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In-situ cobalt nanocrystal synthesis by intense electron beams in TEM

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Abstract. We report the synthesis of cobalt nanoparticles of a range of sizes from raw cobalt fluoride powder using high intensity focused electron beams and their characterisation in-situ in a TEM. A variety of beam intensities with different focussing level in a JEOL JEM 3010 TEM at an acceleration voltage of 300 kV is used. Depending on the beam intensity either a distribution of a large number of nanoparticles of 1-150 nm size or singular/a small number of fine metal particle(s) of ~150 nm up to micron size can be produced. Mechanisms of the nanoparticle formation are discussed. This simple, organic precursor free, non-hazardous and oxide-free fabrication method offers great potential for basic research, as it allows the fabrication of fresh particles “on demand” in a location with a distribution as required. As the size range is tuneable, the full magnetic properties from superparamagnetic, over single domain ferromagnetic, to multi-domain are covered.

1. Introduction
Halide materials have long been identified as one of the most sensitive compounds under electron beam irradiation with the resulting end product of transformation being the reduced metal as the rate of depletion of anions is faster compared to cations [1, 2]. Previous research with a motivation on patterning by resist exposure or fabrication of nanoparticles mostly used thin films as starting material [1-3], and sometimes precursor/powder processing and/or long irradiation durations with both extended and convergence beams were applied [4-10]. It was also suggested that this method may be particularly suitable for nanoparticle production of comparatively low melting point metals [7, 9, 10] or semiconducting lead chalcogenides (IV-VI) [7] while production of high melting point metal nanoparticles is challenging. In this work, we report a cheap and fast one-step synthesis method for the production of either a distribution of multiply facetted magnetic nanocrystals of versatile shape or singular/a small number of fine metal particle(s) of relatively high melting point with a range of 1-1000 nm size using electrons beams placed at various focusing levels onto the micropowders in a conventional TEM.

2. Experimental method
Both CoF2.4H2O and anhydrous CoF2 crystalline powder (Alfa Aesar, 99.99%) were dispersed on a TEM grid covered with carbon film (Agar Scientific, UK) after ultrasonication in isopropyl alcohol.
TEM observation of ambient dried specimens were carried out on some well separated 1-5 µm sized 3D fragments, well different from the continuous thin films used in other work.

The fabrication of particles was carried out in a LaB₆ gun JEOL JEM 3010 TEM at an acceleration voltage of 300 kV with variable electron beam focusing levels. The maximum intensity on the screen for a fully focused beam at the largest condenser aperture was ~180 pA cm⁻². We distinguish two irradiation schedules:

(i) To produce a small number of metal nanoparticles or a singular large particle of >150 nm in size, the electron beam is initially spread to below ~130 pA cm⁻² followed by the maximum intensity with fully focused beam at the largest condenser aperture. The process is observed in real time on the screen, and the threshold focusing level can be adjusted to whatever gun brightness is active in a particular situation. The resulting metal particles are of roundish “molten-like” appearance which corresponds to our earlier studies of NiF₂ irradiation [11], and we call them nano-beads (3.1. below) to distinguish them from crystalline faceted nanoparticles.

(ii) If the highly focused electron beam (~130-180 pA cm⁻²) with the largest condenser aperture inserted or without any condenser aperture (>180 pA/cm⁻²) is directed at the fluorides (CoF₂·4H₂O or CoF₂) without medium-level pre-irradiation, then a distribution of well dispersed nanocrystals in huge numbers and in particular histograms of sizes can be fabricated (3.2. below). The focused electron beam was directed, usually along one edge/corner of a 3D micron sized fragment for a range of sub-second to 5s durations. This results in a distribution of cobalt nanocrystals in the vicinity of the fragment, isotropic in all radial directions. All TEM images were taken after spreading the beam to such reduced intensity as needed to avoid any further dynamic changes of the produced structures. The imaging of all resulting nanostructures was done in the same JEOL JEM 3010 LaB₆ gun, while for analytical TEM, samples were transferred to a JEM 2010F FEG-TEM with EDX and GIF-EELS, with irradiated regions re-centred with the help of mesh-counting and low-magnification mapping.

3. Results and analysis

3.1 Nanobead formation

The initial micron sized CoF₂ fragment (Fig. 1a) was irradiated with a slightly spread electron beam (~130 pA cm⁻²), resulting in an intermediate state of nanocomposite material, which is a mixture of metal cobalt nanoparticles distributed within the amorphous porous CoF₂ (Fig. 1b). Followed by a highly focused electron beam (>180 pA cm⁻²), this mixture turned mostly into a singular roundish or spherical Co metal bead by sweeping out the nearby composite material at the expense of fluorine (Fig. 1c).

![Figure 1.](image1.png)

(a) Initial CoF₂ fragment, (b) partially fluorine depleted nanocomposite, (c) end product metallic Co nanobead with stacking fault fringes.
3.2 Distribution of nanocrystal formation and diversity of shapes
Various distributions of in-situ electron beam synthesised Co nanocrystals are shown in figure 2(a-d). In projection, they are mostly hexagonally (Fig. 2(c,d)), octagonally (Fig. 2b) or less likely heptagonally (Fig. 2a) faceted nanocrystals, with regular or irregular shape. These structure differences are believed to be dependent on the beam parameters. Examples for various projected shapes of individual nanocrystals, selected from distributions of the kind of figure 2(a-d), are listed in figure 2(e-l). From 2D TEM images, only a footprint (support or shadow) of particle shape can be extracted, while tilting experiments using a high-tilt tomographic holder can reveal the 3D shape. However, sometimes (e.g. Fig. 2(g,h)), the 3D shapes can be estimated without a tilt series because edges appear as dark lines and top/side facets differ in grey values due to scattering contrast.

![Figure 2](image)

**Figure 2.** (a-d) Various distributions of the synthesised Co nanocrystals. (e-l) Variously shaped Co nanocrystals produced by electron beam (JEM 3010 at 300 kV).

3.3 Particle size distribution analysis
Two dispersions of nanocrystals, along with their size distribution histogram analysis chart in insets with fitted Gaussian in red, are shown in figure 3(a,b). These distributions correspond to mean sizes of 12.0 nm and 6.4 nm particles, respectively, with (a) being closer and (b) further away from the fluoride edge and electron beam centre. The two standard deviations indicating the spread of sizes were $\sigma = 6.3\text{ nm}$ and $\sigma = 4.4\text{ nm}$.

![Figure 3](image)

**Figure 3.** (a,b) Size distribution analysis of the synthesised Co nanocrystals.

For this, first, a numerical histogram was built using the data obtained from ImageJ [12] analysis by counting the number of well defined particles with diameters falling into given size ranges. Then, the numerical histogram was calculated into the normalized discrete function $F(D)$ of the size
distribution and a bar chart representing the size distribution was plotted (insets, Fig. 3(a,b)). Finally, this discrete function was approximated to the continuous normalized Gaussian profile (with $D_o$ the mean size and $\sigma$ the standard deviation): 

$$G(D) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{(D-D_0)^2}{2\sigma^2} \right].$$

### 3.4 Co nanocrystals decorated by nanoclusters on their surface

Selected images of a tilt series of a $\sim100$ nm sized cluster-decorated Co nanocrystal, acquired between $+30^\circ$ and $-45^\circ$ at $5^\circ$ steps, are shown in figure 4. This nanocrystal shows $\sim2-5$ nm sized nanoclusters on the surface with a quite regular distance indicating self-organisation. Two-stage irradiation of differently centred and focused beams is likely to cause the two hierarchy levels of Co nucleation.

![Figure 4.](image)

**Figure 4.** (a-d) Tilt series of a $\sim100$ nm Co crystal itself decorated by $\sim2-5$ nm Co nanoclusters, selected from a distribution of nanocrystals.

### 4. Discussions and conclusions

*In-situ* synthesis of porous composite and metallic nanoparticles/crystals by electron beam irradiation is demonstrated. The intensity of the beam and its focusing level are the main factors contributing to the formation of singular/a small number of nanoparticle(s), a distribution of nanocrystals or a hierarchical two-stage assembly of clusters on particles. It is believed that a highly focused electron beam induces sputtering with evaporation/sublimation and subsequent far-reaching diffusion followed by nucleation/growth, while a moderate intensity beam induces “quasi-melting” and local conversion of salt to metal via intermediate composite materials stages. Prospective applications of the phenomena described can be envisaged in the fields of magnetic data storage, nanoparticle sensors, and for surface-plasmon enhanced light coupling or wave-guiding in the context of photonic devices.

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**References**