The contribution of g, arising due to the instrumental effects, is computed by recording the XRD pattern of a polycrystalline large grained, strain free standard sample. In the present study, Si is used as the standard, where the crystallite size and strain effects are insignificant. The broadening of the pattern is thus only due to the instrumental effects. The contribution of the size and strain profiles in the structurally broadened profile f can be found by fitting Cauchy and Gaussian distribution, respectively. Again considering h, f and g profiles to be Voigt functions we can write

$$H_c = g_c * f_c \text{ and } h_G = g_G * f_G. \quad (2)$$

The subscripts C and G represent the Cauchy and Gaussian component of the respective Voigt profiles. The integral breadth (β) of f_c and f_G are given by

$$B^f_c = \beta^h_c - \beta^g_c \text{ and } (\beta^f_G)^2 = (\beta^h_G)^2 - (\beta^g_G)^2 \quad (3)$$

The constituent Cauchy and Gaussian components were obtained from the ratio '2w/ β for h and g profiles, where'2w' is full width at half maximum intensity of the peak and β is the integral breadth. Considering the most intense XRD peak, the crystalline size D, computed using SLA analysis, is given by

$$D = \lambda / \beta^f_c \cos\theta \text{ and strain } e = \lambda / \beta^f_G \, 4\tan\theta, \quad (4)$$

Where β is measured in radians, λ is the K∞1 radiation used and θ is the Bragg angle.

The microstructure, crystallite size were studied using the JEM 2100 HRTEM operated at an acceleration voltage of 200 kV in bright field modes. Selected area diffraction (SAD) patterns were obtained to identify the phases at specific locations using appropriate aperture and tilt.

3. Results and Discussion

The particle size distribution of the TiO_2 powder prior to mechanical milling is shown in Figure 1. The size distribution profile of the powder clearly shows that the distribution is fairly wide ranging from 0.195μm to 23.08μm

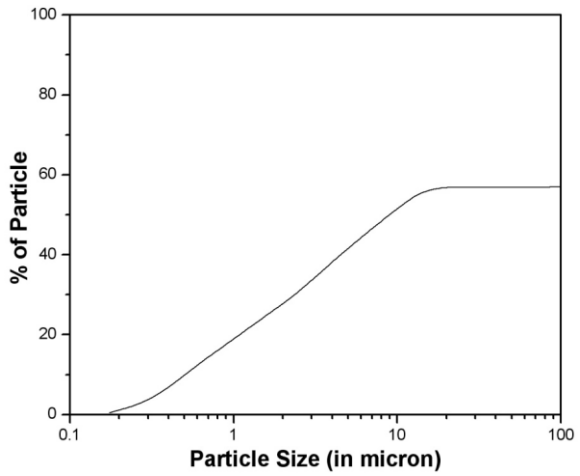

Figure 1: Particle size distribution of TiO_2 powder sample before ball milling

Figure 2 and 3 shows the results of XRD analysis of the mechanical milled TiO_2 powders in dry and wet condition. The pattern clearly shows that initially TiO_2 particles possess tetragonal crystal structure, which transform partially to orthorhombic and hexagonal crystal structure with the increase in dry milling and wet milling time. It has been further observed that the XRD pattern gets broadened with the increase in milling time, which suggest reduction in TiO_2 particle size and increase in lattice strains in the crystallites. This effect appears to be more prominent in the XRD pattern of the dry milled sample than the XRD pattern of the wet milled TiO_2 powder. This can be further corroborated by the results of the XRD pattern of the ball-milled sample by analyzed by the single line profile analysis technique.

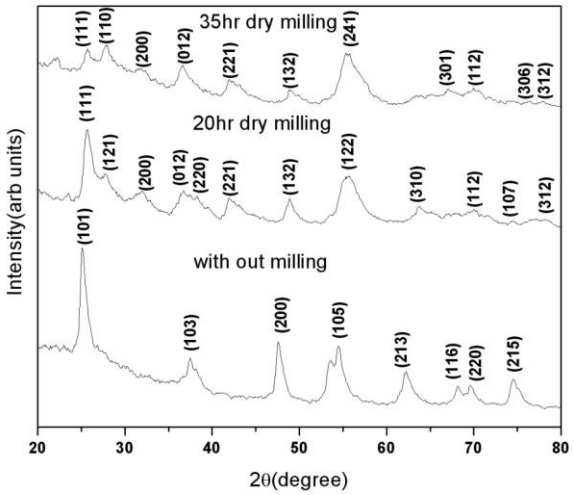

Figure 2: XRD spectra of TiO_2powder (a) After 20h dry milling (b) After 35h dry milling (c) without milling.

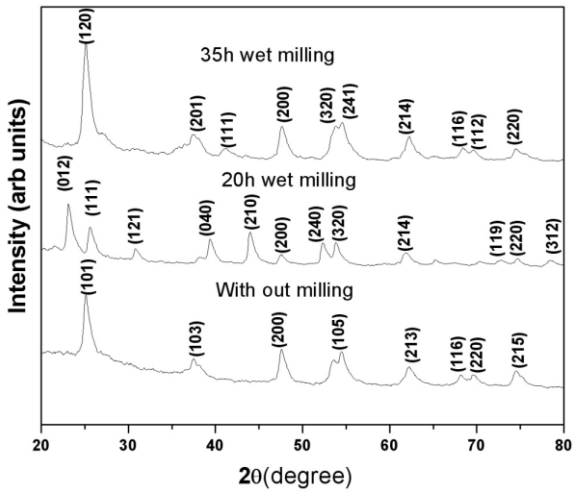

Figure 3: XRD spectra of TiO_2powder (a) After 20h wet milling (b) After 35h wet milling (c) without milling

Table 1: Influence of different milling condition and time on the variation of particle size and strain as measured by single line profile analysis of XRD spectra

Milling time (hrs)	*Milling condition*	*Particle size (nm)*	*Strain*
20	Dry	16.15	0.012
35	Dry	11.86	0.0109
20	Wet	893	.0019
35	Wet	16.17	.0091

Table 1 summarizes results of the single line profile analysis, which shows the variation of particle size and lattice strain with respect to milling condition and time. From the table it is quite clearly evident that with the increase in milling time the particle size of TiO_2 powder decreases and corresponding lattice strain increases. It has been also seen that dry milling is more effective technique in reducing the particle size to the nanometric length scale as compared to wet milling.

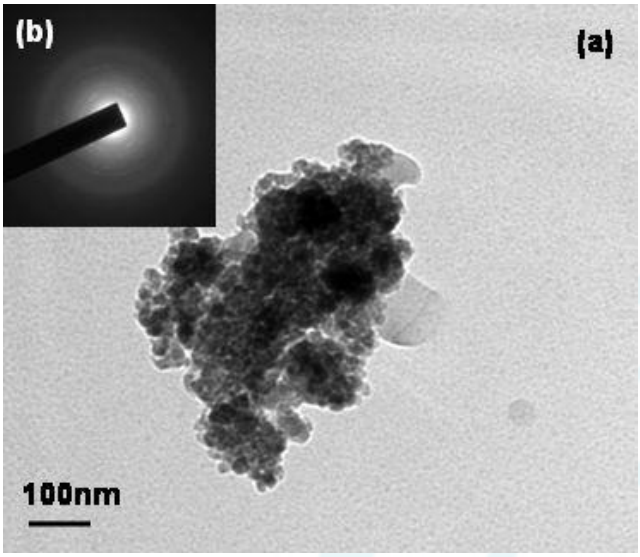

Figure 4(a): Bright field TEM image and inset (b) the corresponding SAD pattern of the powder dry milled after 35 hr.

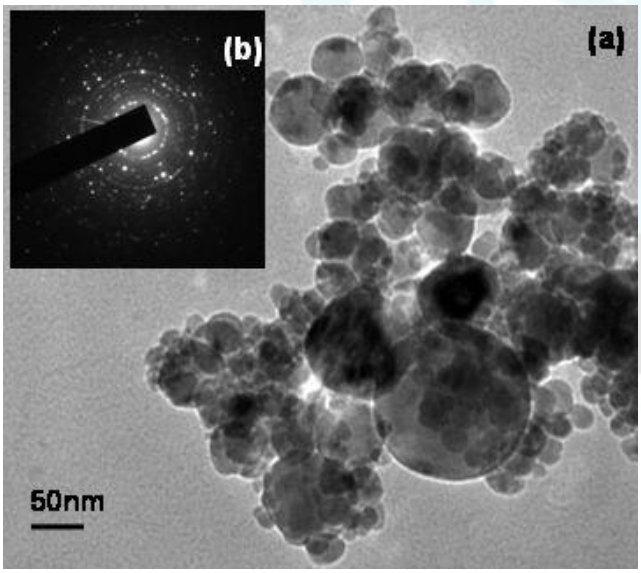

Figure 5(a): Bright field TEM image and inset (b) the corresponding SAD pattern of the powder wet milled after 35 hr.

A bright field TEM image and the corresponding SAD pattern from the powder dry milled after 35 hr are shown in Fig. 4. Examination of the TEM image (Fig. 4a) and indexing of the Debye rings in the corresponding SAD pattern (Fig. 4b) indicate that nano-sized (~10 nm). Fig. 5 shows the bright field TEM image and the corresponding SAD pattern of the dry milled after 35 hr. Comparison of the TEM images in Fig. 4a and 5a suggests that dry milling is the better process for obtaining minimum crystal size TiO_2. In fact, the SAD pattern from the powder wet milled after 35 hr (Fig. 5b) shows many spot with Debye rings which confirm larger crystallite Size.

4. Conclusion

The conclusions that are drawn from this investigation are:

a) Nano-TiO_2 powders have been prepared by mechanical milling method successfully. By controlling the conditions properly, nano-TiO_2 powders with the grain size less than 12 nm could be obtained.
b) Micron sized TiO_2 particles which initially possesses a tetragonal crystal structure, transform partially to orthorhombic and hexagonal crystal structure with the increase in milling time.
c) Dry milling technique has been found to be more effective method of particle size reduction of TiO_2 then the wet milling technique

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