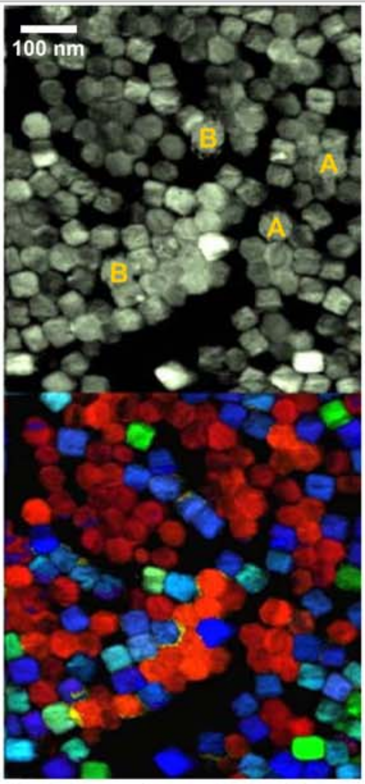
Revealing nanoparticles texture at nm level helps to understand and predict their optical properties

Texture Secrets of nanoparticles



Nanoparticles are now a hot topic in several different fields for their astonishing and unusual properties compared to bulk materials. New sciences like nanochemistry, nanomedicine and nanotoxicology are born and an accurate knowledge of the nanoparticle structure is required to model properly their useful properties. Among these, the grain size, the defects and the particle shape are of major importance, since they easily correlate especially with optical properties.

The knowledge of the grain size of nanoparticles can be easily obtained with conventional TEM techniques, but the coherent domains, those inside where the structure is defect free (no twinning or grain boundaries), are much more difficult to recognize and measure.

The nanoparticle shape is another important factor to be known, since it drives the self-assembly. All these structural details call for a characterization technique that is able to furnish crystallographic information with nanometric resolution. ASTAR technique is able to supply this information.

Two examples of orientation mapping obtained by ASTAR on nanoparticles are here displayed. In fig. 1 is showen an orientation map obtained on $NaYF_4$ nanoparticles. These nanoparticles are known as upconverting, since they are able to emit visible and near-infrared light when excited with near-infrared radiation. They are very promising as fluorescent targets for biological imaging. $NaYF_4$ crystallizes in two forms one cubic and one hexagonal. ASTAR identifies all the nanoparticles as hexagonal. Those that have a hexagonal shape are oriented with the c axis (the 6 fold axis) normal to the plane, while those that are rectangular are oriented with the c axis parallel to the plane. This indicates that the nanoparticles are hexagonal prisms with a height comparable to the base sides. The second example shows an orientation map of nanogold (fig. 2).

figure 1

Orientation map of $NaYF_4$ nanoparticles (Top) Index map (Bottom) Orientation map. The hexagonal (A) nanoparticles are 'red', corresponding to an orientation with the c axis normal to the plane. The rectangular (B) are 'green – blue', corresponding to orientations with the c axis on the plane.

ASTAR identifies most of the nanoparticles as oriented with the [100] direction normal to the plane, indicating that they have well developed flat {100} faces on which they fall. Some of them exhibits {111} twinning as shown by the pole figure plot at the right (fig. 2c).

The challenge: Identify orientation & phase of nanoparticles with < 40 nm that crystallize in two different phases

Solution: ASTAR technique coupled with precession electron diffraction

Experimental Data

TEM type: Zeiss Libra 120
Map resolution: 10 nm
Scanned area: 2 x 2 µm

Crystal Structure

NaYF4: Hexagonal $P\bar{6}$
a= 5.91 Å c= 3.50 Å

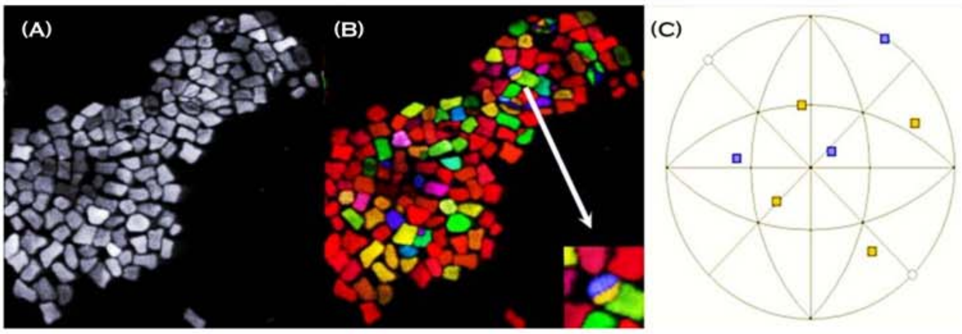


figure 2

Orientation map of Au nanoparticles.
a) Index map b) Orientation map
c) Pole figures of [111]. Equivalent directions of the two twins displayed in the box at the center. Most of the nanoparticles have a "red" orientation corresponding to the [100] direction parallel to the plane normal. Therefore most of them have {100} flat faces on which they fall.

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