

# SURFACTANT-ASSISTED BALL MILLING: A NOVEL ROUTE TO NOVEL MATERIALS WITH CONTROLLED NANOSTRUCTURE - A REVIEW

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**Abstract.** Controlled Structure nanomaterials have played important roles in the advancement of targeted drug-delivery, gene silencing, therapeutics, catalysis, water purification and optoelectronics. These are probably because of their convenient and versatile sizes and shapes, large specific surface area, desirable surface properties, high chemical reactivity and physical affinity as well as attractive opto-electrical and electro-magnetic properties. However, the synthesis of materials with controlled micro/nano-structures and desired surface properties have been remaining a challenging task. Various approaches have been proposed for the commercial production of nanostructured particles from solid state. Chemical methods to synthesis controlled nanostructured nanoparticles from rare-earth solid compounds have numerous limitations. Recently, surfactant assisted high energy ball milling has been exploited for the synthesis of various nanomaterials, nanograins, and nanocomposites from solid bulk materials. Promising results have been obtained in terms of nanostructure assembly, micro/nano-environment, surface functionalities and dispersion. In high-energy ball milling, plastic deformation, cold-welding and fracture predominantly contribute to bring a change in size, shape and microenvironment of nanoparticles. This review systematically presented the basic concept and applications of surfactant assisted mechanical milling in the synthesis of various nanomaterials and nanocomposites.

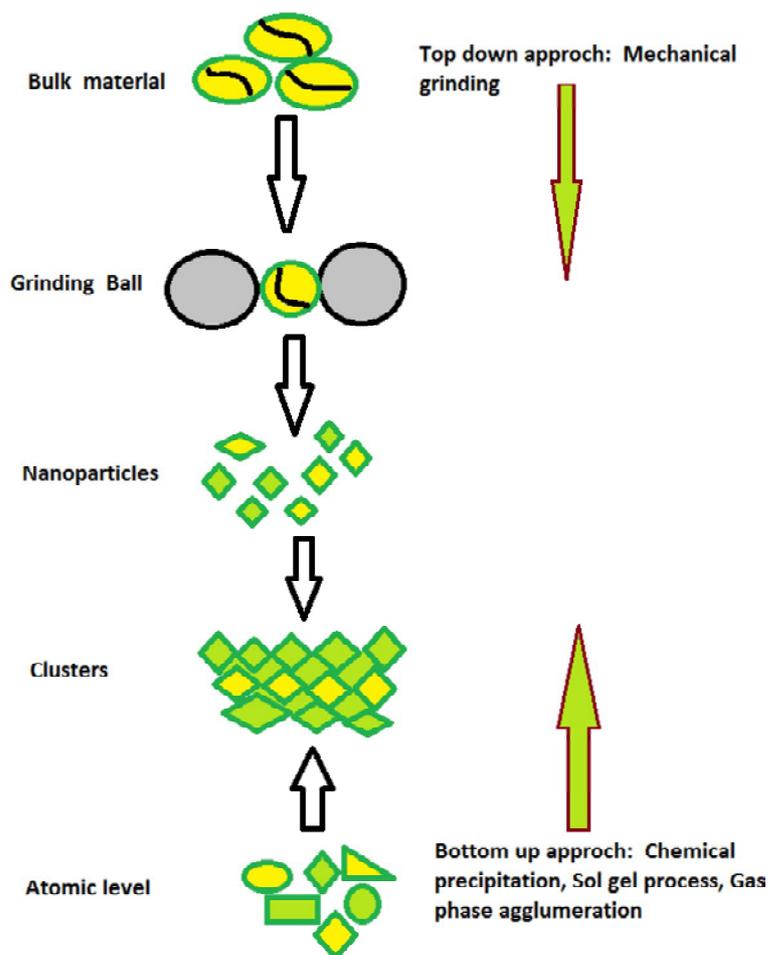
## 1. INTRODUCTION

Recently, synthesis of nanoparticles have received huge attention from various corners because of their high surface to volume ratios, attractive electronic and optoelectronic properties, and suitable sizes and shapes for various applications including green catalysts, green adsorbents, targeted drug delivery, sensors and chips, biomedical imaging [1,2]. Both bottom up and top down approaches (Fig. 1) have been proposed for the size and shape controlled synthesis of nanoparticles [3]. The bottom up approach starts with atoms, ions or molecules as building blocks and assembles them into nanoscale clusters with molecular or atomic precision [4]. In contrast, a top down approach involves decomposition

of bulk solid materials into nanoscale regimes using a mechanical force in the presence or absence of a catalyst [4]. Precise control of size and shape is not obvious using a top down approach [5]. However, it is a fast and suitable method for large scale production in industry [5].

The reduction of particle size by high energy ball milling is termed as mechanical milling [6]. The method was developed in 1970 by John Benjamin and was used to synthesize oxide dispersion strengthened (ODS) alloys capable of withstanding high temperature and pressure [7]. In this process, particle size was reduced along with the generation of new phases and surface properties [8]. The operation is performed by placing a suitable powder in

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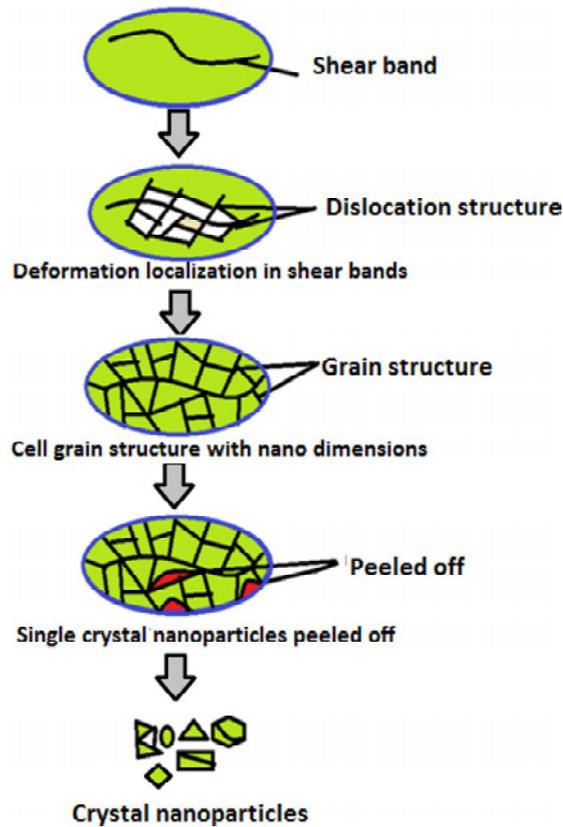
**Fig. 1.** Schematic representation of a typical top down and bottom up approach for nanoparticle synthesis.

a suitable medium in a high energy ball mill where the balls roll down the surface of the chamber in a series of parallel layers and energizes the powder during the milling process. Various factors including nature of powder, type of mill, milling speed, size distribution of ball, dry or wet milling, temperature of milling and duration of milling regulate this energy transfer process. The periodic fracture and coalescence events continue throughout the milling process [9,10]. In the long milling process, the particle size becomes larger than their primary particle due to agglomeration [11]. These particles have strong tendency to agglomerate owing to having large specific surface area and other properties. Surfactants play crucial role to prevent this close contact of the fine particle by providing steric barrier and reducing surface tension [12]. The surfactant molecules form a thin organic layer around the newly formed surfaces to protect the exposed surface from cold welding when they come into contact with another surface during the milling process. The powder surfactant ratio brings new properties in the structure, morphologies and features of the final prod-

uct [13-15]. This surfactant assisted mechanical milling is an economical process for the production of large scale controlled size particle. In this review, we have highlighted the mechanism of ball milling and role of various surfactants for the large scale synthesis of controlled structure nanoparticles.

## 2. MECHANISM OF BALL MILLING

Ball milling is a powerful non-equilibrium processing method capable of producing dispersion strengthened alloys with fine microstructures as well as metastable structured materials [16]. The milling process, which can be either (1) mechanical milling or (2) mechanical alloying, refines the grain size of all solid elements into nanoscale [17,3]. The success of this operation depends on a number of process variables and properties of the milling powder. The minimum grain size can be obtained by a balance between the defect introduced by plastic deformation of milling and its recovery by thermal cases [18].



**Fig. 2.** Schematic representation of ball milling mechanism for the formation of crystalline nanoparticles.

Fecht *et al.* (1990) [19] first described the mechanism of formation of nano crystalline materials by mechanical milling in three stages. In stage 1, the particles were subjected to deformation localization in shear bands that resulted in high dislocation density. Stage 2 produces cell/sub grain structure with

nano scale dimensions through dislocation annihilation, recombination or rearrangement. It might be considered as a self assembly that forms dense dislocating arrays in the sub grain boundaries to lower the energy of the system. In Stage 3, the orientation of the grain becomes random. The high angle grain boundaries replace the low angle grain boundaries by boundary rotation or sliding. Finally, the grain boundaries near the sample edge are broken and single crystals nanoparticles are peeled off the edge of the samples (Fig. 2). The rod shape particle may be evolved through anisotropic growth mechanism [19]. Lie *et al.* (1992) proposed a model for the reduction of grain size during high energy ball milling using the following relationship [20]:

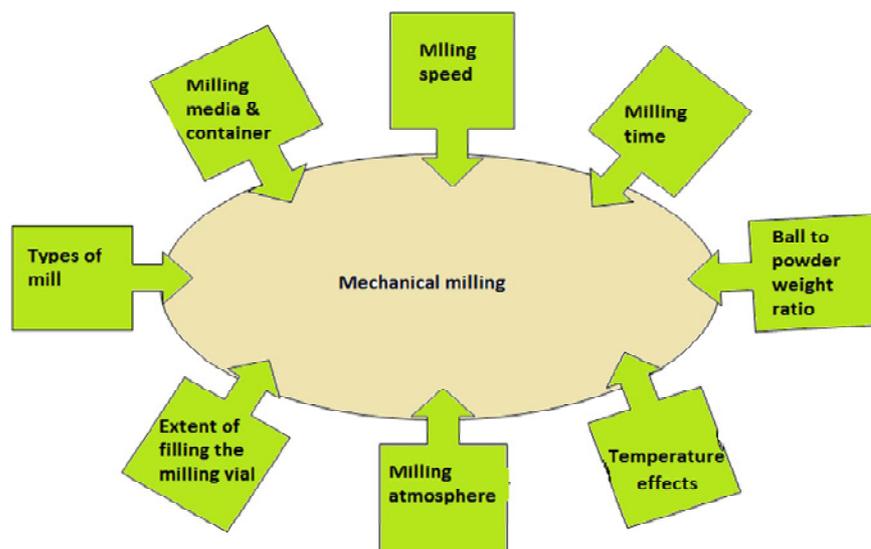
$$d = kt^{-2/3},$$

where  $d$  is grain diameter,  $t$  indicates milling time and  $k$  is constant. This hypothesis was based on the assumption that the particle size reduction was due to shear band formation.

The main advantages of ball milling include large scale production of high purity nanoparticles with improved physical properties in a cost effective way. The ball milling treatments can also bring new properties to the matter depending on the grain size and materials composition [21].

### 3. INFLUENCING FACTORS IN THE MILLING PROCESS

Different variables responsible for obtaining optimum product phase or microstructure are shown in (Fig. 3) and are discussed in the following texts.



**Fig. 3.** Factors influencing the milling process.

**Table 1.** Different types of ball mills and their applications with shortcomings.

Types of ball mills	Major application	Shortcomings	References
Vibratory ball mills	Preparation of very fine powder	Poor yield	22
Tumbler ball mills	Large scale production of commercial alloys	Consumption and wastage of huge energy: only 20% of the consumed energy is utilized in comminution and the rest is wasted	23,32
Planetary ball mills	Laboratory based nanoparticle synthesis	Insignificant for large scale production	25,31
Jet mills	Produce particle sizes between 1-10 $\mu\text{m}$ and are widely used in pharmaceutical and mineral industries	Consumption and wastage of huge energy: only 2% of the energy supplied is used for particle breaking	33, 34

### Type of mills

Recently, ball milling process is performed in different types of high energy ball mills such as vibrator mills, planetary ball mills, attritor mills, tumbler ball mills etc. Among them, the vibrator and planetary mills have been used for the processing of small amount of materials (less than 100 g) within a short span of time. On the other hand, the attritor mills can process higher quantities of powders (between 100 g and 10 kg) and takes several hours for the large scale production of nanoparticles in commercial premises [22]. Tumbler mills are more economical than the high energy ball mills for the large scale synthesis [23]. On the other hand, vibration mills are frequently used for synthesis of very fine powders [22]. However, it is no longer attractive because of its poor yield [24]. Nowadays, planetary ball mill are used for research purposes [25]. Several research groups have already designed their own ball milling devices depending on the needs. For example, Nanotech uniball mill, which is widely used at present, was developed by Australian Scientific Instruments (Canberra, Australia). This ball mill consists of a stainless steel horizontal cell with hardened steel balls [26,27]. In addition to the above mills several other mills such as rod mill, modified rod mill, a single large ball in a vibrating frame mill and other specially designed mills have been developed following mechanical milling operations [28-30]. Generally, the capacity of the mill, operation speed, temperature and contamination controls are taken into accounts while developing or selecting a ball mill for a particular operation [17]. The various types of ball mills along with their major applications and shortcomings are given in Table 1.

### Milling media and container

The composite of the inner milling container is important because materials may dislodge from the inner wall due to the impact of milling. Cross contamination might be avoided by using the same material for the grinding vessel and the grinding medium. The inner wall of the container should be thick and high enough to allow the ball to create high impact force on the grinding material [17]. Different types of materials, such as – hardened steel, tempered steel, stainless steel, chromium, tungsten carbide lined etc. are commonly used for the milling container. The internal design of the container also play important role during the milling process. Harring *et al.* (1992) [35] found that flat ended container are more efficient than the round ended ones for alloy formation. Most of the researchers use the same size ball for the milling medium. However, it has been assumed that different size of balls may produce the highest collision energy and thus produce fine particles. Therefore it is beneficial to use a combination of smaller and larger balls to randomize the effects of the balls. Additionally, the milling ball should be denser than the milling powder [36]. The milling media play key role to control the size of the particle. Dolgin *et al.* (1986) reported that the wet grinding process synthesise fine particles more efficiently than the dry grinding one due to the adsorption of the solvent on the newly formed particle surfaces, lowering the surface energy that prevents agglomeration [37].

### Milling Speed

In ball mill, increasing the rotation speed of the ball might pin down the ball, exerting no effects on the particle. Therefore, the milling speeds should be just

below this critical speed to keep the ball moving. Additionally, high speed yields high temperature that might contaminate the powder or re-crystallizes the nanoparticle [17].

#### **Milling time**

To obtain desirable results, powder should be milled for an optimal time. If the powder is milled longer than the required time, unwanted contamination and phase transformation might take place. The required milling time for a particular sample can be found based on the parameter such as type of mill, ball to powder ratio, temperature of milling and intensity of milling [38].

#### **Ball to powder weight ratio**

The ball to powder weight ratio (BPR) or charge ratio is one of the important variables for the milling operation. It plays significant effects on time required to obtain a fine particle from powder. The higher the BPR the shorter the time required. Different researchers have used the BPR as low as 1:1 to as high as 220:1 [39]. At high BPR, the collision of ball in the grinding medium increases per unit time, evolving more energy that lead to the phase transformation of the particle [17].

#### **Extent of filling the milling vial**

The fine powder particles produce due to impact forces exerted on them. For this action, milling vial should be 50% filled and 50% empty to allow the free moving of the milling ball and the powder particles around the chamber. If the quantity of the ball and powder particles is large, there will be not enough space for balls to move. This would produce less impact on powder particles. Thus special care has to be taken during the filling of milling machine with ball and powder [17].

#### **Milling atmosphere**

The milling atmosphere is one of the factors responsible for contaminating the milling powder. Generally, the milling chamber is evacuated or filled with inert gas such as argon or helium to avoid this contamination. Different atmosphere can be used in the milling media if particular effects are desired [17]. Nitrogen, hydrogen and air have been used to produce nitrides, hydrides and oxides in the powder [40].

#### **Temperature effects**

The temperature of the milling container depends on the characteristics of the milling powder, milling vessels and the kinetic energy of the milling ball. In the milling process, two types of temperature effects are usually taken into consideration: (1) local temperature arises due to collision and friction of the ball and (2) overall temperature in the milling container. The arising temperature induces diffusion

and defects in the milling powder followed by particle phase transformation. During the milling, one part of the powder is attached to the vial walls and the other part is attached to the balls, keeping the rest of the powder in free-state moving. All these three parts have different temperatures [17].

Reduction of particle size increases surface to volume ratios and brings new properties to particles surfaces which are very desirables for many technological operations. Generally, the milling process produce dry and liquid disperse particles with reduced size. The ball milling process has two opposite characteristics. Firstly, the large particles are broken down due to internal strained created by high pressure. Secondly, the fine particles agglomerate in order to reduce their surface energy and form a size larger than that of the primary particles [41]. Yadav and Srivastava (2012), synthesized pure spherical nanocrystalline CeO<sub>2</sub> powders (10 nm) using high energy ball milling in 30 h. When they further extended the milling process for 50 h, the particles started to agglomerate and a mixture of nanocrystalline and amorphous phases were obtained [42]. Particle agglomeration behavior was also observed by Tolia *et al.* (2012) in the synthesis of ZnS nanoparticle in a 10 h milling operation [43]. Particle contamination is another problem in the long hour milling operations. For example, extended milling time in a high energy shaker mill can result in >10% iron contamination in some refractory metal powders [44].

## **4. SURFACTANT ASSISTED BALL MILLING**

Surfactants are surface active agents having both hydrophobic and hydrophilic properties [45]. They can be classified as – anionic, cationic, zwitterionic and nonionic depending on the surface charge character of the hydrophilic group as shown in (Fig. 4).

The cationic surfactants adsorb onto the negatively charged surface through its positively charged hydrophilic head keeping its hydrophobic end away from the surface. Thus they constitute a new surface that repels polar solvents including water. A hydrophobic surface is also constituted when anionic surfactants bind to a positively charged surface. Depending upon the nature of surfaces, nonionic surfactants can adsorb onto the surface with either the hydrophilic or the hydrophobic group oriented toward the surface. Zwitter ionic surfactants owing to having both positive and negative charges can adsorb onto both a negatively charged and posi-

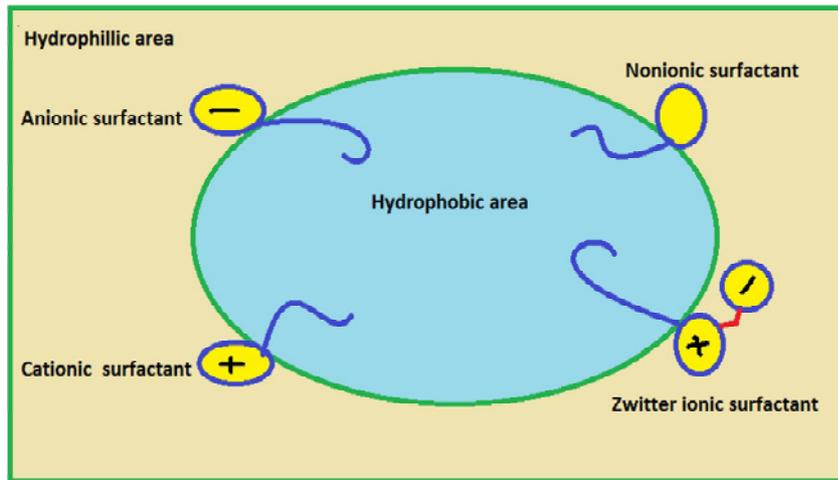


Fig. 4. Schematic representation of various surfactants.

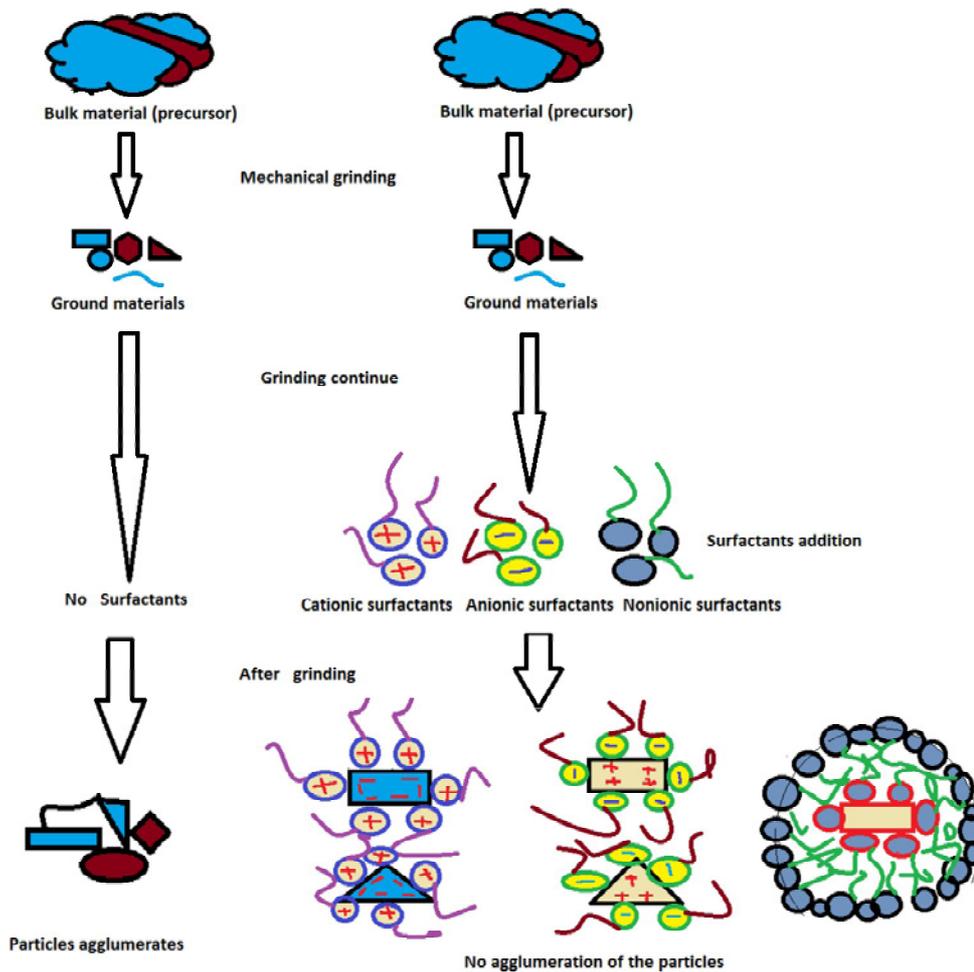


Fig. 5. Schematic representation of nanoparticle synthesis in the presence and absence of surfactants.

tively charged surface without significantly changing the charge profile of the surface [46]. Upon being adsorbed on material surfaces, surfactant molecules provide electrostatic and steric forces to stabilize the particles in milling media, minimizing the uncontrolled breakdown of particles [47]. Surfactant can also lower the surface energy of the freshly

formed fine particles by forming thin organic layer and introducing long range capillary forces that lower the energy for crack propagation. This prevents the particles from agglomeration and cold welding that substantially increase particle sizes in high energy ball milling operations [48]. The nature and quantity of the surfactant as well as the type of grinding

material determine the size, shape and purity of the final product. Increasing the surfactant volume normally reduces the particle size usually by a magnitude of the second or third order. For example, grinding of aluminum for 5 h with 1% steric acid resulted in 500  $\mu\text{m}$  particle. When surfactant volume was increased to 3%, the particle size was reduced to 10  $\mu\text{m}$  [49]. Fig. 5 represents the grinding effect in the presence and absence of surfactant.

## 5. EXAMPLES OF SURFACTANT ASSISTED SYNTHESIS OF NANOPARTICLES

The synthesis of rare-earth metal based nanoparticles has got huge attention because of their enhanced magnetic properties and essential role in the high technology industry such as computers, audio, video, and other consumer electronics [50-55]. However, the chemical synthesis processes (bottom up) of rare- earth compounds have many limitations including the controllability of size and composition. Furthermore, the rare- earth containing systems are very active and prone to oxidation which have made it difficult to prepare the monodisperse nanoparticles under ambient conditions [56,57]. In the last few years, different research groups have made some advancement in the synthesis of rare earth based nanostructure using surfactants assisted ball milling. Well stabilized rare earth intermetallic nanoparticles with smaller than 30-nm in diameter were obtained in presence of organic liquid and surfactants [21, 57-59].

Liyun Zheng *et al.* (2012) prepared  $\text{Sm}_2\text{Co}_{17}$  nanoparticles by surfactant assisted high energy ball milling from  $\text{SmCo}_5$  precursors, where oleic acid

and oleylamine were used as a surfactant. The synthesized nanoparticles were a mixture of single crystal and poly crystalline structures [60]. One step high energy ball milling of the precursor  $\text{SmCo}_5$  for 5 h in heptane in presence of oleylamine as surfactant produced single crystal spherical and rod shape nanoparticle with smooth edges. Increasing in milling time to 8 h produced a mixture of single crystal and poly crystalline nanoparticles. Here, the milling time had no effect on the particle size but had great influence on the crystalline microstructures. In contrast, when oleic acid was used as a surfactant in the milling process of 5 h, the resulted nanoparticles had triangle or rod shape edges and corners. The particles sizes were much smaller than those obtained with oleylamine. This was probably due to the different binding capacity of oleylamine and oleic acid [60].

$\text{Nd}_2\text{Fe}_{14}\text{B}$  nanoparticles of 15 nm in diameter were successfully synthesized from 40- $\mu\text{m}$   $\text{Nd}_2\text{Fe}_{14}\text{B}$  precursors under argon atmosphere using in 20 h high energy ball milling. Improved magnatocrystalline properties were obtained. However, when the milling was performed for 100 h, elongated nanorods with amorphous morphology were realized [61].

The molecular weight of surfactants has remarkable effect on morphology of the synthesized nanomaterials (Fig. 6) [62]. Valeric acid produced smaller nanoflakes (22 nm) in comparison to oleic acid and other higher molecular weight surfactants. The particle sizes and surfactant molecular weight showed proportional relation from stearic acid to valeric acid. This was probably due to the availability of increased number of molecules in low molecular weight surfactants which adhered on new surfaces during the milling operations resulting in

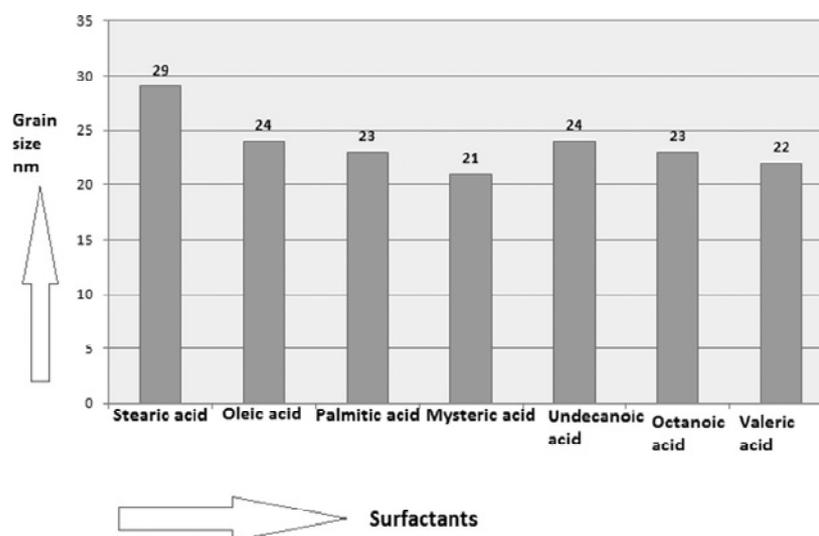
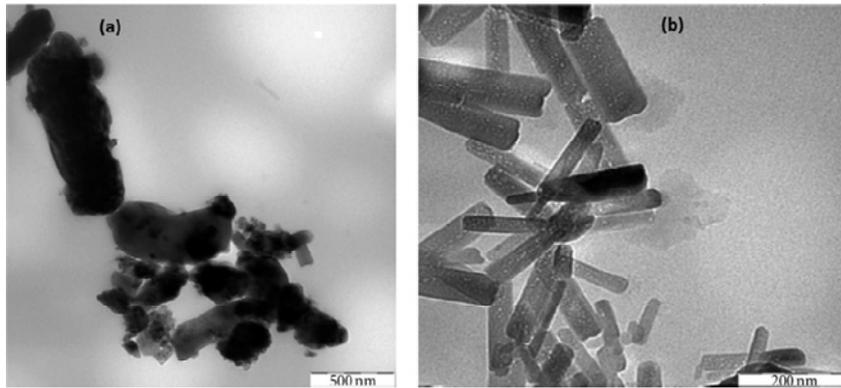
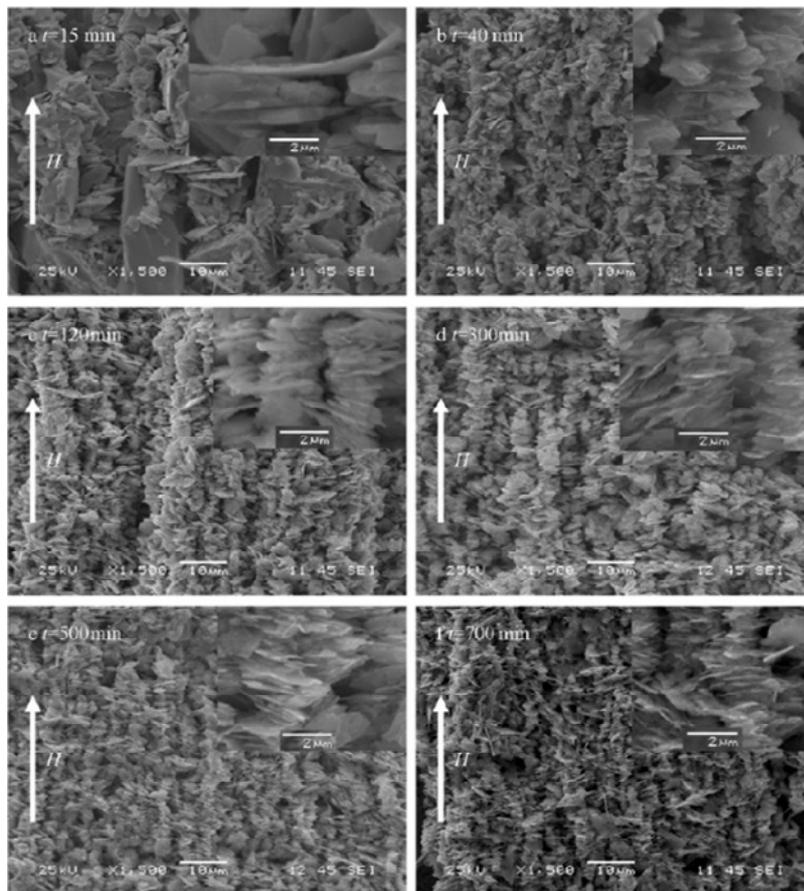


Fig. 6.  $\text{SmCo}_5$  nanoparticles produced through high energy ball milling using various surfactants.



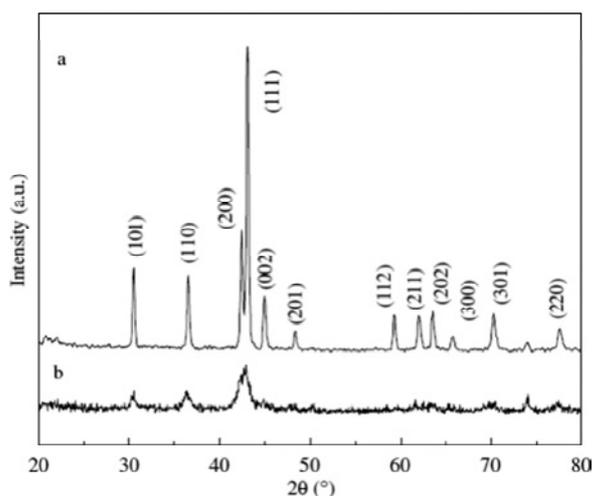
**Fig. 7.** TEM image of cockle shells powders before (a) and after (b) the addition of BS-12. The micron-sized rough rod-like crystals were observed before adding surfactant (a), the clear nanosized rod-like crystals were synthesized after adding BS-12 (b). Reprinted with permission from [Kh. Nurul Islam, A. B. Z. Zuki, M. E. Ali, M.Z. B. Hussein, M. M. Noordin, M. Y. Loqman, H. Wahid, M. A. Hakim, and S. B. A. Hamid, *Journal of Nanomaterials*, Volume 2012, Article ID 534010, 5 pages, (2012)]. Copyright (2012) by Hindawi Publishing Corporation.



**Fig. 8.** SEM images of  $\text{CeCo}_5$  flakes milled at various times. Shown are (a) 15 min, (b) 40 min, (c) 120 min, (d) 300 min, (e) 500 min, (f) 700 min). Reprinted with permission from [J.J. Zhang, H. M. Gao, Y. Yan, X. Bai, F. Su, W. Q. Wang and X. B. Du, *J. Magn. Magn. Mater.* Volume 324, 3272-3275(2012)]. Copyright (2012) by Elsevier.

particles with higher specific surface area [62]. Lower molecular weight surfactants have additional advantages over high molecular weight ones in removal and recovery of particles after the milling. Usually, a

vacuum annealing process involving high temperature that causes particle grain growth and oxidation is necessary for the product recovery when high molecular weight surfactants are used. Thus a suit-



**Fig. 9.** XRD patterns of arc-melted  $\text{CeCo}_5$  ingots (a) and aligned granular film after 40 min of milling (b). Reprinted with permission from [J.J. Zhang, H.M.Gao, Y.Yan, X.Bai, F.Su, W.Q.Wang and X.B.Du, *J. Magn. Mater.* volume 324,3272-3275(2012)]. Copyright (2012) by Elsevier.

able surfactant of lower molecular weight should be employed to avoid unwanted effects on particle and cost [63,64].

Surfactant assisted top down approaches were also used for synthesis of various biomaterials like  $\text{CaCO}_3$  nanoparticles for applications in bone paste, anticancer drugs, advanced drug delivery system and tissue scaffolds [65,66]. Generally,  $\text{CaCO}_3$  nanoparticles are produced in solution route or carbonation route [67]. However, none of the route can produce pure nanoparticles with suitable sizes and shapes without additional impurities [68]. The extra cost, time and skill are also major concern. Islam *et al.* (2012) synthesized pure  $\text{CaCO}_3$  nanoparticles (30 nm in diameter) from cockle shells using dodecyl dimethyl betain (BS-12) (Fig. 7) in a simple and low cost approach [69]. The method was suitable for the large scale production of  $\text{CaCO}_3$  nanoparticles from natural sources. In absence of surfactant, calcium carbonates were agglomerated and the resulted bead size was 300 nm. Opposite scenario was observed when calcium carbonate was treated with polyacrylate surfactant. The surfactant prevented severe agglomeration and helped to reduce the particle size. The resulted minimum size of calcium carbonate particle with this surfactant was about 40 nm [70].

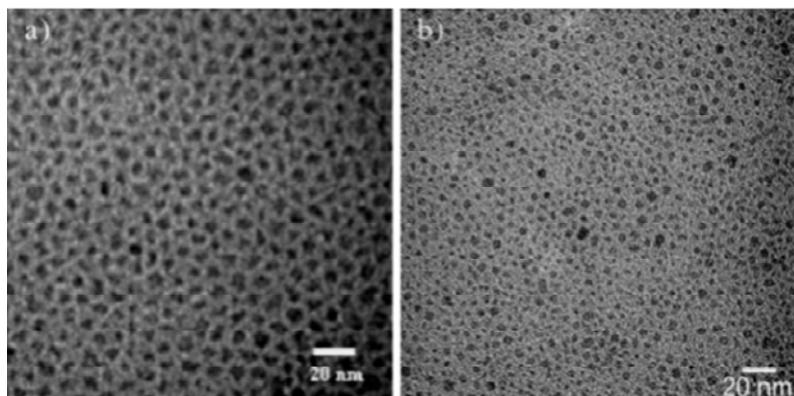
Zhang *et al.* (2012) synthesized flake like  $\text{CeCo}_5$  powder with tens nm in thickness from  $\text{CeCo}_5$  alloys by surfactant assisted high energy ball milling. The maximum coercivity of 3.3 kOe was found from

sample milled for 40 min [71]. The SEM images (Fig. 8) represent  $\text{CeCo}_5$  particle from different milling times where the flakes stick to each other, forming a 'kebab' like morphology aligned in a field of 27 kOe. The thickness of the particle reduced rapidly for several  $\mu\text{m}$  to 100-200 nm under prolong ball milling ( $t < 120$  min). At 700 min the thickness reached at about a few tens nm with slow speed. On the other hand, the length and width of  $\text{CeCo}_5$  particles remain unchanged in the whole milling process. The  $\text{CeCo}_5$  particles were synthesized by the layer by layer peeling or plane splitting cleavage of  $\text{CeCo}_5$  micro particles [71]. The newly formed peeled layers no longer agglomerated in presence of surfactant. The XRD pattern (Fig. 9) showed that the  $\text{CeCo}_5$  flakes were well crystalline as well as anisotropic [71]. Similar effects were observed when  $\text{NdFeB}$ ,  $\text{PrCo}_5$  and  $\text{SmCo}_5$  particles were produced using surfactant assisted high energy ball milling [63, 72-74].

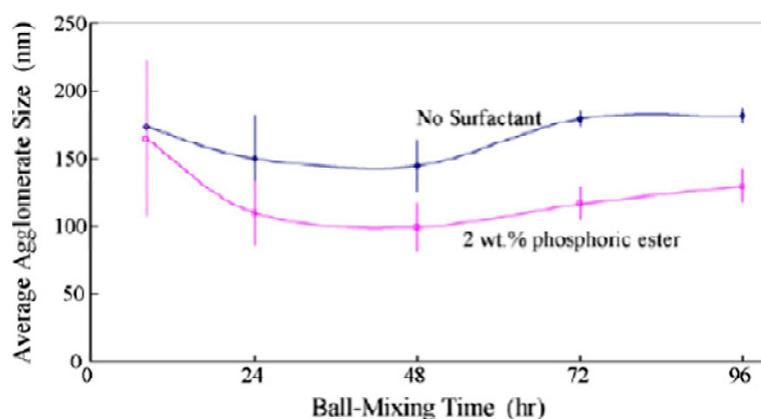
The application of ferromagnetic nanocrystals with controlled size and shape are increasing in advanced materials and devices such as microwave devices, magnetic recording media, ultrahigh density magnets and biomedicines. Due to large permeability and high saturation magnetization, the synthesis of soft magnetic particles such as Fe, Co and FeCo has got extra attention [55,75-77]. Poudeyal *et al.* (2011) synthesized Fe, Co and FeCo nanoplates and nanoparticles by surfactant assisted ball milling in organic solvents. The thickness of the nanoplates was in the range of 20-200 nm, whereas the diameter of nanoparticles was 6 nm with super paramagnetic properties [78].

Chakka *et al.* (2006) also synthesized Fe, Co nanoparticles (size < 30 nm) with surfactant assisted ball milling in an organic solvent (heptane). At room temperature, the synthesized nanoparticles showed super paramagnetic behavior [59]. Fig. 10 represents the TEM image of Fe nanoparticle of size ranging from 3 to 9 nm obtained from 1-5 h grinding in the presence of oleic acid as a surfactant. The morphology of the particles remained constant up to 50 h of ball milling [59].

The long ball milling operation may lead to formation of large agglomerate size. Graphitic size of 1-30  $\mu\text{m}$  which is larger than their primary particle size (tens of nanometer range) were obtained when milled with water and phosphate ester (surfactant) [79]. When the milling time exceeded 48 h, the graphite particle size increased remarkably. At 2 wt.% surfactant (phosphate ester) the size of the agglomerate was reduced below 100 nm with a mix-



**Fig. 10.** TEM images of the nanoparticles prepared by milling Fe powders for (a) 1 h and (b) 5 h. Reprinted with permission from [V. M. Chakka, B. Altuncevahir, Z. Q. Jin, Y. Li, and J. P. Liua, *J. Appl. Phys.* Volume 99, 08e912, (2006)]. Copyright (2006) by American Institute of Physics.

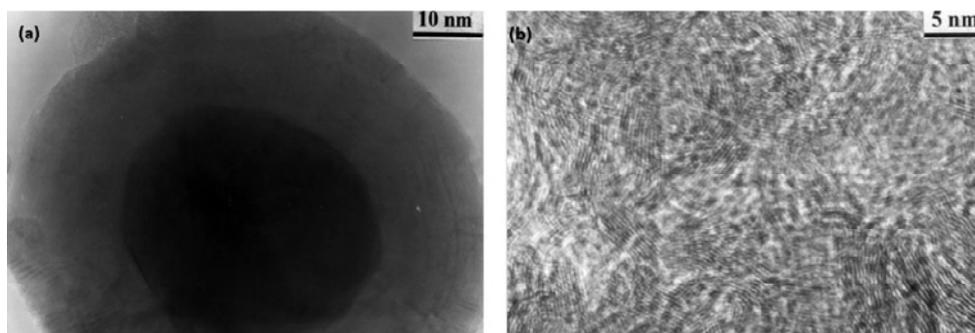


**Fig. 11.** Mean agglomerate size of the ball milled graphitic carbons at prolonged milling time. Reprinted with permission from [Chun-Nan Chen, Ya-Lang Chen and Wenjea J. Tseng, *J. Mater. Process. Technol.* Volume 190, 1-3,(2007)]. Copyright (2007) by Elsevier.

ing operation of 48h. Fig. 11 clearly demonstrates that long milling time does not reduce the agglomerate size of graphite in spite of having sufficient phosphate ester concentration [79]. The authors explained two reasons for the formation of large agglomerate. First, the high collision frequency between particles and grinding media reduces molecular chain of the surfactant to an average shorter length reducing steric hindrance. Second, the high collision tendency of the particle would induce cold welding during the high energy milling. These two steps induced large mean agglomerate size in long time milling [79]. Then graph shows (Fig. 11) clear increase of agglomerate size when time exceeds to 48 h. It can be assumed that the cold welding of graphite particles may be the dominant mechanism which inhibits the reduction of agglomerate size in the long milling operation.

Nowadays, Carbon nanomaterials are being widely used for a variety of process and environment applications such as –electrodes, electronic materials, sensors, solar cells, pollution control

strategies and so on [80]. Various methods such as electric arc discharge, laser ablation, chemical vapor deposition and ball milling have been proposed for the synthesis of carbon-based materials [81-84]. Among the methods, ball milling provides the possibility of synthesizing nanostructured carbon materials in a cost effective way. Chen *et al.* (2000) produced closed shell carbon nanostructures by ball milling of graphite for 150-250 h [85]. At 150 h milling, polyhedral or spherical shapes closed shells graphite nanoparticles were observed [85]. Similar features were obtained by arc discharge method which is expensive and complicated [86]. Fig.12a represents quasi –spherical graphitic particle with metal impurities which were synthesized using 150 h ball milling. These graphite particles were similar to those obtained by electron irradiation process which is not a cost-effective method [85]. Compared to 150 h milled graphites, 250 h one showed strong exploitation and crumpling of the graphite sheets (Fig.12b) [85]. These high crumpling layers were also found in annealed carbon shoot prepared by



**Fig. 12.** HRTEM image for graphite grounded for 150 h (a) and 250 h (b) with inner metal particles. Reprinted with permission from [X.H Chen, H.S Yang, G.T Wu, M Wang, F.M Deng, X.B Zhang, J.C Peng and W.Z Li, *J. Cryst. Growth*, volume 218,57-61(2000)]. Copyright (2000) by Elsevier.

**Table 2.** List of surfactants used in ball milling operation for various nanoparticle synthesis.

Surfactants	Nanoparticle	Nanoparticle sizes	References
Oleic acid	$\text{Sm}_2\text{Co}_{17}$	Average size 9 nm	60
	$\text{CeCo}_5$	tens nanometer in thickness	71
Oleylamine	$\text{Sm}_2\text{Co}_{17}$	Average size 26 nm	60
Oleic acid and Oleylamine	Fe, Co, FeCo	Average nanoparticle size 6 nm and nanoplate thickness 20 to 200 nm Sizes <30 nm	78 59
Mixture of Oleic acid and oleylamine	$\text{Nd}_2\text{Fe}_{14}\text{B}$	15 nm	61
Stearic acid, Oleic acid, Palmitic acid, Myristic acid, Undecanoic acid, Octanoic acid, Valeric acid	$\text{SmCo}_5$	Range (21 to 29 nm)	62
Dodocyl dimethyl betaine	$\text{CaCO}_3$	30 nm	69
Poly(acrylic acid, sodium salt)	$\text{CaCO}_3$	Around 40 nm	70
Phosphate ester	Graphite	Tens of nanometer range	79
Sodium dodocyl sulphate(SDS) /Sodium dodocyl benzene sulphonate (SDBS)	Nano carbon from graphite	Ranges (80 to 500 nm)	88

carbon arc method at 1700 °C [87]. The similar curved nanostructures were also reported by Huang *et al.* (1999) [84] by high energy ball milling. Nandhini *et al.* (2012) reported nanoscale carbons from graphite by surfactant assisted ball milling for 10-30 h [88]. They used anionic surfactants SDBS and SDS. The synthesized nanoparticles were in the range of (80-500 nm). The high energy ball milling created high shear forces in the graphite followed by formation of nanoscale carbon with some exfoliation [88]. Here, surfactants played multiple roles such as cold-welding prevention, dispersion of nanoparticles and reduction of contamination which are common in the ball milling process [57,89,90]. Some important examples of

nanoparticles synthesis by different surfactant assisted ball milling are summarized in Table 2.

## 6. CONCLUSIONS

High energy ball milling processes for the controlled structure synthesis of various nanoparticles were described. Various factors that play key roles in the milling process are presented in a simple diagram. Different types of surfactants along with their roles and mechanisms of actions are discussed. We believe this review would help the potential researchers and academics to efficiently use ball milling along with various surfactants for the synthesis of various particles with controlled nano/microstructures.

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