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Preparation of barium sulphate nanocrystals in ethanol - water mixed solvents

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Precipitation of nanoparticles is an important production procedure in industry to receive nano materials that are widely used in many fields. The product properties are strongly dependent on the properties of the particles i.e., average size, size distribution and morphology. The specific properties and applications of barium sulphate nanoparticles have attracted intensive investigation. There are numerous tedious techniques for synthesis of nano particles. However, in this study, barium sulphate nanoparticles were successfully synthesized using an ordinary chemical precipitation technique. Barium sulphate nanoparticles were synthesized using barium chloride and ammonium sulphate as reagents by an ordinary precipitation process in the presence of ethanol/water mixed solvents. Different compositions of ethanol/water mixed solvents were taken for this synthesis process. Precipitated samples were characterized using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and X-ray diffraction (XRD) techniques. The size and morphology were determined using XRD and SEM techniques respectively. From the XRD results, the sizes of the particles ranged from 85nm to 54nm. The particle sizes are decreased when the vol.% of ethanol is increased.

Key words: Barium sulphate, mixed solvents, ordinary chemical precipitation, ethanol/water.

Introduction

A major trend in research and development has been the shift of interest towards smaller and smaller particles. This can be summarized under the general term "nano-technology". Nanotechnology is concerned with manipulating matter to near atomic scales between 1 to 100 nanometres. This technology has recently gained popularity due to its potential in altering the behaviour of individual molecules and opened the door to new applications [1]. The typical application of nanoparticles can be found in many fields such as heterogeneous catalysis, semiconductors, microelectronics, information storage, pharmaceuticals, paints and ceramics [2]. Nanoscale materials can be made up by numerous ways. Among these, a chemical synthesis method has numerous advantages such as a simple technique, inexpensive, less instrumentation, doping of foreign atoms is possible and large quantities of materials can be obtained. This chemical method could be classified as sol-gel [3], chemical vapour deposition [4], micro emulsion [5], and chemical precipitation [6] etc., Among these different types of synthesis processes a chemical precipitation technique was used in the present study. Barium sulphate commonly referred to as barite, is suitable for many diverse uses because of its high specific gravity (4.5), opaqueness to X-rays, inertness and whiteness. It is mainly used as radio contrast agent, filler in plastics, extender in paints and an additive in pharmaceutical products and printing ink.

In the present study, $BaSO_4$ nanoparticles were synthesized using ethanol/water mixed solvents by a precipitation method. By changing the volume percentage of ethanol in the mixed solvent, the size of $BaSO_4$ particles can be decreased into nanometre range, without doing any additional treatments. The precipitated $BaSO_4$ nanoparticles were characterized using XRD and SEM-EDS techniques.

Experimental Method

Analytical reagent grade of barium chloride, ammonium sulphate and ethanol were used directly without any further purification. The solutions used in the experiments were prepared using distilled water.

The $BaSO_4$ nanoparticles were prepared from a barium chloride solution and ammonium sulphate solution. Firstly, $BaCl_2$ and NH_4SO_4 were dissolved in ethanol/water mixed solvents to form saturated solutions. In this study five different compositions of ethanol/water mixed solvents were used with 30%, 50%, 60%, 65% and 70% of ethanol. Secondly, the reaction was made by quickly mixing the ammonium sulphate solution with the barium chloride solution with vigorous stirring. The $BaSO_4$ suspension was aged for 12 hours. Finally, the precipitate was washed with the mixed solvent several times and dried at 100 °C for 6 hours. The powdered samples were taken for characterization using different techniques, such as XRD and SEM-EDS. The X-ray patterns were recorded using XPERT-PRO PAN alytical with a source of Cukα (λ = 1.5406 Å) and over 2θ values in the range $20^o \leq 2\theta \leq 50^o$. The SEM micrographs were recorded using a JEOL

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SEM model JSM 5610 LV manufactured by JEOL Ltd., TOKYO, Japan. Elemental analysis of samples was also performed using an energy dispersive spectrometer (EDS) attached to the SEM instrument.

Results and Discussion

X-Ray Diffraction

X-ray diffraction study was used to identify the crystal structure and determine the particle size [7]. XRD patterns were recorded for the synthesized samples in the mixed solvents with volume percentages of ethanol 30%, 50%, 60%, 65%, and 70% and are shown in Fig. 1. From this figure the characteristic peaks are identified as from (101), (111), (021), (121), (002) and (212) planes which shows the orthorhombic structured $BaSO_4$ (JCPDS card No.: 24-1035). It is also observed that no interaction takes place with the various concentrations of ethanol. This strongly infers that ethanol can only moderate the physical properties of the reaction medium without changing the reaction paths and arrangements of the crystal structure. It is very clear that the width of the characteristic peaks are broadened with an increasing percentage of ethanol in the mixed solvent. The crystallite size of the $BaSO_4$ was calculated using the Debye-Scherrer equation as follows:

$$D = \frac{0.942\lambda}{\beta cos\theta} \tag{1}$$

where D, λ, β and θ are the average diameter, the X-ray wavelength,the half width of the peak (full width at half maximum) and the Bragg's diffraction angle respectively. The average sizes of the $BaSO_4$ particles were estimated and the particle sizes are tabulated in Table 1.

From this table, the particle sizes are decreased with an increase in the volume content of ethanol. The size of the $BaSO_4$ particles for 30% ethanol is 85 nm. However, a 54 nm particle size is obtained when the ethanol volume percentage is increased to 70%.

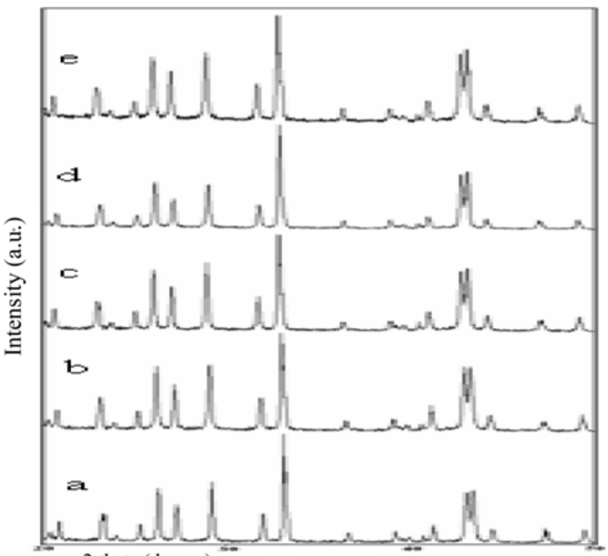


Fig. 1. The XRD spectrum for $BaSO_4$ powders prepared in the mixed solvents with the volume percentage of ethanol (a) 30%, (b) 50%, (c) 60%, (d) 65% and (e) 70%.

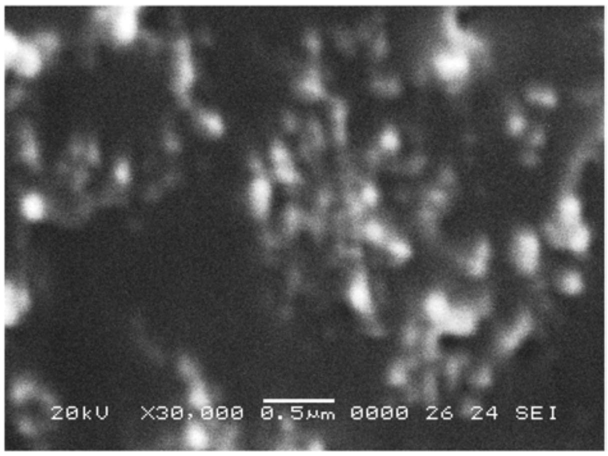
Table 1. Average size of the Barium sulphate nanoparticles using mixed solvents

Percentage of ethanol mixed with water	Average particle sizes (nm)
30%	85
50%	69
60%	63
65%	60
70%	54

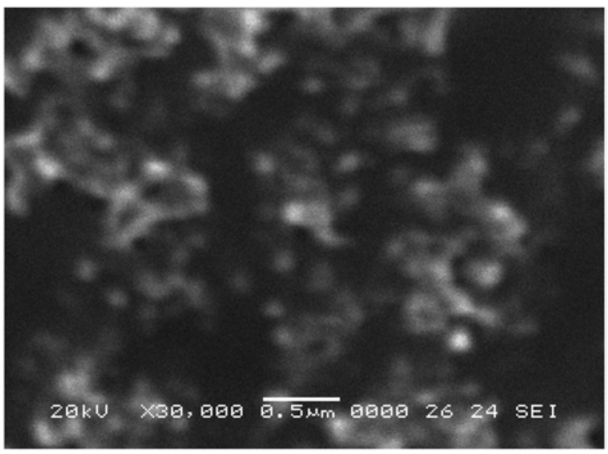
SEM-EDS

SEM micrographs of the $BaSO_4$ nanoparticles are shown in Fig. 2(a) and 2(b). This clearly shows that the particles are spherical in shape.

The water content greatly affects the shape of the $BaSO_4$ particles. According to Qi et al., [8] spherical particles are obtained when the water content is a minimum, while cubic particles can be obtained with a higher water content.



2(a)



2(b)

Fig. 2. SEM images of the $BaSO_4$ powder prepared in the mixed solvents with the volume percentage of ethanol (a) 30% and (b) 70%.

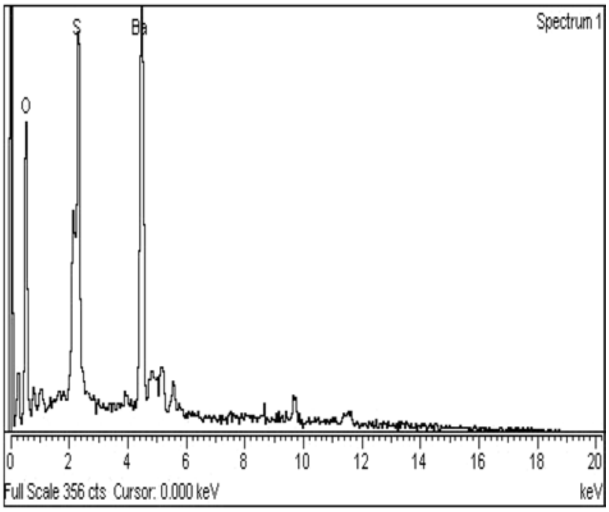


Fig. 3. EDS spectrum of the Barium sulphate nanoparticles using 70% of ethanol in the mixed solvent.

Thus in the present study, the water content is at a minimum since the particles obtained are spherical in shape. This dictates the reduction of water content in the precipitation process. The water content in the precipitation process can be reduced by increasing the volume percentage of ethanol. When the volume percentage of ethanol increases then the particles becomes smaller in size, weaker in aggregation and growth behavior. It can be seen that the SEM observations are consistent with the XRD analysis. The spherical nanoparticles are uniform in size, shape and arranged systematically. Particles in Fig. 2(a) appear to be ultra-fine and largely independent with an absence of any comprehensive agglomeration. Ethanol plays an important role for the absence of agglomeration. From SEM image 2(b), it is clearly seen that the size of the particles is less than the 100 nm range.

Fig. 3 shows the energy dispersive spectrum of a synthesized $BaSO_4$ sample which confirmed the presence of Ba, S and O elements.

Conclusions

$BaSO_4$ nanoparticles were successfully prepared using an ordinary chemical precipitation technique with sizes ranging from 85 nm to 54 nm in ethanol/water mixed solvents. Five different compositions of ethanol/water mixed solvents were employed as the reaction media. The XRD and SEM-EDS analyses shows that ethanol can reduce the particle size and restrain the particle growth and aggregation during the precipitation process without changing the particle nature.

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