Magnetic particles and clusters through a cross-disciplinary approach

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Abstract

Magnetic particles play nowadays an important role in different technological areas with potential applications in fields such as electronics, energy and biomedicine [1, 2]. The production of monodisperse magnetic nanoparticles (NPs) down to few atoms is one of the most important challenges in Nanotechnology. The microemulsion technique is a powerful method to prepare simple metallic and oxide NPs, as well as, core-shell and "onion-like" NPs [3]. Although microemulsions cannot be considered as real templates, they constitute an elegant technique, which can provide a very good control of the final particle size. The reason for that is complex interplay mainly between three parameters, namely, surfactant film flexibility, reactant concentration and reactant exchange rate [4]. By adequately choosing these three parameters one can get a homogeneous distribution of particle sizes down to few atoms.

Metal atomic clusters consist of groups of atoms (usually less than 100-200) with well-defined compositions and one or very few stable geometric structures. They represent the most elemental building blocks in nature – after atoms – and are characterized by their size (below circa 1-2 nm) [5]. Below such size range the free electrons of the metal nanoparticles become frozen and the metals lose their metal behavior, which is clearly detected by the disappearance of the characteristic plasmon bands of the metals. This size scale is comparable to the Fermi wavelength of an electron, which makes them a bridge between atoms and nanoparticles or bulk metals. Novel and fascinating properties, which strongly differ in many cases from the properties of bulk and nanoparticles of the same material, appear at this nanometer/sub-nanometer transition. For example, fluorescence [6], catalysis [7], magnetism [8], and circular dichroism [9] have been found in such clusters, which are not exhibited for the same material in larger sizes. In such range, a bandgap is opened at the Fermi level, increasing the magnitude of the gap as the cluster size is reduced. Due to this bandgap, which can be as high as 3 to 4 eV for the smallest clusters having only 2 to 3 atoms, and the extra-stabilization by electronic closing shells, clusters –contrary to the general belief- are very stable. However, studies involving metallic clusters are still very limited because of the procedures used for their synthesis. Only very small amounts of highly polydisperse samples can be obtained after difficult separation procedures. In the last years we developed, among others, novel microemulsion-based methods for the synthesis of clusters, which allows their production with relatively good monodispersity [10, 11].

In this talk we will describe the microemulsion synthesis procedure, focussing on some particular examples showing how the magnetic properties of materials change from particles to atomic clusters. Moreover, special emphasis will be done on different applications of nanoparticles and clusters related to the biomedical field. In particular, biocompatible iron oxide nanoparticles are being increasingly used as heating sources in magnetic hyperthermia, since they fulfill the chemical and physical requirements to allow treating more efficiently tumoral tissues by means of magnetically induced heat under an oscillating magnetic field [12]. This remotely controlled temperature increases are also very interesting for thermally induced growth factors release systems in bone regeneration applications [13-15]. On other hand, although nanotechnology is already being applied successfully in dentistry through the use of nanocomposite materials such as adhesives, cements and resins, we will introduce the use of subnanometric metallic clusters as potential antimicrobial agents in dental applications.

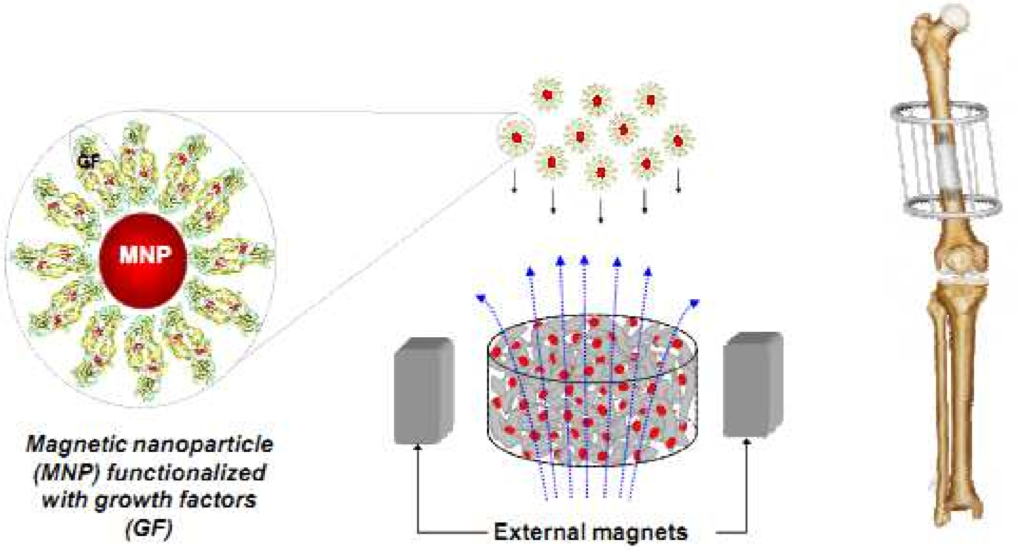

Figure 1. Scheme about the use of magnetic nanoparticles in bone regeneration applications by using magnetic hyperthermia. *European Community's FP7 under grant agreement no. NMP3-LA-2008-14685 project MAGISTER (www.magister-project.eu).*

References

[1] Reiss, G. and Hütten, A. *Nature Materials* 4, 725 - 726 (2005)
[2] Gao, J., Gu, H. and Xu, B. Accounts of chemical research 42 (8), 1097-1107 (2009)
[3] See e.g. López-Quintela, M.A. and Rivas, J. *J. Colloid Interface Sci.* 1993, 158, 446; Ibid, Curr.Opìnion Colloid Interface Sci. 1996, 1, 806; López-Quintela, M.A., Rivas, J., Blanco, M.C. and Tojo, C. "*Nanoscale Materials*", Ed. by L.M. Liz Marzán and P.V. Kamat. Kluwer Academic Plenum Publ., Chapter 6, 135-155 (2003).
[4] See e.g. López-Quintela, M.A. *Curr. Opin. Colloid Interface Sci.*, 8, 137 (2003)
[5] Calvo, J.; Rivas, J.and López-Quintela, M.A. *Encyclopedia of Nanotechnology*, Bhushan, Bharat (Ed.), Springer Verlag. 2639-2648 (2012).
[6] Zheng, J.; Zhang, C.; Dickson, R.M. *Phys.Rev.Lett*., 93, 77402 (2004).
[7] Vilar-Vidal, N; Rivas, J.; López-Quintela, M.A. *ACS Catalysis*, 2, 1693 (2012).
[8] Yamamoto, Y.; Miura, T.; Suzuki, M,; Kawamura, N.; Miyagawa, H.; Nakamura,T.; Kobayashi,K.; Teranishi,T.; Hori,H. *Phys.Rev.Lett.*, 93, 116801 (2004).
[9] Schaaff, T.G.; Whetten, R.L. *J.Phys.Chem.B*, 104, 2630 (2000).
[10] Ledo-Suárez, A., Rivas, J., Rodríguez-Abreu, C.F., Rodríguez, M.J., Pastor, E., Hernández-Creus, A., Oseroff, S.B., López-Quintela, M.A. *Angew.Chem.Int.Ed*., 46, 8823 (2007).
[11] Vázquez-Vázquez, C., Bañobre-López, M., Mitra, A., López-Quintela, M.A. and Rivas, J. *Langmuir* 25, 8208–8216 (2009).
[12] Rivas, J., Bañobre-López, M., Piñeiro-Redondo, Y., Rivas, B. and López-Quintela M. A. *J. Magn. Magn. Mater.* 324, 3499-3502 (2012).
[13] Tampieri, A., D'Alessandro, T., Sandri, M., Sprio, S., Landi, E., Bertinetti, L., Panseri, S., Pepponi, G., Goettlicher, J., Bañobre-López, M. and Rivas, J. *Acta Biomaterialia* 8 (2), 843-851 (2012).
[14] Bañobre-López, M., Piñeiro-Redondo, Y., De Santis, R., Gloria, A., Ambrosio, L., Tampieri, A., Dediu, V. and J. Rivas. *J. Appl. Phys*. 109, 07B313 (2011).
[15] Gloria, A., Russo, T., Dámora, U., Zeppetelli, S., D´Allesandro, T., Sandri, M., Bañobre-Lopez, M., Pineiro-Redondo, Y., Uhlarz, M., Tampieri, A., Rivas, J., Herrmannsdorfer, T., Dediu, V. A., Ambrosio, L. and De Santis, R. *J.R.Soc. Interface,* 10, 20120833 (2013).