

# Jornada Jóvenes Investigadores en Magnetismo

29 - 30 November 2018

### **BOOK OF ABSTRACTS**

THE SPANISH MAGNETISM CLUB AND THE SPANISH CHAPTER OF THE IEEE MAGNETICS SOCIETY ANNUAL JOINT MEETING







Universidad de Oviedo



### SESSION 1 (16:00 - 17:30H)

CHAIR: Mariona Escoda

*1*. The AC susceptibility of the overlapping thermomagnetic phase transitions in Ni-Mn-In Heusler alloys. **Álvaro Díaz-García**. Universidad de Sevilla.

2. Magnetic microwires for contact-less sensing application. **Diego Archilla**. Instituto de Magnetismo Aplicado (UCM-ADIF-CSIC).

*3*. Influence of the magnetic field parameters on the magnetic properties of magnetostatically-coupled Fe-based microwires. **Valeria Kolesnikova**. Universidad Estatal Immanuel Kant.

*4*. Analysis of the order of the phase transition and critical composition of La(Fe,Ni,Si)13 magnetocaloric compounds. **L.M. Moreno-Ramírez**. Universidad de Sevilla.

5. Magnetization reversal of Ni-Co alloy nanowires modulated in geometry and composition. **Miguel Méndez**. Universidad de Oviedo.

*6*. Magnetization ratchet in cylindrical nanowires. **José A. Fernández-Roldán**. Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC).

7. Non-contact monitoring of composite polymerization through the impact on magnetic properties of magnetic microwire inclusions. **Paula Corte-León**. Universidad del País Vasco.

*8*. Influence of sputtering conditions on La0.5Sr0.5CoO3 thin films properties. **Miriam Sánchez-Pérez.** Universidad de Castilla-La Mancha.

*9*. A magnetic field gradient to enhance the signal in magnetic lateral flow immunoassays. **María Salvador**. Universidad de Oviedo.

### SESSION 2 (18:30 - 20:00H)

CHAIR: Marìa Salvador

1. FORC study of the ferromagnetic impurities in Na and K Feldspars of "El Realejo" mine. **José Antonio Montiel-Anaya.** Universidad de Sevilla.

2. Detection and quantification of exomes by means of carbon-coated superparamagnetic nanoflowers. **Amanda Moyano**. Universidad de Oviedo.

3. High frequency hysteresis losses on γ-Fe2O3 and Fe3O4: susceptibility as magnetic stamp for chain formation. **Irene Morales.** Instituto de Magnetismo Aplicado (UCM-ADIF-CSIC).

*4*. Unlocking the potential of Magnetotactic Bacteria as Hyperthermia agents. **David Gandía**. Universidad del País Vasco – BCMaterials.

5. On the magnetosomes chain configuration: a magnetic and structural study. **Lourdes Marcano**. Universidad del País Vasco.

*6*. Nd-Fe-B magnetic particles obtained by sol-gel method. **Maitane Maisterra**. Universidad Pública de Navarra.

7. Challenges in the synthesis of magnetic and plasmonic nanoparticles. **Mariona Escoda.** Universitat de Barcelona.

8. Self-assembly of iron oxide precursor micelles driven by magnetic stirring time in sol-gel coatings. **Jesús López-Sánchez.** Universidad Complutense de Madrid.

# The AC susceptibility of the overlapping thermomagnetic phase transitions in Ni-Mn-In Heusler alloys

Álvaro Díaz-García<sup>1</sup>, Jia Yan Law<sup>1</sup>, Victorino Franco<sup>1</sup>, Alejandro Conde<sup>1</sup>, Anit K. Giri<sup>2</sup>

- <sup>1</sup>Dpto. Física de la Materia Condensada, Universidad de Sevilla. Seville (Spain)
- <sup>2</sup> Weapons and Materials Research Directorate, US Army Research Laboratory (USA)

Ni-Mn-In, one of the Heusler alloys, has been considered to exhibit an enhanced total entropy when their structural and magnetic transitions coincide [1]. As their transition temperatures are highly compositional dependent, the overlap of both Curie and magneto-structural transitions can be achieved.

In this work, a series of Heusler alloys with nominal compositions Ni<sub>49-x</sub>Mn<sub>36-x</sub>In<sub>15</sub> (x=0-2) was studied. They show a low temperature direct magnetocaloric effect (MCE), followed by an inverse MCE due to the martensitic transition, and a high temperature conventional MCE associated to the Curie temperature of the austenite. For Ni<sub>49.8</sub>Mn<sub>34.8</sub>In<sub>15.5</sub>, a tight overlap of the magneto-structural and Curie phase transitions was found. The isothermal entropy change ( $\Delta S_{iso}$ ) shows a spike embedded in the region of the high temperature conventional MCE (Figure 1). The martensitic transition and the Curie transition of austenite result in the different nature and signs of  $\Delta S_{iso}$ , thus give rise to the tight phase competition as observed by this embedded spike feature. Figure 2 shows the real part of the AC susceptibility ( $\chi'$ ) for various bias magnetic fields. For 0 T, a decrease of  $\chi'$  with increasing temperature is observed, while for larger fields  $\chi'$  initially increases and then decreases with higher temperatures. The increase of  $\chi'$  indicates the martensitic transformation, which occurs close to the Curie transition of austenite.



Figure 1: Magnetocaloric response of Ni<sub>49.8</sub>Mn<sub>34.8</sub>In<sub>15.5</sub> alloy at 1.5 T showing a spike embedded in the high temperature conventional MCE region.

Using the field dependence of its AC susceptibility, we could separate the overlapping transitions and also demonstrate that the observed spike is attributed to the martensitic transition of the alloy. The magnetic field stabilizes the austenitic phase and shifts the martensitic transition to lower temperatures, thus deconvoluting the two otherwise competing transitions (Figure 2). In this case, the concurrence of magneto-structural and Curie thermomagnetic phase transitions in Ni<sub>49.8</sub>Mn<sub>34.8</sub>In<sub>15.5</sub> leads to a tight phase overlap which shows that the inverse MCE is compensated by the conventional MCE [2].



Figure 2: Field dependence of the real part of the AC susceptibility, with  $T_M$  being the temperature of the martensitic transformation.

### References

[1] E. Stern-Taulats, A. Planes, P. Lloveras, M. Barrio, J.L. Tamarit, S. Pramanick, S. Majumdar, S. Yuce, B. Emre, C. Frontera, L. Manosa, Tailoring barocaloric and magnetocaloric properties in lowhysteresis magnetic shape memory alloys, Acta Mater 96 (2015) 324-332.

[2] J. Y. Law, A. Díaz-García, L. M. Moreno-Ramírez, V. Franco, A. Conde, and A. K. Giri, How concurrent thermomagnetic transitions can affect magnetocaloric effect: the Ni<sub>49-x</sub>Mn<sub>36+x</sub>In<sub>15</sub> Heusler alloy case, Submitted (2018).

### Magnetic microwires for contact-less sensing application

D. Archilla<sup>1</sup>, P. Marín<sup>1,2</sup>

<sup>1</sup>Instituto de Magnetismo Aplicado (UCM-ADIF-CSIC) P. O. Box 155 28230, Las Rozas, Madrid, Spain. <sup>2</sup>Dpt. Física de Materiales, Fac. CC. Físicas, Univ. Complutense de Madrid 28040, Madrid, Spain.

Amorphous magnetic microwires (AMMW) presents unique magnetic properties. They present a soft magnetic behavior with low coercive field and high permeability, but in particular, the giant magneto-impedance effect present in this type of microwires allows to detect the interaction of the sample with microwaves [1]. The changes of this interaction due to variation of the physical properties, like temperature, stress, current etc., of the microwire makes them useful as elements for contact-less sensing application [2,3].



#### REFERENCES

[1] A. Hernando; V. Lopez-Dominguez; E. Ricciardi; K. Osiak, and P. Marín, IEEE Trans. Antennas Propag. 64, 1112–1115 (2016).

[2] C. Herrero-Gómez; A. M. Aragón; M. Hernando-Rydings; P. Marín, and A. Hernando, Appl. Phys. Lett. 105, 092-405 (2014).

[3] A. M. Aragón; M. Hernando-Rydings; A. Hernando; and P. Marín 2015, AIP Adv. 5, 087-132.

# Influence of the magnetic field parameters on the magnetic properties of magnetostatically-coupled Fe-based microwires

V. KOLESNIKOVA<sup>a,\*</sup>, J.C. MARTINEZ-GARCIA<sup>b</sup>, V. RODIONOVA<sup>a</sup>, M. RIVAS<sup>b</sup>

<sup>a</sup> Immanuel Kant Baltic Federal University, 236004, Nevskogo 14, Kaliningrad, Russia

<sup>b</sup> Department of Physics, University of Oviedo, Polytechnica School of Engineering, 33203 Gijón,

### Spain

### \*kolesnikova-va@rambler.ru

Amorphous ferromagnetic microwires are interesting materials because of their unique magnetic properties. To study their promising properties it is critical to find correct and right procedures of measurements, and to understand the behavior of the magnetic response to the applied magnetic field. The effect of the amplitude and frequency of the magnetic field on the features of hysteresis loops has been studied in the wide range [1, 2]. This work complements knowledge with information on properties at low frequency up to 50 Hz, at high frequency with manipulations of the sampling rate, and with FORC (Firs Order Reversal Curves) analysis.

Measurements were carried out in an inductive magnetometer setup. We analyzed the hysteresis loops of single microwires and systems of two glass-coated  $Fe_{74}B_{13}Si_{11}C_2$  microwires, just separated by their glass shell. To study the magnetostatic coupling of these samples we used 5 cm long and 2cm long microwires and put them into a pick-up coil which is 7 cm long.

The single Fe-based microwire has a perfect rectangular loop while the array of two coupled wires has a step-wise hysteresis loop characterized by two Barkhausen jumps. These steps are according to the magnetostatic interaction between these wires. The arising of additional smaller steps can be related to a temporary pinning of the domain wall on defects, this effect enhanced by the magnetostatic interaction. From the hysteresis loop, we can estimate the value of the magnetostatic interaction. In order to observe the correct shape of the loop with steps, even with large amplitude of the field or frequency, it is necessary to increase the sampling rate. The steps remain with increasing amplitude and frequency, but due to too rapid changes in the parameters, the hysteresis loop instead of the stepped one takes on a "smoothed" appearance. Also, we did the FORCs measurements with high value of frequency where the internal curves corresponding to the magnetostatic interaction should be obtained. And the FORCs analysis will help to deepen the knowledge in the field of magnetostatic interaction, which will help to further improve the properties of magnetic field sensors.

- 1. V. Rodionova et al, J Supercond Nov. Magn. (2011).
- 2. V. Rodionova et al, J. Appl. Phys. 111, 07E735 (2012).

### Analysis of the order of the phase transition and critical composition of La(Fe,Ni,Si)<sub>13</sub> magnetocaloric compounds

L.M. Moreno-Ramírez<sup>1</sup>, I. Radulov<sup>2</sup>, J.Y. Law<sup>1</sup>, V. Franco<sup>1</sup>, A. Conde<sup>1</sup>, K. P. Skokov<sup>2</sup>, O. Gutfleisch<sup>2</sup> (lmoreno6@us.es)

> <sup>1</sup>Condensed Physics Department, Sevilla University <sup>2</sup>Institut für Materialwissenschaft, TU Darmstadt

### ABSTRACT

La(Fe,Si)<sub>13</sub> compounds is one of the most promising family of magnetocaloric (MC) materials. They are based on abundant, non-critical and non-contaminant elements. For these compounds the formed NaZn<sub>13</sub>-type structure (for which Si incorporation is needed to stabilize the phase) show a temperature-induced first order ferro-paramagnetic transition (as well as field-induced para-ferromagnetic transition) around 200 K. However, some issues have to be solved before commercialization, for example, the material degradation under cycling or reducing the thermal hysteresis. The MC response is tunable by the additions of different dopants (mainly, rare earths substitution to La or transition metals to Fe).

In this work, we study the effect of Fe substitution by Ni on the magnetocaloric properties of  $La(Fe,Si)_{13}$  compounds. For Ni additions, the MC response can be tuned in the same way as Co additions but the former avoids using critical raw materials and at the same time reducing material cost (Co is a critical element). Sample quality has been optimized by a combination of induction melting and suction casting techniques, which allowed to shorten the annealing time by an order of magnitude and expand the compositional range. With increasing Ni concentration, the transition temperature increases and the order of the phase transition changes from first to second order type. We show that the magnetic field dependence of magnetocaloric effect enable a clear analysis of the order of phase transition even for compositions near the critical point, surpassing the accuracy of conventionally used techniques for determining the order of magnetic phase transitions (e.g. Banerjee's criterion).

L.M. Moreno-Ramírez et al., The role of Ni in modifying the order of the phase transition of La(Fe,Ni,Si)<sub>13</sub>, Acta Materialia 160 (2018) 137-146

## Magnetization reversal of Ni-Co alloy nanowires modulated in geometry and composition

Méndez, Miguel, Caballero-Flores, Rafael, Prida, Víctor M. (miguel.mendez82@gmail.com)

### Depto. de Física, Universidad de Oviedo, Federico García Lorca nº 18, 33007-Oviedo, Asturias, Spain

### ABSTRACT

The usage of magnetic nanowires (NWs) for applications in ultra-high density magnetic data storage has gained increased attention in the last years due to the growing need for the miniaturization of devices<sup>1</sup>. In arrays of high aspect ratio ferromagnetic NWs, the information is stored along the wire axis, as a sequence of magnetic domains (bits of information), where magnetization pointing upward or downward represent a different state of a magnetic bit of information. The precise control of the NWs geometries and/or compositions<sup>1,2</sup>, allows for the tuning of the magnetization reversal mode by external parameters, such as the direction of the applied magnetic field or the spin-polarized current, and the pinning of magnetic domain walls (DWs)<sup>3</sup>. This fact is of extreme importance for the implementation of these magnetic memories in novel devices.

For a better understanding of the magnetization reversal processes in magnetic NWs, we propose in this work to study the influence of geometrically modulated single isolated Ni and Co NWs, with a diameter-modulated ratio 1:2, by micromagnetic simulations using the open source software called Mumax3<sup>4</sup>. The narrow and wide diameter segments of the NWs are 40 nm and 80 nm, respectively, and the total NW length is 4  $\mu$ m. The micromagnetic simulations were done for different length segments that are ranging from 2 to 3.6  $\mu$ m for the narrow segment and 0.4 to 2  $\mu$ m for the widest one. To determine the contribution of NWs geometry and composition to the domain wall pinning effect, single isolated NW with modulation in composition were simulated, changing the segment composition for same geometries, to study its magnetic behavior and the changes that effective magnetic anisotropy produces in the magnetization reversal effect.



Fig. 1.a) Selected hysteresis loop simulated for a modulated Ni NW with the following geometry: 40 nm of diameter and 3.6 um length for the narrow segment, and 80 nm of diameter and 0.4 um length for the wide segment. b) Hysteresis loop simulated for a modulated Ni-Co NW with the following geometry: Ni, 40 nm of diameter and 3.6 um length for the narrow segment and Co, 80 nm nm of diameter and 0.4 um length for the wide segment.

The simulated hysteresis loops (Fig. 1), shows a rich variety of magnetization reversal processes that ranges from magnetization rotation for almost any NW length to several kinds of domain wall displacements that depend on the NW diameter, length segments

and magnetic material. For example, vortex domain walls can be nucleated at the edge of the wider segment and propagated to the interface, while the magnetization in the shorter segment remains unmodified, producing a fast two-step magnetization reversal. It can also be seen that combining geometry and composition modulations lead to asymmetric hysteresis loops with different reversal modes, when the right dimensions are chosen.

Magnetization reversal processes have been studied in Ni and Co NWs with different length segments for those diameter modulated NWs by micromagnetic simulations, which can give a better understanding of the fundamental physics behind the magnetic behavior observed for this kind of nanostructures. We expect in the near future to extend this work to studies related with the propagation velocity of the magnetic domain walls under the action of either an applied magnetic field or a spin polarized current.

### REFERENCES

- 1. Y. P. Ivanov et. al, Scientific Reports 6, 24189 (2016).
- 2. M. Susano et. al, Nanotechnology 27, 335301 (2016).
- 3. Y. P. Ivanov et. al, ACS Nano 10, 5326 (2016).
- 4. A. Vansteenkiste et. al, AIP Advances 4, 107133 (2014).

### Magnetization ratchet in cylindrical nanowires

Cristina Bran<sup>1</sup>, Eider Berganza<sup>1</sup>, <u>Jose A. Fernandez-Roldan</u><sup>1</sup>, Ester Palmero<sup>1</sup><sup>†</sup>, Jessica Meier<sup>1</sup>, Esther Calle<sup>1</sup>, Miriam Jaafar<sup>1</sup>, Michael Foerster<sup>2</sup>, Lucia Aballe<sup>2</sup>, Arantxa Fraile Rodriguez<sup>3,4</sup>, Rafael P. del Real<sup>1</sup>, Agustina Asenjo<sup>1</sup>, Oksana Chubykalo-Fesenko<sup>1</sup> and Manuel Vazquez<sup>1</sup>

<sup>1</sup> Institute of Materials Science of Madrid, CSIC. 28049 Madrid. Spain

<sup>2</sup> ALBA Synchrotron Light Facility, CELLS. 08290 Barcelona. Spain

<sup>3</sup> Departament de Física de la Matèria Condensada, Universitat de Barcelona. Spain

<sup>4</sup> Institut de Nanociència i Nanotecnologia (IN2UB). 08028 Barcelona. Spain

ABSTRACT. The unidirectional motion of information carriers such as domain walls in magnetic nanostrips is a key feature for many future spintronic applications based on shift registers.

This magnetic ratchet effect has been so far achieved in limited number of complex nanomagnetic structures for example by lithographically engineered pinning sites. Here we report on simple remagnetization ratchet originated in the asymmetric potential from the designed increasing lengths of magnetostatically coupled ferromagnetic segments in FeCo/Cu cylindrical nanowires. The magnetization reversal in neighboring segments propagates sequentially in steps starting from the shorter segments, irrespective of the applied field direction. This natural and efficient ratchet offers alternatives for the design of three-dimensional advanced storage and logic devices.



**Figure 1.** (*Left*) Selected magnetization configurations showing the sequential reversal process during the hysteresis loop obtained by micromagnetic simulations. (*Right*) Selected sequence of PhotoEmission Electron Microscopy images of a multisegmented FeCo/Cu nanowire under an increasing applied field. The inset graph shows the reconstructed hysteresis loop from Magnetic Force Microscopy measurements.

### Non-contact Monitoring of Composite Polymerization Through the Impact on Magnetic Properties of Magnetic Microwire Inclusions

P. Corte-León<sup>1</sup>, S. Allue<sup>2</sup>, K. Gondra<sup>2</sup>, V. Zhukova<sup>1,3</sup>, M. Ipatov<sup>1,3</sup>, J.M. Blanco<sup>3</sup>, J. Gonzalez<sup>1</sup>, M. Churyukanova<sup>4</sup> and A. Zhukov<sup>1,3,5</sup>

(paula.corte@ehu.eus)

<sup>1</sup>Dpto. Fisica de Materiales, Fac. Quimicas, UPV/EHU, 20018, San Sebastian, Spain
<sup>2</sup>Gaiker Technological Centre, 4170, Zamudio, Spain
<sup>3</sup> Dpto. de Fisica Aplicada, EUPDS, UPV/EHU, 20018, San Sebastian, Spain
<sup>4</sup> National University of Science and Technology «MISIS», Moscow, 119049, Russia
<sup>5</sup>IKERBASQUE, Basque Foundation for Science, 48011, Bilbao, Spain

### ABSTRACT

A novel sensing technique for non-destructive and non-contact monitoring of the composites utilizing ferromagnetic glass-coated microwire inclusions with quite soft magnetic properties and tunable magnetic permittivity sensitive to tensile stress and temperature is proposed.

We provide the in-situ studies of the evolution of the hysteresis loop of arrays consisting of Co- and Fe-rich microwires as well as transmission and reflection parameters of the composites with microwire inclusions during the composites matrix solidification.

Changes of shape of hysteresis loops of linear microwire arrays upon thermoset matrix polymerization are observed. For the arrays containing Co-rich microwires we observed transformation of linear hysteresis loop to rectangular and a remarkable change of coercivity from 6 to 35 A/m. In the case of the arrays containing stress-annealed Fe-rich microwires we observed even more remarkable change: the hysteresis loops change from rectangular to linear and the coercivity drops from 40 A/m to 3 A/m.

Using the free space technique, we observed considerable variation of the Reflection in the range of 4-7 GHz and Transmission upon the matrix polymerization.

Observed dependencies are discussed considering variation of temperature and stresses during the thermoset matrix polymerization and their influence on magnetic properties of glasscoated microwires.

### INFLUENCE OF SPUTTERING CONDITIONS ON La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> THIN FILMS PROPERTIES

M. Sánchez-Pérez<sup>1</sup>, O. J. Dura<sup>1,2</sup>, J. P. Andrés<sup>1,3</sup>, R. López Antón<sup>1,3</sup>, J. A. González<sup>1,3</sup>, and M. A. López de la Torre<sup>1,2</sup> (miriam.sanchez23@alu.uclm.es)

<sup>1</sup>Dto. de Física Aplicada, University of Castilla-La Mancha, Ciudad Real, Spain <sup>2</sup>Instituto de Investigaciones Energéticas y Aplicaciones Industriales (INEI), Ciudad Real, Spain <sup>3</sup>Instituto Regional de Investigación Científica Aplicada (IRICA), Ciudad Real, Spain

#### ABSTRACT

Perovskite oxides have received considerable attention due to both fundamental and technological aspects. They show a large variety of interesting phenomena as superconductivity, ferroelectricity or ferromagnetism. From a technological point of view, they emerge as excellent materials for Solid Oxid Fuel Cells (SOFCs) or spintronic devices. Among perovskite oxides, cobaltites show remarkable magnetic properties as spin-state transitions or an unusual glassy ferromagnetic behavior.  $La_{(1-x)}Sr_xCoO_3$  (LSCO) is one of the most widely studied example. For LSCO, it is possible to induce a transition from an insulator-non magnetic state to a metallic-ferromagnetic state through temperature or Sr doping. Moreover, there is a great motivation for the study of LSCO in thin film form. The dimensional confinement of the magneto-electronic phase separation, the oxygen stoichiometry or the strain effects provide the possibility of tuning the properties and potential applications of LSCO.

In this work, we present a physical characterization of  $La_{0.5}Sr_{0.5}CoO_3$  thin films. For this purpose, a family of samples with different structure and thickness was deposited by reactive RF magnetron sputtering from LSCO target. The influence of deposition parameters as temperature, time, oxygen partial pressure and substrate composition, was checked by structural, electric and magnetic characterization. [1] [2] [3]

- [1] M. A. Torija et al., J. of Appl. Phys. **104**, 023901 (2008)
- [2] H. W. Yang et al., Sci. Rep. 4:6206 (2014)
- [3] P. Mandal et al., J. of Appl. Phys. 100, 103912 (2006)

# A magnetic field gradient to enhance the signal in magnetic lateral flow immunoassays

### M. Salvador<sup>a,d</sup>, A. Moyano<sup>b</sup>, J.C. Martínez García<sup>a</sup>, M.C. Blanco-López<sup>b</sup>, Vlad Socoliuc<sup>c</sup>, Ladislau Vékás<sup>c</sup>, Davide Peddis<sup>d</sup>, M.P. Morales<sup>e</sup> and M. Rivas<sup>a</sup>

<sup>a</sup>Departamento de Física, Campus de Viesques – Universidad de Gijón, 33204 Gijón, Spain. <sup>b</sup>Departamento de Química Física y Analítica, Universidad de Oviedo, 33006 Oviedo, Spain <sup>c</sup>Romanian Academy - Center for Fundamental and Advanced Technical Research, 300223 Timisoara, Romania <sup>d</sup>Institute of Structure of Matter (CNR), 00015 Monterotondo Scalo (RM), Italy <sup>e</sup>Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049, Madrid, Spain *E-mail: <u>U0247670@uniovi.es</u>* 

Lateral Flow Inmunoassays (LFIs) are spreading fastly as *point-of-care* bio-testing because of their quickness, portability, easy use and low cost. As a paper-based technology, they basically consist of a nitrocellulose strip across which a reagent is immobilized in the test-line to specifically capture the molecule of interest (bio-analyte) contained in the fluid sample that flows along the strip by capillarity. The bio-analyte is labelled by a recognition probe usually gold or latex nanoparticles that make it visible and so provide a qualitative result (presence/absence test). The need to also quantify the test line arises in cancer, miocardial infartaction, and other diseases to get a better diagnosis, prognosis and decision-making during treatment, etc. For this purpose, magnetic nanoparticles (NPs) have been proposed as an efficient label [1]. The magnetic perturbation they produce can be detected by a magnetic sensor to quantify them and correlate the signal with the concentration of the bio-analyte. Besides the quantifying advantage, their capability for pre-concetration (in the liquid sample) or post-concentration (in the test line) makes them even more attractive to increase the sensitivity of the technique.

In this work, we explore the posibility to enhance the sensitivity of the LFI by means of the application of a magnetic field gradient to the test line once the sample is run and dried. First, a small volume of fresh running buffer is dropped in the test line to enable the mobility of the particles. Secondly, the strip is placed in one of the poles of a electromagnet providing a -0.43 T/m magnetic field gradient. The particles, which had been immobilised across the thickness of the nitrocellulose membrane, are reaccomodated by the field gradient, and concentrated closer to the visible surface. To evaluate the magnetic signal of the LFIs a magnetic reader [2] has been used which basically consists of an inductive sensor on which the magnetic moments of the particles produce an increase of impedance that is continuosly measured. The method has been tested with different kind of particles (all of them magnetite based nanoparticles) functionalised with neutravidin, on a lateral flow strip across which a biotin test line has been printed. A remarkable increase of the measured signal in the order of 30% was observed for all the particles. The effects of the gradient amplitude and time have been analysed to optimise the procedure. The results lead to the conclusion that post-concentration of the magnetic labels of the LFI by a magnetic field gradient is an efficient approach to enhance their sensitivity.



**FIGURE.** A schematic view of a cross section of the membrane of the strip after the sample has been run. The magnetic NPs are caught by the interaction Biotin-Neutravidin and accommodate whithin all the section. After applying a magnetic field gradient, the NPs are move along the nitrocelulose fibers of the membrane towards the most external layer.

#### **Notes and References**

- 1 Wang, Y., et al. Materials Science and Engineering C, 2009, 29, 714.
- 2 Lago-Cachón, D. et al., IEEE Magnetics Letters, 2017, 8, 1-5.

### FORC study of the ferromagnetic impurities in Na and K Feldspars of

### "El Realejo" mine

Jose Antonio Montiel-Anaya, <sup>1</sup> V. Franco, <sup>1,</sup>

<sup>1</sup> Dpto. Física de la Materia Condensada, ICMSE-CSIC, Universidad de Sevilla, Apdo. 1065. 41080-Sevilla, Spain

<sup>2</sup> Avda. Reina Mercedes, Spain

#### Abstract:

Feldspar is a Na-K-Ca-Al tectosilicate, generally poor in iron or other elements with strong magnetic moments. Being the post abundant constituent minerals in Earth's crust, from the technological point of view, feldspars are used in a broad variety of applications, which include glass manufacturing, fabrication of ceramics elements, fillers in paintings, enamels, floors, etc. However, most applications require the absence (or minimization) of Fe inclusions, being this a very relevant factor that controls the price of the mineral.

Typically, Fe content in the mineral produced at a mine is determined by chemical analysis, which implies an off-site test and small sampling volume. Separation of magnetic inclusions is usually made by crushing the rocks and applying a magnetic field gradient that, in combination with gravity, guides the magnetic particles out from the production line.

In this work we focus on two aspects of the production of feldspars extracted from the "El Realejo" mine in Cazalla de la Sierra, Sevilla, Spain; 1.- we evaluate an alternative characterization technique for the determination of the content of the magnetic phases that eventually, can be made on-site during production; and 2.- the reliability of the separation methods that, indirectly, affect the final price of the product.

Magnetic characterization of the produced mineral is a reliable way of identifying the content of Fe-containing phases in feldspars, mainly hematite, magnetite and goethite. While saturation hysteresis loop give a general idea of the presence of magnetic phases, we show that FORC diagrams are useful for determining the presence of different uncoupled phases. In addition, it provides a way to demonstrate that the conventional separation methods are selective in the extraction of magnetic particles, as evidenced by the different FORC distribution of the natural rock and that of the separated particle.

### **Keywords:**





### Detection and quantification of exomes by means of carboncoated superparamagnetic nanoflowers

### Amanda Moyano<sup>\*a,b</sup>, M. Salvador<sup>b</sup>, J.C. Martínez-García<sup>b</sup>, M. Rivas<sup>b</sup>, M.C. Blanco-López<sup>a</sup>, M. Gónzalez-Gómez<sup>c</sup>, Z.Vargas Osorio<sup>c</sup>, Y. Piñeiro<sup>c</sup>, J. Rivas<sup>c</sup>.

<sup>a</sup> Dpto. de Química Física y Analítica, Universidad de Oviedo, C/Julián Clavería, 8, 33006 Oviedo, Spain.

<sup>b</sup> Dpto. de Física, Universidad de Oviedo, Edificio Departamental Este, Campus de Viesques, 33204 Gijón, Spain.

<sup>o</sup>Dpto. Física Aplicada, Fac. Física, Universidad de Santiago de Compostela, Campus Vida, 15782 Santiago de Compostela, Spain.

#### uo210018@uniovi.es

Lateral flow immunoassay (LFI) is a rapid, simple and cost-effective test used in fields such as diagnostics in medicine<sup>1</sup> or environmental control. It is a paper-based platform for detection of analytes which consists of three parts for a *dipstick format*: absorbent, nitrocellulose membrane and conjugate (Figure 1). Traditionally, this kind of immunoassays has been used only as qualitative tests using gold or latex nanoparticles to label the analyte and display a visual signal (positive or negative result as in a pregnancy test). A quantifying capacity can be added by replacing the usual labels by superparamagnetic nanoparticles.

For this purpose, superparamagnetic nanoparticles coated by a black carbon layer have been used in lateral flow immunoassays to detect exomes.

Exosomes, also known as extracellular vesicles, are potential and non-invasive biomarkers for diagnostic, prognosis and monitoring response to treatment in certain diseases including vascular disorders, neurodegenerative diseases and cancer.

Firstly, to develop the test, the nanoparticles were functionalized with a specific antibody against exosomes using the carbodiimide crosslinker chemistry. Furthermore, the functionalization process was followed by dynamic light scattering measurements and it was demonstrated that the hydrodynamic diameter increases from 267 nm to 304 nm after the addition of the antibody. Once the nanoparticles were bound to the antibody, they were mixed with exomes in solution to capture them forming the complex nanoparticles-antibody-exomes. The conjugate pad of the LFI was introduced in the solution, so that it flew along the nitrocellulose membrane by capillarity. The complexes were retained at the test line where a second specific antibody against exosomes had been immobilised. In order to prove the correct operation of the test, a second line was used as control (it consists of anti-IgG antibodies which recognize the anti-exomes antibody that coat the nanoparticles.) This kind of immunoassay is known as sandwich format and the signal of the test line increases with the concentration of exomes (Figure 2). Finally, this line was quantified by an electromagnetic sensor based on the increase of the impedance induced by the varying magnetic moment of the particles on a RF current-carrying copper conductor.<sup>2</sup> The conclusion of the study was that carbon-coated iron oxide nanoparticles present excellent characteristics to be used in LFIA, displaying very good optical and magnetic signals, as well as easy functionalisation.





Figure 1. Lateral flow immunoassay scheme

Figure 2. Test for different concentrations of exomes. The signal of the test line increases with the concentration of exomes

### **Notes and References**

Oliveira-Rodríguez, M.; Serrano-Pertierra, E.; García, A. C.; SorayaLópez-Martín; Yañez-Mo, M.; Cernuda-Morollón, E.; M.C.Blanco-López., Point-of-care detection of extracellular vesicles: Sensitivity optimization and multiple-target detection. *Biosensors and Bioelectronics* 2017, *87*, 38 - 45.
Lago-Cachón, D.; Oliveira-Rodríguez, M.; Rivas, M.; Blanco-López, M. C.; Martínez-García, J. C.; Moyano, A.; Salvador, M.; García, J. A., Scanning Magneto-Inductive Sensor for Quantitative Assay of Prostate-Specific Antigen. *IEEE Magnetics Letters* 2017, *8*, 4.5.

1-5.

### High frequency hysteresis losses on γ-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>: susceptibility as magnetic stamp for chain formation

I Morales<sup>1</sup>, R Costo<sup>2</sup>, P de la Presa<sup>1, 3</sup>, N Mille<sup>4</sup>, J Carrey<sup>4</sup>, A Hernando<sup>1,3</sup>

<sup>1</sup>Instituto de Magnetismo Aplicado (UCM-ADIF-CSIC), P.O. Box 155, 28230, Las Rozas, Madrid, Spain.
<sup>2</sup>Dpt. de Biomateriales y Materiales Bioinspirados, ICMM/CSIC, Sor Juana Inés de la Cruz 3, 28046, Madrid, Spain.
<sup>3</sup>Dpt. Física de Materiales, Fac. CC Físicas, Univ. Complutense de Madrid, 28040, Madrid, Spain.
<sup>4</sup>Université de Toulouse, INSA-CNRS-UPS, LPCNO, 135 Av. Rangueil, 31077 Toulouse, France.
irenemorales@ucm.es

In order to understand the properties involved in the heating performance of magnetic nanoparticles during hyperthermia treatments, a systematic study of different  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles has been done. High-frequency hysteresis loops at 50 kHz carried on particles with sizes ranging from 6 to 350 nm show susceptibility  $\chi$  increases from 9 to 40 for large particles and it is almost field independent for the smaller ones. This suggests that the applied field induces chain ordering in large particles but not in the smaller ones due to the competition between thermal and dipolar energy. The specific absorption rate (SAR) calculated from hysteresis losses at 60 mT and 50 kHz ranges from 30 to 360 W/g<sub>Fe</sub>, depending on particle size, and the highest values correspond to particles ordered in chains. This enhanced heating efficiency is a not consequence of the intrinsic properties like saturation magnetization or anisotropy field but to the spatial arrangement of the particles.



**Figure 1:** 50kHz hysteresis cycles and  $\chi$  calculated at H<sub>c</sub> with increasing ac-field in samples (A)  $\gamma$ Fe2O3-12nm and (B) Fe3O4-35nm.

### Unlocking the potential of Magnetotactic Bacteria as Hyperthermia agents

David Gandia<sup>1,3</sup>, Lucia Gandarias<sup>2,3</sup>, Alicia Muela<sup>1,2</sup>, Javier Alonso<sup>1,4</sup>, Ana García Prieto<sup>1,5</sup>, Raja Das<sup>6</sup>, Manh-Huong Phan<sup>6</sup>, Hariharan Srikanth<sup>6</sup>, Daniel Shore<sup>7</sup>, Bethanie Stadler<sup>7</sup> and M. Luisa Fdez-Gubieda<sup>1,3\*</sup>

- 1. BCMaterials, UPV/EHU Science Park, 48940 Leioa, Spain
- 2. Departamento de Inmunología, Microbiología, y Parasitología, UPV/EHU, 48940 Leioa, Spain
- 3. Departamento de Electricidad y Electrónica, UPV/EHU, 48940 Leioa, Spain
- 4. Departamento de Física Aplicada I, UPV/EHU, 48940, Spain
- 5. Departamento CITIMAC, Universidad de Cantabria (UC), 39005 Santander, Spain
- 6. Department of Physics, University of South Florida (USF), 33620 Tampa, USA
- Department of Chemical Engineering & Materials Science, University of Minnesota Twin Cities (UMN), 55455 Minneapolis, USA

Magnetotactic bacteria (MTB) are a diverse group of microorganisms with the ability to orient and migrate along the geomagnetic field due to the presence of a chain of magnetic nanoparticles that behave as a compass needle. In particular, *Magnetospirillum gryphiswaldense* MSR-1 species synthesize cubo-octahedral shape magnetite (Fe3O4) nanoparticles with a mean diameter of 45 nm. These nanoparticles are arranged forming a chain of  $\approx$  20 nanoparticles. In the last years, one of the most interesting approaches for cancer therapy is devising nano-robots capable of targeting and destroying cancer cells. In this work we want to prove the capabilities of *Magnetospirillum gryphiswaldense* bacteria as self-propelled biorobots for cancer treatment, evaluating the magnetic hyperthermia response. Figure 1a shows the Specific Absorption Rate normalized by the frequency, SAR/f, as a function of the magnetic field. Magnetotactic bacteria were dispersed in water with concentration of 0.15 mg<sub>Fe3O4</sub>/ml reaching SAR/f values as high as 8  $Wg^{-1}kHz^{-1}$  (see figure 1a). We have developed a model considering that the magnetic energy of bacteria depends on the cubic magnetocrystalline anisotropy of magnetite, shape anisotropy, intra-chain dipolar interactions, and



the Zeeman term. Figure 1b reflects the good agreement of this model with experimental results.

Figure 1. (a) SAR/f values as a function of the applied magnetic field for bacteria dispersed in water. (b) Experimental hysteresis loops measured at 302 kHz and simulation.

### On the magnetosomes chain configuration: a magnetic and structural study

I. Orue<sup>1</sup>, <u>L. Marcano<sup>1</sup></u>, P. Bender<sup>2</sup>, A. García Prieto<sup>1,3</sup>, S. Valencia<sup>4</sup>, M. A. Mawass<sup>4</sup>, D. Gil-Cartón<sup>5</sup>, D. Alba Venero<sup>6</sup>, D. Honecker<sup>7</sup>, A. García-Arribas<sup>1,3</sup>, L. Fernández-Barquín<sup>2</sup>, A. Muela<sup>1,3</sup>, M. L. Fdez-Gubieda<sup>1,3\*</sup>

1 Universidad del País Vasco - UPV/EHU, 48940 Leioa, Spain,

2 CITIMAC, Universidad de Cantabria, 39005 Santander, Spain

3 BCMaterials, UPV/EHU Science Park, 48940 Leioa, Spain

4 Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany

5 Structural Biology Unit, CIC bioGUNE, CIBERehd, 48160 Derio, Spain

6 ISIS, STFC Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, United Kingdom

7 Institut Laue-Langevin, 38042 Grenoble, France

lourdes.marcano@ehu.eus

Magnetospirillum gryphiswaldense is a microorganism able to biomineralize high quality magnetite nanoparticles, called magnetosomes. These helical cells contain a variable number of 45 nm cuboctahedral single domain magnetite magnetosomes arranged in a chain. Thus, the chain behaves like a large single permanent magnetic dipole able to passively orient the whole bacteria along external magnetic field lines. Due to the large magnetic anisotropy, such arrangements show potential for biomedical applications and actuation devices as nanorobots.

Rather than the *a priori straight* lines, magnetosome chains are slightly bent, as evidenced by electron cryotomography (ECT). The present work is devoted to shed light on the underlying mechanisms that determine the arrangement of the magnetosomes and consequently the geometry of the chain. For that reason, we have explored the direction of the magnetic moment using state-of-the-art techniques carried out on a set of different bacterial arrangements: *i*) small angle neutron/x-ray scattering (SANS/SAXS) on a bacterial colloid, *ii*) macroscopic magnetometry on 3D and 2D fixed arrangements of randomly distributed and aligned bacteria, and *iii*) x-ray photoemission electron microscopy (XPEEM) on an individual chain of magnetosomes extracted from bacteria. Our experimental and theoretical findings<sup>1</sup> indicate that the effective magnetic moment of individual magnetosomes is tilted out of the chain axis ([111] crystallographic easy axis of magnetite) about 20<sup>o</sup>.

This tilt does not affect the direction of the chain net magnetic moment, which remains along the chain axis, but turns out to be the key to understand the arrangement of magnetosomes in helical-shaped chains. In fact, by considering a interplay between the magnetic dipolar interactions between magnetosomes and a lipid/protein-based mechanism, modelled as an elastic recovery force exerted on the magnetosomes, we were able to reproduce the experimental chain geometry imaged by ECT, see figure 1.



Fig.1: Left) Schematic representation of the force involved in construction of the chain; Right) Experimental reconstruction from ECT images and 3D simulation of the chain

1. I. Orue et al; Nanoscale 10 (2018) 7407, DOI: 10.1039/c7nr08493e

### Nd-Fe-B magnetic particles obtained by sol-gel method

M. Maisterra, I. Reyero, F. Bimbela, I. Pellejero, L.M. Gandía, J.I. Perez-Landazábal, C. Gómez-Polo

Departamento de Ciencias, Universidad Pública de Navarra, Campus de Arrosadia, 31006, Pamplona, Spain.

Institute for Advanced Materials (INAMAT), Universidad Pública de Navarra, Campus de Arrosadia, 31006, Pamplona, Spain.

NdFeB magnets are widely employed in different electromagnetic devices for the conversion between electricity and mechanical energy [1]. Most of the employed fabrication procedures of NdFeB magnets are physical metallurgy methods, where high purity elements as starting materials are required. However, the fabrication of these magnetic materials by chemical synthesis represents a current research challenge due to the large reduction potential of Nd<sup>3+</sup> and the high oxidation tendency of the NdFeB compounds. Chemical synthesis procedures have associated certain advantages such as lower energy consumption, higher particle homogeneity, controllable particle size, and lower cost of the initial materials [2, 3]. Furthermore, it allows the design of bonded magnets employing new processing technologies such as additive manufacturing or 3D printing [4].

In this work, Nd<sub>2</sub>Fe<sub>14</sub>B magnetic particles were synthesized by sol-gel and reduction-diffusion processes. Nd-Fe-B gel was prepared using Nd(NO<sub>3</sub>).6H<sub>2</sub>O, Fe(NO<sub>3</sub>).9H<sub>2</sub>O, H<sub>3</sub>BO<sub>3</sub> and citric acid. Firstly, the gel was calcined during 3 h at 400°C followed by 3h at 800 °C. The X-ray diffraction patterns indicate a complex distribution of oxides, with main reflections associated to NdFeO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>B. The characteristic tetragonal Nd<sub>2</sub>Fe<sub>14</sub>B phase was obtained through a reduction-diffusion process of the calcined sample, using CaH<sub>2</sub> as a reducing agent (800 °C for 2 h under He flow). The phase distribution was further analyzed through Transmission Electron Microscopy (TEM) and the magnetic response (room temperature hysteresis loops) through SQUID magnetometry. The characteristic permanent magnetic parameters, such as coercive field, remanence and energy product (*BH*)<sub>max</sub> are analyzed on terms of the magnetic phase distribution under the performed reduction process.

### Acknowledgents

The authors thank Gobierno de Navarra for the financial support under project Pernanomag 0011-1365-2017-000118.

[3] H. Rahimi et al., J.Magn. Magn. Mat. 444 (2017) 111-118

<sup>[1]</sup> O. Gutfleisch et al. Adv. Mater. 23 (2011) 821–842.

<sup>[2]</sup> P.K. Deheri et al. Chem Mater. 22 (2010) 6509-6517

<sup>[4]</sup>C. Huber et al. Appl. Phys. Lett. 109 (2016) 162401

# Challenges in the synthesis of magnetic and plasmonic nanoparticles

M. Escoda-Torroella<sup>1,2</sup>, A. Fraile Rodríguez<sup>1,2</sup>, A. Labarta<sup>1,2</sup>, X. Batlle<sup>1,2</sup>

<sup>1</sup>Departament de Física de la Matèria Condensada, Universitat de Barcelona, Barcelona, 08028 (Spain)

<sup>2</sup>Institut de Nanociència i Nanotecnologia (IN2UB), Barcelona, 08028 (Spain)

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles (NP) are versatile building blocks due to their good magnetic performance, ease of production and functionalization by chemical routes, and low toxicity. However, controlling the electronic and magnetic properties remains a challenge because of their crucial dependence on composition, structure, surface chemistry, and interparticle interactions. For this reason, careful control of the synthesis conditions is required.

On the other hand, gold nanoparticles, which exhibit strong localized surface plasmon resonance (LSPR) absorption, have attracted much interest due to their biocompatibility, low toxicity and plasmonic properties which made them good candidates for biomedical applications.

The combination of these two materials pave the way to synergies between magnetic and plasmonic properties. Therefore, this work is focused on the synthesis of hybrid structures to achieve multifunctional materials. Magnetite NPs are synthetized thermal decomposition method, which allows obtaining monodispersed nanoparticles with high-crystal quality. Then the NPs are transferred to water to improve the biocompatibility and finally functionalized to allow the attachment of gold nanoparticles, which are also synthesized in aqueous media.

### Self-assembly of iron oxide precursor micelles driven by magnetic stirring time in sol-gel coatings

J. López-Sánchez<sup>1,2,3</sup>, A. Serrano<sup>4,5,6</sup>, A. del Campo<sup>4</sup>, J. de la Figuera<sup>2,7</sup>, J. F. Marco<sup>2,7</sup>, M. Abuín<sup>8,9</sup>, A. Muñoz-Noval<sup>6,7</sup>, N. Carmona<sup>1,2,3</sup>, O. Rodríguez de la Fuente<sup>1,2,3</sup> and P. Marín<sup>1,3</sup>

<sup>1</sup>Departamento de Física de Materiales, Universidad Complutense de Madrid (UCM), 28040 Madrid, Spain

<sup>2</sup>Unidad asociada IQFR (CSIC)-UCM, 28040 Madrid, Spain

<sup>3</sup> Instituto de Magnetismo Aplicado, UCM-CSIC-ADIF, 28230 Las Rozas, Madrid, Spain

<sup>4</sup> Instituto de Cerámica y Vidrio, ICV-CSIC, 28049 Madrid

<sup>5</sup> SpLine, Spanish CRG BM25 Beamline, ESRF, 38000 Grenoble, France

<sup>6</sup> Instituto de Ciencia de Materiales de Madrid, ICMM-CSIC, 28049 Madrid, Spain

<sup>7</sup> Instituto de Química Física "Rocasolano", IQFR-CSIC, 28006 Madrid, Spain

<sup>8</sup> Instituto de Sistemas Optoelectrónicos y Microtecnología, ISOM-UPM, 28040 Madrid

<sup>9</sup>CEI Campus Moncloa, UCM-UPM, 28040 Madrid, Spain

jesloppez@gmail.com

### Abstract

The purpose of this work is to fabricate self-assembly microstructures and study the structural properties of epsilon iron oxide nanoparticles when glycerol (GLY) [1] and cetyl trimethylammonium bromide (CTAB) [2] are added as steric agents simultaneously. The combined action of a polyalcohol and a surfactant significantly modifies the morphology of the sample giving rise to a different microstructuring in each case studied (1, 3 and 7 days of magnetic stirring time). This is due to the fact that the addition of these two compounds leads to a considerable increase in gelation time as glycerol can be found interacting with the alkoxide group on the surface of the iron oxide precursor micelle and/or being incorporated into the hydrophilic chains of CTAB. This last effect causes the iron oxide precursor micelles to be interconnected forming aggregates whose size and structure depend on the magnetic stirring time of the sol-gel recipe (Figure 1). The crystalline structure, composition, purity and morphology of the sol-gel coatings treated at 960 °C are examined by SEM, AFM, CRM, XAS and Mössbauer spectroscopy. Emphasis is placed on the nominal percentage of the different iron oxides found in the samples and the differences between them are also analyzed correlating their magnetic properties. This work supposes the possibility of patterning epsilon iron oxide nanoparticles in coatings by an easy one-pot sol-gel method.



**Figure 1.** SEM images acquired at an inclination of 60° from the XY plane of samples prepared at 960°C for (a) 1 day, (b) 3 days and (c) 7 days of magnetic stirring.

#### References

[1] López-Sánchez J, Muñoz-Noval A, Castellano C, Serrano A, del Campo A, Cabero M, Varela M, Abuín M, de la Figuera J, Marco J F, Castro G R, Rodríguez de la Fuente O, Carmona N. Origin of the magnetic transition at 100 K in ε-Fe<sub>2</sub>O<sub>3</sub> nanoparticles studied by x-ray absorption fine structure spectroscopy. Journal of Physics: Condensed Matter 2017;29:485701. doi:https://doi.org/10.1088/1361-648X/aa904b.

[2] López-Sánchez J, Serrano A, Del Campo A, Abuín M, Rodríguez de la Fuente O, Carmona N. Sol-gel synthesis and micro-Raman characterization of  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> micro- and nanoparticles. Chemistry of Materials 2016;28:511–8. doi:10.1021/acs.chemmater.5b03566.