

Green Synthesis of Ag Nanoparticles in Large Quantity by Cryomilling

Electronic supplementary information

i) Free standing nature of cryomilled Ag NPs

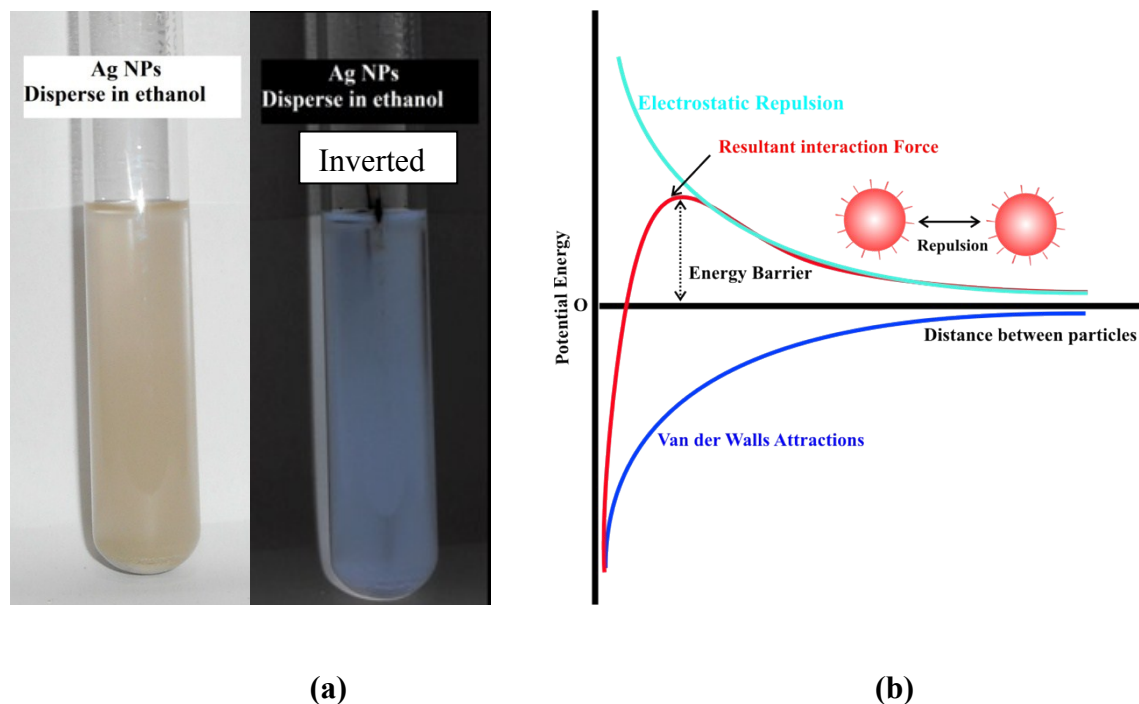


Figure S1. (a) Optical image of test tube showing free standing nature of Ag NPs prepared by cryomilling; (b) Repulsive and attractive forces as a function distance between two particles¹. In (a), both normal and inverted images are shown.

The Figure S1 (a) depicts the dispersion of Ag NPs in ethanol (free standing nanoparticles). The Ag NPs are found to be stable and well dispersed in ethanol due to nanosize and native surfaces. The surfactant free nanoparticles have been observed to be stable for weeks. The said stabilization called electrostatic stabilization¹, where many types of forces such as force of attraction (closer force significant very short distance -particles almost touching to operate this force) and electrostatic repulsion (longer distance force) operate. Here, gravity is considered to have negligible effect due to extremely small size of the nanoparticles. The Brownian motion of the NPs can make them colliding each other all time in solvent. Figure

S1(b) indicates that the combination of Van der Waals attractive force and electrostatic repulsion force acting on the NPs. When NPs come closer, they repel each other due to similar charge. If the repulsive force between them dominates, the resultant energy barrier develops a little away from the surface of NPs (as indicated on Figure S1 (b)). The kinetic energy produced by Brownian motion will not be sufficient to allow the NPs to cross the barrier if the barrier height is more than $10 kT$, where k = Boltzmann constant and T = absolute temperature. Thus, the NPs remain well dispersed for a longer time and exhibit free standing nature. The zeta potential (potential at slipping plane) of the Ag NPs (-17 mV at 7 pH) indicates free standing nature of the Ag NPs in ethanol. Similar studies in methanol and water show the free standing nature of the Ag NPs.

ii) Surface plasmon resonance of cryomilled Ag NPs

The Ag NPs exhibit surface plasmon resonance band due to resonance of the conducting electron with incident laser beam. The cryomilled Ag NPs dispersed in ethanol shows a band at $\lambda_{\max} = 465$ nm as shown in Figure S2 (The measurements were done using Thermo scientific evolution 201 UV-visible spectrophotometer). The presence of specific SPB indicates the nanocrystalline nature of the cryomilled Ag particles.

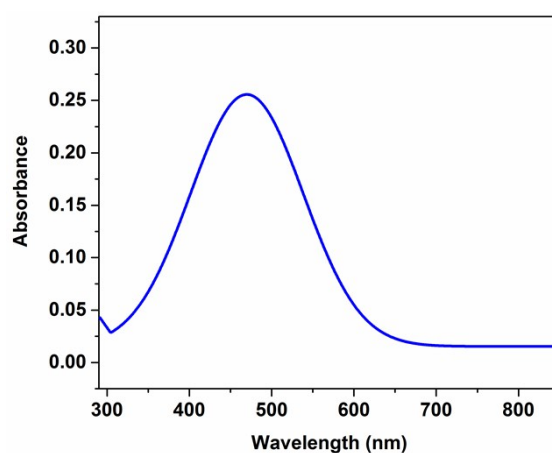


Figure S2. UV-Visible absorption spectrum of Ag NPs dispersed in ethanol ($\lambda_{\max} = 465$ nm)

It is to be noted position of surface plasmon band (SPB) depends the shape, size of nanoparticles, dielectric constant of environment (solvent) as well as functionality of nanoparticles^{2,3}. Additionally, the NPs with irregular shape and roughened surface strongly affect the surface plasmon resonance.⁴⁻⁶ It is well known that the top down approach (milling) produces nanoparticles having irregular shape and roughened surfaces. The tendency is increasingly observed in cryomilling because of decreases in ductility at extremely low temperature. Therefore, it is not possible to correlate λ_{max} with the mean size of Ag NPs.

iii) Thermal stability

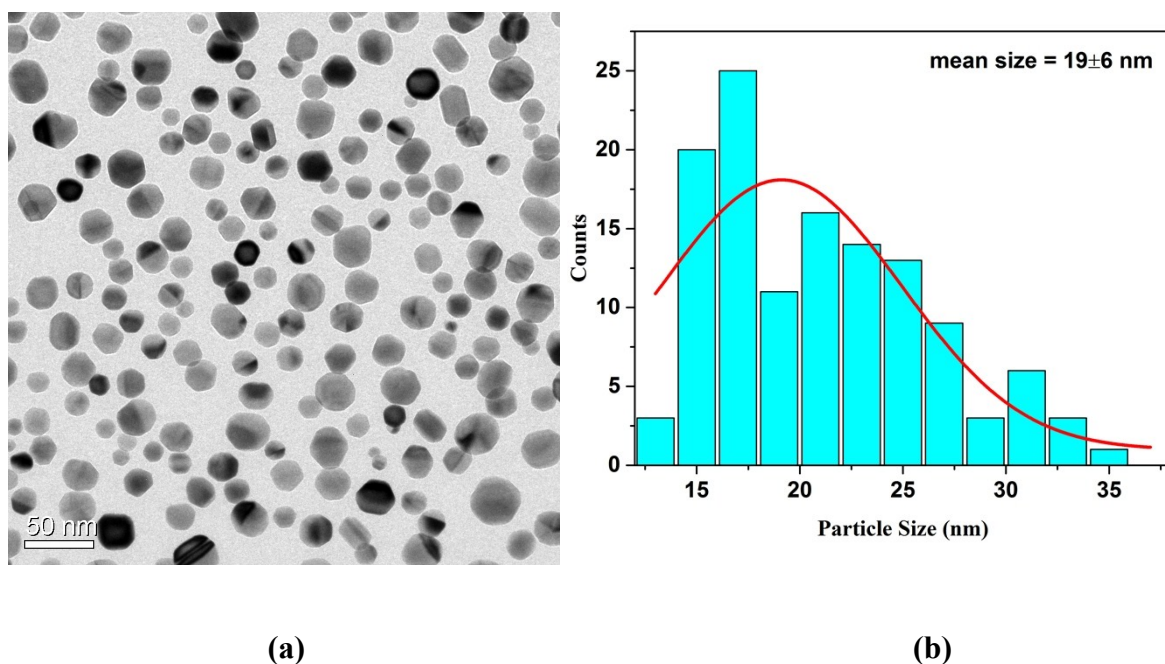
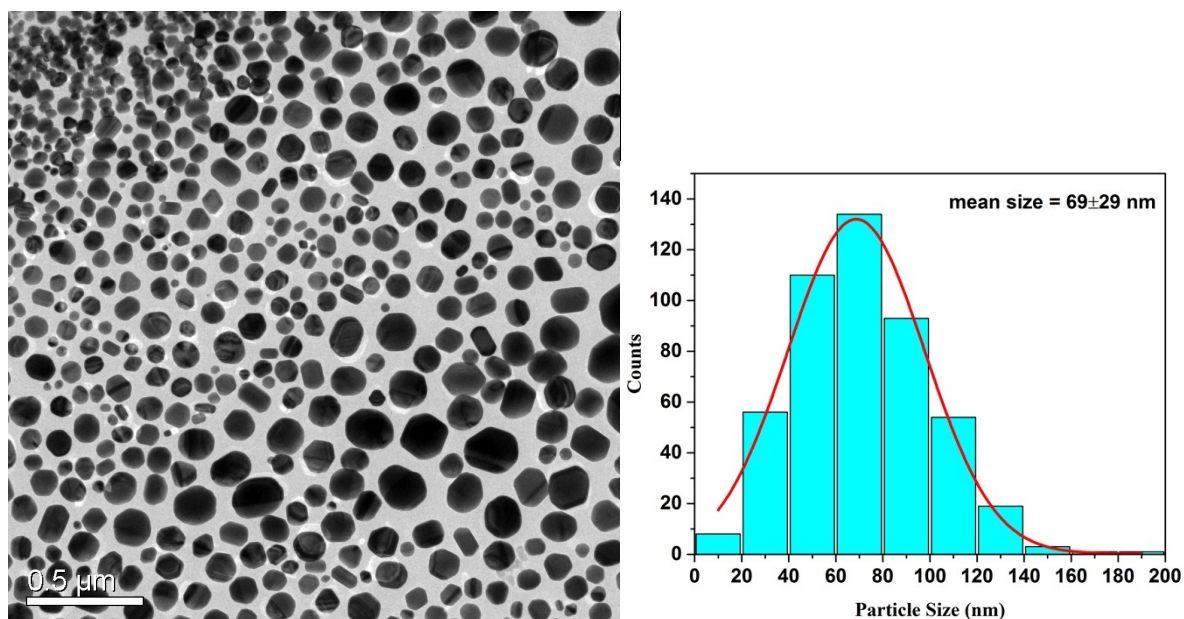
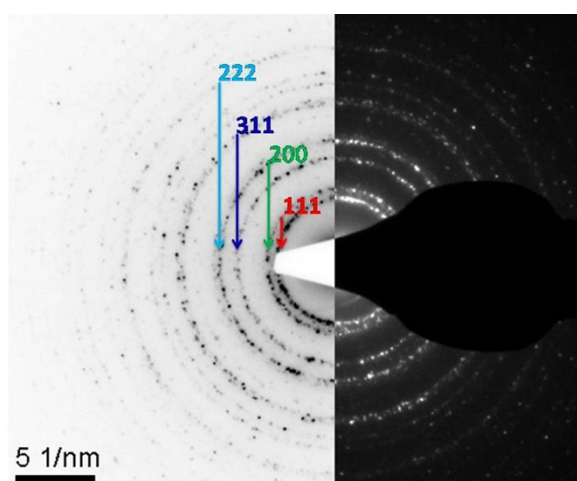


Figure S3. Cryomilled powder annealed under vacuum sealed at 350°C for 2 hours: **(a)** Bright field TEM image of Ag NPs; **(b)** corresponding particles size distribution.



(a)

(b)

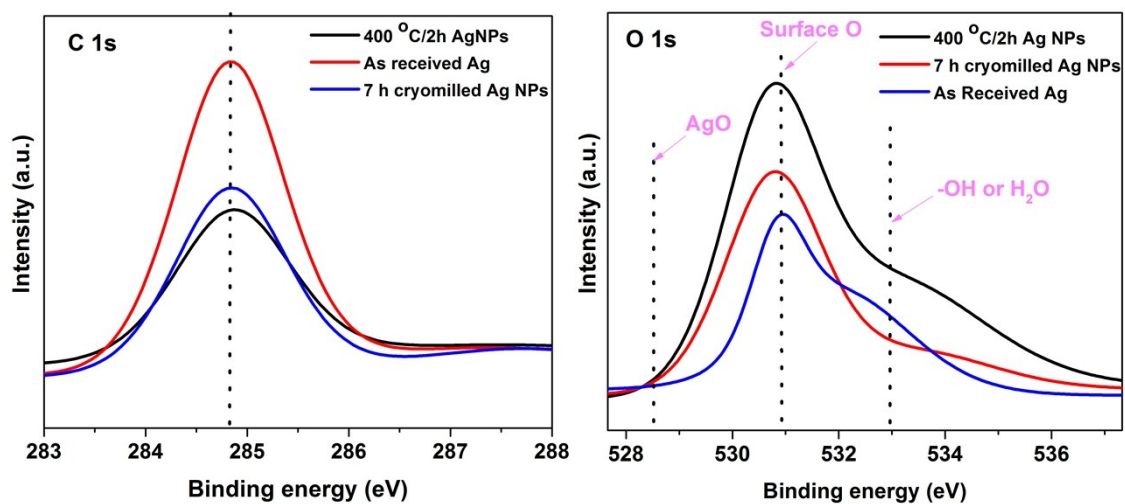


(c)

Figure S4. Cryomilled powder annealed under vacuum sealed at 400°C for 2 hours: **(a)** Bright field TEM image of Ag NPs; **(b)** corresponding particles size distribution **(c)** corresponding SAED (selected area electron diffraction)

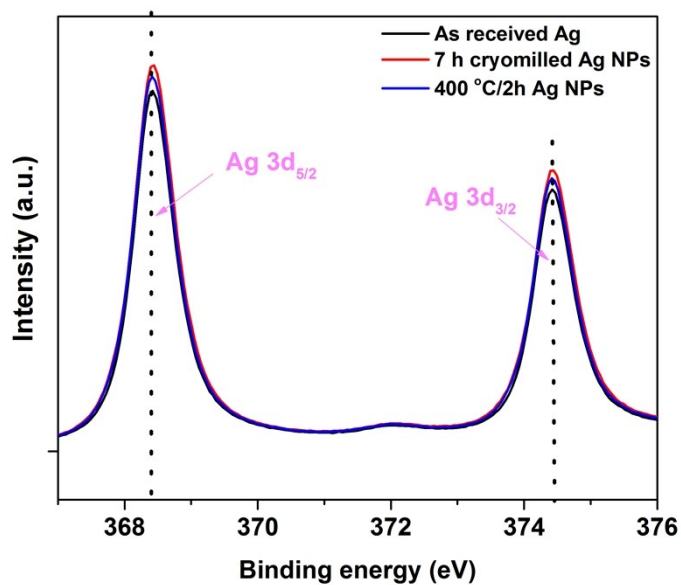
Production of large scale thermally stable nanoparticles is a challenge to the research community. Other synthesis methods (chemical, arc discharge) can produce thermally stable nanoparticles. However, these NPs are stabilized using polymers having cross linkers, which are not stable for higher temperature (>200°C). Thermally stable NPs above 200°C are still

scarce^{7, 8}. It has been reported from the in-situ TEM studies that Ag NPs starts coalescence at 200°C and form micron sized particle after even 30 minutes of annealing treatment⁹. In the present investigation, annealing of the surfactant free Ag NPs at different temperatures (350 and 400°C) has been carried out for 2 hours to systematically study the stability of the NPs. For this purpose, the as milled powder was vacuum sealed at 10⁻⁶ bar in a quartz tube prior to annealing in an electric furnace. The results are shown in Figures S3 and S4. The cryomilled, Ag NPs are found to be thermally stable at higher temperature (up to 400°C). The SAED pattern as shown in Figure S4(c)[400 °C for 2h] indicates that crystal structure of Ag NPs is same as that of the as- received silver powder. Furthermore, the annealed (400 °C for 2 h) powder has been characterized by X-ray photoelectron spectroscopy (XPS) to find out oxidation state or other impurities in the nanoparticles. The silver peaks (Ag3d) of the as prepared and annealed powder look similar to those of the as-received powder (Figure S5 (c)). The detailed analysis of O1s spectra from the as received as well as synthesised samples have been reported in the manuscript. In fact, there is no peak corresponding to silver oxide (AgO) in O1s spectrum.^{10, 11} (Figure S5 (b)). Therefore, the adventitious C and O have come from the environment, when sample was exposed to the atmosphere during handling the powder for investigation. Thus, C and O are present on the surfaces of the Ag NPs. We have carried out compositional analysis of the powder samples. Table S1 shows the composition of prepared Ag NPs and annealed (400 °C for 2h) Ag NPs have been compared with precursor powder (as received). The O content has been increased in the as synthesized Ag NPs and annealed Ag NPs as compared to the as received Ag. This is mainly due to increase in the surface area of nanoparticles and handling of the nanocrystalline powder. The shape of peaks remain similar in all case as shown in Figure S5(b). Therefore, it is evident that the annealed powder has not been oxidized and O is due to surface adsorbed oxygen.



(a)

(b)



(c)

Figure S5. Comparison of XPS spectra of cryomilled powder and annealed Ag NPs [400 °C/2h] with as received Ag **(a)** C 1s; **(b)** O 1s; **(c)** Ag 3d.

Table S1. Composition of Ag NPs using XPS

Name of sample	Ag (atom%)	C (atom%)	O (atom%)
As received Ag	70.57	18.97	10.46
7 h cryomilled Ag NPs	69.03	18.84	12.13
Annealed (400°C for 2h) Ag NPs	65.38	20.82	13.80

iv) Crystallite size analysis by X-ray diffraction

The peak broadening in X-ray diffraction patterns is constituted by different type of broadening [15]

$$\beta_{\text{total}} = \beta_{\text{instrumental}} + \beta_{\text{microstrain}} + \beta_{\text{crystallite size}} \quad (\text{S1})$$

,where β is FWHM (full width at half maxima), indicator of peak broadening. The Hall-Williamson analysis^{12,13} is represented by

$$\beta_c \cos(\theta) = 4\varepsilon \sin(\theta) + \frac{K\lambda}{D} \quad (\text{S2})$$

$$y = mx + c$$

$$\text{Crystallite size} = \frac{K\lambda}{\text{intercept}} \quad (\text{S3})$$

,where θ = diffraction angle, λ = wavelength of X-rays, ε = microstrain, D = diameter of the nanoparticle, K = shape factor(= 0.9 for spherical shape particles). β_c is calculated as follows:

$$\beta_c = \beta_{\text{total}} - \beta_{\text{instrumental}} = \beta_{\text{crystallite size}} + \beta_{\text{microstrain}} \quad (\text{S4})$$

The peak broadening due to instrument ($\beta_{\text{instrumental}}$) has been measured by using X-ray diffraction pattern from annealed (strain free) microcrystalline Ag particles. Mathematically, β_c has been calculated using following relation.

$$\beta_c^2 = [\beta_{measured}^2 - \beta_{instrumental}^2] \quad (S5)$$

In the process of cryomilling, all these broadening dominate and thus, we need to carefully subtract or deconvolute them from the peak to obtain precise crystallite size. On the other hand, similar case is not required for the chemically synthesized metal nanoparticles (bottom up approach) as the chemically synthesized metal nanoparticles might have negligible broadening contributed from the micro-strain. As particles size becomes smaller (~ 10 nm or less) for FCC metals, micro-strain is also observed to exhibit decreasing trend¹⁴ due to the instability of partial Shockley dislocations, when grain size becoming smaller than the equilibrium distance between these partial dislocations [15].

v) See multimedia file for more information about the green synthesis of Ag NPs using cryomilling

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