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Gallium Nanoparticles by Surface Wet Disaggregation and Abrasion

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Nanoparticles of zerovalent Gallium have been produced by surface disaggregation carried out by means of mechanical abrasion in aqueous phase where capping agents have been dissolved. The particles have been characterized in diameter by dynamic light scattering. At a constant grinding force acting on metal surface, it has been observed that the dimension of the as-produced particles is correlated with the physico-chemical properties of the capping agents. Green and eco-friendly stabilizers like glucose and urea showed a higher efficiency than standard capping agents. Such technique proves that metal particles can be obtained without resorting to complex processes relying upon expensive and energy-wasting mechanical apparatuses based on autogenous and non-autogenous disaggregation. The present method, owing to the absence of toxic or noxious reagents usually employed in standard wet chemical etching processes, may represent a cost-effective and environmentally friendly technique for the synthesis of soft metal particles dispersions with application in theranostics and for heat transfer technologies in mechanical and electronic engineering.

1. Introduction

The synthesis of nanoparticles (NPs) has become object of intense investigations in last decades. In 1959, with a prophetic intuition, the Nobel prize Richard Feynman predicted the possibility of creating new materials by assembling structures atom by atom. Nowadays, many research areas are involved in nanotechnologies, with important implications on a broad industry spectrum related to smart materials (Pascariu, 2013). In fact, nanomaterials often show unexpected physico-chemical properties typically absent in conventional bulk materials having the same chemical composition. In the specific field of NPs, chemical and physical methods are the cornerstones of the relevant manufacturing techniques, with variants depending on NPs stability, reactivity, safety (Fabiano et al., 2019) and environmental compatibility (Reverberi et al., 2017). The choice of the schemes adopted for NPs production by chemical methods depends primarily on their cost-effectiveness, joined with the possibility of a satisfactory quality control of the final product without requiring exceedingly complex apparatuses. Chemical processes for NPs synthesis may be carried out in liquid or in gaseous phase, with a prevailing diffusion of the former. In fact, the latter method generally needs an energy input supplied by heating that, in turn, requires the presence of flames, electrical heating, discharges and plasma, often leading to higher fixed and operating costs, introducing as well novel hazards at extreme and unexplored conditions (Pasman and Fabiano, 2021). Nevertheless, compounds giving thermally stable NPs are produced at a large scale by sprayed flames, and this is perhaps one of the most important process for the synthesis of NPs of refractory materials such as Al_2O_3, TiO_2, and many others.
The excellent review paper by Cushing et al. (2004) is an exhaustive summary of methods for the synthesis of NPs embedded in liquid solvents. In these cases, in order to limit or even prevent NPs aggregation, organic molecules are adopted as stabilizing agents, containing amino, hydroxyl and carboxyl functional groups

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having affinity with the single NP. The stabilization occurs according to different mechanisms depending on the concentration of the capping agent forming a shell surrounding the NP at low concentrations or giving rise to micelles covered by NPs at higher concentrations. In other cases, the solvent itself acts as a stabilizer, owing to its rheological properties often combined with specific chemical properties having a direct role in the synthesis, as in redox processes (Reverberi et al., 2018). These techniques are of great importance for the synthesis of metal NPs (El-Berry et al., 2021), as the precursors usually adopted contain the metal in ionic form requiring proper reductants generally exerting toxic effects on upper organisms and on the environment. For these reasons, in the last years, many studies have been proposed where toxic electron-donors like hydrazonium salts or borohydrides have been replaced by more environmentally friendly reagents of natural origin (Das et al., 2020), usually deriving from vegetal (Jasrotia et al., 2020) or even animal products. On that note, Asmathunisha and Kathiresan (2013) reviewed many green techniques for NPs manufacturing by marine organisms and their derivative products. Among them, fish oil was proven to be useful in the preparation of Ag NPs (Khanna and Nair, 2009) owing to its properties of both reductant and capping agent. As a general consideration, such techniques relying upon “green reductants” led to satisfactory results in the synthesis of NPs made of noble metals (Reverberi et al., 2017), with more questionable results concerning NPs of more electropositive elements, except for zerovalent Fe NPs (Mondal et al., 2020), much used in water decontamination. In the same context of green NPs synthesis, other authors proposed the use of bacteria and microorganisms as “nanofactories”, where the redox reactions leading to the formation of zerovalent NPs are carried out by metabolic processes of living cells (Tsekhmistrenko et al., 2020).

Electrochemical methods represent an interesting variant to liquid-phase chemical methods (Stępniowski et al., 2019), as they allow to produce agglomerates of metal NPs of high purity with possibility of tuning shape and dimension by acting on several parameters like precursor concentration, current density and temperature (Raja, 2008). Despite these processes were considered as a marginal technique in past years (Cushing et al., 2004), they have attracted a growing number of scientists in recent times, owing to the possibility of operating in mixed phases.

Physical methods are essentially top-down processes, as they usually start from a bulky material which is subject to a disaggregation process carried out by different mechanisms of surface ablation (Intartaglia et al., 2016). Plasma processes proved to be suitable in many cases, but the costs related to this technology may be demanding in view of a large scale transfer. For these reasons, alternative methods relying upon more economical process have been proposed, where NPs are produced by shear stress, impact and comminution of a starting material, irrespective of its composition. In their review, Gorrasi and Sorrentino (2015) surveyed several techniques of mechanical milling for the preparation of nanocomposites and they described the related apparatuses relying upon solid-state mixing. The energy transferred to the particulate phase depends on the type of equipment (Yadav et al., 2012) and it may be high enough to trigger chemical reactions between different solid phases mixed together in the inner hold-up.

When the comminution is carried out in the presence of a liquid medium, the powder is milled by the action of hard spheres colliding in the suspension, where they realize a low-energy comminution releasing primary particles from NPs agglomerates (Ogi et al., 2017). Indeed, low-energy bead-milling media-assisted apparatuses seem somehow to overcome the commonly accepted rule of thumb that the minimum achievable final diameter of produced NPs in these grinding systems is 1/1000 of the primary particles (Reverberi et al., 2020), although further investigation is still needed to optimize the system parameters (Trofa et al., 2020).

The presence of surfactants has a beneficial effect, same as in chemical methods, by damping the kinetics of re-aggregation (Ullah et al., 2014). Such mechanical disaggregation processes have extended application in the manufacture of nanofluids used in heat exchangers, as an unexpected growth in the overall heat exchange coefficient was observed even for low concentration of the dispersed solid phase. A crucial drawback stems in the progressive fall of stability for growing concentration of NPs, which may lead to deposits and fouling along the duct walls with serious implications in plant management. Despite the presence of surfactants and capping agents, such phenomenon remains an open problem to be faced possibly by inherent safe approaches.

All the aforementioned mechanical processes are characterized by a moving solid phase subject to disaggregation, which can be carried out by autogenous impact/attrition or in the presence of milling beads. The impacting bodies are usually made of ZrO_2, Al_2O_3, SiC or other materials having a surface hardness high enough to avoid the contamination of powders with impurities deriving from their own abrasion.

In a slightly different context, even though always concerning purely physical methods, some authors have observed that some materials, when subject to soft grinding or simple polishing, may release NPs under certain conditions. On that note, Mandal and Saha (2020) prepared carbon and graphene nanoflakes by simple surface abrasion using fine sand paper, thus avoiding both noxious chemicals and complex physical apparatuses realizing a sustainable process. The present study fits into an analogous scheme, in that it describes how NPs from metallic Ga can be produced by simple surface attrition and fretting, without resorting

to milling devices. The process is carried out at a temperature below the melting point of Ga. The paper is divided as follows: in Section 2, the experimental apparatus is outlined in detail and the operative conditions are described. In section 3, the results are presented and the as-prepared particles are characterized in diameter, according to the type of capping agent adopted in the disaggregation process. In Section 4, the conclusions are drawn in view of future developments of the present technique.

2. Materials and methods

2.1 Experimental setup

Gallium metal (Ga, ≥99.5%, Sigma-Aldrich, Milano, Italy); polyvinyl-pyrrolidone (PVP, $(C_6H_9NO)_n$, 25kDa and 40kDa, 99%, La Farmochimica, Genova, Italy), Sodium dodecyl sulphate (SDS, $NaC_{12}H_{25}SO_4$, 99%, Sigma Aldrich, Milano, Italy), urea (CON_2H_4, 99%, La Farmochimica, Genova, Italy), glucose ($C_6H_{12}O_6$, 99%, La Farmochimica, Genova. Italy), were used as purchased. The relevant concentrations are listed in Table 1.
The choice of the aforementioned capping agents aims to ascertain and compare the performances of eco-friendly compounds like glucose or urea with those of standard stabilizers like PVP or SDS, widely used in many technical applications (Grytsenko et al, 2019).
The process of abrasion was carried out with a customarily built apparatus that is schematically represented in Figure 1. A Ga metal plate of 3 cm diameter is blocked at the bottom of a beaker containing a solvent, acting as a dispersing medium for the particles. Different capping agent have been used, to test which of them is the most appropriate to prevent particle agglomeration. The beaker is firmly locked on a fixed support. A backing pad of fabric, located at the edge of a shaft, is kept in contact with the metal plate. The fabric is made of pressed, non-woven polypropylene wires, fixed to the pad by an adhesive joint whose layer is thin enough to ensure only a contact between the fabric and the metal surface undergoing disaggregation. The shaft is integral with a moving arm describing orbital trajectories while keeping the pad in contact with the solid metal surface, which undergoes the process of surface disaggregation. The force exerted by the pad on the metal surface is kept constant at a value corresponding to a pressure of ~ $3.6 \cdot 10^5$ Nm^{-2}. For all samples, the process of abrasion has a duration of 10 min. Afterwards, the solvent is allowed to settle for 6 h in order to let the debris resulting from the pad wear to deposit on the bottom. The process is performed at room temperature.

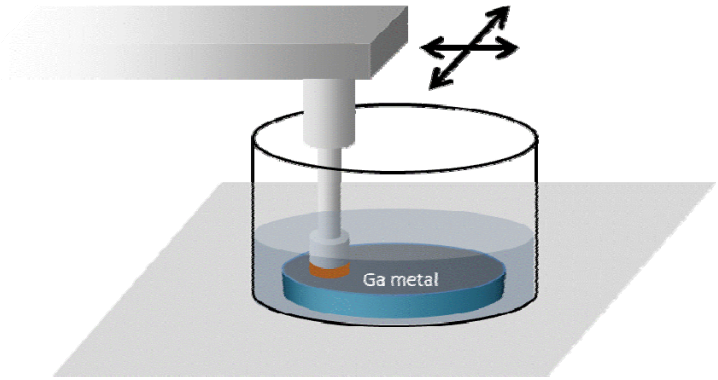

Figure 1: Scheme of the experimental apparatus adopted in the present study. The orange disc is the abrasive fabric pad

Table 1: Data concerning the capping agents adopted in the present experiments.

Capping agent	Molar mass [Da]	Type	Concentration [g/cm^3]
Polyvinyl-pyrrolidone (PVP)	25 k	Non-ionic	0.033
Polyvinyl-pyrrolidone (PVP)	40 k	Non-ionic	0.033
Sodium dodecyl sulphate (SDS)	288.37	Anionic	0.033
Urea	60.06	Non-ionic	0.066
Glucose	180.16	Non-ionic	0.033

2.2 Analytical methods

A Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) was used to determine the probability distribution function of the $Ga^{(0)}$ NPs diameters by means of DLS measurements. Given the little amount of capping agent, the liquid medium of the suspended NPs was considered in all cases to be the same as pure water,

with a viscosity and a refractive index (at 22°C) of 0.954 cP and 1.33, respectively. For the NPs material, we assumed a refractive index (at the instrument lamp wavelength, 633 nm) of 1.62 (Hass and Hadley, 1972); in the absence of available clear literature data for metallic Ga, a tentative absorption coefficient of 0.01 (i.e. different from zero yet very low, as suggested by the solution transparency) was adopted.

3. Results and discussion

NPs of Ga compounds have found extended application in optoelectronics and solar cell technology (Barbé et al., 2016). However, Ga metal or its alloys, owing to their low melting point (29.8 °C for elemental Ga, and even lower for Ga alloys), are confined to a more specific research topic concerning liquid metal nanoparticles (Liu et al., 2020), with uses in cancer therapy and bioimaging (Li et al., 2020). Ga metal has the intriguing property of being essentially non-toxic for man and animals, thus making it very attractive according to the recent protocols of sustainable nanotechnology. Tevis et al. (2014) prepared liquid-metal NPs by a simple and cost-effective physical method based on a turbine as a rotary tool creating a dispersion of a Ga alloy droplets in aqueous medium where organic acids were dissolved as stabilizers. They obtained a wide distribution of particle diameters, ranging from 6.4 nm to over 10 μm. As a general trend, bottom-up methods allow obtaining metal NPs with a better size control and they represent a good trade-off between cost-effectiveness and quality of the final product. Instead, top-down methods based on mechanical comminution from liquid phase produces metal microparticles with a broad distribution, with only a small fraction with diameters <100 nm.

In Figure 2, the results of DLS analysis have been reported, which represent the relevant probability distribution function of $Ga^{(0)}$ NPs diameters (occurring when different capping agents are used), whose detailed data are reported in Table 2. It is interesting to observe that PVP of two different molecular weights, usually very efficient to hinder metal NPs agglomeration, was not particularly satisfying in this context, as only Ga microparticles of diameters greater than 100 nm could be obtained. Even worse results in terms of particle diameters could be obtained using an anionic stabilizer like SDS, leading to the formation of microsized dispersions.

On the opposite, and this is the main achievement of the present paper, eco-friendly additives like glucose or urea proved to be more efficient than standard capping molecules, giving NPs with average diameters of 79 nm and 51 nm, respectively. In the latter case, this result could be explained taking into account the role of amino- groups present in urea, whose affinity towards surfaces of zerovalent metal NPs is well known (Cushing et al., 2004).

The interpretation of the role of a sugar on $Ga^{(0)}$ particles is more puzzling. In many works dealing with $Ga^{(0)}$ particles dispersed in aqueous medium, a formation of a thin layer of GaOOH has been observed at the surface of the metallic phase, enhancing the local basicity of the dispersed particles. On the other hand, glucose, like other reducing sugars in water, has been successfully used as a capping agent for noble metals in basic environment. Admittedly, a limited release of $Ga^{(3+)}$ ions in solution and the formation of the aforementioned oxidized layer may have a synergic action in enhancing the capping role of carbohydrates, leading to the formation of the corresponding glyco-NPs. The latter have already been successfully used in the realization of probes for bacteria detection and decontamination (Adak et al., 2015).

The global mass of NPs produced in each experiment has been determined by weighting the gallium metal sample, which underwent a weight loss in a range of [5-10] mg, according to the type of capping agent adopted. Part of the etched solid remained trapped among the fibers of the abrasive pad and these NPs could not be further dispersed in the liquid phase.

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

Capping agent	Average diameter [nm]	Standard deviation [nm]	Peak position [nm]
Polyvinyl-pyrrolidone (PVP 25k)	177	56	142
Polyvinyl-pyrrolidone (PVP 40k)	221	68	190
Sodium dodecyl sulphate (SDS)	299	46	295
Urea	56	11	51
Glucose	85	17	79

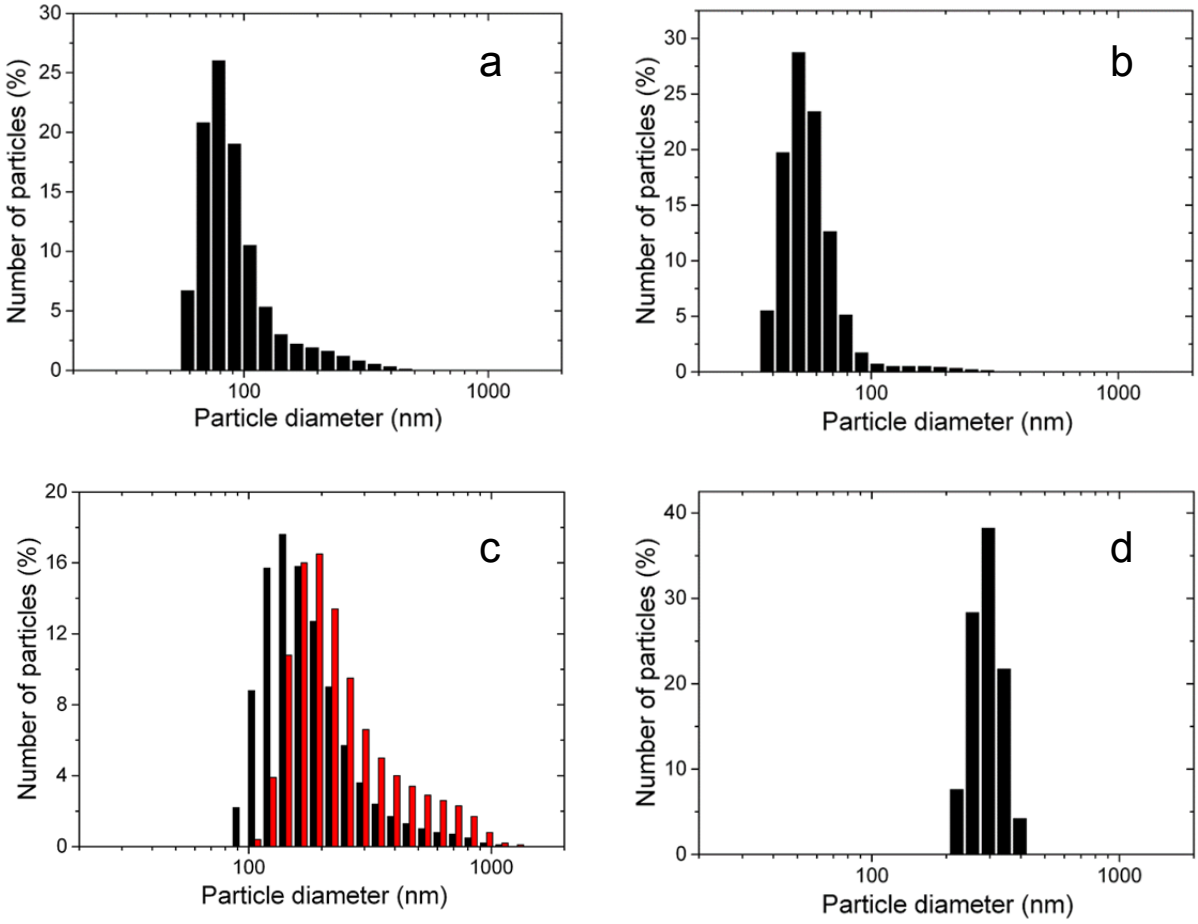

Figure 2: Plot of probability distribution function of $Ga^{(0)}$ particles diameters using different capping agents in water. (a): glucose; (b): urea; (c): PVP 25k (black plot) and 40k (red plot); (d): SDS. Each plot results from averaging on three different runs.

The most important results described in the previous paragraphs can be summarized as follows:

- The physical method proposed here represents an atypical technique different from standard ones for the synthesis of soft metal NPs in aqueous medium. The process is simple and cost-effective, as it does not require complex apparatuses and control systems generally adopted for most physical methods.
- Four different types of capping agents have been tested and the results have proven an unexpected superiority in performances of urea and glucose with respect to standard anionic and non-ionic stabilizers like SDS and PVP, the latter in two different molecular weights.
- Urea and glucose, being green and non-toxic compounds, may advantageously replace other stabilizing molecules, like ionic surfactants, often having irritant properties on mucous membranes.
- The sustainability character of the novel process is demonstrated by low energy consumption and inherent safe configuration in terms of mild operative conditions and hazardous reagent substitution.

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