

A Composite Stirring-Milling Reagentless Process for Soft Metal Micro- and Nanoparticle Production

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A simple, reagentless, eco-friendly and economically viable method to produce metal micro and nanoparticles (NPs) by means of two different wet milling schemes is proposed. With this technique, metal spheroids of millimetric sizes are subject to a tribological disaggregation in liquid phase, with formation of a nanosized solid whose aggregation is damped by a proper capping agent. This procedure has been tested for elemental Bi, using both a new cross-shaped, custom-made and magnetically driven turbine in the presence of a milling medium and an autogenous vibrating miller. All processes were carried out in inert atmosphere to dampen the oxidation of the as-formed metal particles, whose average diameters and shape has been determined by Dynamic Light Scattering and Field Emission Scanning Electron Microscopy, respectively. The average particle diameters obtained by vibrating milling belong to a micro-sized range (237-433 nm), irrespective of the capping agent used, as are those produced by wet bead milling in the presence of polyvinyl pyrrolidone as capping agent. Instead, Bi NPs with average diameter of 75 nm have been obtained by bead milling with Na lauryl ether sulphate. Finally, a discussion about possible applications of the designed process is proposed.

1. Introduction

Technology related to the use of nanomaterials has seen a rapid development in the last few years (Mangifesta et al., 2021). In particular, the evolution of processes for nanosynthesis has gone through several stages, where the physicochemical methods always represent a still valid benchmark for many reasons. Wet chemical methods (Baig et al., 2021) offer several advantages, namely low cost of apparatuses, easy controllability and they lend themselves to large-scale transfer of production (Thacharon et al., 2022). Among them, bottom-up methods are the most successful and they have been largely adopted in the manufacture of refractory materials, organic nanocomposites and zerovalent elements dispersions, including noble and non-noble metals (Khan et al., 2022). The recent protocols are inspired by the implementation of sustainable and eco-friendly processes, according to the guidewords of substitution and attenuation, aiming at a cleaner production (Reverberi et al., 2018) minimizing as well the opportunity for operator violations related to those risks which are considered less serious, e.g., failure to use personal protection equipment (Fabiano et al., 2022). For this reason, many toxic reagents commonly employed in chemical synthesis are going to be replaced by less noxious reactants that proved to be satisfactory in many cases, specifically pertaining to redox reactions typically adopted in zerovalent element synthesis. Current nanotechnology is generally oriented to a multiobjective optimization, as it is not necessarily limited to the aforementioned chemical aspects. In fact, highly energy-demanding synthesis techniques, like thermolysis or other pyrolysis-based methods, (Chiarioni et al., 2006) are being progressively replaced by non-energetic schemes. For this reason, purely physical techniques based on cost-effective apparatuses (Reverberi et al., 2020) are considered as a valid alternative to bottom-up wet chemical processes. The advantages in terms of variable costs are considerable, thanks to the use of economical precursors and the setup of milder operating

conditions, with important benefits as far as industrial safety is concerned (Fabiano et al., 2019). The side effect of such an approach stems in the quality of the final product that, in case of NPs, is often affected by a distribution of average diameters much wider than obtained by traditional bottom-up processes. This trendline concerns also the synthesis of zerovalent metal NPs which, initially based on redox methods, is progressively shifting towards top-down methods based on reagentless processes, with a particular attention to mechanosynthesis. In particular, zerovalent Bi particles and their composites are in the hotspot for their catalytic (Chen et al., 2017) and photocatalytic properties, the latter with promising results in the abatement of polluting gases like nitrogen oxides by visible light (Guo et al., 2020). Interestingly, Mourdikoudis et al. (2022) developed original protocols for synthesizing Bi-based nanoalloys, showing performances in oxygen reduction and in hydrogen production comparable to those offered by noble monometallic electrocatalysts. Bi particles, irrespective of their size, have a good tolerability and low toxicity for man and mammals. For this reason, Bi dispersions and nanodispersions have important biomedical applications as radiosensitizers, multimodal theragnostic, imaging contrast agent (Gomez et al., 2021) and antibiofilm techniques (Vazquez-Munoz et al., 2020a). On that note, the importance of elemental Bi in many aspects of technology and the need of synthesizing Bi dispersions with alternative techniques is the main motivation leading to the realization of the present study, where two different mechanosynthesis techniques for the production of Bi micro and nanoparticles are proposed and compared. Specifically, a precursor made of Bi granules is adopted and subject to comminution in a liquid phase where capping agents have been dissolved to damp particle aggregation. The disaggregation process is carried out in the presence of Y_2O_3 – stabilized ZrO_2 balls as a milling medium in case of liquid-immersed rotating milling, while this milling medium is absent in case of autogenous disaggregation by vertical vibration. The remainder of this paper is organized as follows. In Section 2, the materials and the techniques are described, together with technical details pertaining to the realization of the experimental set-up. In Section 3, the results are presented and discussed in comparison with analogous studies reported in literature. In Section 4, the conclusions are drawn and a forward-looking view of future research is proposed.

2. Experimental

2.1 Materials and methods

Bi metal flakes (Bi, 99.95%, Specialty Metals Corp., Kent, 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, $(C_6H_9NO)_n$, 40 kDa, 99%, La Farnochimica, Genova, Italy); Sodium lauryl ether sulphate (SLES, 27% in water, $C_{12+2n}H_{25+4n}NaO_{4+n}S$, Andrea Gallo, Genova, Italy) have been used as purchased, except for the Bi metal precursor which has been reshaped into granules by a customarily made technique as follows. Specifically, Bi metal has been melted in an alumina crucible and further poured into a mold so as to make sticks from it. They were then cut into cylinders subsequently remelted and converted into spheroid-shaped granules having an average diameter of 4 mm. Deionized water has been deaerated by stripping the dissolved oxygen with argon. All experiments have been carried out at room temperature. The particles have been characterized in diameter by Dynamic Light Scattering (DLS) using a Zetasizer Nano ZS instrument (Malvern Instruments, Malvern, UK), holding a 2 cm³ sample in a suitable polymethyl methacrylate (PMMA) cuvette. A built-in software allowed determining the relevant distribution curve by averaging on different sampling times. The particle shape has been investigated by Field Emission Scanning Electron Microscopy (FESEM), using 20 kV as a maximum voltage to avoid spurious signals in the image acquisition. The samples have been prepared by sonication of the pristine liquid dispersion, followed by drop-spreading on a mica substrate, with further vacuum drying and final sputtering by graphitic carbon by physical vapor deposition (PVD).

2.2 The milling setup

Two different milling apparatuses have been utilized, differing according to the physical principles governing the disaggregation process. The vertical vibrating miller adopted in some of the experiments here proposed has been already described in a previous work (Reverberi et al., 2022a) and its technical details will not be any more discussed. Instead, a new bead miller assembly has been realized here, according to the scheme reported in Figure 1. Briefly, a round-shaped vessel of 36 mm diameter, equipped with a glass cover connected with a pipe for gas recirculation, serves as a container for a holdup comprising 50 YSZ balls, 20 spheroids of metal Bi precursor and 6 cm³ of water containing a single capping agent for each experimental test. The novelty introduced in this study consists in a new type of magnetically driven cross-shaped stirrer, made of a polytetrafluoroethylene (PTFE)-coated stirring bar inserted in an orthogonal PTFE cylinder. The latter element has the function of intercepting the collective motion of the solid holdup subject to the entrainment of the rotating liquid inside the container. In this way, the overall precursor disaggregation

efficiency can be increased with respect to those typical of bead millers operating with a purely cylindrical stirring bar. The YSZ balls, whose hardness is considerably higher than the one of Bi metal spheroids, promote a surface disaggregation of the precursor by a combination of impact and shear stress. Owing to the limited torque offered by the magnetic stirrer, the diameter and number of the milling ceramic spheres have been accurately selected in preliminary experiments, as these two parameters determine univocally the maximum admissible value ω_m of the stirring speed ω in all experiments here proposed. In fact, for $\omega > \omega_m$, the turbine tends to rotate by floating on the solid hold-up with chaotic random jumps, dramatically dropping the comminution efficiency. With all these consideration in mind, a value $\omega = 500 \text{ min}^{-1}$ has been kept in all experiments. It is worth stressing that the cross-shaped stirrer cannot assume a horizontal position in the miller, as one of the two cross arms was designed with a length greater than the diameter of the vessel.

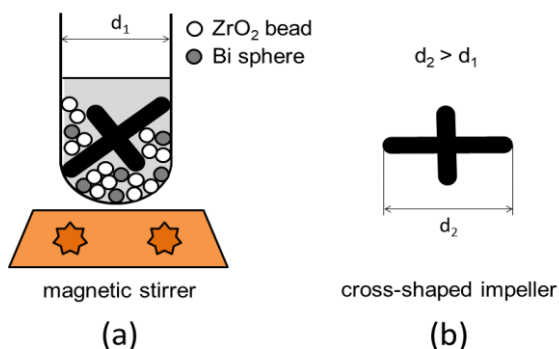


Figure 1: (a): scheme of the designed bead milling technique. (b): designed cross-shaped stirring element.

3. Results and discussions

A common point to many works devoted to the synthesis of $\text{Bi}^{(0)}$ NPs by wet chemical methods is the use of PVP as capping agent, proving its effectiveness in a wide choice of experimental conditions (Vazquez-Munoz et al., 2020b). This finding motivated the choice of PVP as a capping agent also for the present study, but the results are different from the one typical of bottom-up standard processes, as it is observable by inspection of Figure 2. In it, the particle diameter distribution function by number is plotted for $\text{Bi}^{(0)}$ particles obtained after two hours of comminution carried out by the two different milling apparatuses. The supernatant, collected after 12 hours of settling in argon atmosphere to minimize surface oxidation of the solid phase, has been primarily tested by DLS analysis.

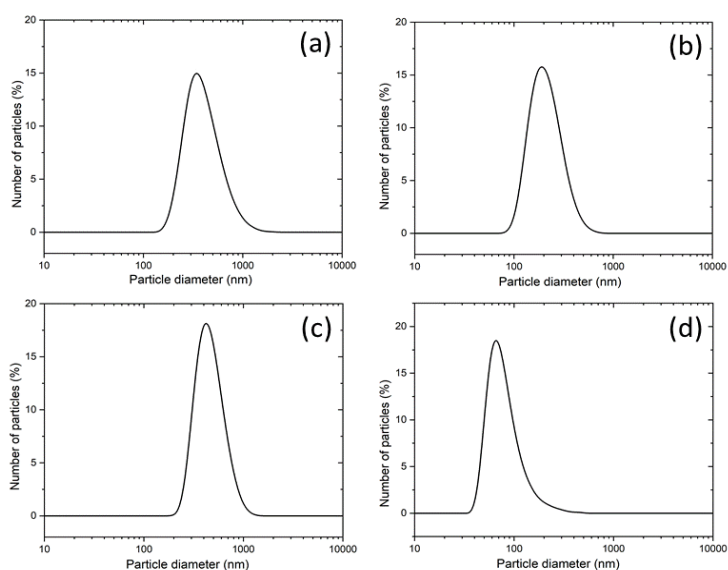


Figure 2: Upper plots: particle diameter distribution function of Bi particles obtained by vertical vibrating milling using PVP (a) and SLES (b). Lower plots: particle diameter distribution function of Bi particles obtained by bead milling using PVP (c) and SLES (d).

Upper and lower plots refer to dispersions obtained by vertical vibrating milling and bead milling, respectively. Left and right plots refer to PVP and SLES, dissolved in water at concentrations of 5% and 4.5%, respectively. The average diameters obtained by vertical vibrating milling have values in a range 237-433 nm, namely typical of microdispersions, irrespective of the type of capping agent used. The situation is different when the disaggregation is performed in the bead milling apparatus of Figure 1. In fact, while PVP-capped $\text{Bi}^{(0)}$ particles still have an average diameter of 505 nm, SLES-capped $\text{Bi}^{(0)}$ can be considered as NPs, having an average diameter of 75 nm. In this case, the shock and abrasion exerted by a milling medium, here represented by YSZ balls, proved to be much more efficient than the reciprocal collisions between precursor spheroids in autogenous disaggregation for the synthesis of NPs. The reasons are connected to the physical properties of the metallic precursor, whose hardness and plasticity may have a basic role. This hypothesis can be confirmed by the fact that, at the end of grinding, it has been observed that many YSZ spheres are superficially covered by an adherent metallic Bi layer to the point of determining an almost complete surface metallization. On the opposite, metals like Ag, namely harder than Bi, did not give rise to an appreciable surface metallization on ceramic spheres and produced dispersions of much finer particles by autogenous disaggregation in aqueous solvent (Reverberi et al., 2022b). For the sake of completeness, the statistical properties of the diameters pertaining to the distribution curves plotted in Figure 2 were reported in Table 1.

Table 1: Data concerning statistical properties of $\text{Bi}^{(0)}$ particles diameters distribution function with different synthesis techniques and capping agents.

Technique and capping agent	Average diameter [nm]	Peak position [nm]	Standard deviation [nm]
Vibrating milling with PVP (Figure 2-a)	433	345	180
Vibrating milling with SLES (Figure 2-b)	237	192	88
Bead milling with PVP (Figure 2-c)	505	424	182
Bead milling with SLES (Figure 2-d)	75	66	23

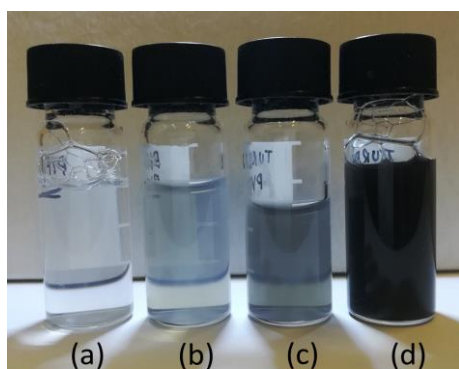


Figure 3: Images of four zerovalent Bi dispersions obtained with two different equipments and capping agents. (a): PVP in vibrating milling. (b): SLES in vibrating milling. (c): PVP in bead milling. (d): SLES in bead milling.

In Figure 3, the two vials on the left contain samples produced by vibrating milling, while the others on the right have been obtained by bead milling. All vials contain supernatants separated from the mother solution after the same settling time. By simple visual inspection of the color intensity, bead milling produced darker dispersions, suggesting that vibrating milling is less efficient than bead milling in terms of suspended mass of $\text{Bi}^{(0)}$ dispersion. Intriguingly, within each adopted process, it can be observed that PVP is globally less performing than SLES, both in terms of particle diameter and in concentration. This experimental finding is somewhat unexpected, taking into account that PVP is perhaps one of the most popular capping agents in standard bottom-up wet chemical processes. Varshney et al. (2021) obtained nanosized Bi_2O_3 dispersion of 14 nm diameter, stabilized with Na dodecyl sulphate and oleic acid, proving that an anionic stabilizer is efficient in preventing aggregation of Bi_2O_3 . Taking into account that $\text{Bi}^{(0)}$ particles in water unavoidably tend to superficially form a very thin oxide layer if residual oxygen is present, one may explain why SLES, a likewise anionic stabilizer, is efficient in capping also zerovalent Bi particles here produced. In Figure 4, two FESEM analyses of $\text{Bi}^{(0)}$ particles synthesized by bead milling are reported. Left and right images refer to PVP- and SLES-capped particles, respectively. In left image, the particles in the field of view are somewhat rare and

this fact is consistent with a greater dilution for PVP-stabilized samples already observed in Figure 3. Some nanosized particles are visible, with diameters in a range 23-34 nm, and this result is seemingly in contrast to the findings reported in DLS analysis. The origin of this discrepancy can be ascribed to a likely clustering effect in solution, which is damped during the FESEM sample preparation procedure where a brief sonication has been adopted before dropping the dispersion on the mica substrate. As expected, the SLES-capped Bi⁽⁰⁾ particles of right image are significantly more numerous, with diameters in a range 22-95 nm, again in contrast, for the aforementioned reasons, with the DLS curves. In all cases, the shape is irregular and a recurrent pattern is not detectable, with a frequent clustering of primary particles. In Figure 5, the EDS analysis of solid particles is reported in the two cases analysed in the previous figure. The presence of a visible oxygen peak can be ascribed to the composition of the mica support and only marginally to a surface oxidation, owing to the protective layer of capping agents irrespective of their chemical structure. The presence of sulphur, whose peak is almost completely superposed to the one of Bi in panel (b) of Figure 5, is due to the anionic group SO₄⁽²⁻⁾ of SLES.

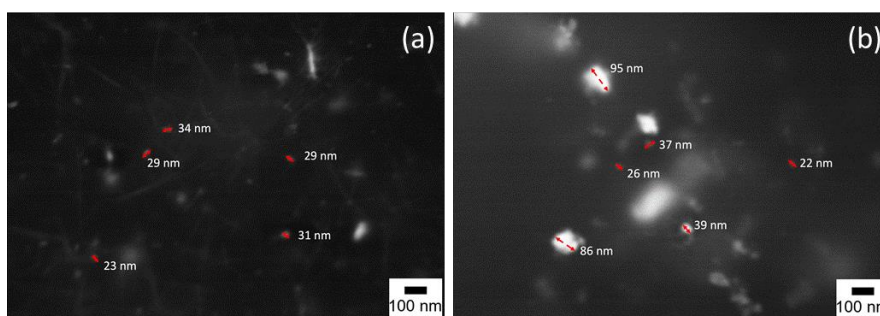


Figure 4: FESEM images of zerovalent Bi particles synthesized by bead milling in aqueous solvent using PVP (a) and SLES (b).

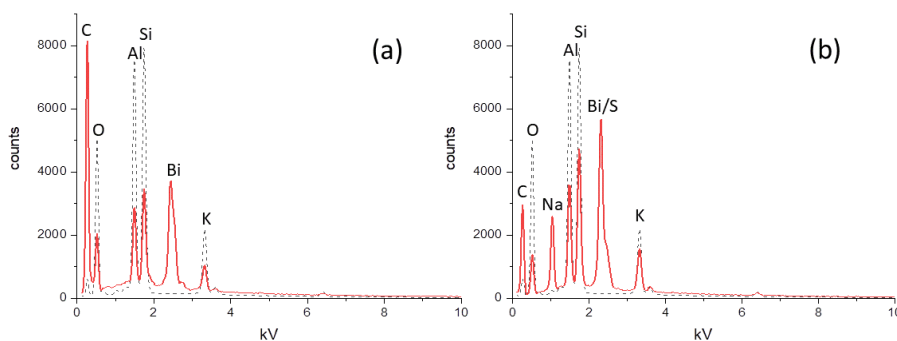


Figure 5. EDS compositional analyses of Bi particles obtained by bead milling in aqueous solvent using PVP (a) and SLES (b). Dashed curves refer to a blank signal (mica), while red curves refer to particle analysis.

4. Conclusions

Bi metal dispersions in water have been prepared by two top-down reagentless processes based on a tribological disaggregation of a bulky metal precursor in the presence of capping agents preventing particle aggregation. Two capping agents have been adopted, differing from one another according to the polar or nonpolar character of the relevant molecule. The performances of these stabilizing agents showed a clear superiority of SLES with respect to PVP in the stabilization of zerovalent Bi NPs. The most important findings can be summarized in the following points:

- A sustainable, energy-saving and safety affordable process for zerovalent Bi particles synthesis has been set up as a valid alternative to standard bottom-up wet chemical processes.
- The process is environmentally friendly, as only capping agents are used and no chemical reaction is needed for metal particles synthesis.
- The process is designed by an inherent safety approach through the practical concept of eliminating or minimizing hazards. In fact, the synthesis of zerovalent Bi particles by bead milling, irrespective of their

dimension, can be carried out at room temperature. In this aspect, the present process is considerably inherently safer than standard bottom-up wet chemical methods, often based on solvothermal schemes operating at temperatures higher than 100 °C, under conditions more favourable to oxidation of metal particles.

- This technique may represent a cost-effective alternative to standard bottom-up processes for the realization of catalysts and electrocatalysts in water splitting technology. In view of plant scale-up, upon proper implementation with suitable sensors, the production set-up allows obtaining reliable dynamic control of process conditions, product quality and early warning signals for process deviations.

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