

Experimental investigation on the use of highly charged nanoparticles to improve the stability of weakly charged colloidal system

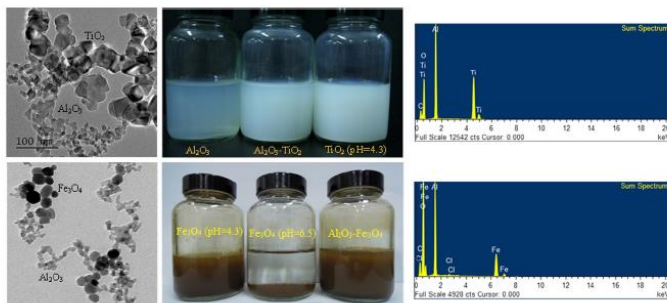


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GRAPHICAL ABSTRACT



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ABSTRACT

The present work highlighted on the implementation of a unique concept for stabilizing colloids at their incipiently low charge potential. A highly charged nanoparticle was introduced within a coagulated prone colloidal system, serving as stabilizer to resist otherwise rapid flocculation and sedimentation process. A low size asymmetry of nanoparticle/colloid serves as the new topic of investigation in addition to the well-established large size ratio nanoparticle/microparticle study. Highly charged Al₂O₃ nanoparticles were used within the present research context to stabilize TiO₂ and Fe₃O₄ based colloids via the formation of composite structures. It was believed, based on the experimental evidence, that Al₂O₃ nanoparticles interact with the weakly charged TiO₂ and Fe₃O₄ colloids within the binary system via absorption and/or haloing modes to increase the overall charge potential of the respective colloids, thus preventing further surface contact via van der Waal's attraction. Series of experimental results strongly suggest the presence of weakly charged colloids in the studied bimodal system where, in the absence of highly charged nanoparticle, experience rapid instability. Absorbance measurement indicated that the colloidal stability drops in accordance to the highly charged nanoparticle sedimentation rate, suggesting the dominant influence of nanoparticles to attain a well-dispersed binary system. Further, it was found that the level of colloidal stability was enhanced with increasing nanoparticle fraction within the mixture.

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1. Introduction

It is evident that bottom-up engineering approach for fabrication and processing has grown tremendously since the inspiring lecture by Nobel laureate, Feynman [1] who highlighted on the possibility of manipulating molecules and atoms to gain unlimited authority over scale and functionality of the final product. As such, he also underlined the persisting challenges in working within sub-micron scale which include dealing with new jargon of physics such as gravity, surface tension and particle interaction, far dominant relative to macro-scale behavior. Thus, from the technological perspective, the key toward successful implementation of this concept strongly lies on the ability to produce and control the particles to achieve specific task.

Within the aspect of colloidal science, one of the underlying disciplines is associated to the study colloidal stability which plays a central role in numerous physicochemical processes. It is evident that the demand to attain highly dispersed colloidal suspension has spread to numerous technological applications ranging from coating, printing, drug carriers, catalysis, etc. [2–4]. A well-known approach to mitigate flocculation between suspended colloids is by tailoring the pH of the solvent away from the colloids isoelectric point to give coulombic repulsive force as well as via steric route with the help dispersant and polymeric binder. Nanoparticles have also been used in unconventional way to stabilize colloids via electrostatic self-assembly mode [5,6].

The concept of using nanoparticles for colloidal stabilization has long been pursued for both emulsion and solid particles [7–9]. In solid particle, the nanoparticles adsorbed onto the colloidal surface via charge asymmetry which promote better dispersion and less aggregation as highlighted earlier by Homola and co-workers [10]. The key toward successful application of nanoparticles in emulsions stabilization lies on the surface modification of the nanoparticles to contain both hydrophilic and hydrophobic segments which will interact at oil water interface, further preventing phase separation [11].

In recent years, hybridized colloids (i.e. colloidal system consisting of two or more particles of different type and morphology) have been used as additive in heat transfer media for thermal application [12,13]. The hybridization also leads to the formation of anisotropic colloidal structure which is favorable to suit specific application [14,15]. It was also proven that the addition of magnetic particles onto carbon nanotube via a simple two step mixing method with the help of surfactant enabled direct control of the thermal conductivity of the hybrid mixture in magnetic field environment [12,16].

While absorbing colloid–nanoparticle interaction has been widely studied, a new research paradigm on the subject of nanoparticle mediated colloidal assembly has been laid by Tohver et al. [17] which is based on weakly repulsive nature of colloidal interaction. Its fundamental theory lies on self-manipulating of highly charged nanoparticles on negligibly charged microparticles of the same polarity to form a halo structure. Nanoparticle haloing concept has been explored for various types of colloidal entities namely ceramic based microparticles, phospholipid, emulsions and carbon nanotubes [17–22]. Interestingly, recent work by Tian and Synder [23,24] highlighted the formation of thermodynamically stable silica nanoparticles close to their isoelectric point.

The stability of the colloid produced using a sol–gel method was attributed to the residual lysine linked to the silica surface.

Much works based on experimental [25–27], theoretical [28–30] and numerical [31–35] approaches have been pursued since the first reported finding on this newly exciting phenomenon. Several prominent progresses of research findings in nanoparticle stabilized colloids via haloing mechanism are worth mentioning here. Tohver et al. [17] elucidated on the ability of the stabilized binary system to generate a much ordered crystal structure under gravitational sedimentation colloidal assembly. Further, a dramatic transition of flow signature manifested from shear thinning associated with the nanoparticle free colloidal system toward Newtonian behavior in stable bi-dispersed system, indicating tremendous drop of viscosity. Chan and Lewis [27] laid an insight on the interaction between binary system at three different conditions namely strongly attractive, weakly interacting and strongly repulsive which give rise to bridging, haloing or depleting effects.

Research by Luijten and co-workers has been dedicated toward validating the phenomena via numerical approach [31–33]. They discovered that the interaction between nanoparticle–microparticle in haloing mode is dominated by electrostatic attraction which gives relatively close agreement to the experimental results. In contrast, Karanikas and Louis numerically highlighted the role of electrostatic repulsion between nanoparticles in solution as dominating factor in the halo formation [28]. However, this condition requires much higher Debye screening length to match the existing experimental results.

Martinez et al. [36] and Lee et al. [37] used a confocal laser scanning microscopy technique to obtain imagery proof on the structural evolution and formation of colloidal crystal in a system containing particles with size and charge asymmetry. Lee et al. [37] further highlighted that the use of nanoparticle haloing technique enables microparticles to deposit on the substrate at much lower separation distance relative to the traditional approach of tailoring the pH away from the isoelectric points. Further, this gap can be regulated by simply changing the nanoparticle size and concentration within the binary system to give much broader range of physical property of the final product. By using ultrasmall-angle X-ray scattering technique, Zhang et al. [38] conducted quantitative validation on the nanoparticle halo formation by measuring the anterior and lateral separation distances between microsphere–nanoparticle and between segregated nanoparticles as well as the spatial distribution and concentration of nanoparticles within the halo structure.

The prediction on the halo formation has also been put forward via elementary analysis on the interaction potential within binary mixture which is based on the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [39,40]. The analysis highlighted the existence of weak repulsive barrier that forms a basis to further quantifying the strength of micro/nanoparticle interaction in experimental, numerical and theoretical approaches [17,26,30].

Ji et al. [30], McKee et al. [41], Hong and Willing [42] and Huang and Ruckenstein [34] investigated the aspect of interactive forces in binary system at different pH which represent different colloidal strengths and highlighted that nanoparticles absorption remained an underlying challenge to achieve ideally reversible colloidal stability. In corroboration to the results obtained by Ji et al. [30], Xing et al. [43] discovered that the haloing phenomena could also

manifest in a highly charged nanoparticle–microparticle/plate system in contrast to the previously known attractive depletion force. They reasoned that the nanoparticle may have converged on the plate due to its low charge potential resulting into effective repulsive force which becomes more pronounced with decreasing separation distance. Herman and Walz [44] conducted rigorous experimental observation on the polarity aspect of the individual nanoparticle and microparticle in the formation of stable binary system. He underlined that similar charge polarity for each particle constituents promoted better stability in comparison to the oppositely charged nanoparticle/microparticle which formed rapid flocculation and sedimentation upon mixing.

Lewis and co-workers in their patent application [45], and review article [46], furnished comprehensive details on the general mechanisms of nanoparticle haloing along with description on how it can be employed to address the current technological limitations particularly in the subject of electronics packaging, photonics and pharmaceuticals. They also outlined the general rules in realizing halo shells, covering aspects such as preferable effective charge, nano/microparticle type, size and its corresponding ratio and the state of carrier liquid.

It is acknowledged that the current use of surfactant and polymer as means of promoting colloidal stability suffers from series of drawbacks. Particularly in the fabrication of close-packed colloidal crystal via gravitational sedimentation technique, the use of surfactant generates irreversible contamination to the primary particles which implicates the fracture and thermal strength of the final product due to the increase in lattice spacing between the sedimented colloids. Further, increasing the surfactant loading primarily screen the inherent potential of the particle especially with regard to the heat and electron transport [18,47]. In addition, the fact that inevitable foam manifests upon heating and mixing process of surfactant stabilized colloids poses detrimental effect on the overall system performance especially in the area of heat transfer [48]. The use of polymer on the other hand is constraint by the increase in viscosity due to its intrinsically high molecular weight which limits its application particularly within thermal transport system that require the viscosity increment be less than the thermal conductivity to induce favorable enhancement in convective heat transfer [49,50]. Likewise, it also demonstrates characteristic disadvantages to that of surfactant in terms of thermal and electrical conducting performances.

Motivated by the above challenges in the use of steric stabilization technique, the present work would explore on the potential of incorporating highly charged nanoparticle toward improving the solubility weakly charged colloidal aggregates. By diverting from the conventional norm of surfactant based colloidal stabilization, it is believed that major impediments associated with thermal, electrical and mechanical properties of the colloids can be efficiently addressed. At present, a substantial amount of work has been dedicated on the use of engineered colloidal based heat transfer media that principally involves the dispersion of mostly ceramic based particles within base fluids [51]. In this light, it is worthy to mention that most of ceramic based colloids (metal oxide or nitrides) used within the existing research domain occupy a broad segment of low stability colloidal nature with respect to pH based on the documented zeta potential measurement [52,53]. While it is necessary to maintain both appropriate pH and stability of the colloids, it has become a persisting challenge for the researcher to meet both requirements simultaneously without steric intervention.

Thus, the present work aims adopt a newly discovered 'halo stabilization' approach by incorporating a highly charged nanoparticle into aggregated prone colloidal system to improve its overall stability particularly near its isoelectric point. Recently Ji et al. [30] highlighted that the force profile measurement of highly charged

nanoparticle/microparticle-plate binary system was found to be higher (i.e. more repulsive) in comparison to nanoparticle free colloidal system. This interesting finding suggests that highly charged nanoparticles promote colloidal stability at both low and high asymmetrically charged systems. This also implies that the inclusion of nanoparticles would pave favorable attributes on the colloidal rheological aspect which may lead to much improved thermal and electrical properties due to the formation of stable solution [54]. The ability to synthesize and functionalized nanoparticles of different types (i.e. metal, polymer and semiconductors) having extremely high charge has broaden the opportunity for this concept to prosper in multidisciplinary fields, particularly in the thermal transport system where stability induced viscosity and conductivity determines the viability of the colloids to be incorporated within the current heat transfer media.

2. Methodology

2.1. Material and sample preparation

Three different materials have been selected for the present investigation namely TiO₂, Al₂O₃ and Fe₃O₄. These materials come in powder form and were purchased from Sigma Aldrich. Details of each material are given in Table 1. HCL and NaOH reagents were purchased from Merck. The water used in the experiments was filtered and deionized by using a Bamstead EASYpure II system (Thermo Scientific). The water had a resistivity of 18.2 MΩ-cm.

Two hybrid colloidal mixtures were tested (i.e. Al₂O₃–TiO₂ and Al₂O₃–Fe₃O₄) within the present research context by which Al₂O₃ serves as the stabilizer while the other two elements represent the weakly charged colloids (see Table 2). The procedure begins by preparing DI water in 100 ml sampling bottles. Al₂O₃ and TiO₂ particles were then mixed in specific weight proportions and the mixture subsequently underwent 10 min sonication inside ultrasonic bath. The total weight of the mixture was kept at 0.1wt.% to standardize and facilitate characterization and property measurement. The mixtures were then titrated to the desired pH in stirring mode using a combination of 0.1 M HCL and NaOH solution. Similar protocol was adopted for preparing Al₂O₃–Fe₃O₄ hybrid complexes. The pH was adjusted to be within the low stability region of TiO₂ and Fe₃O₄ while maintaining the highly charged nature of Al₂O₃ for investigating the ability of Al₂O₃ nanoparticles to act as stabilizer to improve the solubility of negligibly charge colloids (i.e. in this case TiO₂ and Fe₃O₄).

2.2. Stability measurement and analysis

Investigation of colloidal stability of the hybrid mixture was conducted using different techniques. Series of colloidal sedimentation images were taken for each single and hybrid mixtures of different materials at the specific pH of interest. Measurement of the hydrodynamic size and zeta potential of the composite was made using a Malvern Zetasizer Nano-ZS (Malvern Instruments, Ltd., Worcestershire, UK). Further investigation on the stability aspect of the colloidal system was performed by measuring the elemental concentration using Energy Dispersive X-ray (EDX) spectroscopy. Investigation on the morphological structure of the

Table 1
List of materials used for the present investigation.

Element	Particle size (nm)	Density (g/cm ³)
Al ₂ O ₃	13	4.000
TiO ₂	25	4.260
Fe ₃ O ₄	50–100	4.800–5.100

Table 2
List of elements with corresponding abbreviation used for the present study.

Element	Ratio Al ₂ O ₃ : (...)	pH	Total weight (wt%)	Abbreviation
Al ₂ O ₃ + TiO ₂	1:1	6.5	0.1	TIAL11
	1:2	6.5	0.1	TIAL21
	1:3	6.5	0.1	TIAL31
Al ₂ O ₃ + Fe ₃ O ₄	1:1	6.5	0.1	FEAL11
	1:2	6.5	0.1	FEAL21
	1:3	6.5	0.1	FEAL31
TiO ₂		4.3	0.1	TIO43
Fe ₃ O ₄		4.3	0.1	FE043
Al ₂ O ₃		6.5	0.1	ALO65

material was accomplished using Transmission Electron Microscopy (TEM) model TEM LEO LIBRA-120 (Carl Zeiss, Oberkochen, Germany). A UV-vis spectroscopy technique (Varian carry® 50 UV-vis spectrophotometer, Agilent Technology) was further used to quantify the colloidal stability with respect to time. Finally rheological investigation was performed using Anton Paar Rheometer (model Physica MCR 301, Anton Paar GmbH) to study the effect of adding highly charged nanoparticles on mitigating the rapid aggregation in weakly charge colloids.

3. Results and discussion

3.1. Investigation of colloidal stability using particle sedimentation technique

Figs. 1 and 2 provide a clear picture of the sedimentation level of each single and hybrid colloidal systems. As evident in Fig. 1(a) and (b), both TiO₂ and Fe₃O₄ colloids experience rapid agglomeration with time as soon as the sonication procedure

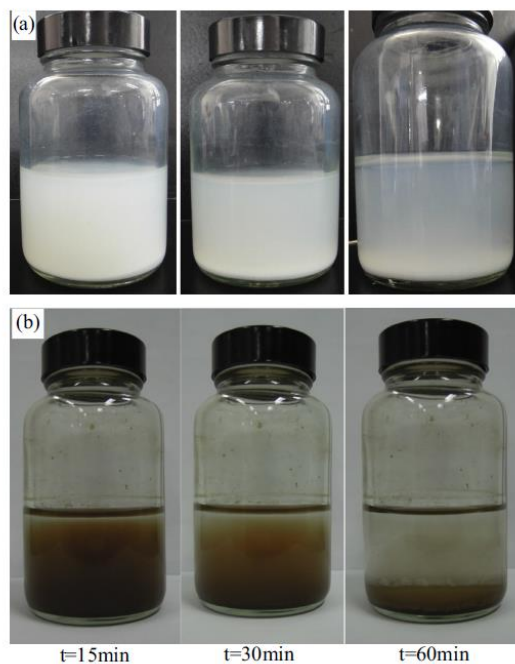


Fig. 1. Chronological sedimentation progress of (a) TiO₂ and (b) Fe₃O₄ colloids in aqueous solution. The pH was adjusted in between 6.4 and 6.5 prior to observation.

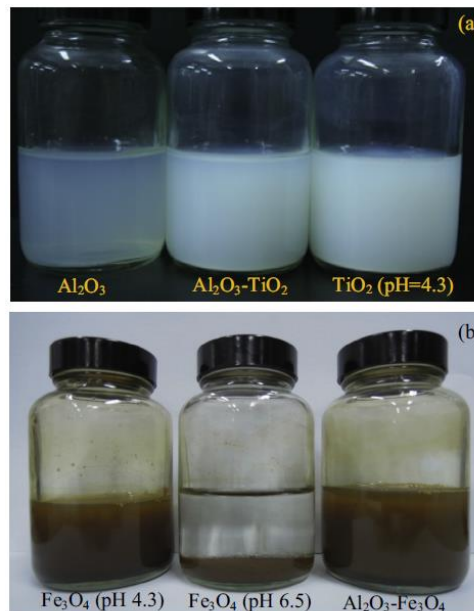


Fig. 2. Sediment photograph results for 1:1 mixing ratio of (a) Al₂O₃-TiO₂ and (b) Al₂O₃-Fe₃O₄ mixtures at pH = 6.5 along with single element colloids at highly stable pH. All pictures were taken after two days of sample preparation.

was terminated. The pH of each constituent was regulated to be relatively close to the isoelectric point as documented within the literature [55,56]. In contrast, as shown in Fig. 2(a), the addition of Al₂O₃ nanoparticles, owing to its highly charged nature at the pH of investigation [57], into solution containing weakly charged TiO₂ particles improves the suspension stability of the resultant binary system based on the color evidence of the solution which resembles TiO₂ colloid at pH = 4.3 (i.e. stable solution). In addition, solution containing single Al₂O₃ element shows rather dim color indicating that there is a strong evidence of interaction between TiO₂ and Al₂O₃ particles to form a colloidal matrix that help to suspend the TiO₂ within the solution. This also consolidates the previous findings on the ability of particles with high surface potential to improve the dispersion behavior of low stability particle of different size ratios [26]. A similar result also transpires for the Al₂O₃-Fe₃O₄ mixture as shown in Fig. 2(b). The color of the mixture was maintained its brownish incandescence after two days and this is in contrast to the original Fe₃O₄ colloidal solution which rapidly flocculated and sediment upon discontinuation of the sonication. This also implies that the Al₂O₃ nanoparticles remain in close contact with the Fe₃O₄ aggregates to resist further proliferation in the chain like structure of the weakly charged particles which leads to phase separation.

3.2. Investigation of colloidal stability using micrograph technique

A series of TEM photographs were taken to observe the particle morphological structure, aiming to shed light on the possible interaction between each individual element within the binary system. Each hybrid solution was prepared at the weakly charged state of both Fe₃O₄ and TiO₂ (i.e. at pH 6.5) and left for one day after preparation to minimize any possibility of getting considerable traces of coagulated aggregates induced by the isoelectric condition. Each of

the solution was dropped on a copper grid and left for 3 days in dry air prior to the viewing.

Fig. 3 shows the TEM micrograph of aggregation structure within the hybrid complexes. It can be summarized from the above results that TiO_2 particles form an isolated cluster and remain in close proximity to the Al_2O_3 nanoparticles, potentially due to electrostatic interaction. It was postulated that this event occurred during the sonication process where the primary particles (i.e. TiO_2) were segregated into much smaller aggregate, thus increasing the overall surface area and creating potential sites for interaction with the secondary particles (i.e. Al_2O_3) via columbic attraction. The encapsulation of highly charged nanoparticles prevents rapid flocculation of TiO_2 aggregates and leads to a formation of binary complexes with size remaining in nanometer range. It is believed that the haloing phenomenon between high and low charged particles is much more pronounced in colloidal solution by the fact that the particles were surrounded by electrical double layer. It is worthy to mention that while the ideal theoretical foundation on this stabilization concept relies on the segregation of individual nanoparticles around the weakly charge colloids [58], the aggregated structure of Al_2O_3 nanoparticles even in its highly charged state produce a relatively different hybrid complexes which can be observed from TEM micrograph. Likewise, a relatively similar morphological structure was formed within the Al_2O_3 - Fe_3O_4 composite, indicating the ability of Al_2O_3 nanoparticles to mitigate rapid size expansion of Fe_3O_4 agglomerates by grafting onto or remaining close to them. This leads to the enhancement in the overall surface charge intensity of the bimodal system, thus preventing further contact.

3.3. Investigation of colloidal stability using quantitative elemental analysis

A series of EDX results provide a quantitative explanation on the ability of highly charged nanoparticles to stabilize weakly charged colloidal system. In essence, it is worthy to mention that the material sampling for EDX measurement was performed in the colloidal state in order to preserve the hybrid complexes in their original form. Each sample was prepared and left for one day at room temperature to remove non-interacted element which may rapidly sediment upon the removal of the sonication process. The supernatant was subsequently transferred onto a separate petri dish using a pipette and allowed to dry at 60 °C prior to the measurement.

As shown in Figs. 4 and 5, the presence of TiO_2 and Fe_3O_4 components at their coagulation pH within the bimodal system strengthen the theoretical prediction of the role of highly charged Al_2O_3 nanoparticles to form hybrid complexes. For Al_2O_3 - TiO_2 mixture at 1:1 ratio (Fig. 4), it was observed that TiO_2 particles remained in suspension in almost equal weight percentage as to the Al_2O_3 . This implies that the primary element (TiO_2) was mostly in contact or remaining close to the secondary element (Al_2O_3) to form a small chain like structure that remain suspended owing to the high surface potential of the secondary particles.

A slightly different scenario manifests for Al_2O_3 - Fe_3O_4 colloidal solution prepared at 1:1 ratio (Fig. 5) wherein the Fe_3O_4 concentration appears less than Al_2O_3 . This strongly suggests that percolation between Fe_3O_4 particles dominates which leads to the formation of large aggregated structures. As such, the prescribed amount of Al_2O_3 was insufficient to sustain the gravitational force which later pulls the structures downwards and cause settling of the colloids. It is believed that major factors that contribute to this phenomenon are the density, size and dipole-dipole interaction between Fe_3O_4 particles which is the highest among the selected materials. The rapid aggregation among Fe_3O_4 particles itself due to dipole-dipole moment interaction on top of the van der

Waal's attraction causes high tendency of the particles to sediment due to accumulated mass that surpasses the columbic forces of the bimodal system. Nevertheless, this result reflects the ability of highly charged nanoparticle to prevent phase separation and prolong the stability of negligibly charged colloids.

Furthermore, metal element distribution measured via X-ray mapping mode vindicates the TEM findings on the state of particle distribution within the bimodal system. The pigments shown in Figs. 4 and 5 clearly indicate the presence of Al_2O_3 nanoparticles together with TiO_2 and Fe_3O_4 aggregates within the domain. The Al_2O_3 nanoparticles act as barriers to prevent further contact between the weakly charged colloids. This translates into much lower colloidal size which further subside the gravitational effect and extend the stability of the weakly charged colloids.

3.4. Investigation of colloidal stability using zeta potential measurement

Another conventional technique commonly adopted to investigate the suspension stability is via the measurement of zeta potential and particle size by which the results can be used to describe the overall particle mobility and surface potential. These components are among the key factors that determine the stability within colloidal system.

Series of plots representing average particle size and zeta potential were established to observe the stability of the colloids. The plots are summarized in Figs. 6–9 respectively. The plots reveal a noticeable trend for both properties which provide the footprint of the binary system stability. In essence, it was observed from the particle size plots that the effective diameter for individual particle in aqueous solution measured by using dynamic light scattering technique was significantly higher in comparison to the original particle size given by the manufacturer. This also consolidates the TEM micrograph finding that the particles coalesce and form bigger aggregates but remain small enough for the columbic force to overwhelm gravitational and van der Waal's attraction that govern the physics of the nanoparticles in suspension.

As depicted in Fig. 6, both TiO_2 and Fe_3O_4 colloids experience dramatic transition in particle size as well as stability as the pH moves closer to isoelectric points for each individual particle. Further, it is evident that the incipient point of instability for both colloids falls within a similar range (i.e. $\text{pH} \approx 6$), indicating these particles require external stabilizing intervention to prevent further agglomeration. The registered pH at point of zero charge (i.e. pH_{pzc}) for TiO_2 and Fe_3O_4 is approximately 6.8 and 6.9 respectively which is close to the documented value from the literature [55,56].

Figs. 7 and 8 highlight results of size and zeta potential distribution curves for each hybrid complexes which serve as another quantitative evidence on this interesting stabilizing concept. The results show relatively minimal transition of hydrodynamic size for both TiO_2 and Fe_3O_4 colloids when Al_2O_3 is added as oppose to the single component colloids that grow rapidly near their isoelectric points as presented in Fig. 6. Furthermore zeta potential distribution curve also indicates similar trend of results by which the magnitude of both hybrid complexes remains high as a result of incorporating highly charged Al_2O_3 nanoparticles into the system. These results coupled with the above imagery findings strongly suggest the stabilizing effect of highly charged nanoparticles on poor colloidal systems as alternative to widely known surfactant and polymer.

In addition while dynamic light scattering technique indicates a stabilized phase for both bimodal systems, the TEM and EDX results show that Al_2O_3 nanoparticles are mostly in contact with each weakly charged component (i.e. TiO_2 and Fe_3O_4). It is believed that the contact is established during the drying stage of the

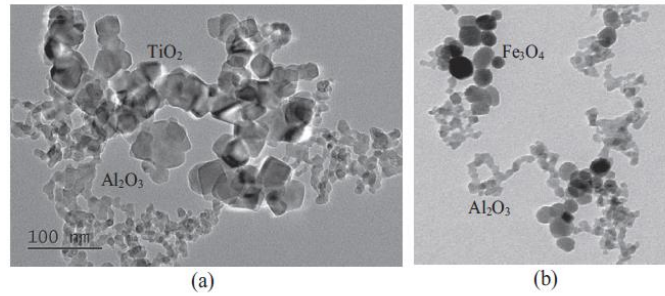


Fig. 3. TEM micrograph of (a) Al_2O_3 - TiO_2 and (b) Al_2O_3 - Fe_3O_4 aggregation structure.

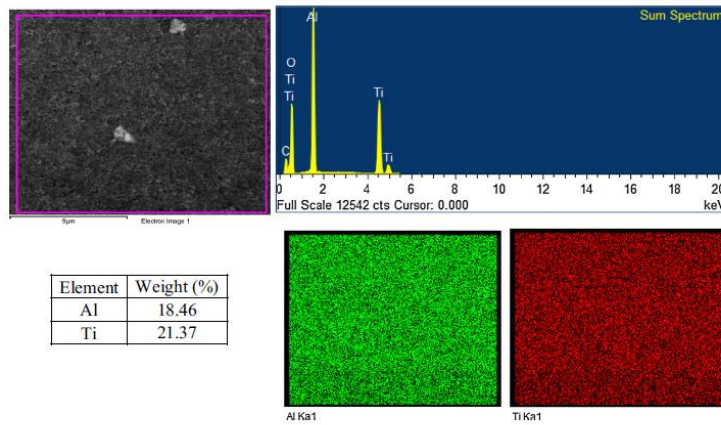


Fig. 4. EDX results for Al_2O_3 - TiO_2 mixture at 1:1 ratio prepared at pH = 6.5. The green and red pigments represent X-ray mapping of Al_2O_3 and TiO_2 individual element within the measured domain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

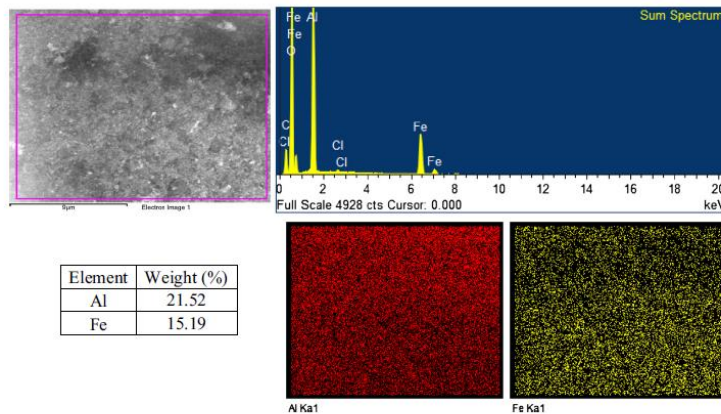


Fig. 5. EDX results for Al_2O_3 - Fe_3O_4 mixture at 1:1 ratio prepared at pH 6.5. The yellow and red pigments represent X-ray mapping of Al_2O_3 and Fe_3O_4 individual element within the measured domain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

samples which reduces the surface tension leading to an increase in the aggregation tendency of the particles.

Further, As highlighted in Fig. 9, the plot of hydrodynamic diameter for single and binary colloids suggest that the above

mentioned aggregation phenomenon manifests for both conditions, even as the single colloids were prepared at pH far away from the isoelectric point. It is also evident that, as time progresses, the aggregates show a decreasing trend of hydrodynamic diameter

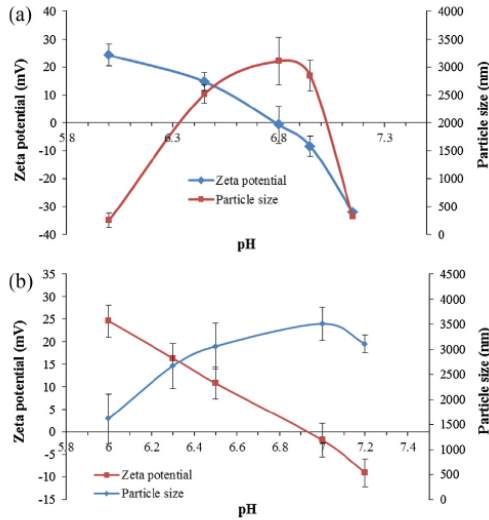


Fig. 6. Plot of particle size and zeta potential against pH for (a) TiO₂ and (b) Fe₃O₄ colloids.

toward the end of the observational period. This explains the reduction of the solution turbidity indicating that gravity driven sedimentation dominates which causes larger agglomerates to settle down. It is also shown that hydrodynamic diameter for hybrid colloidal aggregates remains close to their single element counterpart (Al₂O₃, TiO₂ and Fe₃O₄) which justifies the ability of Al₂O₃ nanoparticles to interrupt the growth of negligibly charged colloids and consequently prolonged their stability. These findings indicate that the binary system demonstrate similar sedimentation behavior relative to the highly stable single element colloids.

As given in Fig. 10, plots of zeta potential against time for all mixtures show that the magnitude remains relatively constant throughout the prescribed 30 days period. This also confirms the

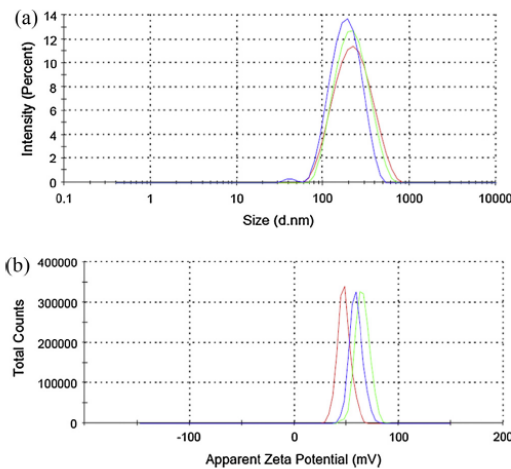


Fig. 7. Results of (a) size and (b) zeta potential distribution for Al₂O₃ (Blue line), TiO₂ at pH 4.3 (green line) and Al₂O₃-TiO₂ at pH 6.5 (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fact that the charge potential of the particles continue to remain strong. In general, the figure show that the zeta potential of the binary mixtures increases with increasing ratio of Al₂O₃ which adopt similar trend as the previous study by Tohver et al. [17]. The magnitude of each hybrid complexes is higher in comparison to the weakly charged colloidal solution in the absence of Al₂O₃ nanoparticles (Fig. 6). Further, the effect of Al₂O₃ concentration is more prominent in Al₂O₃-Fe₃O₄ binary system due to the additional dipole-dipole moment within Fe₃O₄ particles that generate more attractive force. This interaction consequently leads to the formation of bigger agglomerates, thus require much higher amount of dispersant to remain in suspension. This phenomenon suggests that highly charged nanoparticles play a prominent role in stabilizing negligibly charged colloidal aggregates and impede further contact by forming a hypothetical shield surrounding the colloidal parameter.

It is interesting to note that each combination of hybrid mixture shows much lower magnitude of zeta potential relative to the individual Al₂O₃ nanoparticles, indicating that electrostatic interaction manifest between participating elements which tailor the overall charge intensity of the binary system. Further, the plots show that, for 1:3 weight ratio, the zeta potential magnitude of Al₂O₃-Fe₃O₄ complexes is much lesser than that of the Al₂O₃-TiO₂ counterpart. This is expected since the zeta potential value for Fe₃O₄ and Al₂O₃ colloids at specific pH differs due to the difference in surface charge density for different material. Further, as highlighted by Liu and Luijten [31] and further verified by others [44,54], apart for the nanoparticle volume concentration, zeta potential difference between interacting particles also determines the strength of the halo formation and the binary mixture as a whole. Nevertheless, the fact that the zeta potential plots of both hybrid colloidal mixtures remain within the stable region suggests that these complexes possess rather identical characteristic and aggregation behavior reminiscent to the single element highly charged colloids of Fe₃O₄ and TiO₂. In summary, zeta potential and particle size measurements serve as effective tools to describe the stability of binary mixture particularly within a system containing weakly charged colloids. The results provide promising avenues on the ability highly charged nanoparticle to alter aggregation structure

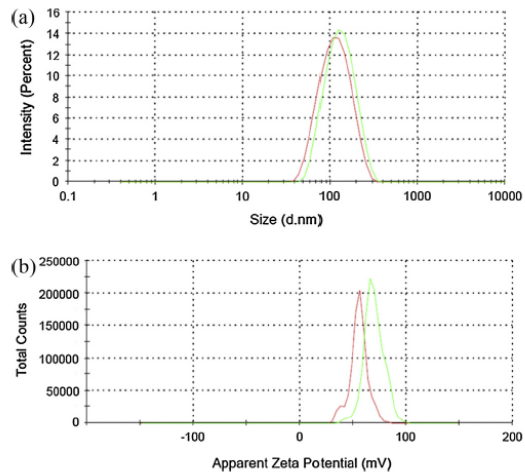


Fig. 8. Results of (a) size and (b) zeta potential distribution for Al₂O₃-Fe₃O₄ at pH 6.5 (red line) and Fe₃O₄ at pH 4.3 (green line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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