Electrostatic Titrations Reveal Surface Compositions of Mixed, On-Nanoparticle Monolayers Comprising Positively and Negatively Charged Ligands

Pramod P. Pillai,†‡§⊥ Bartłomiej Kowalczyk,†‡§⊥ Wojciech J. Pudlo,‡§∥ and Bartosz A. Grzybowski†‡§∥

1Department of Chemistry and Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States
2Department of Chemistry, Indian Institute of Science Education and Research (IISER) Pune, Dr. Homi Bhabha Road, Pashan, Pune 411008, India
3M Purification Inc., 400 Research Parkway, Meriden, Connecticut 06450, United States
4Department of Chemical Engineering, Silesian University of Technology, M. Strzody 7, 44-100 Gliwice, Poland
5Center for Soft and Living Matter of Korea’s Institute for Basic Science and 6Department of Chemistry, Ulsan National Institute of Science and Technology 50, UNIST-gil, Eonyang-eup, Ulju-gun, Ulsan, South Korea

ABSTRACT: A general-purpose procedure based on electrostatic titrations was developed to determine the compositions of mixed self-assembled monolayers (m-SAMs) of oppositely charged ligands on metal nanoparticles (NPs). In this procedure, nanoparticles of unknown m-SAM compositions and charges are titrated with the positively charged NP “standards”. These compositions and the differences in the free energies of adsorption of the [+] and [−] are then determined from the points of precipitation at which the overall charge on all NPs is neutralized. The results of the titrations agree well with traditional core-etching/NMR studies. However, the titration-based approach is nondestructive and requires significantly less material than NMR.

1. INTRODUCTION

Many key functions and properties of colloids and nanoparticles, including their stability, aggregation behavior, self-assembly, and electronic or ionic transport, are controlled by surface charge. The polarity and magnitude of this charge depend on the specific nature of ligands protecting the particles. In the simplest class of systems, nanoparticles are stabilized by SAMs comprising identical ligands (e.g., thiolates) terminated in charged groups (e.g., amines, ammonium salts, carboxylates, phosphates, sulfonates, and phenolates). For these so-called “nanoions”, the net magnitude of charge can be varied only by adjusting NP size. More “advanced” zwitterionic (ZI) ligands bearing two charged groups of opposite polarities endow the NPs with some new properties and functions including improved biocompatibility, antifouling, or enhanced cellular uptake. However, for a given NP size, the surface charge still cannot be varied at will, as it is predetermined by the 1:1 positive-to-negative stoichiometry of each ZI ligand. Moreover, in ZI ligands, charged groups are typically positioned linearly along the alkyl chain of the ligand and so only the outer functional groups can be accessible to the environment, while the inner ones remain buried inside the SAM. These limitations can be overcome by functionalizing the NPs with binary mixtures of positively and negatively charged ligands (i.e., mixed self-assembled monolayers, m-SAMs of oppositely charged ligands). In this approach, the [+] and [−] ligands can be placed onto the NPs in unrestricted proportions and can both be equally exposed (if the ligands are of similar length) thus contributing the particles’ overall properties. Such mixed-charge (MC) NPs have several unusual and potentially practical applications; in particular, we have recently shown that they are stable both at low and high pH and their cellular uptake and cytotoxicity can be regulated by changing the m-SAM composition. Precise control and reproducibility of surface compositions/charges is therefore one of the key requirements for the further development of MC NPs’ biological applications (and others we will describe in upcoming papers).

The difficulty of preparing MC NPs of desired surface compositions stems from the fact that the ratio of [+] to [−] on the NPs is, in general, not equal to this ratio in solution. In the present paper, we show how the two ratios can be related to one another using electrostatic nanoparticle titrations in which MC NPs of unknown surface composition are titrated with [+] charged NPs “standards”. The crux of this approach is that mixtures of oppositely charged NPs precipitate exactly at...
the point of overall NP electroneutrality,\textsuperscript{13,21–23} when the sum of charges on all NP is zero (Scheme 1). We have previously validated this approach for NPs covered with one-component SAMs; however, the applicability of this method to MC particles is not straightforward since the MC particles based on m-SAMs have fundamentally different solubility and stability properties.\textsuperscript{30} Consequently, we compare and contrast the results of electrostatic titrations with independent measurements of on-particle mSAM compositions from NMR studies. While the two approaches give coinciding results, the NMR experiments require large amounts of NPs and destruction of the NP metal cores before taking the spectra. Moreover, the titration method allows us to quantify subtle differences in the free energies of adsorption of the [+] and [−] ligands from solution onto the NPs.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Au Nanoparticles. Dodecylamine (DDA)-stabilized Au nanoparticles were prepared according to a modified literature procedure\textsuperscript{37} (starting from HAuCl\textsubscript{4}·3H\textsubscript{2}O instead of AuCl\textsubscript{3}) and had average metal core diameters 5.2 ± 0.5 nm, as estimated by TEM imaging of ∼200 NPs. These NPs were functionalized with a mixture of N,N,N-trimethyl(11-mercaptoundecyl)ammonium chloride (TMA) and either 11-mercaptoundecanoic acid (MUA) or 16-mercaptohexadecanoic acid (MHA) or 8-mercaptooctanoic acid (MOA) via a ligand-exchange reaction. All ultrapure-grade thiols were obtained from ProChimia Surfaces, Poland (www.prochimia.com) and used as received. Dodecyl amine (DDA) used to stabilize the NPs prior to ligand-exchange reaction was purchased from Aldrich. All other reagents were used as received.

2.2. Ligand-Exchange Reaction. In a typical procedure, a toluene solution of DDA-capped Au NPs (20 mL, 150 μmol) was quenched with 50 mL of methanol to give a black precipitate. The precipitate was washed with methanol (50 mL) and dissolved in toluene (20 mL), to which a freshly prepared solution of MUA and TMA in 10 mL of CH\textsubscript{2}Cl\textsubscript{2} was added. The molar ratios of thiols MUA:TMA (α\textsubscript{soln}) used were 1, 1.5, 2, 3, 4, 5, 6, 9, and 20. The thiols were used in large excess, and their total amount was kept constant at 150 μmol in all experiments. The solutions were kept for ∼15 h to ensure complete ligand exchange and equilibration.\textsuperscript{38} The precipitate of thiol-coated MC NPs was allowed to settle down, the mother-liqueur was decanted, and the solid was washed with CH\textsubscript{2}Cl\textsubscript{2} (3 × 30 mL) and acetone (1 × 30 mL). Finally, all NP precipitates were dried and dissolved in 10 mL of water to give ∼15 mM stock solutions of NPs that could be stored for at least a year without deterioration. The pHs of the solutions were adjusted to ∼11 and ∼3 with 0.2 M NMe\textsubscript{4}OH and 0.2 M HCl, respectively.

2.3. UV−vis Measurements. The UV−vis spectra were recorded on a Cary 300 UV−vis spectrophotometer in a quartz cell (10 mm path length) over the range from 300 to 800 nm. The initial concentrations of NP solutions were 0.2 mM (freshly prepared from stock solutions by dilution and adjustment of pH). In a typical experiment (procedures were analogous for all different ligand ratios), 0.2 mM solutions of MC NPs were titrated in a stirred vial by adding 20–100 μL aliquots of “standard” AuTMA NPs of similar concentration (∼0.2 mM). The titrations were carried out in a stirred vial, and after each addition, the solution was allowed to equilibrate for ∼5 min and then transferred to the UV−vis cell.

2.4. Zeta Potential (ζ) and DLS Measurements. The electrophoretic mobility and hydrodynamic diameter of NPs were measured with Zeta/PALS particle sizer and surface potential analyzer (NanoZS Malvern Instruments) using a universal dip cell. The optical density of all the NP solutions was kept at ca. 0.2. DLS measurements were performed at 90° scattering angle at 514 nm laser wavelength. ζ was determined by measuring the electrophoretic mobility and using Henry’s equation

\[
U_e = \frac{2\pi\varepsilon f(\kappa_m)}{3\eta}
\]
where, \( U_\text{f} \) = electrophoretic mobility, \( \zeta \) = zeta potential, \( \epsilon \) = dielectric constant, \( \eta \) = viscosity, and \( f(\kappa) \) = Henry’s function. Smoluchowski’s approximation was used to measure the zeta potential values of NPs.

2.5. NMR Studies. Before NMR experiments, the Au cores of the MC NPs were etched using molecular I\(_2\), following the procedure of Murray and co-workers.\(^{38}\) Excess of I\(_2\) was removed by washing with methanol and drying at 65 °C to remove the solvent. Subsequently, the thiol mixtures were dried under vacuum for 15 h to remove traces of water and methanol. The purified thiol mixtures were dissolved in deuterated DMSO and \(^1\)H NMR spectra were taken on a 500 MHz Inova apparatus. The composition of the mixture was estimated from the integrals of peaks originating from methylene groups attached to the trimethylammonium group of the TMA thiol (R=CH\(_2\)-NMe\(_3\)+, \( \sigma \sim 3.28 \) ppm) and the methylene group next to the carboxylic group of MUA thiol (R=CH\(_2\)-COOH, \( \sigma \sim 2.17 \) ppm). Note: these studies required large quantities of particles. The amounts of NPs used to obtain each spectrum corresponded to at least 1 mg of thiol.

3. RESULTS AND DISCUSSION

To begin with, dodecylamine-functionalized gold NPs (AuDDA NPs) with average core sizes \(<d> = 5.2 \pm 0.5 \) nm were synthesized according to a previously reported procedure.\(^{37}\) To prepare various MC NPs from these precursors, series of place-exchange experiments were performed using pairs of oppositely charged alkane thiols. In a typical procedure, 11-mercaptopoundecanoic acid (MUA, negatively charged) and \( \text{N}_2\text{N}_2\text{N}_2\)-trimethyl-(11-mercaptopoundecyl)ammonium chloride (TMA, positively charged) were used (Scheme 1a). Au NPs stabilized with DDA were soaked in toluene/dichloromethane (20/10 mL) containing mixtures of various relative concentrations (\( \alpha_{\text{soln}} = \frac{C_{\text{MUA}}}{C_{\text{TMA}}} \)) of the two thiols. The ligand exchange was performed for at least 15 h in order to allow the reaction to equilibrate.\(^{38}\) Afterward, the thiol-coated MC NPs was allowed to precipitate, and the unbound thiols were removed by multiple washings with dichloromethane. Purified MC NPs were then dissolved in water, and the pH was adjusted to \( \sim 11 \) to completely deprotonate the carboxylic groups.

All MC NPs prepared by this procedure were characterized by TEM, UV–vis, DLS, and zeta (\( \zeta \))-potential measurements at both acidic and basic pH values (pH \( \sim 3 \) and 11, respectively). At pH \( \sim 11 \), the MUA’s were deprotonated and \( \zeta \)-potential measurements for \( \alpha_{\text{soln}} = 1, 1.5, 2, 3, 4, 5, 6, 9, \) and 20 showed positive value only for \( \alpha_{\text{soln}} = 1 \); for \( \alpha_{\text{soln}} = 1.5 \) and higher ratios, the potential was negative (Figure 1). At pH \( \sim 3 \), all MUA’s were protonated; the charge was due to the TMA thiols, and the \( \zeta \)-potential was positive for all samples, regardless of \( \alpha_{\text{soln}} \) (Figure 1 and see Table S1 in Section 1). However, there was a gradual decrease in the magnitude of \( \zeta \)-potential regardless of increasing \( \alpha_{\text{soln}} \), which corresponded to at least 1 mg of thiol.

All MC NPs were stable at both pH values for prolonged times. A typical \( \zeta \)-potential (Figure 2a) and DLS (Figure 2b) data for MC AuNPs (\( \alpha_{\text{soln}} = 3 \)) at pH \( \sim 11 \) (red) and pH \( \sim 3 \) (green). MC NPs are highly stable and monodisperse at both high and low pH values. (Scheme 1b). Progress of the titration was monitored by UV–vis spectroscopy recording the changes in the intensity and position of the Au NP SPR peak at each titration point (Figure 3a). In the initial stage of titration, the intensity of the SPR peak increased moderately, followed by a steep decrease accompanying precipitation of NPs (Figure 3b). At the same time, the position of the SPR peak was slightly red-shifted, indicating gradual aggregation of oppositely charged NPs due to attractive electrostatic interactions.\(^{39}\) Clusters of aggregated NPs precipitated from the solution at the point when the total amounts of positive and negative charges on the NPs were equal, \( \Sigma Q^+ + \Sigma Q^- = 0 \). On the basis of a series of such electrostatic titrations, we verified that, as expected, the position of the precipitation point shifted to higher values with increasing value of \( \alpha_{\text{soln}} \) (Figure 3b).

The ultimate objective of the titrations, and indeed, the challenge of this work, has been to relate the solution precipitation point to the composition of the m-SAM on the nanoparticles (\( \alpha_{\text{NP}} = \frac{C_{\text{MUA}}}{C_{\text{TMA}}} \)). We re-emphasize that this on-

Figure 1. Zeta potential of MC AuNPs as a function of \( \alpha_{\text{soln}} \) and pH. Error bars correspond to standard deviations based on at least three experiments from two different samples.

Figure 2. Characterization of MC NPs at low and high pH values. (a) Zeta potential and (b) DLS data for MC Au NPs (\( \alpha_{\text{soln}} = 3 \)) at pH \( \sim 11 \) (red) and pH \( \sim 3 \) (green). MC NPs are highly stable and monodisperse at both high and low pH values.
The equilibrium constant for the adsorption of a thiol onto the surface of gold nanoparticle can be expressed as

\[ K^\text{thiol} = \frac{C_{\text{thiol}}^{\text{NP}}}{C_{\text{thiol}}^{\text{soln}}} \]

where \( C_{\text{thiol}}^{\text{NP}} \) and \( C_{\text{thiol}}^{\text{soln}} \) are concentrations of thiol in the solution and on the NP, respectively, and \( C_{\text{thiol}}^{\text{NP}} \) is concentration of binding sites on the surface of a nanoparticle. Therefore, for mixture of TMA and MUA thiols, the ratio of equilibrium constants (assuming no cooperativity during adsorption) is given by

\[ \frac{K_{\text{TMA}}^{\text{NP}}}{K_{\text{MUA}}^{\text{NP}}} = \frac{C_{\text{MUA}}^{\text{NP}}}{C_{\text{TMA}}^{\text{NP}}} \]

\[ = \frac{C_{\text{MUA}}^{\text{NP}}}{C_{\text{TMA}}^{\text{NP}}} \frac{K_{\text{TMA}}^{\text{NP}}}{K_{\text{MUA}}^{\text{NP}}} \]

\[ = \frac{\alpha_{\text{MUA}}}{\alpha_{\text{TMA}}} \]

\[ = \frac{1}{\alpha_{\text{TMA}}} \]

We next plot the titration curve as a function of a variable \( \epsilon \), which quantifies how many TMA "standard" particles were added to the MC NPs:

\[ \epsilon = \frac{N^{\text{standard}NP}}{N^{\text{MC-NP}}} = \frac{N^{\text{TMA-MC-NP}}}{N^{\text{TMA-MC-NP}} + N^{\text{MUA-MC-NP}}} \]

where \( N^{\text{standard}NP} \) and \( N^{\text{MC-NP}} \) are particle numbers and \( N^{\text{TMA-MC-NP}} \) and \( N^{\text{MUA-MC-NP}} \) are concentrations of TMA and MUA thiols on the TMA "standards" and MC-NPs, respectively. At the precipitation point, the net charge on all the NPs is zero,

\[ 2\Sigma Q^+ + \Sigma Q^- = 0 \]

and so

\[ \frac{C_{\text{TMA}}^{\text{standard NP}}}{C_{\text{MUA}}^{\text{MC-NP}} - C_{\text{TMA}}^{\text{MC-NP}}} \]

Therefore, the precipitation point corresponds to

\[ \epsilon = \frac{C_{\text{MUA}}^{\text{NP}} - C_{\text{TMA}}^{\text{NP}}}{C_{\text{MUA}}^{\text{MC-NP}} + C_{\text{TMA}}^{\text{MC-NP}}} = \frac{\alpha_{\text{MUA}} - 1}{\alpha_{\text{TMA}} + 1} \]

From the last dependence \( \alpha_{\text{NP}} \) can be derived as \( \alpha_{\text{NP}} = \frac{1}{\epsilon + 1} \). Also, because

\[ \frac{1}{\alpha_{\text{NP}}} = \frac{K_{\text{TMA}}^{\text{NP}}}{K_{\text{MUA}}^{\text{NP}}} \times \left( \frac{1}{\alpha_{\text{soln}}} \right) \]

\[ \text{on} \left( \frac{1}{\alpha_{\text{soln}}} \right) \]

With this algebra in place, the experimental results are summarized in Figure 3c. For \( \alpha_{\text{soln}} = 3, 4, 5, 9, \) and 20, there is a clear linear trend with the slope of \( \frac{K_{\text{TMA}}^{\text{NP}}}{K_{\text{MUA}}^{\text{NP}}} \) = 1.22, indicating that TMA thiols adsorb more readily than MUA ones.

Importantly, titration results agree with those of independent NMR experiments. Since spectra of SAMs on NPs exhibit pronounced peak broadening and, despite some previous efforts, cannot provide the basis for precise analyses, we used a well-known procedure of first dissolving the metal cores and only then taking the spectra of the liberated ligand mixtures. In short, the procedure involved initial etching of the NPs’ gold cores with iodide and oxidizing thiols to disulfides, which after purification, were subjected to NMR studies. The ratio of thiols’ concentrations was then calculated from the integrals of the characteristic peaks of both thiols (see Section 2) to give the value of \( \alpha_{\text{NP}} \). When the dependence of \( \left( \frac{1}{\alpha_{\text{soln}}} \right) \) on the NMR-derived \( \left( \frac{1}{\alpha_{\text{NP}}} \right) \) values was plotted (Figure 3d), the slope of the line was \( \approx 1.20 \), in close agreement with 1.22 obtained by electrostatic titrations.

With the NMR validation at hand, we studied whether the titration approach is applicable to m-SAMs comprising thiols other than MUA and TMA. We performed a series of experiments in which MUA was substituted with longer MHA (16-mercaptophexadecanoic acid) or shorter MOA (8-mercaptopoctanoic acid) (Figure 4a). All conditions for these experiments were identical to those previously described for MUA/TMA thiols; \( \alpha_{\text{soln}} \) used were 11, 14, 19, 30, and 55 for MOA-TMA and 14, 19, 25, 40, and 50 for MHA-TMA; these values were chosen high to ensure all MC-NPs had negative zeta potentials in basic pH. After analysis analogous to the MUA/TMA system, we obtained linear trends with the slopes \( \frac{K_{\text{TMA}}^{\text{NP}}}{K_{\text{MUA}}^{\text{NP}}} \approx 6.45 \) and \( \frac{K_{\text{TMA}}^{\text{NP}}}{K_{\text{MUA}}^{\text{NP}}} \approx 2.45 \) (Figure 4b), again showing the preference of TMA thiols to adsorb onto NPs. With the use of the thermodynamic dependence \( \Delta G_{\text{thiol}} = -RT \ln K_{\text{thiol}} \)

\[ \text{this preference can be expressed in the form of the differences in the free energies of adsorption of different thiols on the surface of gold nanoparticle, } \Delta \Delta G = -RT \ln \frac{K_{\text{TMA}}^{\text{NP}}}{K_{\text{MUA}}^{\text{NP}}} \]

This data is summarized in Figure 4c and shows that adsorption of TMA is favored over that of MOA by 1.86kT, over that of MUA by 0.2kT and over that of MHA by 0.9kT. Since there is no obvious trend in how the length of the alkyl chain in the carboxylic acid thiols influences the ratio of equilibrium constants, factors other than chain-length must be involved in the thermodynamics of m-SAM formation (e.g., for approximately equal-length MUA and TMA, the [−] and [+] head groups are proximal at the SAM's surface and adsorption of TMA can "promote" adsorption of MUA). What is worth
Such properties of charged “superstable” MC NPs could be useful in biological applications, where the stability of nanomaterials is often decreased by the interactions with charged macromolecules.42–45

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b12599.

Zeta potential, NMR characterization, and electrostatic titrations of MC NPs (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: grzybor72@unist.ac.kr.

Author Contributions
@P.P.P. and B.K. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Dr. Yanhu Wei for helping with NMR measurements. This work was supported by the Non-equilibrium Energy Research Center, which is an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DESC0000989. B.A.G. gratefully acknowledges personal support from the Institute for Basic Science Korea, Project Code IBS-R202-D1.

REFERENCES


Figure 4. (a) Schematic illustration of MOA-TMA (left) and MHA-TMA (right) MC NPs. (b) Plot of the dependence of 1/ΩNP on (1/σNP) obtained from electrostatic titrations of MOA/TMA (left) and MHA/TMA (right) MC NPs with “standard” AuTMA nanoparticles. (c) Thermodynamic values for three pairs of thiols used in this study. Error bars in (b) correspond to standard deviations based on at least three experiments.

4. CONCLUSIONS

While the obvious extensions of this approach would be to study charged m-SAMs of other types of charged ligands, and on nano-objects of different sizes and shapes, we wish to conclude by pointing out the limitations of the method and, at the same time, an interesting property of the MC NPs. As it turns out, MC NPs covered with lower fractions of MUA thiols (σNP determined by NMR between 1.2 (σMUA = 1.5) and 1.6 (σMUA = 2) do not precipitate until at least 2-fold excess of TMA NPs is added, well above the NP electroneutrality point (see Figure S2). What is interesting about this case is that the net charge of such NPs is still negative but lower than that of σNP > 1.6 particles for which precipitation is observed; this seems to defy the common wisdom of colloidal science stating that the decrease of charge should cause destabilization of colloidal solutions. This phenomenon, however, can be rationalized by taking into account the fact that increasing the fraction of positively charged TMA ligands on the MC NP surface (i.e., decreasing σNP) not only decreases its net negative charge but also creates repulsive (and therefore stabilizing) electrostatic interactions with oppositely charged TMA NPs used in the titrations. An additional factor might be that the head groups of the MUA and TMA ligands on the same MC NP can serve as counterions to each other and thus increase the stability of the NPs by removing the entropically favorable effect of counterion desorption driving NP aggregation.21,41

Table 1. Thermodynamic values for three pairs of thiols used in this study. Experimental zeta-potentials were used to calculate ∆G values (for MOA/TMA): 0.20/0.496/kT, 1.36/4.613/kT, and 0.90/2.225/kT. The data obtained from zeta-potential measurements (Figure S1) are in agreement with the results obtained from electrostatic titrations of MC NPs. The fraction of MUA thiols on MC NPs were obtained from NMR measurements. This work was supported by the Non-equilibrium Energy Research Center, which is an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DESC0000989. B.A.G. gratefully acknowledges personal support from the Institute for Basic Science Korea, Project Code IBS-R202-D1.
Adsorption of Charged Nanoparticles.

1. Introduction

Charged nanoparticles are gaining significant interest due to their unique properties and potential applications in various fields, including biology, medicine, and material science. The interaction between charged nanoparticles and surfaces or other charged particles can lead to complex behavior such as aggregation, dispersion, and adsorption, which are crucial for understanding their functionality and behavior in different environments. This article will discuss the adsorption of charged nanoparticles on different surfaces and the factors influencing this process.

2. Experimental Setup

The experiments were conducted using a combination of spectroscopic and microscopic techniques to study the adsorption behavior. Surface-enhanced Raman spectroscopy (SERS) was used to monitor the changes in the chemical environment of the adsorbed nanoparticles, while atomic force microscopy (AFM) was employed to observe the morphological changes at the nanoscale. Additionally, dynamic light scattering (DLS) was utilized to determine the size and size distribution of the nanoparticles in solution.

3. Results and Discussion

3.1. Adsorption Dynamics

The time-dependent adsorption of charged nanoparticles onto a negatively charged surface was investigated using SERS. The changes in the Raman spectra were monitored over time, revealing the adsorption of nanoparticles onto the surface. The results showed a rapid initial adsorption followed by a slow, gradual increase over a longer period, indicating a kinetic behavior.

3.2. Role of Surface Charges

The interaction between charged nanoparticles and surfaces is influenced by the charge density and the electrical potential of the surface. Theoretical calculations using density functional theory (DFT) were performed to understand the electronic structure and electrostatic interactions at the nanoparticle-surface interface. The simulations revealed that the adsorption energy is significantly dependent on the surface charge density and the nanoparticle charge.

3.3. Aggregate Formation

The aggregation of charged nanoparticles was studied using DLS and AFM. The size distributions of the aggregates were measured, and the morphological changes were observed. The results showed that the aggregation behavior is influenced by the nanoparticle charge, concentration, and presence of electrolytes. The aggregation was found to be a competitive process between attractive and repulsive forces.

4. Conclusions

The adsorption of charged nanoparticles is a complex process influenced by various factors such as the surface charge, nanoparticle charge, concentration, and electrolyte composition. Understanding these interactions is crucial for optimizing the performance of nanoparticle-based applications. Further studies are needed to explore the role of interfacial phenomena and the impact of dynamic environmental conditions on the adsorption dynamics.

References


