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HAADF-STEM imaging of CuAg core-shell nanoparticles

C. Langlois^{1*}, Z.W. Wang², D. Pearmain², C. Ricolleau¹ and Z.Y. Li^{2*}

¹Materials and Quantum Phenomena Laboratory MPQ-CNRS, 10 rue Alice Domont et Léonie Duquet, 75013 Paris (FRANCE)

²Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham B15 2TT (UK)

* Corresponding authors. cyril.langlois@univ-paris-diderot.fr, z.li@bham.ac.uk

Abstract. Scanning transmission electron microscopy (STEM) is used in this study to determine the location of silver in bimetallic CuAg nanoparticles. The Z-contrast effect in STEM is particularly useful in our case because of the large difference in Z number between the two materials. However, the channeling effect that occurs when electrons are transmitted through a crystalline nanoparticle near a zone axis orientation prevents a direct interpretation of the STEM image contrast in terms of silver location. Two simple procedures are presented in this paper to estimate the contribution due to channeling, by varying the detection angle and by tilting the specimen a few degrees from its original orientation.

1. Introduction

Nanoparticles comprising two different metallic elements offer an additional degree of freedom for altering their physical properties compared to monometallic nanoparticles. This could potentially enable a wide range of new materials and properties. However, as physical properties of nanoparticles depend strongly on their atomic arrangements and structures and because in most cases nanoparticles on a specimen can exhibit size/structure distribution, it is crucial to obtain the localized elemental and structural information of a given bimetallic nanoparticle. For example, for the CuAg core-shell nanoparticles that we have prepared, the location of silver within the particles (core-shell or side-segregated) is particularly important because the optical properties of such particles are linked to the plasmon resonance frequency of silver, which often depends on its environment.

Scanning transmission electron microscopy (STEM) has been demonstrated possessing capability of exploring the three-dimensional shape and structure of nanoparticles at atomic-scale [1]. It also has potential to correlate structures with electronic and chemical properties of nanomaterials [2,3]. We focus in this paper on the use of STEM with high-angle annular dark field (HAADF) detector for a direct determination of chemical composition within bimetallic CuAg nanoparticles through an incoherent Z-contrast imaging interpretation. Here, we present two simple procedures developed to rule out the possible artifacts from the true chemical information by controlling the so-called channeling effect that occurs when electrons cross a crystal near zone axis orientation. The effects of the detection angle and small sample tilting on the contrast of HAADF-STEM images are considered.

2. Experimental details

Bimetallic CuAg nanoparticles are prepared under ultra-high vacuum conditions by pulsed laser deposition at MPQ-CNRS laboratory. Copper nanoparticles are first synthesized by condensing Cu atoms onto a thin amorphous carbon film, supported by an electron microscopy grid. Silver is then ablated and deposited on the pre-existing Cu nanoparticles. As neither Cu nor Ag wet easily on the amorphous carbon film, nanoparticles are formed instead of a continuous film. For this study, two samples were prepared. Sample A has been obtained with a deposition of Cu and Ag, with nominal thicknesses of 2 and 1 nm respectively. Sample B is a reference sample with elemental Cu nanoparticles only, obtained simultaneously during the same experiment. For both samples, the substrate temperature was held at 350°C during the deposition. Finally, a 2 nm layer of alumina was deposited to cap the nanoparticles in order to prevent their contamination.

A 200kV FEI Tecnai F20 scanning transmission electron microscope with a field-emission electron source at the University of Birmingham was employed for ex-situ examination. The microscope is fitted with a Fischione model 3000 HAADF detector. The camera length used for this study ranges from 520 to 52 mm, corresponding to the inner collection angle from 12 to 120 mrad.

3. Results and discussion

3.1. Channeling effect

STEM channeling takes place in thin crystals oriented in a zone axis parallel to the electron beam. This effect corresponds to the tendency for the electron beam to stay close to the atomic columns when it crosses the sample [4]. This maximizes the scattered intensity of the crystal and would make the crystal appear brighter than a corresponding crystal of same thickness and composition but in an off-axis orientation. Without taking any particular experimental care, the channeling effect would prohibit a direct interpretation of the images in HAADF-STEM mode in terms of chemical localisation by Z-contrast. This is particularly true for the crystalline CuAg nanoparticles prepared for this study. To illustrate this phenomenon, we carried out HAADF-STEM imaging on both CuAg and Cu nanoparticle samples.

Figure 1 shows a comparison between HAADF-STEM images for the two specimens, acquired using the same experimental conditions with a large camera length of 520 mm. This camera length corresponds to an inner angle of 12 mrad and an outer angle of 60 mrad on the HAADF detector. For the CuAg sample (Figure 1a), strong intensity variations between different particles can be noticed, and also variations of the intensity within a single nanoparticle. The latter could be attributed to the segregation of Cu and Ag inside the nanoparticle, because of the large difference in atomic number between Cu ($Z=26$) and Ag ($Z=47$). However, similar contrast has been identified on images of sample B that has only elemental Cu nanoparticles on. This comparison demonstrates that these intensity variations are not solely due to the Z-contrast. Indeed, a large proportion of the copper nanoparticles of sample B are not monocrystalline [5], and often one of the crystallites composing a copper nanoparticle can be in Bragg orientation relative to the incident electron beam. Channeling effect is then the most probable reason for explaining such a sharp variation of contrast when no chemical contrast presents. The another possible mechanism of intensity variation is strain contrast [6], which is important in this lattice mismatched CuAg bimetallic nanoparticles but does not apply to Cu nanoparticles on the amorphous substrate.

In our present study, we need to avoid channeling effect because here the aim is to get insight on the position of silver atoms over all the area of interest. Because each nanoparticle possesses its own crystallographic orientation, the channeling effect occurs in a different orientation for each of the nanoparticles and it would not be straightforward to deduce useful information about the chemical composition of the bimetallic nanoparticles through simple intensity variation analysis. Care needs to be taken to circumvent the channeling effect.

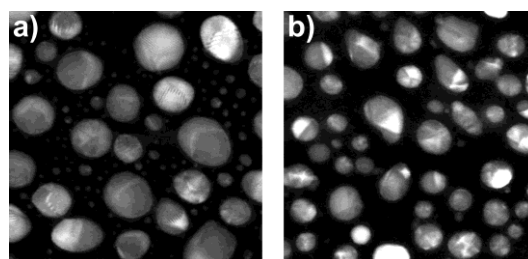


Figure 1. HAADF-STEM images acquired with a camera length of 520 mm (inner collection angle of 12 mrad). a) Sample A with Cu and Ag deposited. b) Sample B with only Cu. Field of view for both: 101 nm.

3.2. Scattering angle variation

Figure 2 shows four HAADF-STEM images of the same area of sample A, CuAg nanoparticles, acquired with different collection angles from ADF to HAADF conditions. Whereas a majority of the nanoparticles have kept their internal intensity contrast variation unchanged when the camera length is varied, it is interesting to note that a few particles undergo a contrast inversion (particles arrowed on the figures). This means that, for small collection angles (large camera length), the Bragg-oriented part of the particle gives an intensity by channeling that is larger than the intensity due to the atomic number contrast. This contrast inversion shows that the collection angle used for Figure 2d is large enough to cancel a large part of the diffracted intensity and to restore a contrast linked to the local chemical composition within the nanoparticle.

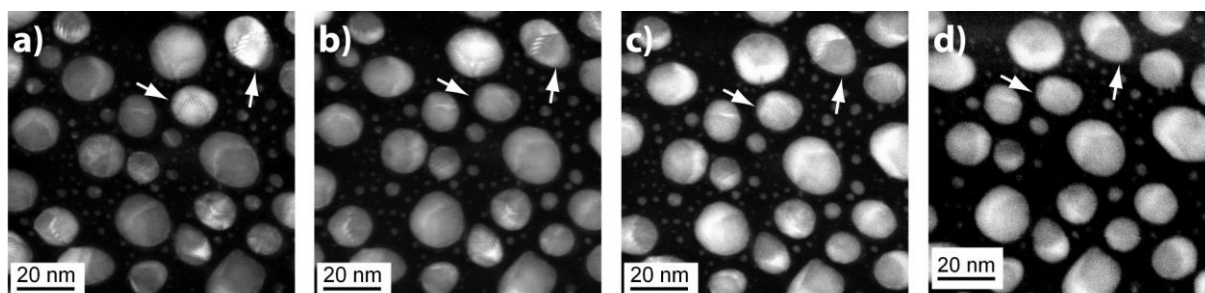


Figure 2. The effect of the detection angle on HAADF image contrast (a) CL = 520mm. (b) CL = 285mm. (c) CL = 100mm. (d) CL = 52mm.

Applying this procedure, it is then possible to discriminate between particles in Bragg orientation giving rise to high intensity through channeling for small collection angles, and off-axis nanoparticles for which the Z-contrast theory can be safely applied for localizing silver because of its big difference in atomic number compared to copper. Clearly, the signal-to-noise ratio of images acquired with such large collector angles is weak. Therefore, optimum conditions need to be carefully assessed and chosen. For bimetallic particles with two metals close in their atomic number, the decreased signal to noise ratio could mask the intensity difference arising from chemical composition.

3.3. Specimen Tilting

The channeling effect is very sensitive to the lattice orientation [7]. It is found that one or two degrees tilt of the specimen is enough to decrease the intensity of on-axis nanoparticles and recover a contrast linked to the local chemistry. Figure 3 displays an example of the specimen tilt effects on CuAg nanoparticles, where intensity variation in the arrowed particle is obvious.

This procedure has some advantages compared to the use of a small camera length. By keeping a reasonable scattering angle, the intensity detected does not fall down quickly as the specimen is tilted, thus the signal-to-noise ratio is largely preserved. Small nanoparticles can then be investigated without

loosing too much resolution. However, the nanoparticles prepared through the approach we take are oriented randomly along the electron beam, therefore, each particle needs to be examined individually.

Again, among all the particles within the area under consideration, only a few of them may show a contrast that can unambiguously be assigned to silver. It is worth of pointing out that the specimen tilting, whatever the amplitude of the tilt is, can easily result in a loss of the region of interest at such high magnification. The specimen should be at an exact eucentric position, and the backlash of the goniometer should be cancelled by pre-tilting the specimen in the same direction of tilt.

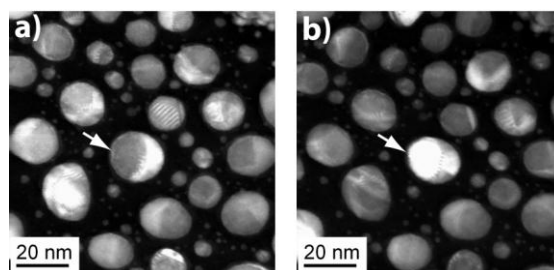


Figure 3. The effect of a small sample tilt on the STEM image contrast (CL = 520mm). (a) 0 degree. (b) 2 degrees.

4. Conclusion

In this paper we detail the use of two different procedures to estimate the channeling effect in STEM observations of CuAg nanoparticles. The first one is to increase the collection angle, in order to decrease any contribution from Bragg diffraction. The second procedure, mostly used for bulk specimen, consists in tilting the specimen out of a zone axis, and relies on the fact that the intensity due to channeling varies rapidly with the tilt angle. Both procedures are applied to the CuAg nanoparticles. It appears that increasing the collection angle by decreasing the camera length can restore a contrast linked to the position of silver atoms but decreases the signal-to-noise ratio of the images. On the contrary, acquiring two (or more) images with a reasonably large detector angle at two slightly different specimen orientations allows one to interpret (with precautions) the contrast in terms of chemical composition qualitatively for each particle. Extra-care is necessary when tilting the sample to keep the area of interest in the field of view. A compromise between the two procedures would be to acquire two images at different tilts with the smallest acceptable detector angle.

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