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Sustainable and Inherent Safe Tribological Process for Metal Nanoparticles Production

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A green and sustainable process is proposed for the synthesis of metal nanoparticles (NPs) by means of a solid disaggregation in a liquid phase. A solid metal substrate, embedded in a solution containing suitable capping agents and surfactants, undergoes comminution carried out by a rotating shaft of hardness greater than the one typical of the eroded substrate. The NPs have been characterized by dynamic light scattering for particle diameter. The effect of a technical solution replacing the presence of an abrading pad and the role of different physicochemical properties of the capping agent employed to damp particle aggregation have been investigated and discussed. In three out of four experiments carried out with different capping agents, the average metal NPs diameter is smaller than 10 nm. The present process does not require a complex experimental apparatus typical of dispersion machines customarily used on an industrial scale, generally relying upon direct or indirect milling equipment. With respect to the latter techniques, the advantages offered by the process proposed here stem from a possibility of monitoring the time trend of the NPs synthesis with minimal contamination of the as-produced NPs deriving from disaggregation of the milling medium.

1. Introduction

The nanotechnology of NPs showed impressive development with significant implications in many sectors of industrial production (Trofa et al., 2020). As a consequence, many different manufacturing activities are now strictly interlinked, and the corresponding branches of scientific disciplines follow the same trend. New ways for process design and shifts in the operation of processes are needed to improve the safety and sustainability of nanomaterials production processes, moving towards Safety 4.0 (Pasman and Fabiano, 2021). The pressing need for innovative nanomaterials (Pascariu et al., 2013) led to a progressive improvement of process synthesis techniques both for zerovalent elemental nanoparticles (ZV-NPs) (Fabiano et al., 2019) and for nanosized organic or inorganic compounds of different chemical composition, having a wide range of applications (Stepniowski et al., 2019). As an example, ZV-NPs are well known in environmental decontamination (Muradova et al., 2016) owing to their specific reactivity towards organic pollutants, which are decomposed with fast kinetics making them useful sorbent for soil remediation. Bi ZV-NPs (Das et al., 2020), thanks to their good tolerability in the human body, have been successfully adopted in organ targeting and in theranostics as efficient drug carriers in cancer therapy and other diseases. Cu ZV-NPs and their related nanostructures (El Berry et al., 2020) have been successfully adopted for the degradation of dyes (El-Berry et al., 2021), owing to marked photocatalytic properties of several transition elements (Nagayothi et al., 2020), including noble metals like Au and Ag, with promising uses as standard catalysts (Nguyen and Nguyen, 2020).
Nanomaterials made of compounds instead of pure elements represent a large subset, with applications even wider than the previously described, including wastewater treatment (Alberti et al., 2021), disinfection (Kayani et al., 2021), decontamination (Basaleh et al., 2021), nanoelectronics (Gorokh et al., 2019) and many others

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where organic and inorganic structures converge to a new and scientifically fascinating merging point, as in the case of metal-organic frameworks (MOF) composites, giving a boost to the photocatalytic efficiency of semiconductors (Zhao et al., 2021).
A problem related to most nanomaterials stems from the techniques adopted for their synthesis. In fact, many chemical processes for NPs production require the use of reagents (and, specifically, reductants for ZV-NPs), being often noxious for the environment or toxic for humans. As an example, the negative effects of hydrazine and its derivatives as proven carcinogens have been widely discussed in the literature.
A growing need for safer and environmentally sound techniques (Jasrotia et al., 2020) and the consequent necessity of sustainable production protocols (Laciok et al., 2021) led to greater attention to green chemical routes (Reverberi et al., 2017) and also to a revamping of reagentless methods of production, essentially based on purely physical processes. These methods often rely upon laser ablation (Intartaglia et al., 2016) and mechanical disaggregation by attrition and shear stress, like milling, grinding and other techniques involving fracture and surface comminution (Mc Mahon et al., 2014). In this context, several strategies can be adopted (Yadav et al., 2012), differing from one another according to the presence/absence of milling media (Gorrasi and Sorrentino, 2015). Generally, the choice of the most suitable equipment depends on the granulometry of the starting material, often in the form of powder, whose size may belong to a range of mm in traditional tumbling millers, or it may directly start from μm sizes in bead milling processes. These methods can be classified as top-down techniques, as the final product of desired granulometry is obtained using a starting material whose initial average diameter is greater than the final one. For the sake of a simple classification, the aforementioned techniques are essentially ascribable to physical processes in that they do not need the use of toxic chemical reagents except for the presence of capping agents, often unavoidable in order to prevent NPs from aggregation.
In this sense, these physical techniques are a promising eco-friendly and sustainable alternative to chemical synthesis processes (Ullah et al., 2014), but the cost of apparatuses required in reagentless physical methods is a real bottleneck restricting their implementation on a large scale. As a consequence, the need for safe and economical equipment is the main target of recent research in top-down NPs synthesis, according to the protocols of substitution and risk attenuation.
In agreement with this trend, this paper reports a simple and cost-effective synthesis of Ag ZV-NPs obtained by means of a tribological process of surface disaggregation. The main novelty of the present work is that no chemical reagents are used, and mild operating conditions are adopted in order to meet sustainable and inherent safe production criteria, nowadays representing a paradigm in process technology and energy optimization (Chew et al., 2015). The paper is organized according to the following scheme: in Section 2, the experimental apparatus is described in its basic components, and the operative conditions are outlined. In section 3, the results are discussed, and the NPs obtained with different capping agents are characterized in diameter. In Section 4, the conclusions are drawn, and the direction for future works is traced.

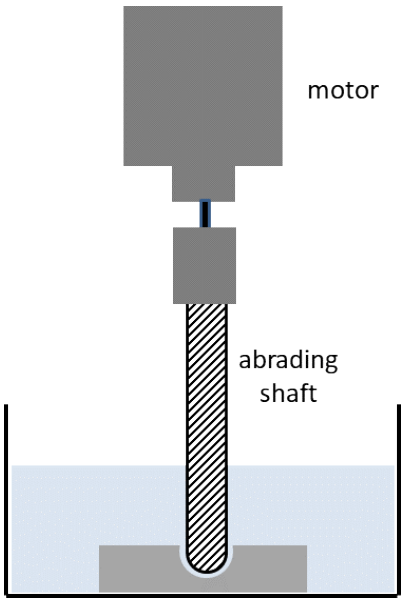

Figure 1: Simplified scheme of the experimental setup for nanoparticles synthesis.

2. Materials and methods

2.1 Experimental setup

Silver metal (Ag, 99.9 %, Sigma-Aldrich, Milano, Italy); myristyl trimethylammonium bromide (MTAB, $C_{14}H_{29}N(CH_3)_3Br$, ≥99 %, Sigma-Aldrich, Milano, Italy), Sodium dodecyl sulphate (SDS, $NaC_{12}H_{25}SO_4$, ≥99 %, Sigma Aldrich, Milano, Italy), polyethylene glycol (PEG, $H(C_2H_4O)_nOH$, 4 kDa, 99 %, La Farmochimica, Genova, Italy), polyvinyl pyrrolidone (PVP, $(C_6H_9NO)_n$, 40 kDa, 99 %, La Farmochimica, Genova, Italy) have been chosen in the present experimental campaign in order to test the action of different capping agents according to their molecular structure and ionic character, which is typical of anionic and cationic molecules like SDS and CTAB, respectively, while it is absent in PEG and PVP (Reverberi e al., 2020). These properties and the relevant concentrations have been indicated in Table 1. All experiments are carried out at room temperature in double replicate. A plate of Ag metal of 2 mm thickness is fixed at the bottom of a vessel containing 10 cm^3 of distilled water, previously deaerated by stripping the dissolved O_2 by a stream of N_2 bubbled in the liquid. The surface of the Ag plate is previously punched by a burin making a spherically shaped cavity intended to serve as a housing for the semicircular tip of a rotating shaft. For the present experiments, a glass shaft of 5 mm diameter has been adopted, forming a 90° angle with the surface of the Ag plate. The shear stress between the tip and the metal surface produces Ag particles that are released in the solution containing the aforementioned capping agents, damping agglomeration between primary particles. The rotating shaft is directly connected with a gearbox, ensuring a proper speed reduction down to approximately 400 rpm.
The present assembly, as depicted in Figure 1, is somewhat different from the one adopted in a previous work (Reverberi et al., 2021), where the surface disaggregation was carried out by a translating orbital motion of a moving arm bearing an abrasive material on its end. The improvements adopted in the present study can be essentially summarized in the following points:

- The absence of a backing pad of synthetic fabric is advantageous, as this component would entrap a considerable amount of NPs among its fibres, thus reducing the global yield of the process;
- A friction material of a synthetic fabric (now absent) would be subject to progressive disaggregation during its use, thus releasing unwanted debris in the solution needing a further separation for NPs purification.

All equipment is located in a gas-tight chamber, ensuring safety operations against airborne NPs dispersions. The force applied by the rotating shaft on the eroded Ag substrate is kept steady at a pressure of approximately $3.75 \cdot 10^5$ Nm^{-2}. A single experiment lasts 1 h, then the solution is allowed to rest for 6 h before separating the supernatant, which is further analyzed for particle characterization.

Table 1: Physicochemical properties and concentrations of capping agents used in the present experiments.

Capping agent	Molar mass [Da]	Type	Concentration [g/cm^3]
Sodium dodecyl sulphate (SDS)	288.37	Anionic	0.02
Myristyl trimethylammonium bromide (MTAB)	336.39	Cationic	0.02
Polyvinyl-pyrrolidone (PVP)	40 k	Non-ionic	0.02
Polyethylene glycol (PEG)	4 k	Non-ionic	0.02

2.2 Analytical methods

The NPs diameters were assessed by means of DLS carried out with a Zetasizer Nano ZS (Malvern Instruments, Malvern, UK). After modelling the material properties (solvent viscosity at the considered temperature, optical properties of both solvent and solid NPs), the size distribution by scattered light intensity was converted first to size distribution by volume and finally to size distribution by number. For water at 22°C, viscosity and a refractive index of 0.954 cP and 1.33 were assumed. For the Ag NPs, a refractive index and absorption of 0.2 and 0.6 were assumed (Hass and Hadley, 1972). For all samples, nine measurements were carried out, and the corresponding values were averaged in order to damp spurious oscillations due to improper thermalization of the system so as to obtain the representative size distributions displayed in Figure 2.

3. Results and discussion

Metallic Ag has been selected for the present experiments for its important implications in theranostics and pharmacology for their promising anti-viral functionalization (Shoaib et al., 2021). Additionally, its hardness estimated at 2.5-3 on Mohs' scale represents a trade-off between soft metals (like Pb and Sn) and hard ones (like Mo, V, W and other transition metals). The capping agents listed in Table 1 are customarily chosen in stabilizing aqueous NPs dispersions of various compositions (Reverberi et al., 2017), but their uses are not

limited to nanotechnology. For example, PVP and PEG are used in biomedicine and pharmacotherapy (Naz et al., 2017), while ionic surfactants like MTAB and SDS are typically adopted in dentistry (Silva et al., 2020) and detergents, respectively. According to the DLS analysis, the size distributions of the NPs obtained with different capping agents have been plotted in Figure 2, and the respective diameters resulting from log-normal fitting are reported in Table 2. It should be noticed that the peak value for MTAB NPs size fell very close to the lower limit for the measuring range of the instrument (0.1 nm – 10 μm). For the sake of clarity, the fitting profiles are not shown in Figure 2. In the case of PEG (Figure 2d), a shoulder on the left-hand side of the peak clearly appeared as a hint of multiple size distribution. However, the fit was still rather good, as the residuals showed R^2=0.976, still high while lesser than the values for the other capping agent samples (0.988, 0.996 and 0.989, for SDS, MTAB and PVP). The curves revealed the formation of NPs with considerably small diameters for PVP (6.0±1.9 nm), PEG (3.9±1.3 nm) and especially for MTAB (1.0±0.2 nm), while for SDS, they were significantly larger (172±48 nm).

Table 2: Data concerning statistical properties of $Ag^{(0)}$ particles diameters distribution function with different capping agents.

Capping agent	Average diameter [nm]	Standard deviation [nm]	Peak position [nm]
Sodium dodecyl sulphate (SDS)	172	48	165
Myristyl trimethylammonium bromide (MTAB)	1.0	0.2	0.9
Polyvinyl-pyrrolidone (PVP)	6.0	1.9	5.2
Polyethylene glycol (PEG)	3.9	1.3	4.0

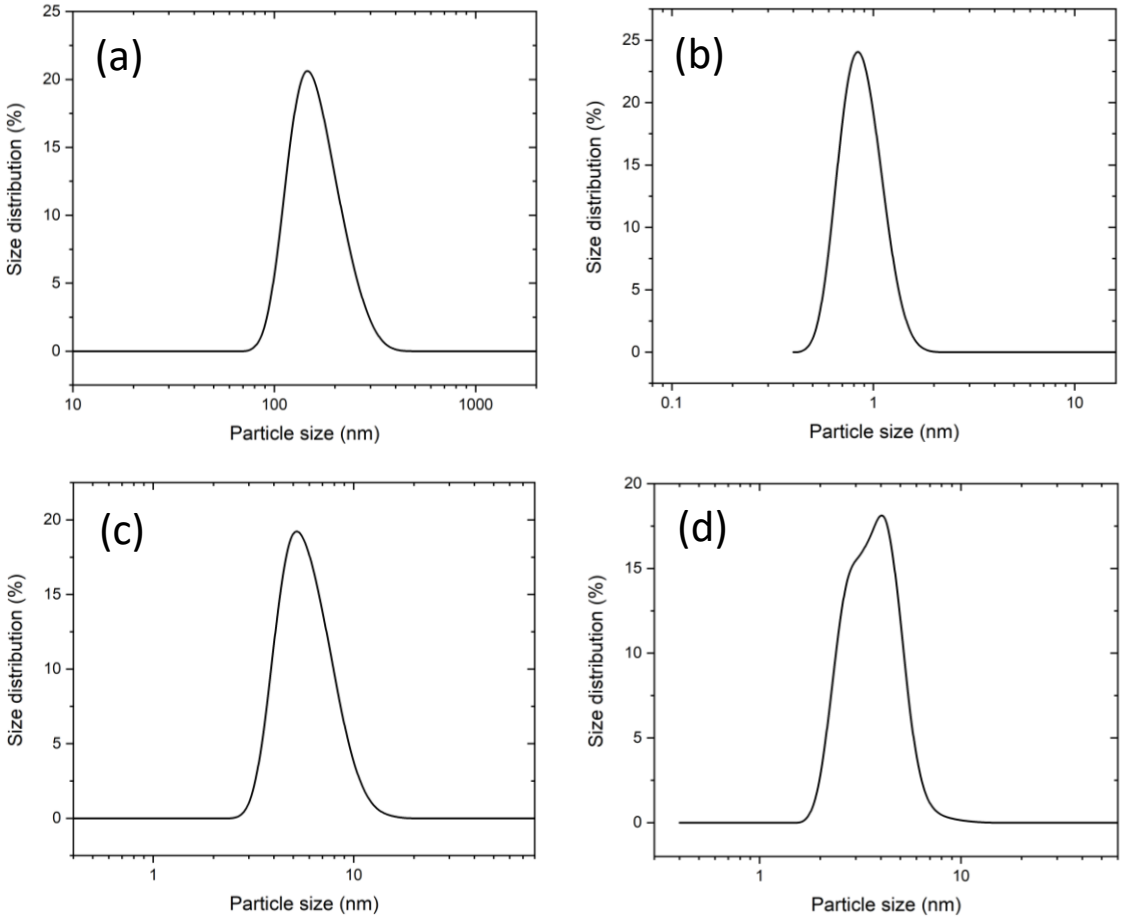

Figure 2: Plot of probability distribution function of $Ag^{(0)}$ particles diameters using different capping agents in water. (a): SDS; (b): MTAB; (c): PVP; (d): PEG.

The action of cationic and anionic capping agents on the formation of Ag NPs has been amply discussed in a context predominantly related to bottom-up synthesis methods by chemical reduction. It has been conjectured that the kind of polarity may interfere with the electron-transfer process between the reductant and the ionic species Ag^+ by complex superposed phenomena, sometimes inhibiting the transfer itself (Khan et al., 2012). Admittedly, in the case of a pure physical synthesis method, as the one here presented, a different stabilization offered by two capping agents of opposite polarity may be reasonably ascribed to local surface affinities with respect to the bulky source material $Ag^{(0)}$.

4. Conclusions

A technique for the production of metal NPs by a simple physical method relying upon shear stress and abrasion in an aqueous medium has been proposed. The method requires the use of capping agents only. The main achievements of the present experimental work can be summed up in the following points:

- The technique discussed in this paper does not require complex and expensive apparatuses usually needed by physical methods, like plasma or laser ablation.
- Four different types of capping agents have been tested, and the results have proven that cationic and non-ionic surfactants have performances much more promising than anionic surfactants like SDS.
- The diameters of the as-prepared metal NPs are very small, with average values <10 nm in three different cases (except for SDS), proving that this method may be an efficient alternative to standard and consolidated bottom-up chemical processes.
- This process, here tested for Ag for the first time, may represent a promising starting point for the preparation of NPs of different metals, exploiting the low energy consumption.
- In view of industrial application, the technique allows the implementation of measures aiming at accident prevention by the use of inherently safer substances and by the inherent safe peculiarity of this sustainable production method. Future development of the present work will be addressed to a scale-up of the technique here outlined in order to improve the productivity of the global process.

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