

# Inorganic Nanoparticles Synthesis by an Aerosol-Assisted Wet Chemical Method

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Many successful methods for nanoparticle synthesis are based on a comminution of the phases containing the precursors prior to the chemical reactions. The beneficial effects of such techniques are well-known in terms of small dimensions and narrow distributions of diameters of the nanoparticles thereby produced. According to specific methods, micelles or droplets behave as segregated micro-reactors where reactants are made to combine with minimization of further aggregation, to improve the quality of the final product. In the present paper, an aqueous solution of a reagent is nebulized on the surface of a stirred liquid containing the second reagent, with formation of a nanosized solid phase with diameter and height ranges of 50-100 nm and 6-8 nm, respectively. We are not aware of other wet-chemical methods based on such a technique, which proves to be simpler and more inexpensive than the typical one of traditional spray processes followed by high-temperature pyrolysis, which are generally carried out in flame reactors.

## 1. Introduction

In recent years, inorganic nanoparticles have been successfully employed in the production of composite materials for sensors (Pascariu et al., 2013), in optical devices (Li et al., 2015), in high-performance catalysts (Cruz et al., 2016) and in environmental decontamination (Tagliabue et al., 2014), thanks to their peculiar physicochemical properties which are often very different from those typical of the same bulk material.

As a first rough classification, chemical methods for nanoparticle synthesis comprise top-down and bottom-up techniques. The top-down techniques, generally based on solid disaggregation by chemical dissolution in a liquid phase until a nanosized solid dispersion is attained, are rarely applied on a large production scale, owing to their intrinsic difficulties in controlling the disaggregation kinetics, leading to unwanted broad size dispersions of the end product. On the opposite, the bottom-up techniques are appealing and promising because of a very good tunability of both nanoparticle shape and diameter according to the operative variables of the process.

Inorganic nanoparticles obtained by wet chemical methods span over a broad variety of composition: pure metals, alloys, composites and salts are produced both at laboratory and at pilot scale, with attractive and unexpected properties in heat, mass, wave and electron diffusivities, which make them practically unreplaceable in the manufacture of innovative materials for industrial and domestic applications.

As an example, magnesium hydroxide (Mg(OH)<sub>2</sub>) nanoparticles have been used in environmental decontamination (Wang et al., 2015), in catalysis (Estrada et al., 2014), in flame retardancy for high profile event mitigation (Vianello et al., 2012) and in many fields related to process safety and loss prevention, thus representing an up-to-date research topic (De Rademaeker et al., 2014). An et al. (2012) prepared ordered structures of Mg(OH)<sub>2</sub> nanoparticles by a slow injection of aqueous ammonia in a precursor solution of magnesium chloride under vigorous stirring, where 0.75% by weight of a suitable surfactant had been previously added to inhibit particles aggregation. The nanosized precipitate was dried and finally embedded in a low-density polyethylene (LDPE) polymer, whose thermal stability was considerably improved by such a mixing. In a different context, Liu and Yi (2009) activated a substrate made of 80 nm Mg(OH)<sub>2</sub> nanoparticles

with a solution of sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ), which was electrostatically adsorbed on particle surface as the initiator for a subsequent in-situ styrene polymerization. The as-prepared inorganic nanophase showed a considerably greater dispersibility in the hydrophobic polymer with respect to the pure nanosized  $\text{Mg}(\text{OH})_2$ . Buesser and Pratsinis (2012) presented a very exhaustive review paper on nanomaterials synthesis by aerosol processes, where the reactants are finely divided in droplets undergoing a further chemical reaction in flame reactors, hot wall reactors, plasma and microwave reactors operating at temperatures generally analogous to those typical of pyrolysis processes (Chiarioni et al., 2006). Incidentally, flame spray pyrolysis is nowadays recognized as one of the most widespread techniques in industrial production of carbon black for tires, nanosized metals, silica and titania. In such a method a solvent carrying the precursor is sprayed in a burner whose flame supplies the heat required by nanoparticles synthesis, followed by their clustering with aggregation/agglomeration (Widiyastuti et al., 2010). The latter phenomena, which may severely condition the quality of the final product, can be successfully minimized by a suitable quenching time control obtained by modifying fuel and comburent flow rates, likewise different processes (Fabiano et al., 2015), high comburent fluxes correspond to highly turbulent flames and short quenching times, leading to smaller particles diameters (Stark and Pratsinis, 2002).

On the other hand, it is intriguing to point out that inorganic nanoparticle synthesis by aerosol-assisted wet-chemical method received far less attention with respect to the aforementioned processes, despite the former relying upon a much easier structure of the plant facility, at least at a laboratory scale. As pointed out by Biskos et al. (2008), atomization of a liquid solution can be obtained by several techniques, such as ultrasonic, pneumatic and electrospray methods. The ultrasonic methods produce nearly monodisperse droplets in the range of 0.25-50  $\mu\text{m}$ , but their small concentration at the output represents a serious draw-back. The pneumatic methods are traditionally the mostly adopted ones for economic reasons, but they produce a polydisperse flow of droplets with 1-10  $\mu\text{m}$  diameter. Finally, the electrospray methods offer some advantages as they give a monodisperse particle population, where the electric charges at particle surface ensure a mutual repulsion between droplets with a considerable gain in stability.

In this study we propose a  $\text{Mg}(\text{OH})_2$  nanoparticle synthesis where one of the reagents is finely dispersed in a pressure-driven aerosol phase impinging the meniscus of a stirred liquid containing the second reactant. The paper is divided as follows: in section 2 we describe the experimental apparatus and we give some details concerning the aerosol-liquid reactor design; in section 3 we present the results with particular attention to the geometrical characteristics of the nanosized solid phase dispersed in the reactor hold-up, and in the last section we draw the conclusions and we trace the direction for future work.

## 2. Materials and methods

### 2.1 Experimental set-up

In Figure 1 a pneumatic atomizer (a), commonly used for drug nebulization, is filled with 2.5 g of 5 M sodium hydroxide ( $\text{NaOH}$ ) solution in distilled water. The air pressure must be kept at values greater than 0.5 bar to ensure a satisfactory nebulization, whose droplets are conveyed by the air stream towards a reactor vessel (b). The length of the tube connecting the reactor vessel with the atomizer must be minimized, in order to reduce the weight loss of the atomized  $\text{NaOH}$  solution as an effect of droplet coalescence along the tube walls. The nebulized phase is only partially captured by the liquid hold-up contained in the reactor; namely a fraction of droplets made of  $\text{NaOH}$  solution comes out from the reactor, requiring a careful abatement to avoid harmful health effects, owing to its noxious and irritating action on the respiratory tract. To this purpose, a sequence of adsorption devices is set downstream the reactor, namely a 0.5 m packed bed height column of dry glass spheres (c), followed by two Drechsel bottles (d) and (e) in series, each containing a dilute solution of ferric chloride ( $\text{FeCl}_3$ ). After the air flow carrying the nebulized phase has passed these units, it is vented into the atmosphere.

Figure 2 represents a scheme of the reactor, which comprises two glass concentric vessels whose inner one has a height  $h=4.4$  cm, an inner diameter  $d=3.1$  cm and contains 28  $\text{cm}^3$  of 0.5 M magnesium sulfate ( $\text{MgSO}_4$ ) solution in distilled water stirred by a magnetic bar. A glass tube, entering the reactor through the moving head, goes down vertically to a few millimeters above the rotating meniscus of the liquid phase contained in the inner vessel. This tube acts as a "droplets gun", shooting the nebulized phase coming from the pneumatic atomizer towards the surface of the liquid phase contained in the stirred tank.

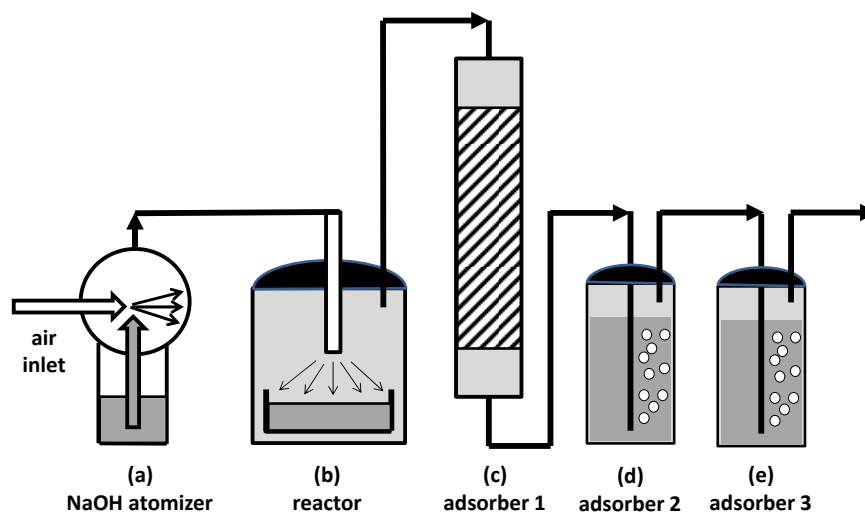


Figure 1: Scheme of the experimental set-up adopted in the present study.

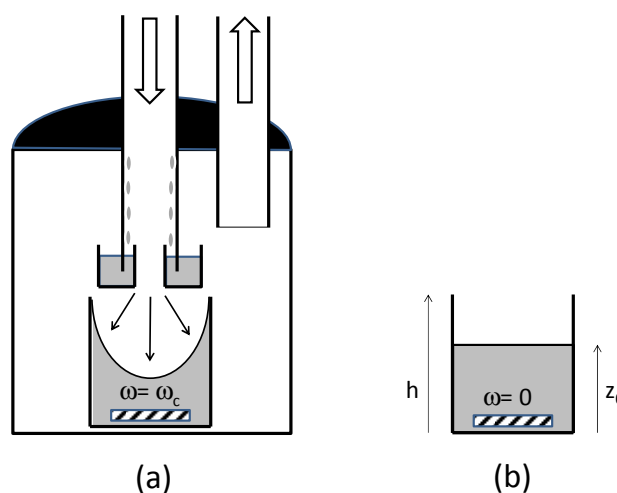


Figure 2: (a): Detailed scheme of the reactor containing a vessel having its inner surface totally wetted by a stirred  $\text{MgSO}_4$  solution. (b): scheme of the vessel containing the same solution at rest.

Unfortunately, the tube is subject to the formation of a liquid film falling along its vertical walls as an effect of coalescence of NaOH liquid fog, which requires a careful control. To this purpose, an annular dam located at the tube outlet collects the aforementioned liquid film, preventing big drops from falling in the  $\text{MgSO}_4$  solution. Similarly, the vertical walls of the inner vessel are subject to the same drawback, which is overcome by tuning the rotation speed of the stirring bar so that the meniscus of the liquid hold-up wets all the inner surface of the reservoir, thus avoiding fog condensation, as it will be explained in the following section.

A solid phase made of  $\text{Mg}(\text{OH})_2$  nanoparticles is formed in the stirred vessel according to the following reaction:



The precipitate obtained after prolonged nebulization is repeatedly washed and centrifuged to eliminate the excess of reagents. Then, it is dried at low temperature ( $120^\circ\text{C}$ ) to avoid the formation of  $\text{MgO}$  coming from thermal dissociation of  $\text{Mg}(\text{OH})_2$ . The dried mass is weighted and finally dissolved in hydrochloric acid in order to estimate its content in elemental magnesium by atomic adsorption spectrometry (AA240FS, Varian Instruments, USA). We calculated a  $99 \pm 0.5\%$  of  $\text{Mg}(\text{OH})_2$  in the aforementioned dried solid precipitate.

## 2.2 Parameters set-up

In a cylindrical coordinate system, the shape of the rotating meniscus is described by the well-known paraboloid equation, which reads:

$$z = ar^2 + k \quad (2)$$

$$a = \frac{\omega^2}{2g} \quad (3)$$

where the z-axis is set along the vertical direction,  $r$  is the radial coordinate around the rotation axis,  $\omega$  is the angular rotation speed, and  $g$  is the gravity acceleration according to the scheme depicted in Figure 2-b. The value of the constant  $k$  is related to the total hold-up volume  $V$  obtained by integration of Eq (1) as follows:

$$V = \int_0^{2\pi} d\theta \int_0^R r(ar^2 + k) dr = \pi R^2 \left( \frac{aR^2}{2} + k \right) \quad (4)$$

where  $R$  is the radius of the inner vessel and  $\theta$  is the angular coordinate. Combining Eq (2) with Eq (4) and remembering that  $z_0 = V/(\pi R^2)$  is the height of the liquid hold-up for  $\omega=0$ , we can write Eq (2) in the form:

$$z = z_0 + a \left( r^2 - \frac{R^2}{2} \right) \quad (5)$$

Defining  $z_R$  as the height of the meniscus at the vessel wall, that is for  $r=R$ , we finally obtain:

$$z_R = \frac{\omega^2 R^2}{4g} + z_0 \quad (6)$$

If  $z_R > h$ , part of the liquid overflows out of the vessel; if  $z_R < h$ , a part of the vessel wall is left unwetted and it may promote an unwanted condensation of the nebulized phase, as previously explained. Therefore, Eq (6) defines a critical rotation speed  $\omega_c$ , which is:

$$\omega_c = \sqrt{\frac{4g(h - z_0)}{R^2}} \quad (7)$$

In the present experiments, we kept the liquid stirring at constant speed  $\omega = \omega_c$ .

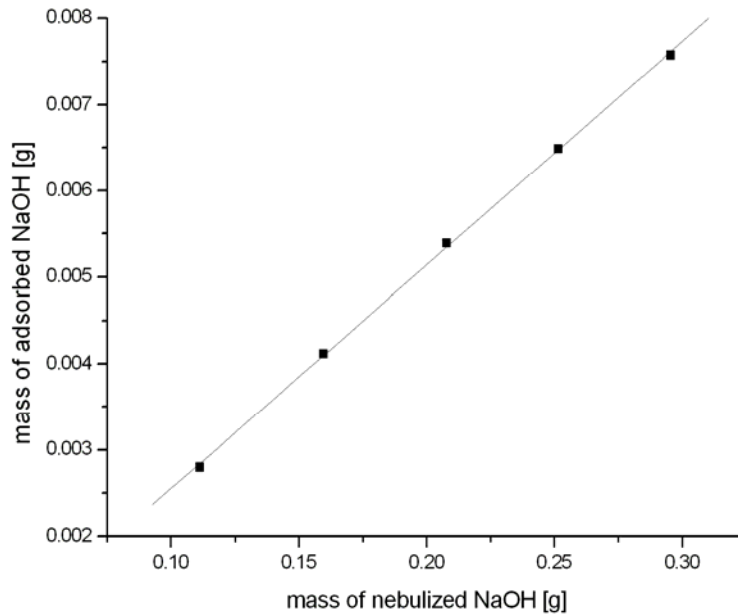


Figure 3: Plot of NaOH mass captured by the stirred vessel versus the mass of the same reagent supplied by the atomizer.

### 3. Results and discussion

In Figure 3 we have reported the mass of NaOH entrapped by the stirred vessel versus the mass of NaOH nebulized by the atomizer. The points correspond to samples collected every 2.5 minutes. The values collapse onto a line with slope  $\alpha=0.0259$ , indicating that only a small fraction (2.59%) of nebulized mass is adsorbed by the reactor, corresponding to a Mg(OH)<sub>2</sub> nanoparticles production of 0.37 mg/min. This process can be mainly ascribed to the inertial forces exerted on the NaOH droplets by the high speed of air flux at the exit of the droplets gun. Admittedly, the droplets are conveyed far from the meniscus, as the drag effect prevails on the capturing power of the liquid surface itself. On the other hand, this fact is beneficial as it hinders a steep rise of NaOH concentration in the MgSO<sub>4</sub> tank at short times, with positive effects in nanoparticles nucleation and agglomeration. Namely, a nebulizing tube outlet nearer to the liquid meniscus would increase the reaction yield, at a price of an unwanted growth in particle size and a larger solid agglomeration.

A sample obtained after 5 minutes of NaOH atomization is extracted from the stirred vessel and, after 6 hours standing, the supernatant is collected and further drop-cast on a freshly cleaved and hydrophilic mica sheet, to characterize the precipitate by atomic force microscopy (AFM). We used an AFM instrument MFP-3D (Asylum Research, Santa Barbara, USA), operating in air in tapping mode with probes NCHR (Nanoworld, Neuchatel, Switzerland). The 3-D topographic image reported in Figure 4 is satisfactorily representative of the Mg(OH)<sub>2</sub> particle population, as they are many in the embedding space with minimal mutual superposition. We measured an average apparent diameter of  $73\pm 25$  nm. This size is overestimated for different reasons. First, the convolution of the particles profile with the tip profile makes the apparent size of the particles larger of roughly the tip diameter itself, i.e.  $\sim 10$  nm in the best case.

Additionally, due to the loose bond of the particles to the substrate, the tip may have captured a few particles by electrostatic interaction, during the surface scan. Thus, the actual working tip diameter was not the nominal  $\sim 10$  nm mentioned above, but probably much larger. On the opposite, the particle height of  $7\pm 1$  nm, with very narrow distribution of the population, as shown by the representative cross section in Figure 5, suggests that this is the true size of the nanoparticles. This result is particularly interesting if we take into account that it has been obtained without using surfactants or capping agents, according to the inherent safety guideword “minimization”, thus avoiding in the process the use of hazardous materials (Fabiano et al., 2012).

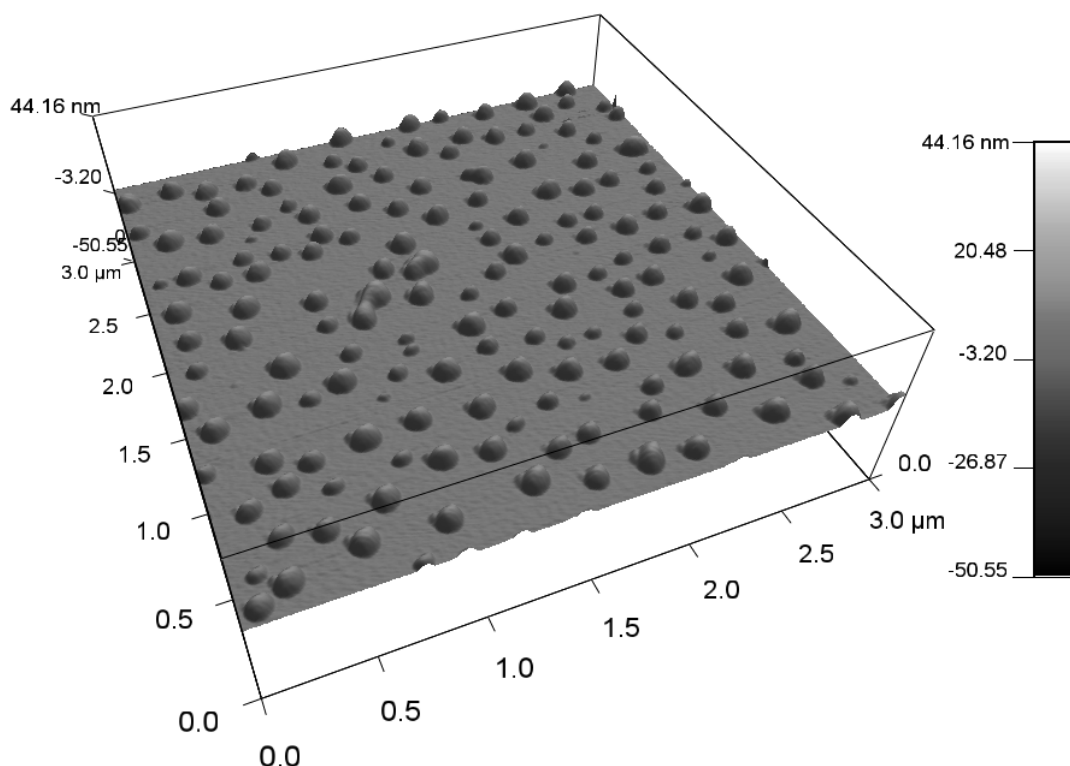


Figure 4: Typical 3D topography of Mg(OH)<sub>2</sub> nanoparticles detected by AFM.

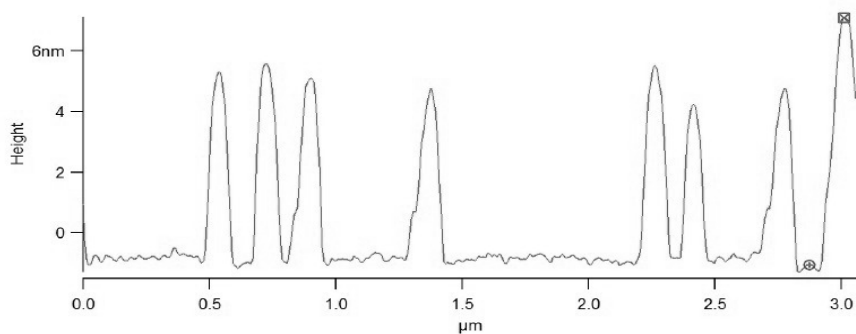


Figure 5: Typical cross-section of a representative AFM image as that presented in Figure 4, showing the plot of nanoparticles heights versus the position along a scan line.

#### 4. Conclusions

We have successfully obtained  $\text{Mg}(\text{OH})_2$  nanoparticles with a very narrow height distribution, without using additives that may be undesirable for some applications. The process here proposed is economical and easily controllable; moreover, following an inherent safety approach, it operates at room temperature unlike many spray-assisted synthesis methods. We are currently investigating the production of magnetic nanoparticles for medical purposes by this technique.

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