

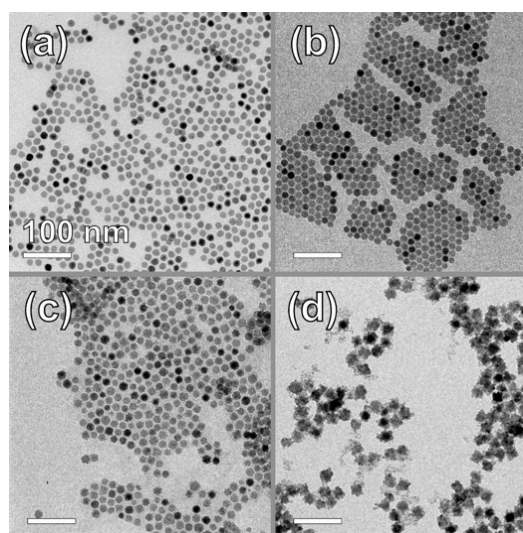
## Structural and magnetic evolution of mixed CE/seeded-grown multilayered Mn/Fe oxides

Ef시오 Zuddas,<sup>a</sup> Sergio Lentijo Mozo,<sup>a</sup> Alberto Casu,<sup>a</sup> Andrea Falqui<sup>a</sup>

<sup>a</sup> Biological and Environmental Sciences and Engineering (BESE) Division, NABLA Lab, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia

Magnetic nanoparticles (NPs) are a well-known and very attractive class of materials, due to the ever-growing number of novel, advanced magnetic nanostructures showcasing different shapes, compositions and properties, thanks to the constant push for a more precise control over compositions and morphologies by enhanced chemo-structural tuning.[1] In this context, the multi-layered core-shell systems represent an interesting route to develop novel materials by combining the properties of an internal layer acting as a seed (core) and one or more external layers (shell) with different properties. The seeded growth method, which revolves around the addition of one or more external layers (shells) to pre-existing seeds, represents the most efficient strategy to obtain such materials, but is usually hindered by a limited control over the desired shape and/or size of the final product. On the other hand, post-synthetic cation exchange (CE) reactions offer a possible solution, by partially or completely replacing the cations of parent NPs while concomitantly preserving the anionic sublattice, thus preserving the seeds shape, while giving rise to new compounds (total CE reactions) [2] or composite, structured systems (localized and/or partial CE reactions).[3]

In our study, we moved from a recent work on bi-magnetic Fe, Mn oxide-based core-shell NPs, synthesized by a seeded-growth approach on pre-synthesized magnetite NPs [4] to develop a bi-magnetic core-shell system based on a mixed CE/seeded growth approach and subsequently push the CE reaction to observe the structural and magnetic evolution of the multilayered system. In particular, we started from single crystalline, monodispersed colloidal iron oxide NPs and substituted the Fe<sup>2+</sup> with Mn<sup>2+</sup> ions by a post-synthetic CE protocol to obtain a mixed Fe/Mn shell, without affecting their crystal structure, shape and size. Further pushing the CE reaction resulted in the growth of a second Mn<sub>3</sub>O<sub>4</sub> shell over the initial cation-exchanged composite core-shell (Fig 1). The evolution from seed to core-shell and finally to a multi-shell system was analyzed by combining chemo-structural characterization by TEM and DC magnetometry studies by SQUID. In fact, the variations in the structure of the Fe/Mn system also implied a drastic change in the resulting magnetic properties, with the initial ferrimagnetic response of the pure seeds leaving place to different interaction-based effects. While the formation of the first, CE-based shell determined a magnetic softening with respect to the starting material, accompanied by a ferrimagnetic coupling between the iron oxide seed and the CE-mixed shell, this was gradually overcome by an antiferromagnetic coupling between the core/CE-shell and the growing external Mn<sub>3</sub>O<sub>4</sub> shell, which gradually resulted in a magnetic hardening of the whole composite system. Then, the structural evolution of this multilayered Mn-Fe system and the subsequent modification of its magnetic features open the possibility to increase or decrease the magnetic hardness of the final product by just varying the reaction conditions.



**Fig. 1.** Conventional TEM images of (a) Fe<sub>3</sub>O<sub>4</sub> NPs, (b, c, d) Mn-exchanged NPs with different Mn<sup>2+</sup>/Fe<sup>2+</sup> molar ratios

- 1) N.A. Frey et al., *Chem. Soc. Rev.*, **2009**, 38, 2532.
- 2) B.J. Beberwyck et al., *J. Phys. Chem., C* **2013**, 117, 19759
- 3) Z. Luo et al., *ACS Appl. Mater. Interfaces*, **2016**, 8, 17435
- 4) M. Estrader et al., *Nat. Commun.*, **2013**, 4:2960