doi:10.1017/S1431927610058721
Microsc. Microanal. 16 (Suppl 2), 2010


# Self-assembled Lanthanide Phosphate/Magnetite Nanocomposites

Jie Fang,*,*** Martin Saunders,*** Yanglong Guo,* Guanzhong Lu,* Colin L. Raston** and K. Swaminathan Iyer**

* Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, P. R. China.
** Centre for Strategic Nano-Fabrication, School of Biomedical, Biomolecular and Chemical Sciences The University of Western Australia, Crawley, WA 6009, Australia.
*** Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Crawley, WA 6009, Australia.

We report a novel protocol to use magnetite ($Fe_3O_4$) nanoparticles stabilised with *p*-sulfonato-calix[6]arene (SC[6] ) [1] to self-assemble doped $LaPO_4$ nanorods into 3-dimensional "koosh nanoballs" as a bifunctional luminescent ferro-fluidic system.

The structure comprises nanorods growing radially (Fig. 1) from the centre, forming a koosh nanoball 200-300 nm in size. Lattice fringes are observed with a repeat spacing of ~0.61 nm along the short axis of the needles, consistent with of the (100) plane of the hexagonal phase of lanthanum phosphate. The corresponding SAED pattern (Fig. 1c inset) also verified the hexagonal phase. A weak (220) diffraction ring from magnetite in the SAED pattern confirmed its presence in the nanocomposite assembly. The elemental composition was analyzed using electron energy loss spectroscopy (EELS) confirming the existence of the elements O, Fe, La, Tb, Ce (Fig. 1b) and O, Fe, La, Eu in the corresponding nanoparticles. The phosphorous signal was not clearly detected due to overlap with the metal signals.

The composition of the $Fe_3O_4$@SC[6]- $LaPO_4:Eu^{3+}$ koosh nanoballs was investigated using energy filtered TEM (EFTEM), Fig. 2. The thickness map (Fig. 2b) validated the 3D structure of the nanocomposite, being thicker in the centre than the edge of the particle. The maps (Fig. 2c-e) revealed that the nanocomposite was made up of nanorods containing lanthanum, europium and oxygen, with iron-rich particles distributed within the structure (Fig. 2f). The SC[6]coated magnetite with multiple free upper rim $–SO_3$ groups presumably serves as an inorganic crosslinker holding the 1D $LaPO_4$ nanorods into a koosh nanoball structure (Fig. 3). Each magnetite nanoparticle within the structure serves as a multiple nucleation site for the growth of high aspect ratio $LaPO_4$ nanorods. The resulting high density of nanorods within a single discrete structure leads to a koosh nanoball spheroidal structure with the nanorods growing radially outwards due to crowding.

References

[1] S. F. Chin, M. Makha, C. L. Raston, M. Saunders, *Chem. Commun*. 2007, 1948–1950.
[2] The work was supported by the Australian Research Council (ARC), the National Basic Research Program of China (2010CB732300) and the China Scholarship Council (CSC). The TEM work was carried out at the Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, supported by University, State and Federal Government funding.

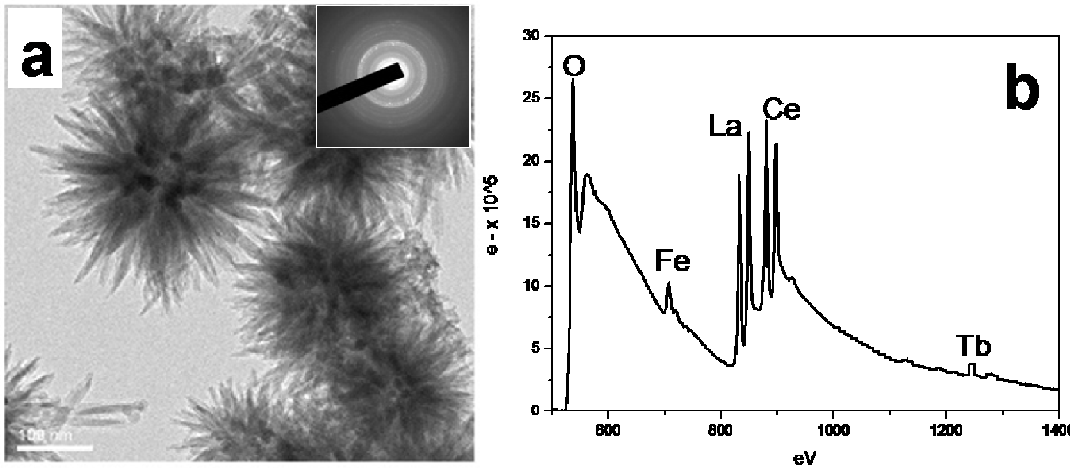


**Fig. 1** a) TEM image of $Fe_3O_4$@SC[6]-$LaPO_4:Ce^{3+}:Tb^{3+}$ nanocomposites (inset: SAED patterns) and b) EELS of the $Fe_3O_4$@SC[6]-$LaPO_4:Ce^{3+}:Tb^{3+}$ nanocomposites.

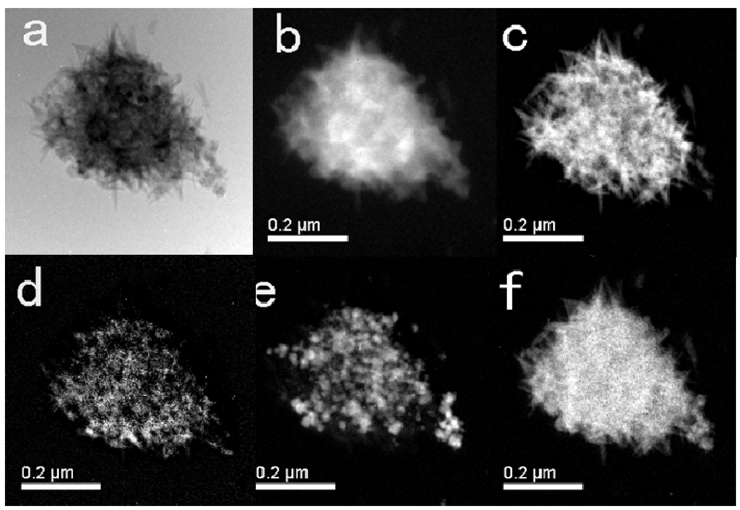


**Fig. 2** EFTEM images of a $Fe_3O_4$@SC[6]-$LaPO_4:Eu^{3+}$ nanocomposite, (a): unfiltered image, (b): thickness map, (c): lanthanum map, (d): europium map (e): oxygen map and (f): iron map.

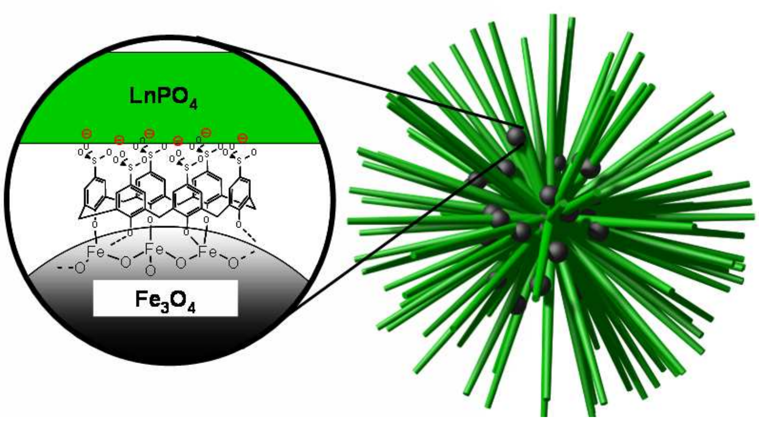


**Fig. 3** A schematic representation of the Koosh nanoball structure of $LnPO_4$ nanorods (Ln = La, Eu, Tb, Ce) held together by SC[6]s stabilized $Fe_3O_4$ nanoparticles.

https://doi.org/10.1017/S1431927610058721 Published online by Cambridge University Press