were qualitatively in agreement. Aqueous-nC<sub>60</sub> and tetrahydrofuran-nC<sub>60</sub> were observed to be more hydrophobic than nano-Ag coated with polyvinylpyrrolidone or gum arabic, followed by nano-Ag or nano-Au with citrate-functionalized surfaces. Fullerol was shown to be the least hydrophobic of seven NPs tested. The advantages and limitations of each method were also discussed.

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## 1. Introduction

As a consequence of the extensive current and foreseen use of nanotechnology in consumer products, industrial applications and health care products, engineered nanoparticles (NPs) are likely to find their way into the natural environment [1]. This potential for environmental exposure suggests the need to evaluate risks to human health and the environment that may accompany nanoparticle releases. Thorough characterization of physical and chemical properties of NPs and methods for performing such characterization are fundamental in the investigation of potential exposure, hazard and hence risk of nanomaterial in the environment [2]. Hydrophobicity, as one of the key properties of NPs, plays a significant role in the fate, transport and bioavailability of NPs [3,4]. Hydrophobic nanomaterials like carbon-base NPs can strongly partition into lipid-rich environments such as the sea-surface microlayer [5] or cell membrane [6] and previous studies have shown that hydrophobicity of NPs can influence the uptake and toxicity of NPs [7,8]. Thus, characterization of NP hydrophobicity facilitates the evaluation of both the potential exposure and hazards presented by NPs.

However there are multiple challenges in the characterization of hydrophobicity for NPs. In many of the risk scenarios of interest, NPs are present in an aqueous medium. Their small size excludes the possibility of conventional in situ measurements of contact angle in an aqueous environment. At the other end of the scale, the theoretical basis for applying methods developed for molecular species, which assume equilibrium, are not necessarily appropriate for nano-scale matter. Also, the design and manufacture of engineered NPs often involves the use of surface coatings for their intended applications [9,10], that are specifically design to render them more or less compatible with carrier fluids such as water or oil [11,12]. A heterogeneous surface that combines with the properties of the nanoparticle core complicates interpretation of interfacial phenomena.

Current characterization methods for hydrophobicity can be summarized as falling into three categories: measurements of surface tension, measurements of the surface adsorption of hydrophobic or hydrophilic probe molecules, and the relative affinity (partitioning) of a compound for reference phases. Measurements of contact angle are frequently used to obtain estimates of surface tension [13], employing the sessile drop Young–Laplace method [14]. Applied under ideal conditions, the tested substance is a macroscopic, flat solid surface, thus requiring modification for NPs. Several methods [15–17] have been proposed for the in situ measurement of the contact angle of NPs, however, most of them are indirect measurement by fitting thermodynamic or optical model to the experimental data and calculating contact angle.

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**Table 1**  
Characteristics and source of NPs.

NPs	Size <sup>a</sup> (nm)	EPM (10 <sup>-8</sup> m <sup>2</sup> /Vs)	Concentration <sup>b</sup> (mg/L)	Source
Aqu-nC <sub>60</sub>	87 ± 11	-0.38 ± 0.02	22	Lab prepared <sup>c</sup>
THF-nC <sub>60</sub>	55 ± 12	-0.71 ± 0.03	14	Lab prepared
Fullerol	98 ± 7	-1.57 ± 0.03	80	Lab prepared
Au-CIT	31 ± 6	-2.60 ± 0.05	60	CEINT
Ag-CIT	52 ± 10	-3.12 ± 0.03	100	CEINT
Ag-PVP	48 ± 12	-1.21 ± 0.05	250	CEINT
Ag-GA	16 ± 7	-0.41 ± 0.03	250	CEINT

<sup>a</sup> The second order average hydrodynamic diameter given by DLS ± standard deviation.

<sup>b</sup> Concentration of NPs in stock solutions.

<sup>c</sup> Preparation methods refer to later discussion.

For the partitioning method, the distribution of tested substance between two immiscible liquid phases, typically water and one organic solvent such as octanol, is measured. Octanol–water partition coefficients for various organic compounds are widely reported in the literature [18]. The surface adsorption method evaluates the relative affinity of tested substances to a standard hydrophobic material. This latter method is potentially the most suitable for nano-scale measurements as it can be easily applied to materials of all sizes, and it takes advantage of an increased sensitivity associated with the high specific surface area of the nanomaterial to be tested.

In this study we compare methods for quantifying surface hydrophobicity of several engineered NPs with the objective of understanding their applicability for nanomaterial characterization.

## 2. Experimental

Seven different carbon- and metal-based engineered NPs, with and without surface coatings, were characterized by three methods. Contact angle measurements were performed on a thin-film of NPs. Large contact angles corresponded to more hydrophobic surfaces. Octanol–water affinity coefficients ( $KA_{OW}$ ) of NPs were measured with the expectation that more hydrophobic materials would preferentially accumulate in the octanol phase. The adsorption of a hydrophobic organic dye and of naphthalene was evaluated with the expectation that such hydrophobic “probe” molecules would preferentially sorb to nanoparticles with more hydrophobic surfaces. The results obtained here provide a quantitative insight into the surface hydrophobicity of coated or uncoated engineered NPs and a reference for establishing a characterization strategy for NPs.

### 2.1. Materials

Fullerene C<sub>60</sub> (99.9%) and fullerol C<sub>60</sub>(OH)<sub>24</sub> were purchased from MER Corp. (Tucson, AZ, USA). Rose Bengal, Nile Blue and naphthalene were obtained from Alfa Aesar (Ward Hill, MA, USA). Octanol was purchased from J.T. Baker (Phillipsburg, NJ, USA). Ultrapure water used to prepare samples were prepared by Barnstead Nanopure Diamond™ system with resistivity greater than 18 MΩ cm and dissolved organic carbon concentration <3 μg/L.

### 2.2. Characteristics and preparation of NPs

Seven NPs were characterized in this work: aqueous nC<sub>60</sub> (aqu-nC<sub>60</sub>), tetrahydrofuran-nC<sub>60</sub> (THF-nC<sub>60</sub>), fullerol, nano-gold coated with citrate (Au-CIT), nano-silver coated with PVP (Ag-PVP), citrate (Ag-CIT) and gum arabic (Ag-GA). These NPs were either prepared in our lab or obtained from sample store of Center for the Environmental Implications of NanoTechnology (CEINT, Durham, NC, USA). The main characteristics of these NPs are presented in Table 1. Particle size was measured using dynamic light scattering with

ALV CGS-3 system (ALV-GMBH, Langen, Germany). Electrophoretic mobility (EPM) measurements were performed using a Zeta Sizer Nano ZS (Malvern, Bedford, MA).

The NPs used in this investigation were dispersed in ultrapure water prior to the hydrophobicity experiments. Aqu-nC<sub>60</sub> and THF-nC<sub>60</sub> were prepared in ultrapure water by extended stirring [19] and solvent exchange techniques, respectively [19]. The fullerol suspension was obtained by adding 80 mg/L of fullerol powder into ultrapure water and then stirring the suspension by magnetic stirrer at 500 rpm for 2 h.

### 2.3. Organic dye adsorption experiment

The adsorption experiments of the hydrophobic dye Rose Bengal (RB) were performed as described previously [20], because RB, a xanthene dye, shows an increased adsorption to particle surface with increasing hydrophobicity. This method has been used in pharmaceutical studies to determine the surface hydrophobicity of nanoparticle drug delivery vehicles [21–23]. Briefly, 20 mg/L of RB was added to each NPs suspension with a range of increasing concentration (10 mM to 1 M). Controls were prepared by adding RB to ultrapure water to account for the adsorption of RB to vials and centrifuge tubes. All the samples were repeated in triplicate. After mixing and incubation in 0.1 M phosphate buffer (pH = 7.4) for 3 h, RB partitioned between NP surface and water. NPs were then separated from the supernatant by ultra-centrifugation at 185,000 g. The concentration of free RB in the supernatant was determined by UV–Vis spectroscopy at  $\lambda = 542.7$  nm. The partitioning quotient (PQ) was then calculated as the following equation (Eq. (1)).

$$PQ = \frac{\text{Mass of RB adsorbed on particle surface}}{\text{Mass of RB in water}} \quad (1)$$

Total surface area (SA) of NPs was calculated by assuming that the NPs suspensions were mono-disperse, with diameter equal to the hydrodynamic diameter measured using DLS. Plotting of PQ against total SA of NPs resulted in straight lines. The slopes of these lines were calculated by linear regression analysis, and are considered as an indicator of the surface hydrophobicity of NPs.

### 2.4. Naphthalene adsorption experiment

For the naphthalene adsorption experiments, 10 mL of each NPs suspension in 0.1 M phosphate buffer (pH = 7.4) was added to a 40 mL sample vial and capped with Mininert™ caps (Sigma–Aldrich, St. Louis, MO). For each sample, a control vial was set up following the same procedure, while using 10 mL ultrapure water instead of the NP suspension, to account for the possible adsorption of naphthalene to the glass and caps. The head space in the vials was approximately 30 mL. Naphthalene-in-acetone stock solutions were then injected with a microsyringe so that the initial naphthalene concentration in aqueous phase was within the range of 0.05 to 1.0 mg/L. The volume fraction of acetone in aqueous

phase in each vial was kept less than 0.002 to avoid possible cosolvent effects [24]. The vials were rotated end-over-end at 20 rpm in the dark at room temperature. After 3 days, the concentration of naphthalene in the head space was analyzed by gas chromatography (GC) using the Shimadzu GC-2010 (Kyoto, Japan) coupled with flame ionization detector (FID). The concentrations of naphthalene in aqueous phase were then calculated based on Henry's Law (with Henry's Law constant for naphthalene at 25 °C = 0.0197 [25]) and the concentrations of naphthalene in gaseous phase. All the samples were repeated in triplicate.

### 2.5. $KA_{OW}$ measurement

The shake-flask method was used to measure  $KA_{OW}$  analogous to  $K_{OW}$  measurements performed for organic compounds. We adopt the notion of  $KA_{OW}$  to underscore the fact that the thermodynamic conditions for equilibrium distribution of the nanomaterial are not likely to be met due to the particulate nature of nanomaterials that imply path-dependency resulting from processes such as mass transport, aggregation and accumulation at phase interfaces. Octanol and water were premixed and equilibrated for 24 h before use. 20 mL of NPs suspension and 20 mL of octanol were added to separatory funnels and shaken at 50 rpm on an orbital shaker for 24 h at room temperature. The mixture was allowed to stand for 3 h, followed by the collection of an aliquot of the aqueous phase. The concentration of NPs in the aqueous phase was measured and used, together with the initial concentration of NPs in the stock solution, to calculate  $KA_{OW}$ . The concentration of fullerene NPs was quantified by liquid–liquid extraction coupled with HPLC–UV/vis spectroscopy [26], and the concentrations of Au and Ag NPs were measured by ICP-OES.

### 2.6. Contact angle measurement

A thin film of NPs was prepared by filtering the NP suspensions through 0.025  $\mu\text{m}$  Pore Size Millipore MF-Millipore Mixed Cellulose Ester membrane (Millipore, Billerica, MA). The membrane with its associated thin film of NPs was freeze dried overnight and then placed on the bottom of a glass petri dish. The petri dish was filled with octanol, and a drop of water was added to the octanol phase. The water drop settled on the NPs film, and the contact angle formed between water, octanol and the film (Fig. 1) was measured by KRÜSS Easydrop FM 40 (KRÜSS GmbH, Hamburg, Germany). All measurements were done in triplicate and angles were measured immediately after contact of the water drops with the NPs film.

## 3. Results and discussion

### 3.1. Organic dye adsorption on NPs in aqueous suspension

Out of seven different NPs tested, RB adsorbed to five (Fig. 2A): Ag-PVP, Ag-GA, Au-CIT, aqu-nC<sub>60</sub>, and THF-nC<sub>60</sub>. However, there was no observable adsorption of RB on Ag-CIT or fullerol. Larger slopes in Fig. 2A indicate more adsorption of RB per unit area of the NP surface, which implies that the NP surface was more hydrophobic. Results in Fig. 2A showed that by this measure, aqu-nC<sub>60</sub> was the most hydrophobic, having the highest slope, followed by THF-nC<sub>60</sub>, Ag-PVP, Ag-GA and Au-CIT. Pristine fullerene is highly hydrophobic, as evidenced by its very low solubility in water (7.96 ng/L)[27]. The extended mixing when preparing aqu-nC<sub>60</sub> leads to partial hydroxylation of fullerene surface [28], hence making it adequately hydrophilic to be dispersed as a stable suspension in water, yet hydrophobic enough that they easily aggregate. The comparatively lower hydrophobicity of the THF-nC<sub>60</sub> may be due to the retention of residual THF on the surface of fullerene, which may form hydrogen bond with water to make THF-nC<sub>60</sub> more

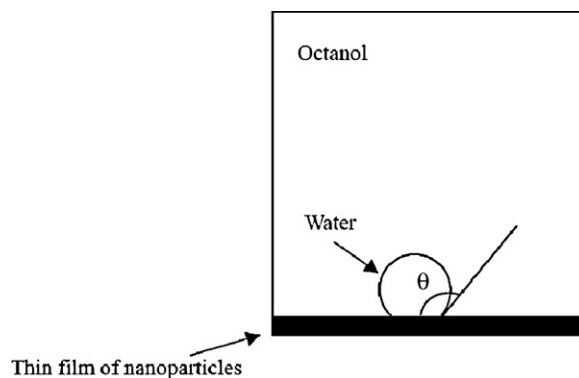


Fig. 1. Contact angle measurement on a thin film of nanoparticles.

hydrophilic than aqu-nC<sub>60</sub> [19]. The coatings of citrate, PVP or GA were meant to stabilize nano-Ag by steric shielding, but our results showed that coatings also changed the surface chemistry of nano-Ag. Ag-CIT was more hydrophilic compared to nano-Ag with PVP or GA as RB hardly adsorbed onto the Ag-CIT surface. PVP and GA made nano-Ag more hydrophobic as a result of the amphiphilic properties of PVP and GA.

The limitation of RB adsorption was that it was not applicable to particle surfaces that were more hydrophilic than carboxylated or hydroxylated polystyrene particles [29] as demonstrated by the failure of RB to adsorb on such surfaces. Thus, as shown in our study, Ag-CIT and fullerol were quite more hydrophilic, consistent with the presence of carboxyl groups in the citrate and the hydroxyl groups on the fullerol. The relative hydrophobicity of fullerol and Ag-CIT can be interpreted from the adsorption of a hydrophilic dye, Nile Blue (NB). Following the same procedure as RB adsorption experiment with NB, the results were shown in Fig. 2B, and the larger slopes in this figure indicate less hydrophobic particle. By this measure, fullerol was much more hydrophilic than either the Ag-CIT or Au-CIT. Compared with aqu-nC<sub>60</sub> and THF-nC<sub>60</sub>, the 24 hydroxyl groups in fullerol made it more hydrophilic and hence an enhanced solubility in water. Interestingly, little difference in hydrophobicity between Ag-CIT and Au-CIT was observed despite the differences in core material. These results demonstrate that the surface hydrophobicity of coated NPs largely depended on the properties of coatings, rather than the properties of the core materials.

Another limitation of using organic dyes adsorption to characterize surface hydrophobicity was the interference of electrostatic interaction. RB was negatively charged under the experimental condition, while NB was positively charged. According to the EPM measurements shown in Table 1, all the NPs investigated in this study were negatively charged. Thus the repulsive or attractive forces between RB or NB and NPs might reduce or enhance the adsorption of dyes on NPs. Although some studies such as Gessner et al. [30] reported that similar amount of RB adsorbed on particles of same material and significantly different surface charge which suggested that surface hydrophobicity might have a larger role in the adsorption, the importance of electrostatic interaction cannot be underestimated. Therefore a neutral hydrophobic molecule such as naphthalene might be a better probe than charged organic dyes.

### 3.2. Naphthalene adsorption on NPs in aqueous suspension

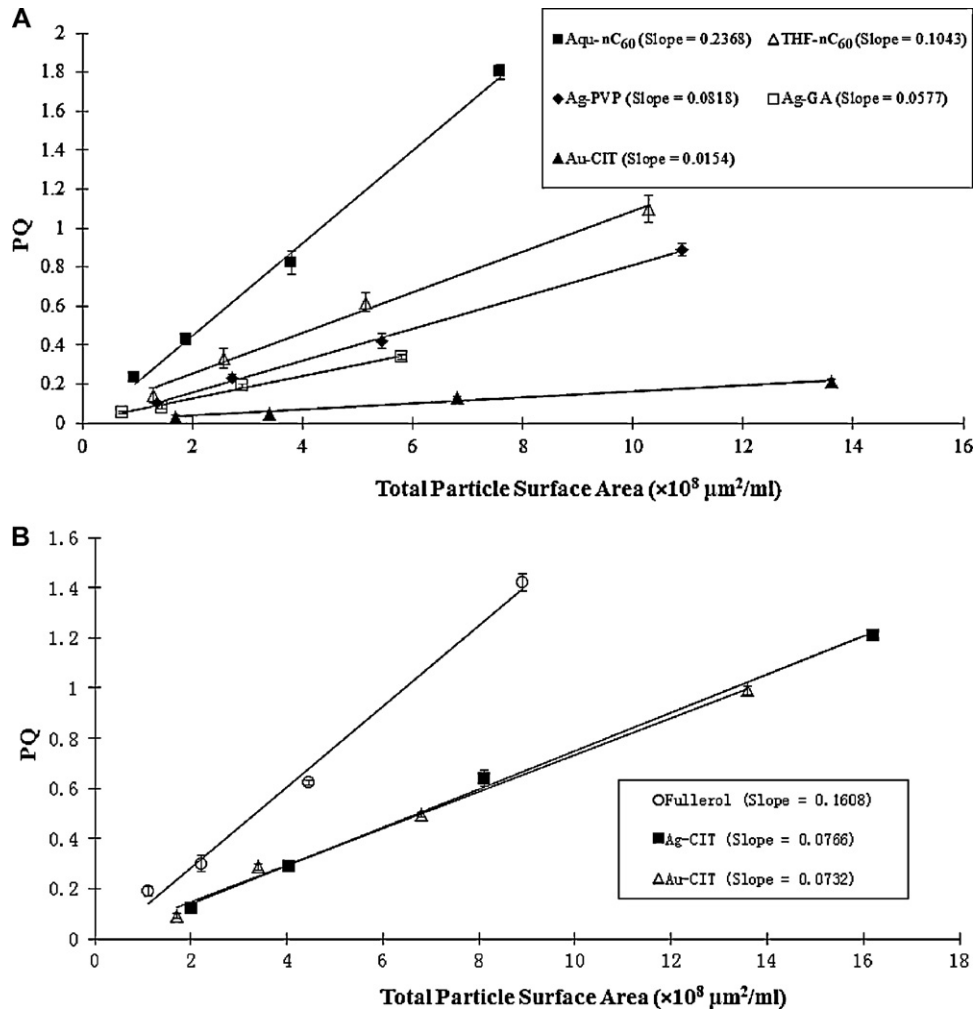
Experimental results for the adsorption of naphthalene on different NPs are summarized in Table 2 and Fig. 3. The adsorption data were fitted to the Freundlich isotherm (Eq. (2)).

$$q = K_F C_W^{1/n} \quad (2)$$

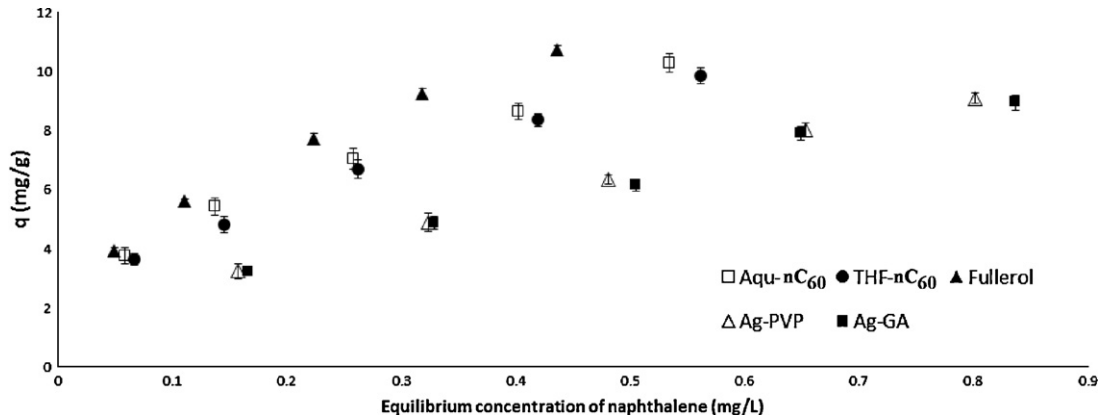
**Table 2**  
Freundlich isotherm parameters for adsorption of naphthalene to NPs.

NP	$K_F$ ( $L^{1-1/n} mg^{1-1/n}/g$ )	$N$	$R^2$
Aqu-nC <sub>60</sub>	13.16 ± 0.24	2.24 ± 0.10	0.997
THF-nC <sub>60</sub>	12.64 ± 0.25	2.10 ± 0.07	0.993
Fullerol	15.56 ± 0.25	2.16 ± 0.01	0.999
Ag-PVP	10.33 ± 0.12	1.56 ± 0.09	0.996
Ag-GA	9.99 ± 0.28	1.55 ± 0.02	0.993

In the Freundlich equation,  $q$  (mg/g) is the mass of naphthalene per unit mass of NPs,  $K_F$  ( $L^{1-1/n} mg^{1-1/n}/g$ ) is the Freundlich constant,  $C_W$  (mg/L) is the equilibrium concentration of naphthalene in aqueous phase and  $1/n$  is the Freundlich exponent.  $R^2$  results in Table 2 (>0.99) suggested that the Freundlich isotherm was a reasonable choice for the adsorption of naphthalene on NPs. No observable adsorption on Ag-CIT and Au-CIT occurred during the experiments which was consistent with the hydrophilic nature of



**Fig. 2.** (A) Relative hydrophobicity as measured by adsorption of Rose Bengal on NPs surface; (B) relative hydrophilicity as measured by adsorption of Nile Blue on NPs surface.



**Fig. 3.** Adsorption of naphthalene on NPs.

**Table 3**  
K<sub>OW</sub> of NPs.

NP	Aqu-nC <sub>60</sub>	THF-nC <sub>60</sub>	Fullerol	Au-CIT
K <sub>OW</sub> (Mean ± 95% C.L.)	3.08 ± 0.18	2.54 ± 0.27	0.12 ± 0.03	0.38 ± 0.07
NP	Ag-CIT	Ag-PVP	Ag-GA	
K <sub>OW</sub> (Mean ± 95% C.L.)	0.03 ± 0.009	2.26 ± 0.17	2.14 ± 0.34	

**Table 4**  
Contact angle on thin film of NPs.

NP	Aqu-nC <sub>60</sub>	THF-nC <sub>60</sub>	Fullerol	Au-CIT
Contact angle/°	82.6 ± 3.8	81.5 ± 3.4	35.7 ± 2.1	41.2 ± 2.6
NP	Ag-CIT	Ag-PVP	Ag-GA	
Contact angle/°	40.4 ± 1.8	78.7 ± 2.9	78.9 ± 3.2	

these two NPs as determined by the previous measures. Comparing with the results of organic dye adsorption experiments, an obvious difference was that more naphthalene adsorbed to fullerol than aqu-nC<sub>60</sub>, which contradicts the common expectation that fullerol is more hydrophilic than aqu-nC<sub>60</sub>. Lin and Xing [31] and Chen et al. [32] proposed a possible explanation to this observation; the adsorption of adsorbates with aromatic rings on carbon-based NPs such as fullerene and carbon nanotubes (CNT) is not solely controlled by hydrophobic interaction, but also by  $\pi$ - $\pi$  interaction. Fullerene and naphthalene are both  $\pi$ -electron rich molecules. The hydroxyl groups of fullerol, acting as electron-donating substituent on fullerene surface, can strengthen the  $\pi$ - $\pi$  interaction hence enhancing the adsorption of naphthalene on fullerol to a larger extent than on fullerene. Except for fullerol, the results agreed well with the organic dye adsorption experiments, in that aqu-nC<sub>60</sub> was the most hydrophobic with more naphthalene adsorption followed by THF-nC<sub>60</sub>, Ag-PVP and Ag-GA.

We note that when characterizing surface hydrophobicity by adsorption, special attention needs to be paid to ruling out other mechanisms which might be involved in the adsorption process, such as electrostatic attraction and other chemical bonding like  $\pi$ - $\pi$  interaction in this case.

### 3.3. K<sub>OW</sub> measurement of NPs

K<sub>OW</sub> values greater than 1 indicate a hydrophobic material, while values less than 1 indicate a preference for the aqueous phase (Table 3). NPs determined to be more hydrophobic in the organic dye adsorption experiment yielded larger K<sub>OW</sub> values, with exception of Ag-CIT which had the smallest K<sub>OW</sub> value of the seven NPs tested, but was not indicated to be the most hydrophilic based on NB adsorption. K<sub>OW</sub> of NPs with PVP or GA coatings were close to 1, suggesting amphiphilic behavior that might have contributed to the emulsion zone between water and octanol in the experiments, with the coatings acting as surfactants. Citrate, PVP and GA were all water-soluble. However, K<sub>OW</sub> of both Ag-PVP and Ag-GA were larger than 1, while Ag-CIT had a K<sub>OW</sub> of less than 1. Others have reported a K<sub>OW</sub> of pristine fullerene to be 10<sup>6.67</sup> [27], which is several orders of magnitude larger than the value of K<sub>OW</sub> we report here and likely highlights the important role of kinetics as well as the effect of sonication on the surface property of fullerene when preparing aqu-nC<sub>60</sub> suspension. The K<sub>OW</sub> of THF-nC<sub>60</sub> was 2.54, falling between K<sub>OW</sub> of aqu-nC<sub>60</sub> reported here and the K<sub>OW</sub> of 1.66 reported for THF [33]. While the process determining K<sub>OW</sub> and K<sub>OW</sub> likely differs, the lower K<sub>OW</sub> value for THF is consistent with the hypothesis that small residual amounts of THF may have explained the reduced hydrophobicity of the THF-nC<sub>60</sub> compared to that of aqu-nC<sub>60</sub>.

Indeed, concerns as to whether or not K<sub>OW</sub> is a suitable notion for NPs [34] reflect a violation in key assumptions. A fundamental assumption of the K<sub>OW</sub> measurement [35] is that tested substances diffuse freely between the phases, and this assumption is likely compromised in the case of NPs. Our results show that despite these limitations, the trends in K<sub>OW</sub> are largely consistent with other measures of NP hydrophobicity.

### 3.4. Contact angle measurement on thin film of NPs

Contact angle measurement results are shown in Table 4. Theoretically, a contact angle greater than 90° suggests that the tested surface is hydrophobic. Surprisingly, all the NPs yielded contact angles of less than 90°, though contact angles of aqu-nC<sub>60</sub>, THF-nC<sub>60</sub>, Ag-PVP and Ag-GA were close to 90°. These results imply the amphiphilic surface properties that are consistent with the previously discussed results. The order of NPs in terms of hydrophobicity given by contact angle was similar to results from other hydrophobicity experiments. Aqu-nC<sub>60</sub> and THF-nC<sub>60</sub> were the most hydrophobic, followed by Ag NPs and Au NPs. Fullerol was the most hydrophilic, as demonstrated by the smallest contact angle.

There were no statistical differences between contact angles obtained for aqu-nC<sub>60</sub> and THF-nC<sub>60</sub>, or Ag-PVP and Ag-GA. The contact angle is an average measure of the surface hydrophobicity and is useful in generally comparing hydrophobicity of different NPs. However, it cannot give any detail about the heterogeneity in hydrophobicity on the surface due to the use of coatings.

## 4. Conclusion

Characterization of key physico-chemical properties of NPs, especially hydrophobicity, is critical to the interpretation, and ultimately, the prediction of nanoparticle behavior in physiological and environmental systems. The methods explored in this work provided a largely coherent description of the relative surface hydrophobicity for the NPs tested. More hydrophilic NPs such as Ag-CIT, Au-CIT and fullerol cannot adsorb dyes, naphthalene or either, indicating that the surface adsorption method is only applicable in a comparative sense for NPs exhibiting some degree of hydrophobicity. Other mechanisms, rather than hydrophobic interaction, responsible for the adsorption such as chemical bonding may interfere the determination of hydrophobicity. Overall, each of the methods evaluated in this study has their advantages and shortcomings. However, based on the consistency with other methods and the more solid grounds for interpretation of the results, we conclude that the adsorption probe method offers some advantages over the other two methods.

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