

Bi Nanoparticles Synthesis by a Bottom-up Wet Chemical Process

Andrea P. Reverberi^{a*}, Marco Vocciante^a, Marco Salerno^b, Valentina Caratto^a, Bruno Fabiano^c

^a DCCI - Department of Chemistry and Industrial Chemistry, Genoa University, via Dodecaneso 31, 16146, Genoa, Italy

^b Nanophysics Department, Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy.

^c DICCA - Department of Civil, Chemical and Environmental Engineering, Polytechnic School, Genoa University, via Opera Pia 15, 16145, Genoa, Italy.

reverb@dichep.unige.it

A process concerning bismuth nanoparticle synthesis by an eco-friendly reductant in mixed solvents is proposed. The method relies upon a redox reaction carried out at mild operative conditions using tin salts as electron donors. The reaction is performed in the presence of polyvinyl-pyrrolidone (PVP) and sodium dodecyl-sulphate (SDS) as capping agents with the aim of investigating the role of such stabilizing compounds on particle average dimension and shape. The particles composition and diameter are determined by standard analytic techniques and by Dynamic Light Scattering. The precursor is dissolved in glycerol to hinder the formation of basic salts typically present in aqueous medium and to enhance the stability of the as-prepared zerovalent Bi nanoparticles. The slow-down of reaction kinetics related to the presence of glycerol is more than offset by its positive effect in terms of stability of the nanoparticles dispersion. From an applicative point of view, this study may help in identifying the best operating conditions for the production of zerovalent bismuth-based nanofluids by an energy-saving technology.

1. Introduction

Owing to a wide variety of applications in different fields of science and technology, the production of metal nanoparticles (NPs) represents one of the most challenging aspects in water purification (Vocciante et al., 2018) as well as in advanced pharmaceutical applications (Pastorino et al., 2016). In most cases reported in literature, wet-chemical methods for metal NPs synthesis are still based on standard powerful inorganic reducing agents, like alkali metal borohydrides and hydrazinium ions ($\text{NH}_2\text{-NH}_3^+$), irrespective of the electrochemical properties of the cations to be reduced (Reverberi et al., 2016). Such technique offers the benefits of a high reaction yield with fast kinetics of reduction even at room temperature, but it poses the problem of a high toxicity and/or reactivity of the reductants. In these last years, a specific attention of researchers is devoted to inherent safety and the development of successful engineering practices for the reduction, suppression and elimination of hazards from the manufacturing processes (Fabiano, 2017). Many efforts are currently directed to minimize safety, health and environmental impact of the synthesis methods by attenuation and substitution protocols (Fabiano et al., 2019). The toxic properties of some metal and metal oxide NPs are well known (Moschini et al., 2010), but there are exceptions. In fact, bismuth is perhaps the sole heavy metal having low environmental impact and good biocompatibility for humans and other mammals, as shown by in-vitro tests assessing low cytotoxicity and by in-vivo experiments based on oral administration in mice (Wei et al., 2016). These peculiarities explain the growing role of bismuth in green nanotechnologies (Reverberi et al., 2018a), with successful applications in X-ray computer tomography, in fluorescence imaging (Bi et al., 2018), in surface disinfection (Badireddy et al., 2013) and in the manufacture of antiseptics. The manufacturing techniques for Bi NPs essentially follow the same trend typical of other metal nanoparticles (Reverberi et al., 2017), with some new intriguing aspects.

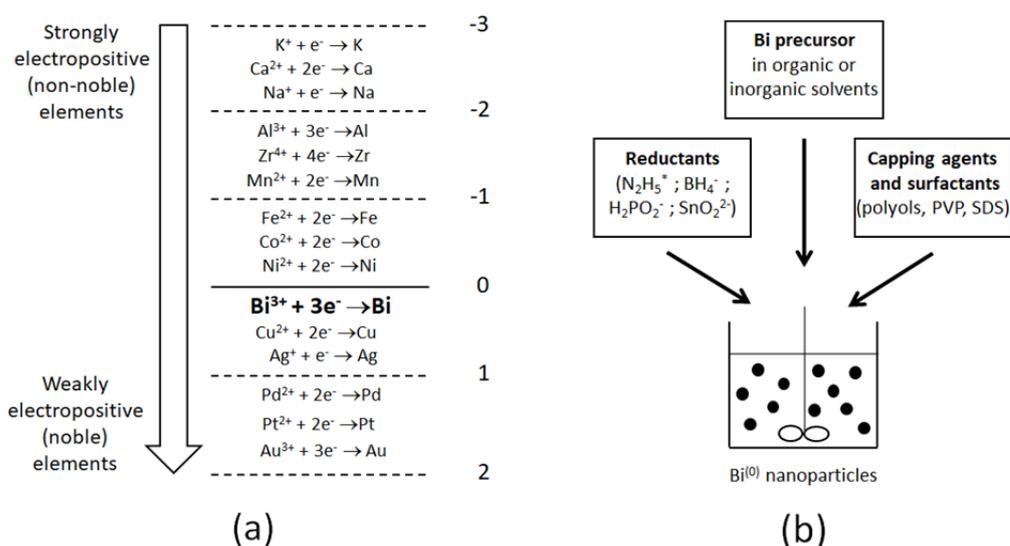
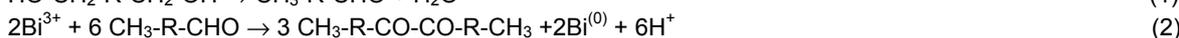


Figure 1: (a): Scheme reporting the position occupied by bismuth in the electrochemical series of the elements according to their redox potentials in volts with respect to the (null) standard hydrogen value. (b): example of different types of reagents usually employed in redox wet-chemical $Bi^{(0)}$ -NPs synthesis.

In fact, the position of Bi in the standard electrode potential series of Fig.1-(a) suggests that Bi has electrochemical activity standing between noble and non-noble metals, thus evidencing an intermediate electron affinity actually opening new scenarios concerning its chemical synthesis processes. For this reason, in redox synthesis processes as the ones indicated in Fig.1-(b), the choice of reductants may span over a wide number of inorganic and organic reagents, whose strength may strongly condition the kinetics of the redox step. In some cases, as for polyols and other hydroxyl-containing molecules, the reductant may act as a stabilizing agent whose joint chemical and physical effects actually prevent nanoparticles from aggregation (Díaz-Álvarez and Cadierno 2013). When polyols are adopted, the reduction process necessarily requires temperatures close to the melting point of the metal and the nanoparticles thus obtained are generally spherical owing to self-diffusion and thermal relaxation processes. Following Li et al. (2009), one can formulate a possible reaction mechanism as follows:



Where R is a generic saturated alkyl group or alkyl chain and $Bi^{(0)}$ is zerovalent Bi, which is obtained in nanosized form. From simple inspection of reaction (1), it can be observed that the reduction of Bi^{3+} ions requires an intermediate step where polyols are initially decomposed forming the corresponding aldehydes. The yield of the process according to the aforementioned reactions may also depend on the type of Bi precursor. It is intriguing to observe that, for many other elements different from bismuth, nitrates tends to be reduced more easily than other inorganic salts. Wang et al. (2014) prepared Bi nanospheres by a thermolysis method using Bi acetate ($Bi(OOCCH_3)_3$) in oleylamine at $T > 300$ °C in inert atmosphere, owing to a non-negligible affinity of Bi for atmospheric oxygen at temperatures needed by kinetic activation of redox reaction. These experimental conditions indicate that, both for polyol- and amine-mediated reductions, the operative conditions are somewhat demanding in terms of laboratory equipment and added-on safety control (Fabiano et al., 2019). As far as oxidation prevention is concerned, organic solvents are advantageous, since oxygen has a solubility usually lower in apolar or weakly polar organic solvents than in water. This is a further reason explaining why the unit operations following the synthesis process like washing, centrifugation and drying are generally carried out in organic solvents.

Recently, other manufacturing processes for NPs synthesis were considered in order to meet more stringent constraints of environmental safeguard (Meramo et al., 2018), resource conservation and energy saving (Chew et al., 2015). That is why some chemical processes like cementation, originally adopted in disciplines apparently far from nanotechnology, gained a greater attention (Rocchetti et al., 2015). When such synthesis method is applied to the production of $Bi^{(0)}$ NPs, a precursor dissolved in water or in organic solvents is put in

contact with a sacrificial element $\text{Me}^{(0)}$ having a suitable redox potential, namely an electron affinity higher than the one of metallic Bi (Reverberi et al., 2018b). The resulting reaction can be described as follows:



Zerovalent Bi is set free at the surface of the sacrificial element and this phenomenon may trigger the reciprocal aggregation of primary $\text{Bi}^{(0)}$ particles produced by reaction (3). This is the most crucial drawback related to cementation processes and many efforts have been made to minimize such side effect with several experimental tricks. The only choice of a vigorous holdup stirring is often insufficient to damp the aggregation, while an appropriate selection of chemico-physical parameters like pH and the use of suitable organic capping agents may help improving the quality of the final product. Regrettably, when reaction (3) is thermodynamically feasible, its kinetics are slowed by the presence of organic molecules dispersed in the solution and this fact counterbalances their beneficial effects as anti-aggregants. Green nanotechnology frequently relies upon the use of organic reductants of vegeta/animal origin for the synthesis of metal NPs (Baiocco et al., 2016). In some cases, $\text{Bi}^{(0)}$ NPs have been produced using bacteria as bio-templates, in which Bi ions are assimilated and further reduced to elemental Bi at the surface of the cell or inside the cell itself. These last methods are efficient at mild temperatures, but the kinetics of reduction are often unpredictable as they are subject to complex biochemical steps whose control is really critical. Moreover, the separation of the as-prepared nanoparticles from the embedding biomass require additional unit operations (Nazari et al., 2012). For these reasons, the setup of a simple process minimizing the items of reagent toxicity, separation costs and unpractical operating conditions is at a premium. In the present paper, a simple process for $\text{Bi}^{(0)}$ NPs synthesis operated by sodium stannite as an unconventional reductant active at mild temperatures is proposed. The remainder of this paper is divided as follows. In section 2, the experimental conditions are described and some details concerning the preparation of the reductant are given. In section 3, the Bi NPs are characterized by dynamic light scattering and by standard analytical techniques. In section 4, the conclusions are drawn and the direction for future works is traced.

2. Materials and methods

2.1 Experimental setup

Bismuth (III) nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 98\%$, Sigma-Aldrich, Milano, Italy); glycerol ($\text{C}_3\text{H}_7\text{O}_3$, $\geq 99\%$, Sigma-Aldrich, Milano, Italy); Tin (II) chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98%, Sigma-Aldrich, Milano, Italy); sodium hydroxide (NaOH, $\geq 97\%$, Sigma-Aldrich, Milano, Italy); polyvinyl-pyrrolidone 25 kDa (PVP, 99%, La Farnochimica, Genova, Italy); sodium dodecyl sulphate (SDS, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$, La Farnochimica, Genova, Italy); cetyltrimethyl-ammonium bromide (CTAB; $\geq 98\%$, Sigma-Aldrich, Milano, Italy) were used as purchased. In all experimental tests, bidistilled water was used after being purged with a stream of nitrogen to strip all dissolved oxygen in order to minimize both reductant and Bi NPs oxidation. The synthesis process is schematized in Fig. 2 and detailed in the following. A solution of NaOH in water is added dropwise to an aqueous solution SnCl_2 0.1 M under nitrogen atmosphere. A white precipitate of stannous hydroxide is suddenly formed, which is further dissolved in the minimum required amount of excess of precipitant to allow the formation of sodium stannite (Na_2SnO_2) according to the following reactions:



The dissolution of $\text{Sn}(\text{OH})_2$ according to reaction (5) must be carried out leaving a perfectly clear solution of Na_2SnO_2 at its final stage. This amount to saying that no turbidity related to a residual presence of $\text{Sn}(\text{OH})_2$ should be accepted, as it will alter the composition of the solid phase of $\text{Bi}^{(0)}$ NPs that will be produced in the further steps. Likewise, an excess of NaOH is not recommended as it could interfere with Bi^{3+} ions added in a second time, giving an undesired precipitate of bismuth oxide contaminating the $\text{Bi}^{(0)}$ NPs by the reaction:



A moderate warming at $T \leq 50$ °C in a stirred reactor is recommended to speed up reaction (5), so as to monitor an unwanted NaOH excess in real time. The Na_2SnO_2 solution is to be stored out of air contact, as the oxygen will deactivate its reducing properties forming sodium stannate as follows:



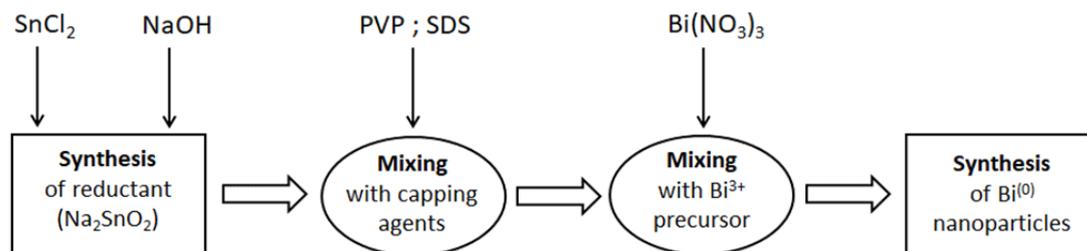


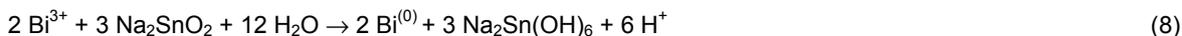
Figure 2: Scheme of process flowsheet for the synthesis of $\text{Bi}^{(0)}$ NPs according to the present study.

It has been observed that the deactivation reaction (7) is complete when the solution of stannite is exposed to the atmospheric oxygen for 24 hours only.

Afterwards, three separated 0.02 M alkali stannite solutions were prepared and mixed with SDS (20 g/L), PVP (20 g/L), and CTAB (10 g/L) respectively. The sample containing CTAB became instantaneously turbid, probably owing to the formation of a compound of addition with the stannite salt. For this reason, it was discarded from further experimental tests. A 0.05 M solution of Bi precursor was obtained by dissolving $\text{Bi}(\text{NO}_3)_3$ in anhydrous glycerol. This non-aqueous solvent has been adopted in place of water for two different reasons, namely:

- $\text{Bi}(\text{NO}_3)_3$ forms clear solution in many organic solvents like glycols without giving off basic salts as in water. The limited solubility of these basic salts is another source of contamination in the final product.
- Aqueous solutions of Bi salts require an acidification to ensure the stability of these solutions. The presence of a free acid may interfere with the redox reaction where nanosized $\text{Bi}^{(0)}$ is formed, as the acid may decompose the alkali stannite thus decreasing the yield of Bi^{3+} reduction.

Finally, each alkali stannite solution containing a single surfactant is mixed with the precursor under stirring at $T=50\text{ }^\circ\text{C}$ giving a dispersion of $\text{Bi}^{(0)}$ NPs:



The presence of water is essential for the realization of the redox reaction (8). In agreement with this statement, no production of $\text{Bi}^{(0)}$ NPs has been observed when the reduction is carried out using anhydrous organic solvents for all reagents involved in reactions (4-5) and (8). The other saline products generated by reactions (4) and (8), namely NaCl and $\text{Na}_2\text{Sn}(\text{OH})_6$ remain dissolved in the solution embedding the solid phase without forming precipitates contaminating the $\text{Bi}^{(0)}$ NPs. The solution of alkali stannite, colorless at initial time, gets progressively yellow, deep brick red and finally dark brown after the beginning of reaction (8), suggesting the formation of a solid nanosized phase of $\text{Bi}^{(0)}$ as analogously reported in other studies using different reductants (Xia et al., 2014). This phase is centrifuged at 6000 rpm, separated and repeatedly washed with oxygen-free water and absolute ethanol in inert atmosphere and finally characterized in its composition by a standard analytic technique described in the following section.

2.2 Analytical methods

The solid phase obtained according to the process here described was characterized for chemical composition by atomic adsorption spectrometry (AA240FS, Varian Instruments, USA).

A Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) was used to determine the probability distribution function of the $\text{Bi}^{(0)}$ NPs diameters by means of dynamic light scattering (DLS) measurements.

3. Results and discussion

In a context different from nanotechnology, Na_2SnO_2 is a well-known electron-donor that makes it a versatile reactant owing to its efficiency and selectivity in specific redox reactions. For example, it has been used for the production of zerovalent Sn to be used in allylation of carbonyl compounds (Sinha et al., 2015) and in the synthesis of fine organic chemicals (Wang and Li, 2012). In analogy with hydrazine and alkali borohydrides, alkali stannites contribute to establishing a basic medium that proves to be experimentally more suitable than an acid solution in damping the kinetics of nanoparticles aggregation (Litmanovich et al., 2014). Additionally, Na_2SnO_2 has a remarkably lower toxicity than hydrazine compounds and borohydrides, which tend to be progressively replaced according to the new protocols of green chemical production (Primerano et al., 2016).

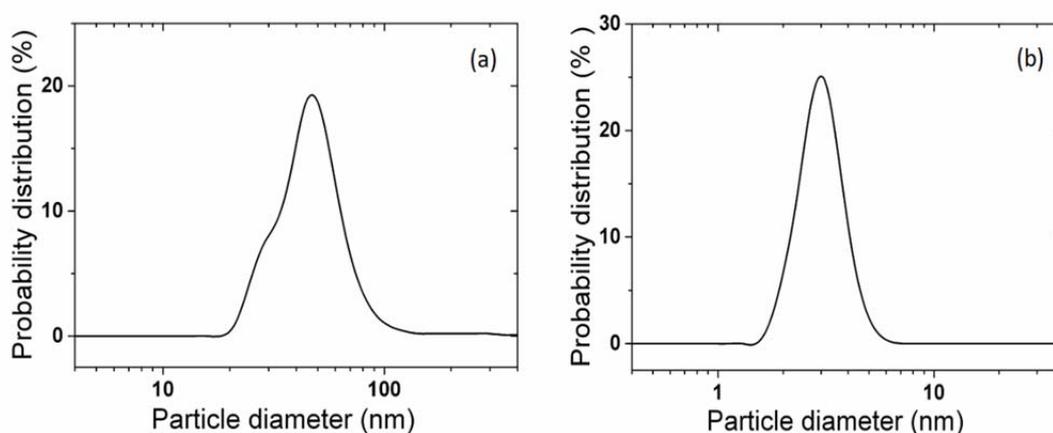


Figure 3: Lot of probability distribution function of $\text{Bi}^{(0)}$ NPs diameters using PVP (left graph) or SDS (right graph) as capping agents.

The solid phase obtained according to the process described in Section 2 is dried in oven under nitrogen flux at $T=120\text{ }^{\circ}\text{C}$ to eliminate all traces of solvents used during washing and centrifugation. Subsequently, it is weighted, dissolved in an excess of nitric acid and finally diluted to a standard volume of water to be analyzed by atomic adsorption spectrometry. The concentration of elemental Bi in the solid phase obtained by reaction (8) was estimated in the range $98.5 \pm 0.5\%$.

In Fig. 3, the probability distribution functions of $\text{Bi}^{(0)}$ NPs diameters are reported according to a DLS analysis for two different types of capping agents, namely polyvinyl-pyrrolidone (PVP) and sodium dodecyl-sulphate (SDS). The first, very widely used to stabilize metal NPs, has a non-ionic character, while the second is a typical anionic surfactant. The effects of these stabilizers are different from one another in terms of $\text{Bi}^{(0)}$ NPs average diameters, which have been estimated at 48 nm and 3 nm in case of PVP and SDS, respectively. The curves in each graph of Fig. 3 has been obtained by averaging on three different measurements. The attainment of ultrafine average NPs dimensions in Fig. 3(b) could be explained taking into account the different polarization of the two capping agents, with a tighter binding strength of SDS compared with the one of PVP, despite the latter has long been considered as a first-rate polymer for $\text{Bi}^{(0)}$ NPs stabilization.

4. Conclusions

From a methodological point of view, the most important results obtained by the process here proposed can be summarized in the following points:

- An unconventional reductant like sodium stannite proves to be efficient in the synthesis of Bi NPs in a mixed water-glycerol solvent at mild experimental conditions ($T \leq 50^{\circ}\text{C}$) following the “attenuation” guideword of inherent safety approach.
- Both non-ionic (PVP) and anionic (SDS) capping agents are satisfactory in hindering zerovalent Bi NPs aggregation, without interfering with the redox reaction.
- The use of sodium stannite may represent a valid eco-friendly and inherent safer alternative to conventional toxic reductants while preserving fast reaction kinetics and low reagent cost.
- The reaction by-products have a low toxicity for man and environment.

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