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A novel approach for the preparation of nanosized Gd₂O₃ structure: The influence of surface force on the morphology of ball milled particles

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**CHAPTER 5: A NOVEL APPROACH FOR THE PREPARATION OF
NANOSIZED Gd₂O₃ STRUCTURE: THE INFLUENCE OF SURFACE FORCE ON
THE MORPHOLOGY OF BALL MILLED PARTICLES**

Due to copyright reasons, Chapter 5 has been omitted from this version of the thesis.

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CHAPTER 5: A NOVEL APPROACH FOR THE PREPARATION OF NANOSIZED Gd₂O₃ STRUCTURE: THE INFLUENCE OF SURFACE FORCE ON THE MORPHOLOGY OF BALL MILLED PARTICLES

5.1. Introduction

Recently, nanoscale and submicron-sized structures of gadolinium (Gd) based compounds, especially Gd₂O₃, have attracted considerable attentions from both scientists and manufacturers due to their special optical and magnetic characteristics [31,35,90]. In application, they are used as fluorescent, luminescent materials for optical glass, plasma display panel of television tube and as radiation sensors and detectors [31,38-40]. Gd₂O₃ can also be used as a clean cooling source for magnetic refrigerators or as a data storage place of computer bubble memory owing to its excellent magneto caloric properties [41-43]. The most important applications of nanosized gadolinium oxide are in medical areas. Because of its safe properties in clinical uses, gadolinium oxides can be used as a gamma absorber and a source in cancer radiation therapy, magnetic resonance imaging contrast agents, magnetic targeting drug carrying, and recently proposed as radiation shielding material for X-ray diagnosis [7,36,44-49,69].

Wet chemical synthesis is the most popular liquid state method to synthesize nanosized Gd₂O₃ particles [139-144]. In this method, Gd compounds with solid state structure are generated from chemical reactions and the reaction yield is controlled by multiple factors such as the concentration and purity of reactants, pH value, temperature, pressure and so on. The product particle size is determined by the parameters that control the nuclei growth such as the external surfactants, thermal decomposition or hydrothermal supporting techniques [43,116,139-147]. Therefore, wet chemical synthesis is a complicated method with low yield, which prevents mass production. Mechanochemical approach employing solid-state reaction during high-energy ball milling process is also used to produce fine Gd₂O₃ particles. Tsuzuki, et al. successfully synthesised nano- and submicron-sized cubic and platelet Gd₂O₃ particles via the reactions between gadolinium chloride (GdCl₃) and sodium hydroxide (NaOH) or calcium oxide (CaO) powder in milling process followed by post heat treatment [158,159]. Unfortunately, there exist many by-products in the reaction from the stoichiometry such as NaCl, CaCl₂ or residual amount of reactants such as NaOH, GdCl₃, CaO, which result in impure substances of the final products [158,159]. In contrast, the top-down mechanical

technique without chemical reactions, such as ball milling, is an effective and low cost method of producing relatively large quantity of fine particles from bulky brittle materials [148-152]. However, this approach has experienced difficulty in producing nanosized gadolinium compounds particles because it completely depends on the nature of material used including physical, mechanical and chemical characteristics [1,153-156].

Gadolinium oxide, being malleable and magnetic, is difficult to mill to nanoscale just simply by ball milling [160-164]. This work reports that an addition of inert NaCl can reduce the size of Gd_2O_3 by attrition and prevent the resulting refined particles from aggregation during the milling process [163]. The inert NaCl could be removed by repetitively washing with distilled water, settling the flocculated particles out and decanting the supernatant NaCl solution. The control of particle-particle interaction and flocculation morphology by using specific polyelectrolyte additives at a distinct surface chemistry condition can stabilize ultrafine dispersion and also support the reproduction of ultrafine grained powder [76]. Although, many studies have used surfactants to control the nuclei growth from reaction, no study has incorporated milling process and colloidal phase study to form Gd_2O_3 nanopowder [139-144]. Anionic sodium dodecyl sulfate (SDS) and cationic cetyltrimethylammonium bromide (CTAB) polyelectrolyte, which are the most widely used in both fundamental scientific studies and industrial products, were employed in this work for investigate their influence on the morphology of Gd_2O_3 in aqueous medium. Additionally, a model is developed to clarify the variation of Gd_2O_3 morphology due to the effects of these surfactants.

5.2. Materials and method

5.2.1. Materials

Premilled gadolinium (III) oxide (Gd_2O_3) powder with a purity of 99.99% with size distribution of $d_{10} = 0.28\mu m$, $d_{50} = 4.34\mu m$ and $d_{90} = 10.6\mu m$, was purchased from Alfa Aesar (United Kingdom). Sodium chloride crystals (NaCl, 99%), sodium dodecyl sulfate (SDS, 99%), cetyltrimethylammonium bromides (CTAB, 99%) and potassium hydroxide pellets (KOH) (85%) were supplied by Aldrich Sigma. Nitric acid solution HNO_3 (40%) was from Chem Alert.

5.2.2. Method

A mixture with 1:1.5 weight ratio of Gd_2O_3 : NaCl was loaded together with harden steel balls (12.5 mm in diameter) in a SPEX 8000M mixer/mill model. The milling with the ball-to-powder weight ratio of 2.8:1 was performed for 70 minutes at room temperature. The washing procedure using deionized water was conducted repetitively for 4 times by dissolution of 100g mixture in 1000g water in a 2-litre beaker. An amount of 2g NaOH pellets was added for the following two reasons. First, NaOH at this dilute level provided mild washing of the particle surface from any adsorbed anionic impurities [172,180-182]. Second, the alkali pH of this solution enhanced the flocculation of the of Gd_2O_3 particles as in this pH region the charge density of these particles is low. The conductivity of upper water layer of cleaned slurry at the end of washing procedure was less than 0.5mS/cm or the concentration of remained NaCl was less than 0.005M [172]. To increase the particle concentration to solid volume fractions (ϕ_s) of 0.30, the washed slurry was separated in a Sigma 2-6 centrifuge (Germany) at 2000 rpm for 15 minutes. The solid concentration was determined by evaporating of a small sample (2 g) of the slurry in an oven for 5 hours at 110 °C

Distilled water was added into centrifuged pristine slurry to create 260ml Gd_2O_3 suspension at solid volume fraction to 0.003 for zeta potential-pH characterization (Colloidal Dynamic Zeta Probe). A Branson sonifier was used to disperse this suspension for 1minute set at 70% amplitude prior to zeta potential measurements. The KOH (0.7 M) and HNO_3 (0.7 M) solutions were used to adjust the pH of the slurry.

Three green samples each containing 30g of centrifuged Gd_2O_3 slurry (solid volume fraction $\phi_s=0.30$) were diluted with 1.91g of distilled water to create slurry at $\phi_s=0.25$. The pH of Gd_2O_3 modified by sodium dodecyl sulfate (Gd-SDS) suspension was adjusted to 8 by adding 1M HNO_3 , then it was added with 0.023g SDS (0.1 dwb% (dry weight basis percentage) of SDS/ Gd_2O_3). Similarly, the pH of Gd_2O_3 modified by cetyltrimethylammonium bromide (Gd-CTAB) slurry was adjusted to 12.5 using 1M KOH, then 0.023g of CTAB (0.1 dwb% of CTAB/ Gd_2O_3) additives was added for surface modification. Dispersion of the particles in solution using Branson sonifier (70% amplitude) was conducted for 2minutes before and after adding surfactants, and theses dispersions were rested for at least a day prior to any measurement. The pH of sample with unmodified milled Gd_2O_3 (unmodified Gd) was adjusted to 8 then it was sonicated at 70% amplitude for 2 minutes.

The yield stress-pH behaviour at $\phi_s=0.25$ of unmodified Gd, Gd-SDS and Gd-CTAB slurries was characterized using a Brookfield vane viscometer. Here, the KOH (0.7M) and HNO₃ (0.7M) were used to adjust the pH value. The vane of viscometer was submerged in the colloids and rotated at a slow rate of 0.4 rpm (revolutions per minute). The maximum values of torque as a function of time of suspensions were recorded and transferred to the shear yield stress at every pH interval. Such a plot of yield stress – pH was used to describe the change in attractive force of surface unmodified and modified crushed Gd₂O₃ in distilled water [173]. The particle size distribution of samples was analyzed by laser diffraction (Malvern Mastersizer Microplus Particle Size Analyzer) to explain the change of Gd₂O₃ particle size in aqueous medium under the effect of surfactants. This technique assumes the particles are spheres.

The samples of unmodified Gd, Gd-SDS and Gd-CTAB were also annealed at 110 °C for 12 hours. The structural characteristics of these samples were examined by scanning electron microscopy (SEM) using a Zeiss 1555 VPSEM microscope and X-ray diffraction (XRD) using a PANalytical EMPYREAN diffractometer with Co K α radiation ($\lambda= 0.1789\text{nm}$).

5.3. Result and discussion

Figure 5.1 A-D shows the SEM micrographs indicating the effect of cationic and anionic surfactants individually on the morphology Gd₂O₃ after ball milling. Figure 5.1B shows the presence of particles with a range of shape; the most majority of particles are cylindrical, some are spherical and a few are cubic for milled unmodified Gd₂O₃ particle. CTAB surfactant causes the Gd₂O₃ particles to agglomerate into large aggregates (Figure 5.1C). In contrast, as seen in Figure Figure 5.1D, the milled Gd₂O₃ particles modified with SDS displays morphology of well-defined uniform 2D nanowire with an average size of approximately 400nm in length and 20nm in diameter.

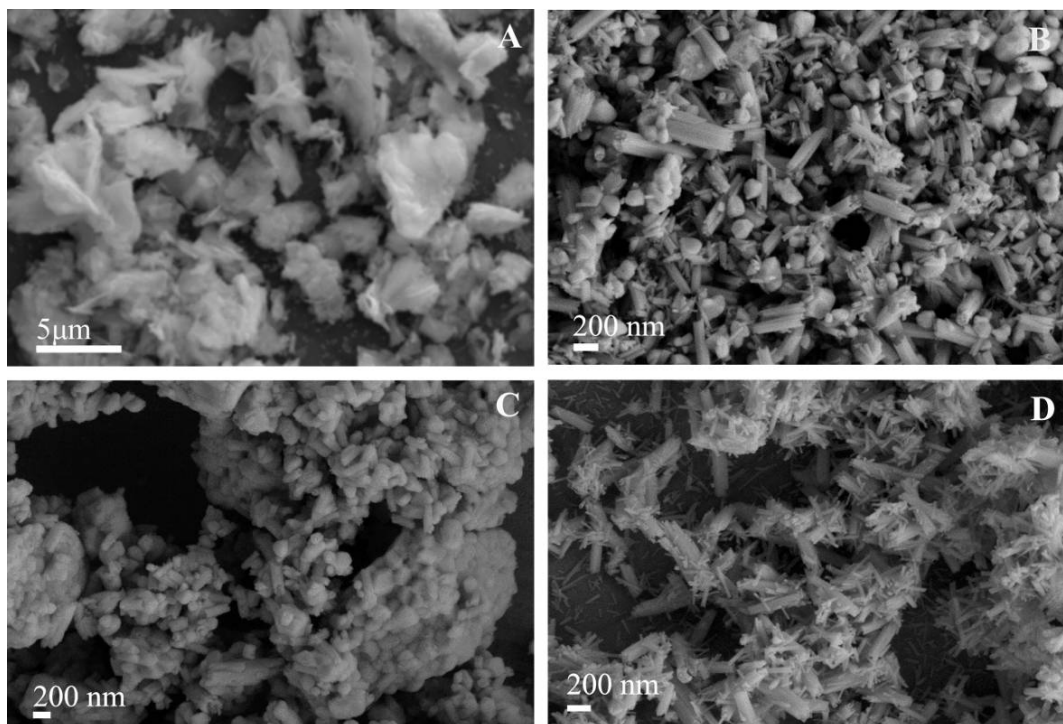


Figure 5.1. SEM images of: (A) premilled Gd_2O_3 , (B) ball-milled unmodified Gd_2O_3 , and (C) and (D) the ball-milled modified Gd_2O_3 under the effect of CTAB and SDS surfactants respectively.

The size distributions of milled Gd_2O_3 particles in aqueous medium before and after surface modification with surfactants are shown in Figure 5.2. The Gd_2O_3 modified with CTAB denoted as Gd-CTAB shows the highest content of coarse particles and its size distribution is the broadest among the three. The particle size of the Gd_2O_3 modified with CTAB ranges from 0.1 to 7.4 μm . The unmodified oxides appear to have the least amount of the coarse materials with a size distribution ranging from 0.1 to 2.6 μm . The Gd_2O_3 with adsorbed SDS or Gd-SDS displays the same size range. The nano-sized rods materials seen in the SEM (Figure 5.1D) are not captured in the size distribution characterization. It is possible that the size given in terms of an equivalent spherical diameter may not be valid for rod-like or needle-like materials or that the volume fraction of these very fine materials being too small to be measurable.

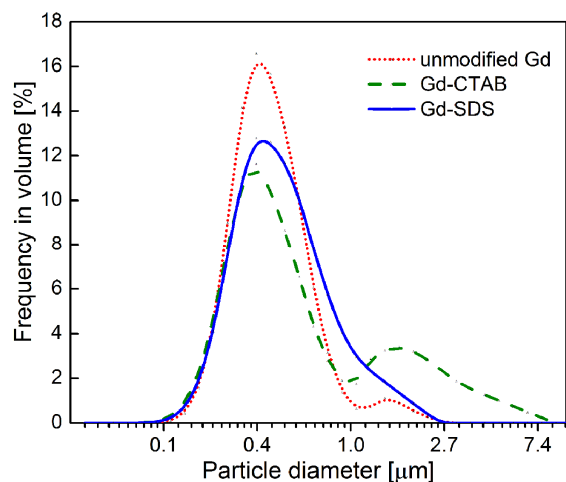


Figure 5.2. Size distribution by frequency in volume (%) of unmodified and modified Gd_2O_3 suspension.

The increase in the fraction of coarse particles by CTAB is consistent with the result of the SEM image (Figure 5.1C). The strong hydrophobic interaction of the adsorbed CTAB is responsible for the particle agglomeration. Adsorbed SDS also gives rise to hydrophobic interaction in suspension but this interaction should be much weaker due to a shorter alkyl chain length [196]. This hydrophobic interaction does not cause strong particle agglomeration thereby resulting in a large amount of fine rod particles being seen in the SEM image (Figure 5.1D).

The XRD patterns of the annealed unmodified Gd and modified by SDS and CTAB (Figure 5.3) show the same pattern of pre-milled commercial Gd_2O_3 (99.99%) [197,198]. No additional peaks of other substances are observed. Therefore, all the annealed unmodified Gd and modified by SDS and CTAB are mainly Gd_2O_3 phase, according to the standard pattern for Gd_2O_3 phase (JCPDS 12-0797). This implies that no unexpected reaction between gadolinium oxides and other chemicals occurs during grinding, washing and modifying procedure. It is clear that the change in the morphology of milled particles (Figure 5.1B-D) is mainly attributed to the surface force and particles interaction arising from adsorbed surfactants in colloidal slurries.

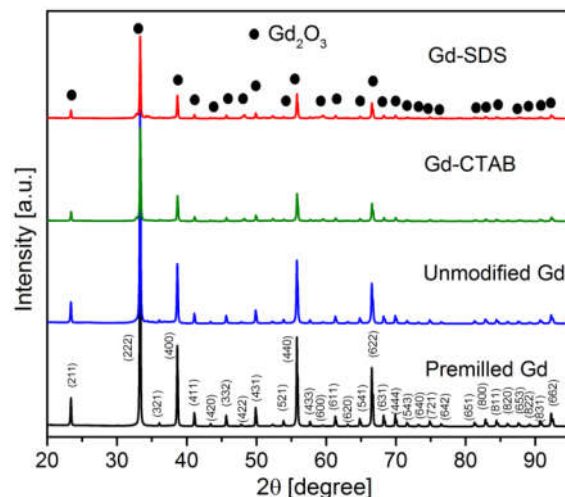


Figure 5.3. XRD patterns of ball milled Gd_2O_3 particles under the effect of surfactants modified SDS, modified CTAB and unmodified milled, and commercial or premilled Gd_2O_3 (99.99%)

Small particles with diameter of less than $1\mu m$ in aqueous medium normally carry electric charge and tend to approach one another under Brownian motion [199,200]. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, when kinetic energy of the colliding particles is high enough to overcome the energy barrier arising from the electrostatic repulsive force, the van der Waals attractive force dominates and makes the particles adhere strongly together. This leads to flocculation or coagulation and hence increasing the size of the colloidal aggregates [172,196,199]. If only the DLVO forces are in play then the stability of the nanosize and submicron-size particles in water is determined by the electrostatic or double layer repulsive forces being much stronger than the van der Waals attractive forces [172,176,199,201]. In this case flocculation of colloidal particles is resisted producing a stable colloidal suspension [201,202]. Zeta potential and yield stress are two indicators of the stability of colloidal dispersions [69,172,199]. A high magnitude of the zeta potential indicates a strong repulsion, and a stable suspension is produced. Meanwhile, the value of yield stress is an indication of the magnitude of the attractive forces acting between particles in dispersion [69,172,199]. A very high yield stress means a strong attractive force being present [172,199]. In addition to van der Waals, there are a range of non-DLVO attractive forces such as hydrophobic, bridging by adsorbed additives, patch charge and hydrogen bonding of function groups of adsorbed additives [203,204].

Figure 5.4A presents a sigmoid relationship with a negative slope between zeta potential or electrostatic charge and pH of premilled ($d_{50}=4\mu\text{m}$) and milled Gd_2O_3 ($d_{50}=0.38\mu\text{m}$). Reduction in particle size by attrition with the inert NaCl from high-energy ball milling increases the surface area to volume ratios of the particles. The subsequent mild alkali and NaCl washing removes the adsorbed impurities or ensure that the new surface is free of adsorbed anionic impurities. As a result, the point of zero zeta potential shifts from pH 9.6 to pH 11 [156]. Additionally, while the inverse S curve of pre-milled powder is symmetrical pattern between positive and negative branches, the corresponding curve of milled particles indicates a prominent high positive charge region in the low pH region, i.e. below pH 9. The high magnitude of the zeta potential suggests that strong repulsive interaction is operating between particles. This leads to a completely dispersed suspension being produced in this low pH region.

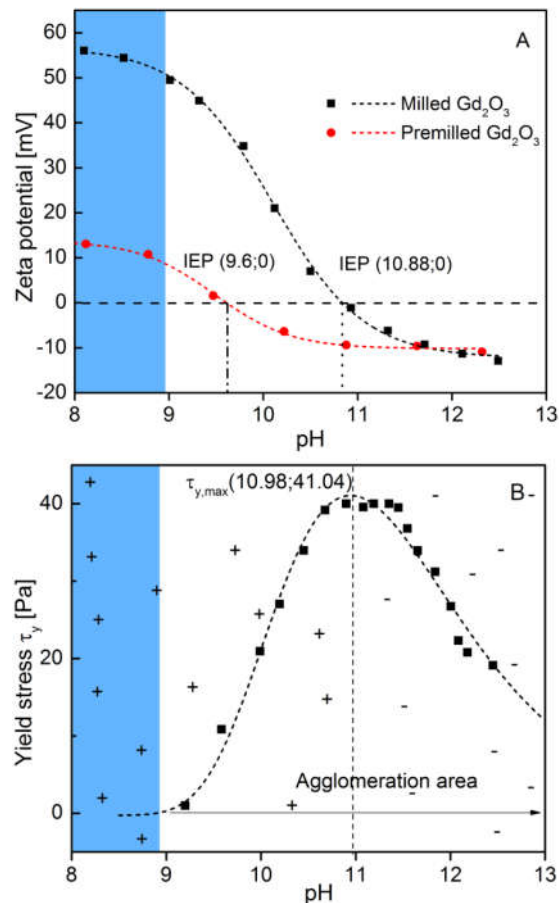


Figure 5.4. (A) The zeta potential and (B) yield stress of milled Gd₂O₃ suspension, describing the change in the surface charge and dispersed-agglomerated state of milled Gd₂O₃ suspension.

At pH greater than 11, the negative charge region displays low negative zeta potential. This suggests that attractive force dominates in the high pH region (pH > 11). This pattern agrees with an asymmetrical bell curve of yield stress in Figure 5.4B which shows that yield stress decreases significantly in the pH range of pH < 11 and quickly reaches to zero at pH ~ 9. Meanwhile, the yield stress in negative branch is still high at pH of 13. As can be seen in Figure 5.4 A-B, the flocculated region of this milled and washed Gd₂O₃ ranges from pH 9.5 to greater than 13. Van der Waal attractive force therefore dominates from pH 9.5 to more than pH 13 and the repulsive force dominates at pH below 9.

Figure 5.6 shows the effect of anionic SDS and cationic CTAB agents with carbon chain length of 12 (C12) and 16 (C16) respectively on the yield stress-pH of Gd₂O₃ suspension ($\phi_s = 0.25$). The adsorption of SDS and CTAB on Gd₂O₃ surface increases the yield stress significantly. This is characterized by large increase in maximum yield stress ($\tau_{y, \max}$). Compared with the unmodified Gd sample with maximum yield stress ($\tau_{y, \max}$) of ~41.4 Pa, the addition of a small amount of 0.1 dwb% of CTAB and SDS results in a 4-fold and 32-fold increase in maximum yield stress, respectively. The large yield stress in the present surfactants is due to the presence of an additional attractive force. This attractive force which is much stronger than the van der Waals force is the main contributor to $\tau_{y, \max}$ [98,185,196]. This attractive force results from the hydrophobic effect of long carbon tails (>7) of two surfactants CTAB and SDS [98,185,205]. Although alkyl chain length of CTAB is 4 carbons longer than SDS, the hydrophobic interaction from CTAB contributes to lower maximum yield stress than SDS (Figure 5.5). This is attributed that the CTAB modified Gd particles produce much stronger hydrophobic interaction thereby leading to agglomeration of the particles in the high pH region. Such large agglomerated particles reduce the concentration of particles for interaction and hence weaken the network structure. However, the presence of CTAB still strengthens interparticle attractive force and this leads to smaller increase in the maximum yield stress compared to the unmodified Gd particle suspension [183,206].

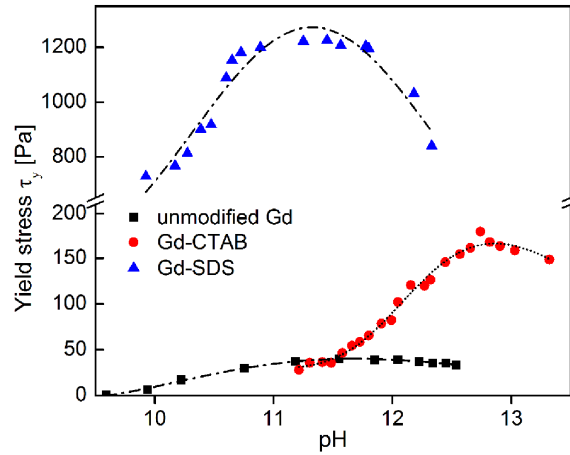


Figure 5.5. The relationship between yield stress and pH value of Gd_2O_3 suspension.

According to the above observations, a schematic illustrating the change in morphology due to the effect of surfactants is interpreted as Figure 5.6. Surfactants are surface-active agents having a hydrophilic head and hydrophobic alkyl tail. While CTAB surfactant gets positively charge on the hydrophilic ammonium group and an alkyl tail of 16 Carbon, anionic SDS surfactant contributed by negatively charge on hydrophilic sulfate group and a hydrophobic tail of 12 Carbon. CTAB is adsorbed onto the negatively charged patch of Gd_2O_3 particles in the pH range exceeding 11 and keeps its hydrophobic end away from the surface. In contrast, SDS is adsorbed onto the positively charged particles in the pH range less than 11.

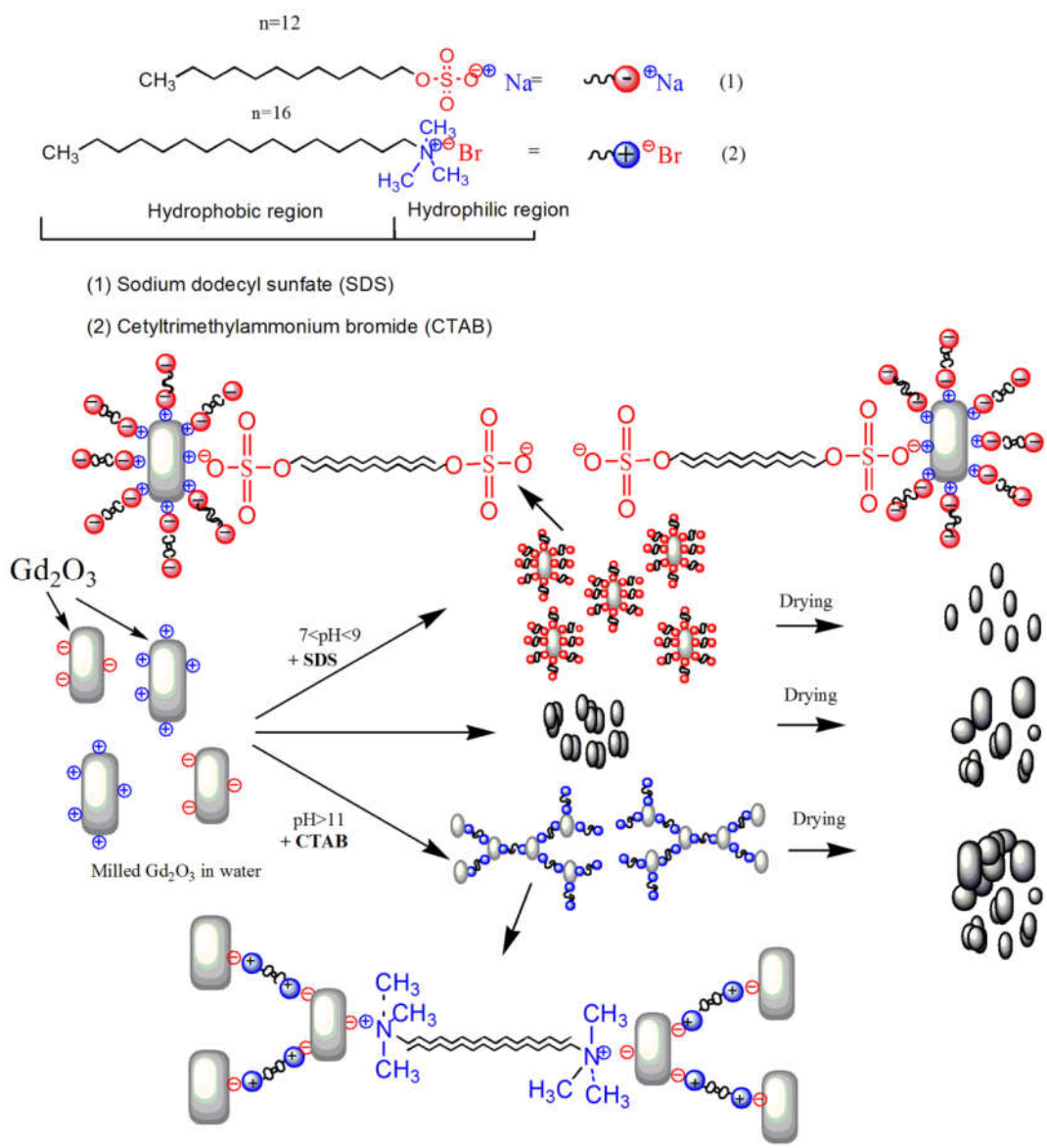


Figure 5.6. Schematic illustration explaining the possible formation mechanism of dried ball milled Gd_2O_3 particles under the effect of surfactants

The high positive zeta potential suggests the presence of high concentration of positive charge sites for SDS to adsorb. This should increase the extent of SDS adsorption stabilizing the smaller particles via steric and charge stabilization. Therefore, the pH of suspension is adjusted to 8 to adsorb SDS. The low negative zeta potential at pH above the point of zero charge suggests a low amount of negatively charge sites available for CTAB adsorption. Adsorption of CTAB or its dimer with the two head groups locate on the opposite

ends of dimeric molecule does not lead to charge or steric stabilization as the amount adsorbed is too low. Particle bridging as a result of low surface coverage of CTAB is a real possibility causing particle agglomeration. The particle morphology is thus evaluated at pH 12.5 for the CTAB modified Gd particles. Sonication was conducted to physically separate the fine particle before addition of surfactants. Unfortunately, the low negative charge of suspension in this pH suggests that the aggregation of the particles is inevitable. Therefore, larger aggregated particles are coated and bound by CTAB. In contrast, a dominance of electrostatic repulsive force at pH less than 9 allows single fine particles to be covered by SDS surfactant. Centrifugal or annealing process increases kinetic energy and reduces the distance between the particles hence increasing the particle size and altering particle shape undergoing agglomeration and coagulation. However, after surface modification, carbon tails of surfactants establish a thin organic layer around particles which is sufficient to keep particles separately [156,205]. As a result, SDS surfactants stabilize the milled Gd₂O₃ in suspension at low pH producing relatively homogeneous nanowire Gd₂O₃ powder.

5.4. Conclusion

This work provides a schematic illustration clarifying the mechanism responsible for the morphology change of the ball milled unmodified and modified Gd₂O₃ particles. The interaction between electrostatic repulsive and attractive force via the zeta potential-pH data can explain very neatly the yield stress-pH behaviour of milled and washed Gd₂O₃ suspension. An additional attractive force due to hydrophobic effect is invoked to explain the large increase in the maximum yield stress by SDS- and CTAB-modified Gd₂O₃ suspensions. Here, the external attractive force due to hydrophobic effect and the extent of surface coverage of adsorbed surfactant indicated by the bare charge density of the particle are the key factor influencing the morphology of final dried Gd₂O₃ particles modified by surfactant. SDS-stabilized Gd₂O₃ particles at pH 8 at high coverage produced stabilised fine nano-rod particles after drying. The organic SDS shell prevents the fine particles from re-welding during the dispersing, drying and sintering process. Due to this mechanism, the simplest, most cost effective, reproducible and high yield procedure for preparing 2D nanowires of gadolinium oxides is proposed as follows. First, the coarse micron-sized Gd₂O₃ powder is ball milled at weight ratio 1:1.5 of Gd₂O₃: NaCl and 2.8:1 of ball-to-powdery mixture for 70 minutes. Then, the removal of NaCl from mixture is carried out by dissolving in distilled water and small amount of NaOH. Afterwards, surface modification of the milled particles

using SDS (0.1% dwb) in water is conducted at the pH ~8 under sonication. Finally, centrifugation and annealing process at 110 °C are employed to produce high purity of Gd₂O₃ nanopowder from above suspension. The final product displays morphology of well-defined uniform 2D nanowire with an average size of approximately 400nm in length and 20nm in diameter.