Supporting Information

Stabilization of Highly Concentrated Colloidal Suspension of Pristine Metallic Nanoparticles

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Stabilization of surfactant free metallic NPs

The stabilization of surfactant free metallic NPs strongly depends on following factors

1) Nanoparticles formation (<10 nm)

2) Interaction of NPs with other nanoparticles and solvent

The nanoparticles are required to be below 10 nm and with native surface, which can directly interact with solvent molecules and form a stable double layer with high potential barrier. In the following, aspect of formation and interaction are discussed.

Nanoparticles formation mechanism

As compared to bottom up approach, the formation of nanoparticles by top down approach (ball milling) has not been studied in details\(^1\). Ballmilling has widely been utilized to obtain nanocrystalline metallic materials. In particular, ball milling at cryogenic temperature has gained wide attention to the scientific community recently\(^2\)-\(^5\). The following section will be devoted to the formation of NPs \textit{via} cryomilling and issues related to it.

During ball milling, the mechanism of refinement of grain size involves repeated deformation, cold-welding, fracturing and dynamic recrystallization, leading to aggregation of micron sized particles containing multiple grains of nanometric size. The powder particles also have relatively strong tendency to adhere to container walls (vials) and to sinter to form bigger particles. In order to increase the efficiency of achieving extremely fine grain size, attempts were made to mill at lower temperature i.e. at cryogenic temperature\(^4\)-\(^5\),\(^7\)-\(^8\). Cryomilling is a mechanical milling technique in which metallic or ceramic powders are milled either in slurry formed by powder, balls and a cryogenic liquid (preferably liquid N\(_2\)) or at cryogenic temperature such that nanostructured materials are obtained. In the latter case, powder is generally milled in a container (vial) cooled by liquid N\(_2\) jacket around it. It is to be noted that the cooling of the milling media
and powder is an effective approach to suppress the recovery and recrystallization and to accelerate the fracture process leading to finer grain structures and more rapid grain refinement. However, the common notion in the literature is that preparation of pure freestanding nanoparticles of different metals and alloys is not possible during milling because of agglomeration\textsuperscript{6, 9-16}. During high-energy milling at room temperature, the powder particles are repeatedly flattened, cold-welded, fractured and rewelded\textsuperscript{6}. Since powders are cold-welded and fractured during milling, it is critical to establish a balance between cold-welding and fracturing during milling for preparation of the free-standing nanoparticles having size less than 10 nm. The ability of cold-welding and fracturing of powder depends on material and milling conditions. These two factors are strongly dependent on the milling temperature.

It is well known that fracturing of any material depends on temperature. Any material when cooled below ductile-to-brittle (DBT) temperature will undergo brittle fracture and break into pieces very easily\textsuperscript{17}. Cooling down to extremely low temperature (<123K) during milling is an effective means to accelerate the fracturing process for many materials having BCC, HCP crystal structure. However, the materials having FCC crystal structure do not exhibit DBT transition\textsuperscript{17}. In any case, the fracturing tendency of these materials will increase at low temperature as compared to that at room temperature. Another critical phenomenon controlling the formation of nanocrystalline particles is cold-welding. The welding process due to collision of balls with powder during milling can be approximated as cold-welding of two plates under pressure. The increase in the pressure during collision increases the real area of contact between the powders. According to cold–welding theory, cold-welding is associated with a particular range of deformation strain of the powders\textsuperscript{18}. The deformation strain required by cold-welding depends on materials systems employed and can occur in cases of welding between two similar or dissimilar metals. Most important aspect of the cold-welding is the fact that the bond strength
between the powders of metals is a function of deformation strain. In the following, the cold-welding aspect has been studied in detail for different metals in order to find out the formation free metallic NPs having size <10 nm. It is evident that the strength of the joint will dictate the agglomeration tendency of the powder particles during ball milling at cryogenic temperature. If the strength of cold-welded joint is low as compared to the energy being transferred due to collision of ball and powder, the joint will break easily, and agglomeration will not occur. Hence, it is essential to estimate the strength of the cold-welded joints formed during ball milling.

**Cold-welding**

During cold-welding phenomenon, two metallic plates are brought together by high pressure (greater than threshold), resulting in the electron cloud of atoms residing in the both plates become common and can form a weld joint\(^{19}\) as shown in Figure S1. Therefore, the strength of the joint depends on the overlap and the applied pressure or stress.

![Figure S1: Cold-welding phenomenon](image)

The cold-welding behavior of metal strips with different amount of stress (corresponding to plastic deformation) at different temperature has been further experimentally analyzed. It is to be noted that during deformation of metals (cold bonding), the temperature can rise instantly at the point of deformation, which can help in cold bond formation or even sintering of the nanoparticles. As a result, it can reduce the advantage of the cryogenic temperature milling (free
particles formation as shown in Figure S2). Hence, the temperature at the joint has first been estimated using available models (Schwarz et al.)\textsuperscript{20}.

**Rise in Temperature (during deformation)**

![Diagram](image)

*Figure S2: Nanoparticles formation and rise in temperature during cryomilling.*

As shown in Figure S2, when metallic NPs are deformed during the ball milling, particles get flattened and fractured. However, during flattening or deformation, the temperature will rise instantly at the point of collision due to conversion of mechanical energy to heat.

The rise in temperature during the process of collision was analyzed by Schwarz et al.\textsuperscript{20} A relationship between the temperature rise due to localized shear of the powder particles entrapped during milling and other parameters has been provided

\[
\Delta T = \frac{F}{2} \left( \frac{\Delta t}{\pi k \rho C_p} \right)^{1/2}
\]  

(S1)

Here, \( \Delta T \) is the rise in temperature, \( F \) the dissipated energy flux = \( \sigma V \), where \( \sigma \) = normal stress caused by the head-on collision and \( V \) is given by the relative velocity of the balls before impact,
\( \Delta t \) is the stress state lifetime, \( \rho \) is the density of powder particle, \( k \) is thermal conductivity of powder and \( C_P \) is heat capacity of powder. Here, \( \sigma \) can be considered as the maximum compressive stress generated during a head-on collision of two balls of diameter \( D \). Hence,

\[
\sigma = 0.616 \left[ P \cdot E^2 \left( \frac{2}{D} \right)^2 \right]^{\frac{1}{3}}
\]

(S2)

Here, \( E \) is the elastic modulus of the ball and \( P \) is the load. Using the values of parameters (provided in Table S1) and the calculated value of \( \Delta T \) is found to vary in the range of 2 to 8K for these metals listed in Table S1. Thus, the temperature rises during localized heating due to impact between ball and vial is not significantly large. As the temperature of the powder is maintained during cryomilling temperature at \(-160\pm10 \, ^\circ\text{C}\) or less, therefore, the rise in temperature at collision point does not really affect the fracture of sintering process because this temperature rise is not enough to overcome the cryo-temperature effect. It is to be noted that the rise in temperature during milling depends on many factors such as number of balls, ball and vial materials, milling speed and shapes of vials\textsuperscript{21}. The calculated values are for the custom built cryomill are provided in Table S1\textsuperscript{8}.

### Table S1: Milling parameters used in the calculation of rise in the temperature during milling

| Milled Powder | Density (g/cm\(^3\)) Balls-vials | Elastic modulus (GPa) | Load (N) | Density of milled powder (kg/m\(^3\)) | Thermal conductivity (w/mk) | Specific heat (C\(_P\)) kJ/kg.K | Rise temperature (K) |
|---------------|----------------------------------|-----------------------|----------|--------------------------------------|----------------------------|-------------------------------|----------------------|
| Al            | 15.63                            | 600                   | 0.4095   | 2700                                 | 205                        | 0.91                          | 4                    |
| Ag            | "                                | "                     | "        | 10490                                | 406                        | 0.23                          | 3                    |
| Cu            | "                                | "                     | "        | 8960                                 | 385                        | 0.38                          | 2.5                  |
| Zn            | "                                | "                     | "        | 7130                                 | 116                        | 0.39                          | 5                    |
| Fe            | "                                | "                     | "        | 7870                                 | 73                         | 0.46                          | 5.5                  |

**Cold bond strength**

Let us now discuss the cold bond strength in these metals as a function of temperature. As mentioned earlier, it is important to measure the strength of cold-welded bonds among different
metals. To probe this aspect, we have adopted the following approach. First, the cold-welded strips were prepared as lap joints and strength of bond has been measured using conventional tensile test of the joint as shown in Figure S3(a). The metallic strips with purity of 99.9% (3 mm thickness) have been used for measurement of cold bond strength. The rolling (Horsburgh and Scott, U.K.) machine has been utilized to prepare cold weld joints, where roll diameter, rolling speed, metal initial thickness, and width etc. were kept constant throughout experiments except temperature of metal strips. Universal Testing Machine (UTM, Instron, model 3369, U.K.) was used to measure strength of the cold weld. It is important to note that the cold bonding is observed to start when the roll pressure reaches the threshold value for bond initiation. At least 10 measurements were carried out in each case to obtain the statistically average value of the bond strength of the joint.

First, let us discuss the behavior of the bonding ability of the metals, which primarily depend on the plastic deformation. The ability to plastically deform basically depends on the available slip systems in the crystal structure. Consequently, dynamic recovery leads to the annihilation of pairs of dislocations\textsuperscript{17}, which can support more deformation during further deformation. Dynamic recovery is normally achieved by the cross slip of screw dislocations and higher temperature vacancy climb dominates\textsuperscript{22-23}. However, the dynamic recovery significantly decreases at low temperature (<123 K) compared to room temperature (300 K) for the most of the FCC/BCC metals\textsuperscript{23}. Therefore, milling at low temperature (cryomilling) will lead to extensive accumulation of dislocations in the milled materials, leading to early fracture of materials. Al is reported to have higher recovery constant compared to Cu at low temperature\textsuperscript{23}. The higher recovery constant means higher deformation ability. Therefore, the Al is expected to have higher cold-welding ability compared to Cu as observed in Figure S3(b).
Although the FCC metals do not show the ductile-to-brittle (DBT) temperature, the ability to deform depends on the dynamic recovery. On the other hand, BCC pure Fe (T\text{DBT}= -50 ^\circ \text{C}) and HCP Zn (T\text{DBT}= <50 ^\circ \text{C}) show sharp ductile-to-brittle transition\textsuperscript{17}. Therefore, they easily fracture at low temperature (<123 K) and exhibit cold bond ability as shown in \textbf{Figure S3(c)}.

It is to be noted that bond strength is the key factor in the formation of free nanoparticles at extremely low temperatures (<123K). The many metals exhibit low deformation ability and as a result, the cold welds do not form. It is important to note that a threshold level deformation is required (40- 70\%) for the bond formation\textsuperscript{18, 24}. Hence, the bond may not form due to lack of enough deformation. There is also a probability to form weak cold bond during repeated
collisions with balls. Such weak cold-welded bond will break as the strength of the bonding will not be enough. Therefore, weak bond formation will promote the formation of free-standing nanoparticles.

During the present investigation, the behavior of cold-welding of Al, Cu, Zn, and Fe has been studied by cold rolling at different temperatures (300K (27 °C), 273K (0 °C) and 77K (-196 °C)). Figure S3(c) illustrates deformation vs. normalized bond strength shows the behavior between bond strength normalized by solid metal strength against percent deformation. The solid metal strength was considered the highest possible bond strength. Figure S3(c) shows the results of the experiment for Al, Cu, Fe and Zn, measured at three different temperatures. The error bars in the Figure indicate the standard deviations in the measurements. It is evident from Figure S3(c) that there is no bond formed between metallic strips the prepared up to 50% reduction at any of three processing temperatures. In case of Cu, the 60% deformation is required to show bond strength at 300 K and 273 K. However, there is no bonding at all at 77 K. Furthermore, at 70% and 80% deformation, there is 40% and 55% suppression in bond strength respectively at 77 K as compared to room temperature. In the case of Al, at 60% deformation, bond strength is subsequently reduced to 40% and 60% at 273 and 77 K respectively as compared to room temperature bond strength. It is to be noted that, at 77 K, results shows some bond strength, possibly due to an instantaneous increase in temperature during rapid deformation (compression energy change to thermal energy). However, the temperature rise during cryomilling can vary from 2 to 8K in one impact and hence, bond strength may further decrease.

**Interaction of nanoparticles with liquid**

Let us now discuss the interaction of the surface atoms of the NPs with liquid in which the NPs are dispersed. We shall discuss the details of the DLVO theory and the application in the present case.
Stability of colloids in a suspension is described by the DLVO theory (Derjaguin, Landau, Verwey and Overbeek)\textsuperscript{25-26}. The net force ($F_{\text{total}}$) acting between surfaces two charged particle surfaces is a resultant of van der Waals attraction ($F_{\text{vdW}}$) and electrostatic repulsion or double layer force ($F_{dl}$),

$$F_{\text{total}} = F_{\text{vdW}} + F_{dl}$$  \hspace{1cm} (S3)

\textbf{van der Waals attraction}

The Van der Waals attraction is a short-range force, generally appreciable within 5-10 nm inter-particle separation distances. For two particles with radius R approaching towards each other, this force can be approximated as,

$$F_{\text{vdW}} = -\frac{RA_H}{12h^2}$$  \hspace{1cm} (S4)

where h is the separation distance between two particles and $A_H$ is the Hamaker constant, which varies for different systems\textsuperscript{27}. Therefore, it is important to estimate $A_H$ to determine $F_{\text{vdW}}$.

\textbf{Hamaker Constant}

The Hamaker constant is a material property, calculated using the Lifshitz theory\textsuperscript{27-28}. In our case, the metal nanoparticles (radius R and dielectric permittivity $\varepsilon_1$) interact in a polar solvent, methanol (dielectric permittivity $\varepsilon_2$).

\textit{Figure S4:} Two metal nanoparticles of radius R are interacting in a polar solvent (methanol). (Dielectric permittivity of metal nanoparticles and methanol is $\varepsilon_1$ and $\varepsilon_2$, respectively.)
According to Lifshitz theory, the Hamaker constant can be expressed as \(^{27-28}\),

\[
A_H = \frac{3}{4\pi} \hbar \omega_1 \tag{S5}
\]

where, \(\hbar \omega_1\) is the Lifshitz constant defined as,

\[
\hbar \omega_1 = \frac{\hbar}{2} \times \int_0^{\omega_{\text{max}}} \int_0^{\infty} \frac{x^2}{x_1(i\omega) x_2(i\omega) + x_2(i\omega) + x_1(i\omega)} \times dx d\omega \tag{S6}
\]

The above equation can further be simplified to,

\[
\omega_1 \approx \int_0^{\omega_{\text{max}}} \frac{[\varepsilon_1(i\omega) - \varepsilon_2(i\omega)][\varepsilon_1 (i\omega) - \varepsilon_2(i\omega)]}{[\varepsilon_1(i\omega) + \varepsilon_2(i\omega)][\varepsilon_2(i\omega) + \varepsilon_2(i\omega)]} \, d\epsilon, \tag{S7}
\]

where \(\varepsilon_1(i\omega)\) and \(\varepsilon_2(i\omega)\) are dielectric permittivity of metal nanoparticles and surrounding medium, respectively. The cut off frequency \(\omega_{\text{max}}\) is chosen to be 200 eV/\(\hbar\), because further increasing the limit of integration to 1000 eV/\(\hbar\) changes the Hamaker constant by only 0.2\%. \(^{27}\)

According to the Drude model, dielectric permittivity of metal nanoparticles is given by \(^{29}\)

\[
\varepsilon_{\text{Drude}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\gamma \omega} \tag{S8}
\]

where \(\omega_p\) is plasma frequency and \(\gamma\) is the electron scattering rate or damping constant. If the mean free path of the conduction electrons in the bulk metal is comparable to or less than that of the radius of the metal NPs, boundary collisions become important. Therefore, the term \(\gamma\) must be modified to take into account the particle size effects on dielectric permittivity, as shown in the following equation \(^{29}\),

\[
\gamma \to \gamma(R) = \gamma + A \frac{\nu \epsilon}{R} \tag{S9}
\]

where, \(R\) and \(\nu \epsilon\) are nano-particle radius and Fermi velocity of electrons, respectively. Substituting \(\gamma\) from eq. (9) to eq. (8), size dependent dielectric permittivity can be expressed as
Different material parameters utilized to estimate the Hamaker constant and dielectric permittivity of metal nanoparticles are reported in Table S2.

**Electrostatic repulsion force**

The electrostatic repulsion force is a long range force and can be expressed as\(^ {25-26}\),

\[
F_{el} = 2\pi\varepsilon\varepsilon_0 k \psi_{eff}^2 e^{-kh}
\]

where \(\varepsilon\) is dielectric constant of the solvent, \(\varepsilon_0\) is the permittivity of the vacuum, \(k\) is the Debye length and \(\psi_{eff}\) is the surface potential.

**Surface charge potentials**

The surface charge potential is given by the Nernst equation\(^ {30}\),

\[
\Psi = 2.303R_g T[(p.z.c) - pH]/F
\]

where, p.z.c is the point of zero charge, \(R_g\) is the gas constant, \(T\) is the absolute temperature, and \(F\) is the Faraday’s constant. At room temperature, eq. (S10) becomes

\[
\Psi = 0.059[(p.z.c) - pH]/F.
\]

The p.z.c or isoelectric point has been calculated by varying the pH and measuring the zeta potential of metal nanoparticles in pure methanol [see Figure (3b) in the main manuscript].

**Table S2: Parameter used in calculation**

| Metal | \(\omega_p\times10^{16}\) s\(^{-1}\) | \(\gamma\times10^{14}\) s\(^{-1}\) | \(\nu_f\times10^6\) ms\(^{-1}\) | Reference |
|-------|--------------------------------|-----------------|-----------------|-----------|
| Ag    | 1.392                          | 1.297           | 1.39            | \[31\]    |
| Al    | 2.228                          | 1.29            | 2.02            | \[16\]    |
| Cu    | 1.343                          | 1.92            | 1.57            | \[16\]    |
| Zn    | 1.44                           | 1.17            | 1.83            | \[32\]    |
Aluminum nanoparticles
In this section, we shall describe the results of Raman, FTIR and UV-Visible spectra of metallic NPs synthesized in the present investigation. In particular, we shall show the case of aluminum NPs to reveal the interactions between Al atoms with methanol. The absorbance spectra of Al nanoparticles (dispersed in methanol) with varying concentration is shown in Figure S5(a) and corresponding optical images of nanoparticles are provided in Figure S5(b). The maximum concentration of Al NPs, which can be dispersed is found to be 33 gm/l. The dispersion stability of the NPs is higher than other metallic NPs. The interaction of NPs has been probed using FTIR and RAMAN spectroscopy. The Raman spectra are shown in Figure S5(c). The most of the band are similar to methanol, as methanol has been used as solvent. However, some new bands are also observed. These bands might be due to formation of AlOOH (diaspore) at nanoparticles surface. The band at 3363 cm$^{-1}$ is active for both Raman as well as FTIR$^{33}$. The band at lower and higher wavenumbers is mainly observed due to presence of surface hydroxyl group for AlOOH bonding$^{33}$. Similar attributes has been reported in X-ray photoelectron spectroscopy analyses of Al NPs and the upper most layer of Al NPs has been found to be consisting of Al(OH)$_3$/hydroxyl group$^5$. 
**Figure S5**: (a) UV absorbance spectra of Al NPs dispersed in pure methanol; (b) optical image Al nanoparticles dispersion in pure methanol with varying Al NPs concentration (c) Raman spectra of Al NPs.
**Size distribution of the cryomilled NPs**

The size distribution of as prepared NPs via cryomilling is shown in Fig. S6. At least 500 nanoparticles have been utilized to obtain the size distribution. It is evident, majority NPs having size less than 10 nm for Ag, Al, Cu, Fe and Zn.

![Particles size distribution of metallic nanoparticles](image)

**Figure S6:** Particles size distribution of metallic nanoparticles (using about 500 nanoparticles to obtain reasonable statistics) Al NPs (average size = 6±3 nm); Ag NPs (average size = 6±2 nm); Cu NPs (average size = 7±2 nm); Fe NPs (average size = 8±3 nm) Zn NPs (average size 3±1 nm).
Molecular Dynamics simulations: varying unit cell size

In order to verify whether artefacts were introduced in the MD simulations by the small number of nanoparticles in the periodic unit cell, we also tested unit cells with 4 and 8 copper NPs. Results are presented in Fig. S7 and discussed in the caption. Each 2 nm nanoparticle contained 456 atoms, and 1896/3784 methanol molecules were used for the system with 4/8 particles. More simulation details can be found in the main text.

Figure S7: Molecular dynamics simulation results. (a) Snapshot of a system composed by eight 2 nm copper nanoparticles immersed in methanol molecules, at the end of an equilibration process (equilibration details can be found in the main text). (b) Charge distribution around copper nanoparticles at the end of the equilibration process, for systems composed by 2, 4, and 8 nanoparticles. (c) Graph presenting the number of atoms located within 2.5 – 3.0 Å of the nanoparticles’ surface versus elapsed simulation time, for a system composed by 4 nanoparticles. Notice that figures for number of atoms are larger in this graph than in figure 4 of the main text, because the number of nanoparticles has increased. The number of atoms per nanoparticle, on the other hand, remains constant. Overall, it appears that increasing system size does not significantly affect simulation results.
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