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# Top-down Cleaner Production of Nanoparticle Dispersions in Liquid Phase by Vibrating Granular Beds

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A mechanosynthesis process aiming at producing stable particles dispersions embedded in a liquid phase is proposed, starting from spheres of a metal precursor subject to a progressive disaggregation carried out by a tribological process. The method consists in using a precursor in metal spheres of millimetric dimensions, placed in a suitable vessel together with a ceramic milling medium in a liquid phase. The vessel is subject to vertical oscillations at variable frequency, leading to a production of a micro- or nanometric dispersion of the pristine material in a liquid medium as a consequence of friction and impact between spheres. The process has been tested for Ag spheres at different operating conditions and the effect of frequency, hold-up fraction and capping agents dissolved in the liquid phase has been considered and related to the quality of the final product. The characterization of the solid phase has been carried out by dynamic scattering for particle diameter, giving distribution curves with average values at 11.7 and 16.9 nm using polyvinyl pyrrolidone as capping agent of two different molecular weights. The present indirect milling technique, as other analogous reagentless methods for the synthesis of nanodispersions, may represent a sustainable alternative to the standard wet chemical bottom-up schemes, owing to its cost-effectiveness and ease of realization.

## 1. Introduction

The setup of new manufacturing techniques in engineering had an impressive development in the last decades. This phenomenon can be ascribed to a growing interlink between many research areas, namely chemical physics, materials science, mechanical and chemical engineering. Nanotechnology is perhaps one of the most involved sectors in this sort of renewed “neural network” between science and technology, with important repercussions in real world. It is difficult to make a categorization of nanotechnology sectors that have benefited from such a fruitful scientific-technological process of exchange. As a first rough analysis, nanotechnology in manufacturing refers to products having different scales of dimensionality, starting from zero-dimensional objects like nanoparticles (NPs), namely representing the lower-dimensionality objects, going on to 2D materials. They found extended applications in electronics (He et al., 2020), optoelectronics (Tan et al., 2021), photocatalysis (Orona-Návar et al., 2020), environmental remediation (Orona-Návar et al., 2018) and medicine. The former is a very promising field, as there are many examples of application of nanoparticles as drug carriers to target organs, with the purpose of mitigating the side effects related to a systemic drug delivery. Of course, this specific use requires the highest level of biocompatibility (Jasrotia et al., 2020), which is one of the most challenging problems in the current research in nanomedicine (da Luz et al., 2020). Within the framework of this discipline, a promising example is offered by elements of the pnictogen group (Mourdikoudis and Sofer, 2021), where Bi is the only heavy cation having a low toxicity and a good tolerability for humans and mammalians, together with a good bactericidal effect towards microorganisms (Das et al., 2020). For its rather unusual properties and its relative ease of preparation at the nanosized

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elemental state (Reverberi et al., 2018), it is nowadays object of intense scientific investigation and many research papers strengthen this statement (Xu et al., 2020). The production of NPs and nanopowders is a starting point for the realization of sintered bulky structures, having innovative mechanochemical or physical properties, like a surface hardness, magnetic susceptivity or electric conductivity very different from that typical of analogous materials realized by traditional processes. The nanochemistry of binary metal oxides of the type AxByOz, where at least one of the two atoms A and B is a transition element (Pascariu et al., 2013), is another field where the scientific investigation led to an actual implementation of results of particular importance for the energy transition.
It should be taken into account that the production of these materials by chemical route is often based on processes that pose serious safety concerns, owing to the use of noxious reagents, requiring removal of hazards by applying inherently safe guidewords (Fabiano et al., 2019). This crucial drawback is particularly evident when NPs are produced by redox methods, which generally require electron-donors having negative effects on health and environment (Reverberi et al., 2017). For this reason, a growing attention of researchers has been devoted to the set-up of new reagentless synthesis methods, as a viable alternative to standard wet chemical techniques. To this purpose, physical methods like laser ablation (Intartaglia et al., 2016), wire explosion, vapor deposition, spray drying or electrospraying have been already experienced in the past, but they need complex and expensive apparatuses for a correct management of the experimental conditions. With the above considerations in mind, the optimal strategy would be producing NPs by reagentless physical methods relying upon simple, affordable and cost-effective facilities, removing hazards to perform risk-based lay-out optimization and provide an inherently safer design minimizing the reliance on add-on safety barriers (Pasman and Fabiano, 2021). In order to achieve this challenging target, top-down tribological techniques (Yadav et al., 2012) have been proposed, which have already given promising results in the production of photocatalysts. For example, Volnistem et al. (2020) utilized a highly efficient ferroelectric photocatalyst obtained by mechanosyntesis carried out in a high-energy planetary miller where two different solid phases, namely Bi ferrite ($BiFeO_3$) and $Fe_3O_4$ were subject to mechanical comminution (Volnistem et al., 2018). The as-produced photocatalyst was successfully tested in the photodegradation of an environmentally noxious pigment under visible light.
Many different mechanosynthesis techniques may be adopted and their classification is generally based on different structural realizations of the apparatuses where the comminution is carried out (Gorrasi and Sorrentino, 2015). This study is inspired to analogous techniques of comminution, based on a vertical vibrating milling device where Ag NPs are formed by Ag spheres subject to a non-autogenous milling process in liquid phase, carried out by hits between them and abrasive ceramic spheres. The paper is structured according to the following scheme: in Section 2, a description of the experimental apparatus is provided and some assembly details are outlined. In Section 3, the operating conditions are analyzed with respect to the fluidization threshold and the particles thereby produced with different capping agents are thoroughly characterized in diameter. In Section 4, the conclusions are presented and the direction for future studies is traced.

## 2. Materials and methods

### 2.1 Experimental setup

Silver metal spheres of 3 mm diameter (Ag, 99.9 %, American Elements, Los Angeles, USA), yttria-stabilized zirconia spheres of 4 mm diameter (YSZ, $ZrO_2$ 95 % + $Y_2O_3$ 5 %, Pingxiang Zhongtai Environmental Chemical Packaging Co. Ltd., Pingxiang, Jiangxi, China), polyvinyl-pyrrolidone (PVP, $(C_6H_9NO)_n$, 10 kDa and 40 kDa, 99 %, La Farmochimica, Genova, Italy), propylene glycol (PG, $C_3H_8O_2$, 99 %, La Farmochimica, Genova, Italy), methylene diiodide (MD, $CH_2I_2$, 99 %, Thermo Fisher Scientific, Powai, India), have been used without any other purification step. Bidistilled water as solvent was used in all milling experiments.
The apparatus here adopted is described in Figure 1. It consists of an adjustable power supply, with output voltage in a range 0-30 V, with double controls in voltage and current for a better tuning of the operating conditions. A 50 W brush-type permanent magnet motor, powered by the aforementioned device, is linked to a mechanical cinematism transforming the rotatory motion of the motor shaft into a reciprocating motion of a vertical bar. The latter is screwed on a shatterproof plastic box, whose come-and-go motion is constrained between two guides in order to avoid spurious vibrations of the oscillating equipment. A glass vessel of 27.5 mm outer diameter, containing Ag and YSZ spheres in a liquid medium, is fixed in turn inside the above-mentioned box. With these mechanical tweaks, the vessel is subject to cyclic vertical oscillations, whose frequency $\omega$, which is measured by an electromechanical counter, can be adjusted by varying the voltage of the current generated by the power unit. The hits and friction between Ag and YSZ spheres, here representing

the milling agent, produces micro- and NPs of the metal precursor in the liquid phase. In all experimental tests, the amplitude of oscillations cannot be modified and it remains fixed at 0.7 cm. For the above considerations, this comminution technique can be classified as an indirect milling process (Gorrasi and Sorrentino, 2015).

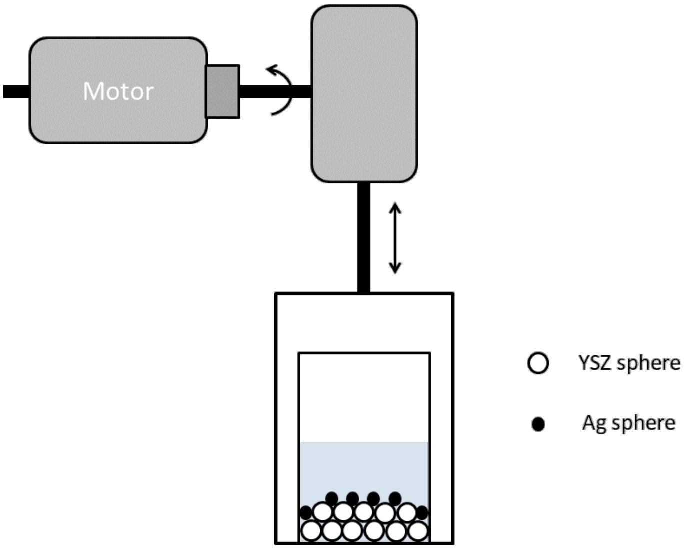



*Figure 1: Simplified scheme of the vertical vibrating miller adopted in the present study.*

### 2.2 Analytical methods

The probability distribution function of the Ag particle diameters was determined by dynamic light scattering (DLS) measurements realized by a Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) instrument. It has been assumed that the physical properties of the liquid medium embedding the suspended metal NPs are the same as pure water in the mechanosynthesis experiments of 3.2. For the solid Ag material suspended in the liquid phase, the refractive index (at the instrument lamp wavelength, 633 nm) was taken to be approximately equal to 0.2, while the absorption coefficient was fixed at the value 0.6 (Dengler et al., 2012).

*Table 1: Solvents used for the fluidization tests in the vertical vibrating miller.*

| Solvent | Molar mass [Da] | Density [kg $m^{-3}$] at 20 °C | Dynamic viscosity [mPa·s] at 20 °C |
|---|---|---|---|
| Water | 18.015 | 998.2 | 1.0016 |
| Propylene glycol (PG) | 76.09 | 1030 | 45 |
| Methylene diiodide (MD) | 267.836 | 3325 | 2.76 |

## 3. Results and discussion

### 3.1 Dynamical tests at the fluidization threshold

The beds of granular materials, when subject to vertical oscillations at frequency $\omega$ in the wet state, namely in the absence of a liquid phase embedding the granular material, exhibit a critical oscillation frequency $\omega_0$ such that:

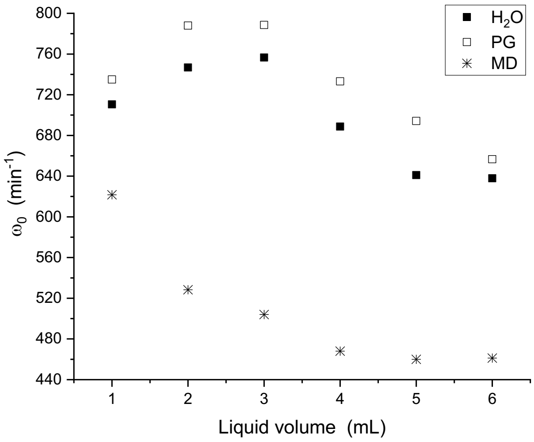
- For $\omega \leq \omega_0$, the particles at the upper layers of the bed change their reciprocal position in time, but there is still a compact layer at the bottom of the vessel preserving its original configuration;

- For $\omega > \omega_0$, the above condition is broken and all granules start moving randomly. In this situation, all layers are fully fluidized (Götzendorfer et al., 2006).

The existence of such a critical oscillation frequency has been checked for the presently adopted equipment, using 50 YSZ spheres and various volumes of liquid in the vessel in the absence of Ag spheres. Three different liquids have been tested and their physico-chemical properties are listed in Table 1. PG and MD have been intentionally chosen for their physical properties in comparison with those of water. Namely, PG has a viscosity $\mu_{PG} >> \mu_{H_2O}$, with a density $\rho_{PG} \cong \rho_{H_2O}$. MD, being one of the densest organic liquids, with a viscosity not very far from that of water, has properties symmetrical with respect to those of PG, namely $\mu_{MD} \cong \mu_{H_2O}$ and $\rho_{MD} \gg \rho_{H_2O}$.

In Fig. 2(a), $\omega_0$ is plotted versus the volume of liquid present in the vessel, for different liquid species. It can be seen that, for water and PG, the scatter graphs have a similar shape, characterized by a growing trend for small liquid volumes, followed by a decreasing trend for higher liquid volumes. In fact, small amounts of water and PG tend to stabilize the bed of YSZ spheres, requiring a growing $\omega_0$ for fluidization owing to the liquid-spheres cohesion forces. This phenomenon ceases for higher liquid volumes, whose oscillatory flow destabilizes the bed of YSZ spheres, thus requiring a lower $\omega_0$ for fluidization. The curve for PG is shifted above that of water as a growing viscosity of the liquid tends to make the spheres stick together.

The case for MD is totally different from the previous ones, as the corresponding curve decreases monotonically for growing liquid volume. This trend can be explained taking into account the exceptionally high density of MD, whose liquid oscillations destabilize the bed of spheres at all regimes, thus damping the sticking effect between spheres. Figure 2(b) provides a visual representation of the exceptional MD density, that makes glass spheres float on it, while YSZ spheres sink down into it.




(a)

(b)

*Figure 2: a) Plot of the threshold fluidization frequency versus the volume of liquids of different composition contained in the vibrating vessel. b) Image of a vessel where glass beads are floating in MD (left vessel) and where YSZ beads are sunk (right vessel).*

### 3.2 Metal NPs synthesis

In the following experimental samples, Ag metal spheres have been chosen as precursor owing to their multipurpose applications both in nanomedicine and in pharmacology. Additionally, Ag NPs proved to be fairly resistant to oxidation in air, when stabilized with carbohydrates (Reverberi et al., 2022) or with other capping agents of ionic or non-ionic properties. The present results can be compared with those of analogous studies where Ag NPs have been synthesized using different mechanosynthesis techniques relying upon direct milling processes (Reverberi et al., 2020). It is intriguing to observe that the research on ball-milling techniques in top-down disaggregation processes is mostly focused on rotary equipment (Ullah et al., 2014), while studies on vibrating/reciprocating millers are more uncommon in the same mechanosynthesis context.

In this Section, experiments have been carried out with the following materials contained in the vessel:

- 50 YSZ balls, as in the previous Section;
- 5 mL of water, where 0.33 g of capping agent have been dissolved;
- 20 Ag spheres of 3 mm diameter.

The milling process has been prolonged for 1 h at ω = 1,240 $min^{-1}$, namely at an oscillation frequency considerably higher than that corresponding to the fluidization threshold for YSZ balls in water, as observable in the scatter graph of Figure 2(a). Afterwards, the solution has been collected and allowed to stand for 12 h in order to separate the microparticles unavoidably present and clearly visible at the naked eye. The supernatant underwent a DLS analysis and the relevant distribution functions for particle diameter are reported in Figure 3, for two non-ionic capping agents of the same chemical composition but differing in molecular weight.
The curves in Figure 3 have diameter peaks and average values at 12.6 and 11.7 nm for PVP 10 kDa and at 17.8 and 16.9 nm for PVP 40 kDa. These particle diameters, despite being larger than those obtained by disaggregation of Ag spheres with the same capping agents by a direct milling technique, show the same trend observed in a previous study (Reverberi et al., 2020), where the particle diameters grew for increasing molecular weight of PVP. For a plausible explanation, it should be taken into account that, in the present experiments where spheres of a metal precursor are disaggregated by collisions induced by a fluidized vibrating bed, new phenomena like convection rolls, undulations and granular Leidenfrost effect are present, which do not have the correspondent in standard shaft-equipped millers (Tabet, 2016). In particular, the latter phenomenon may have a basic role, as it damps the disaggregation of Ag spheres by collisions, while promoting their disaggregation by friction.

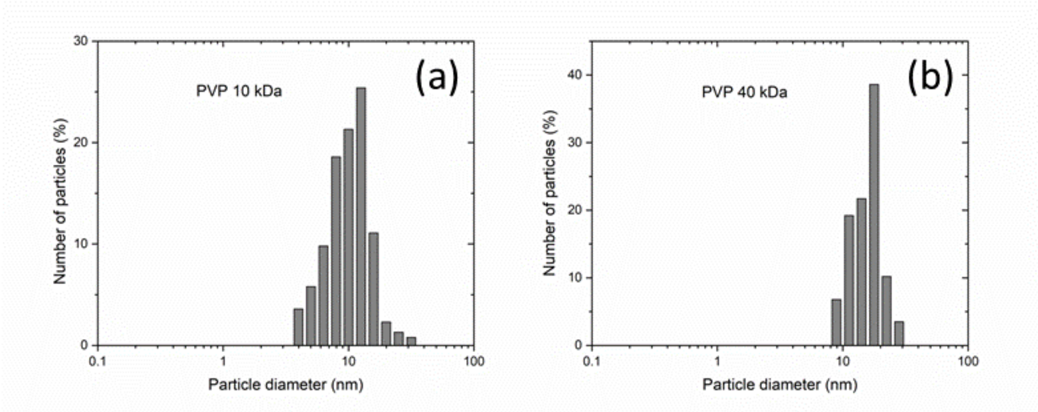



*Figure 3: Plot of probability distribution function of Ag NPs diameters for PVP of two different molecular weights in water. (a): PVP 10 kDa; (b): PVP 40 kDa.*

## 4. Conclusions

The most important outcomes of this study can be resumed in the following points:

- A top-down disaggregation method, exclusively relying upon a physical process, has been proposed as a technique alternative to a standard chemical route for the preparation of metal nanoparticles dispersed in liquid phase. The method is simple, sustainable and inherently safer than amply explored methods and much more economical than many other standard milling techniques based on rotating shafts.
- The present method, where a nanosynthesis is realized in liquid phase, may represent a variant of other indirect milling processes generally operating on dry powders.
- A non-ionic capping agent like polyvinyl pyrrolidone is confirmed to be efficient in stabilizing Ag NPs in top-down mechanosyntesis.
- A future development of the present study will be aimed at determining the fluidization regimes for a maximization of NPs productivity in case of autogenous and non-autogenous disaggregation.

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