

## Photovoltaic LiNbO<sub>3</sub> particles: Applications to Biomedicine/Biophotonics

B. J. Ramiro<sup>2</sup>, A. Blázquez-Castro<sup>1</sup>, A. García-Cabañes<sup>1</sup>, L. Arizmendi<sup>1</sup>, A. Méndez<sup>2</sup>, A. Alcázar<sup>2</sup>, J. C. Stockert<sup>3</sup>, F. Agulló-López<sup>1,4</sup>, and M. Carrascosa<sup>1</sup>

<sup>1</sup>Depto. de Física de Materiales, Universidad Autónoma de Madrid, 28049 Madrid, Spain

<sup>2</sup>Depto. Aerotecnia, Universidad Politécnica de Madrid, 28040 Madrid, Spain

<sup>3</sup>Depto. de Biología, Universidad Autónoma de Madrid, 28049 Madrid, Spain

<sup>4</sup>CMAM, Universidad Autónoma de Madrid, 28049 Madrid, Spain

[j.ramiro@upm.es](mailto:j.ramiro@upm.es)

### Abstract

Recently, a novel method to trap and pattern ensembles of nanoparticles has been proposed and tested. It relies on the photovoltaic (PV) properties of certain ferroelectric crystals such as LiNbO<sub>3</sub> [1,2]. These crystals, when suitably doped, develop very high electric fields in response to illumination with light of suitable wavelength. The PV effect lies in the asymmetrical excitation of electrons giving rise to PV currents and associated space-charge fields (*photorefractive effect*). The field generated in the bulk of the sample propagates to the surrounding medium as evanescent fields. When dielectric or metal nanoparticles are deposited on the surface of the sample the evanescent fields give rise to either electrophoretic or dielectrophoretic forces, depending on the charge state of the particles, that induce the trapping and patterning effects [3,4].

The purpose of this work has been to explore the effects of such PV fields in the biology and biomedical areas. A first work was able to show the necrotic effects induced by such fields on He-La tumour cells grown on the surface of an illuminated iron-doped LiNbO<sub>3</sub> crystal [5]. In principle, it is conceived that LiNbO<sub>3</sub> nanoparticles may be advantageously used for such biomedical purposes considering the possibility of such nanoparticles being incorporated into the cells. Previous experiments using microparticles have been performed [5] with similar results to those achieved with the substrate. Therefore, the purpose of this work has been to fabricate and characterize the LiNbO<sub>3</sub> nanoparticles and assess their necrotic effects when they are incorporated on a culture of tumour cells.

Two different preparation methods have been used: 1) mechanical grinding from crystals, and 2) bottom-up sol-gel chemical synthesis from metal-ethoxide precursors. This later method leads to a more uniform size distribution of smaller particles (down to around 50 nm). Fig. 1(a) and 1(b) shows SEM images of the nanoparticles obtained with both method.

An *ad hoc* software taking into account the physical properties of the crystal, particularly donor and acceptor concentrations has been developed in order to estimate the electric field generated in nanoparticles. In a first stage simulations of the electric current of nanoparticles, in a conductive media, due to the PV effect have been carried out by MonteCarlo simulations using the Kutharev 1-centre transport model equations [6]. Special attention has been paid to the dependence on particle size and  $[Fe^{2+}]/[Fe^{3+}]$ . First results on cubic particles shows large dispersion for small sizes due to the random number of donors and its effective concentration (Fig 2).

The necrotic (toxicity) effect of nanoparticles incorporated into a tumour cell culture subjected to 30 min. illumination with a blue LED is shown in Fig.3. For each type of nanoparticle the percent of cell survival in dark and illumination conditions has been plot as a function of the particle dilution factor. Fig. 1a corresponds to mechanical grinding particles whereas 1b and 1c refer to chemically synthesized particles with two oxidation states. The light effect is larger with mechanical grinding nanoparticles, but dark toxicity is also higher. For chemically synthesized nanoparticles dark toxicity is low but only in oxidized samples, where the PV effect is known to be larger, the light effect is appreciable.

These preliminary results demonstrate that Fe:LiNbO<sub>3</sub> nanoparticles have a biological damaging effect on cells, although there are many points that should be clarified and much space for PV nanoparticles optimization. In particular, it appears necessary to determine the fraction of nanoparticles that become incorporated into the cells and the possible existence of threshold size effects.

This work has been supported by MINECO under grant MAT2011-28379-C03.

### References

- [1] H. A. Eggert, F. Y. Kuhnert, K. Buse, J. R. Adleman and D. Psaltis, Appl. Phys. Lett., **90** (2007) 241909.
- [2] J. Villarroel, H. Burgos, A. García-Cabañes, M. Carrascosa, A. Blazquez-Castro ad F. Agullo-Rueda, Opt. Express, 19 (2011) 24321.
- [3] X. Zhang, J. Wang, B. Tang, X. Tan, R. A. Rupp, L. Pan, Y. Kong, Q. Sun and J. Xu, Opt. Express, 17 (2009) 9981.
- [4] H. Burgos, M. Jubera, J. Villarroel, A. Garcia-Cabañes, F. Agullo-Lopez and M. Carrascosa, Opt. Mat. **35** (2013) 1700.
- [5] A. Blazquez-Castro, J. C. Stockert, B. Lopez-Arias, A. Juarranz, F. Agullo-Lopez, A. Garcia-Cabañes and M. Carrascosa, Photochem. Photobiol. Sci., **10** (2011) 956.
- [6] Kukharev N.V., Markov V.B., Odulov S.G., Soskin M.S., Vinetskii V.L., Ferroelectrics 22, 949 (1979).

## Figures

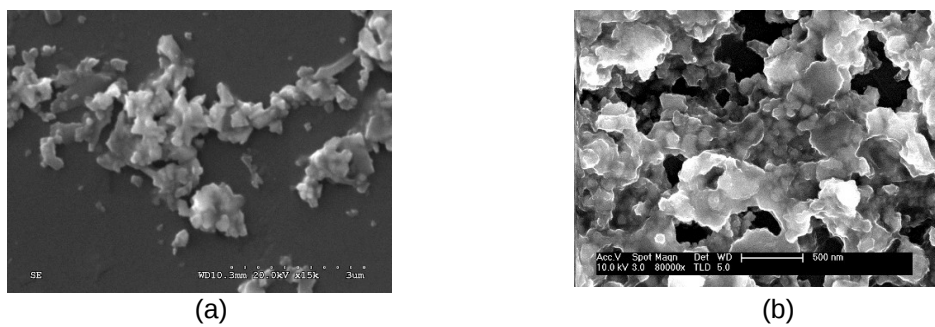


Figure 1.- SEM imagines of  $\text{LiNbO}_3:\text{Fe}$  nanoparticles obtained by: (a) mechanical grinding, (b) chemical synthesis.

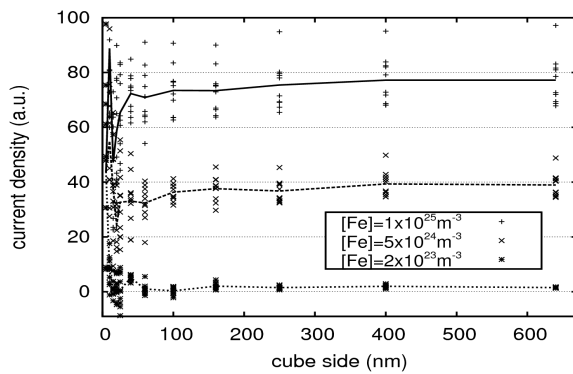


Figure 2.- Current density as a function of particle size. Dots represent individual particles. Lines connect mean current density for each size.

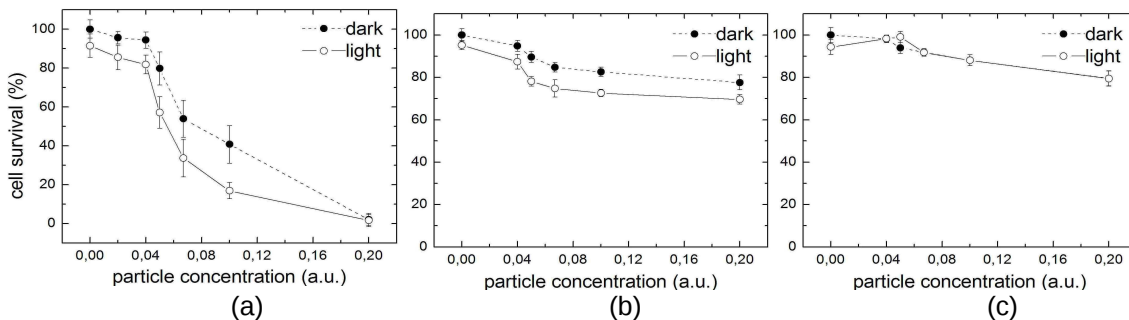


Figure 3.- Percent cell survival versus nano-particles concentration in solution obtained by mechanical grinding (a) and obtained by chemical synthesis and oxidized (b) and reduced (c) by thermal treatments.