TOP-DOWN SYNTHESIS OF METAL NANOPARTICLES BY SURFACE DISAGGREGATION IN A STIRRED TANK

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INTRODUCTION

The methods for the synthesis of nanoparticles (NPs) at small or large scale are generally based on physical, chemical and biological processes. In Fig. 1, a schematic representation of the most important synthesis processes is proposed according to this basic scheme. The choice of a specific production route is generally related to the physico-chemical properties of the materials which the nanoparticles are made of. For example, inorganic NPs are manufactured according to processes which are generally very different from the ones adopted for the synthesis of organic NPs, owing to an intrinsic thermal instability of the latter. Physical and chemical synthesis methods are usually considered as the first choice and a huge literature focused on such techniques proves this statement. The former often require expensive apparatuses and instrumentation and they pose some problems in matter of scalability of the final product. On the opposite, chemical processes are more economical and they allow a satisfactory controllability of shape and dimensions of the as-produced NPs. One of the most crucial drawback related to a chemical synthesis method is the use of reagents having noxious properties for man and environment. This negative aspect of chemical synthesis method is perhaps the main reason leading to an increasing interest towards biological processes, where cells of bacteria, yeasts and fungi act as living nanofactories for the synthesis of NPs. Such processes proved to be useful for the production of zerovalent nanostructures of noble metals like gold, platinum, palladium and silver, owing to the weak electropositive character of the corresponding element. However, biochemical methods proved to be somewhat inefficient when non-noble metal NPs are to be synthesized, as the electron-donors in biochemical processes are considrably weaker than the typical inorganic reductants like hydrazonium compounds or alkali borohydrides.
In the present work, a purely physical synthesis method relying upon a mechanical friction between bulk copper spheres and zirconia (ZrO_2) balls in a liquid medium is described. The process is carried out at room temperature and it proved to be successful for the synthesis of very fine Cu-NPs.

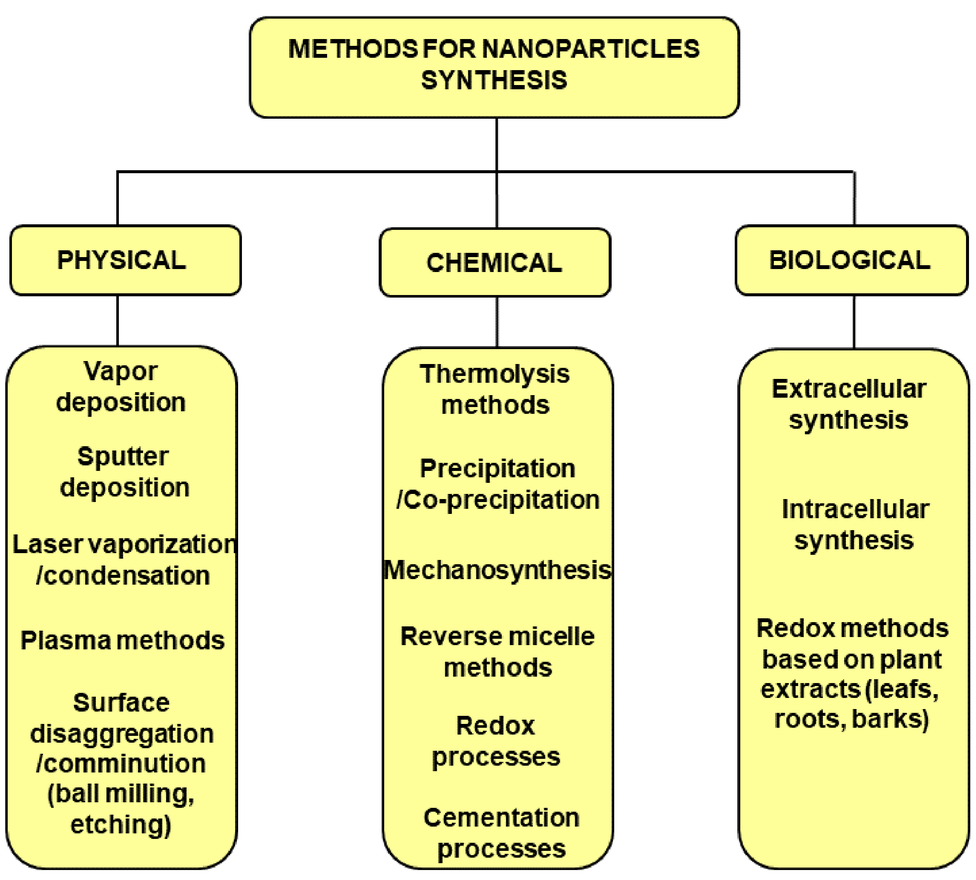

Figure 1 – Scheme of typical methods adopted for the synthesis of NPs

THE METHOD

In Fig.2, a simplified scheme of the process is proposed. A glass vessel of 34 mm diameter containing 100 ZrO_2 spheres of 3 mm diameter and 5 Cu spheres of equal dimension is filled with 3 cm^3 of anhydrous ethanol where a surfactant (polyvinyl-pyrrolidone PVP 0.1g; mol.wt: 25kDa) has been previously dissolved. The temperature of the vessel is kept constant at 25°C by a suitable thermostatic control. A rotating shaft, located at the axis of the vessel, is equipped with a glass turbine of asymmetric shape dipped in the hold-up of spheres at its lower end. Such turbine allows a vigorous stirring of the system Cu-ZrO_2 spheres in ethanol and promotes reciprocal collisions leading to surface disaggregation of the copper spheres. At its upper end, the shaft is dragged by a magnetic bar, rotating inside the vessel without any contact with the stirred solution. In its turn, such magnetic bar is driven by an external magnetic stirrer with variable speed in order to control the frequency of collisions.

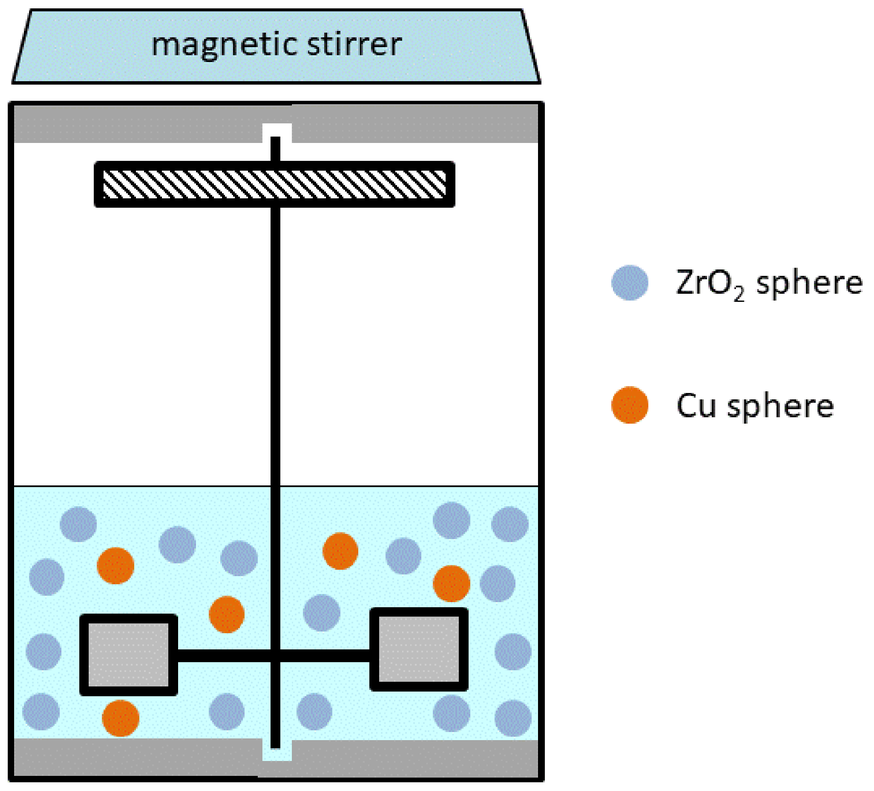

Figure 2. Scheme of the stirred tank miller adoped in the top-down synthesis method here described .

RESULTS AND DISCUSSION

The milling tank assembly described in Fig.2 is advantageous with respect to the classical constructive solution where the hold-up is stirred by a magnetic bar located at the bottom of the sphere bed. In fact, the present stirring assembly allows to overcome problems related with the lift force exerted on a free stirring bar, which tends to floats on the surface of the sphere bed for growing values of the angular rotation speed., with obvious drop of milling efficiency.
After a five-hours stirring, the vessel is opened and the solution is separated from the spheres. Such liquid phase, containing a dispersion of copper particles, is centrifuged at 6000 rpm for 20 min. The supernatant is further separated and it is analyzed for the determination of NPs diameter by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments, UK). In Fig.3, the particle diameter distribution function is plotted; different curves refer to plotting times shifted by 10 mins from one another. In all cases, the average NPs diameter remains smaller than 10 nm. It is intriguing to observe that the solution, colorless at the start of the process, assumes a definite yellow color preserving its transparency to the naked eye.

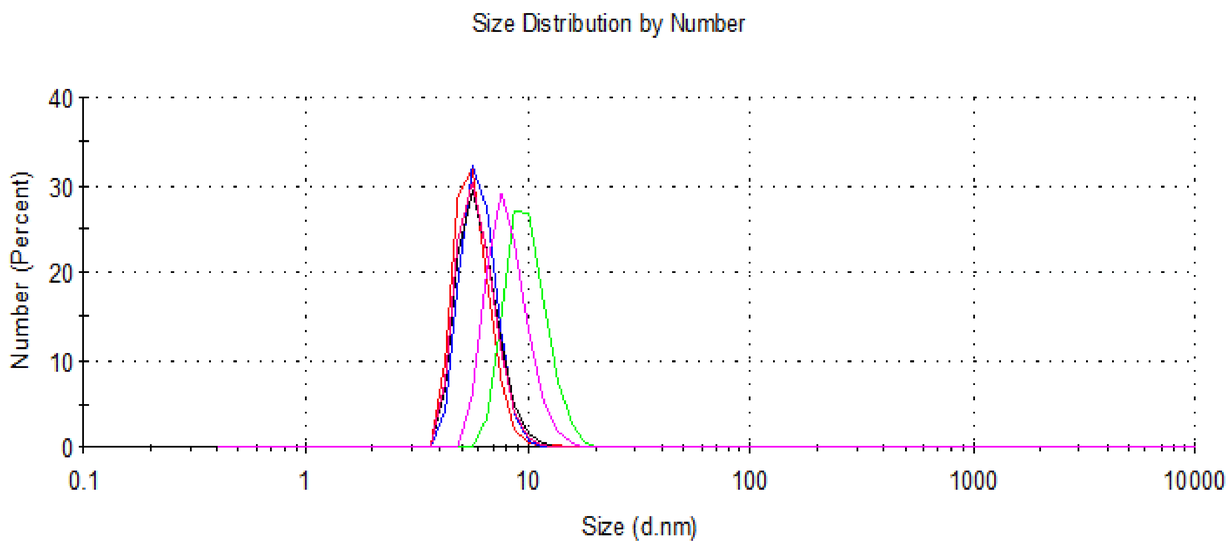

Figure 2. Probability distribution function of Cu-NPs diameters for different sampling times. The average diameters are <10 nm in all cases.

CONCLUSIONS

In the present work, we have described a wet milling process carried out in a sealed stirred tank where copper spheres are etched at their surface by mechanical friction with zirconia spheres of equal diameter in an ethanol liquid phase. From a methodological point of view, we can draw the following conclusions:
- A low-energy milling process in liquid phase may represent a simple, eco friendly and economical process for Cu-NPs synthesis.
- The PVP is confirmed as a very efficient surfactant for obtaining a product of good quality in terms of Cu-NPs diameters and stability.

REFERENCES

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