Iron nanoparticle formation in a metal–organic matrix: from ripening to gluttony

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Abstract

A simple method for the fabrication of metal nanoparticles is introduced. Heating metal–organic crystals in vacuum results in the formation of well-defined metal particles embedded in a carbon matrix. The method is demonstrated for iron phthalocyanine. At 500 °C homogeneously distributed iron nanoparticles with a reasonably narrow size distribution form by nucleation and ripening. After this initial phase the formation kinetics changes drastically. The particles move in the matrix to incorporate material. The 'gluttony' phase shows astonishing similarities with the search for nutrition of living micro-organisms. Particle formation, ripening and gluttony are followed in situ by transmission electron microscopy.

Supplementary data are available from stacks.iop.org/Nano/18/215601

Nanometre-sized particles of magnetic metals have been attracting substantial interest in basic and applied research for many years [1–4]. This activity is mainly driven by the envisaged application of such nanoparticles in high-density data storage [5], in magnetic resonance imaging [6, 7], and as catalysts [8, 9]. In many cases they show improved or even new properties due to their size in the nanometre range [10]. State-of-the-art production methods of metal nanoparticles include arc discharge [2], colloidal chemistry [11], sputtering or laser ablation [12], and ripening from gel-like films [8]. Each method has its specific advantages and disadvantages. Critical issues are the stability of the particles with time, their protection against oxidation [13], and the control of their size and shape [14]. Here we present a novel, simple method to produce inherently protected iron nanoparticles. They are generated by heating iron phthalocyanine crystallites in vacuum. The particles exhibit a narrow diameter distribution and ferromagnetic hysteresis. The obtained structures and particles were imaged by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) after the heat treatment. In situ TEM observations show that the formation process is a complex mechanism, taking place basically in two phases: a first classical nucleation, growth and ripening phase, and a second phase in which the particles move in the matrix to incorporate material. The second phase shows astonishing similarities with the search for nutrition of living micro-organisms.

Iron phthalocyanine (C\textsubscript{32}H\textsubscript{16}N\textsubscript{8})Fe (FePc, figure 1(a) (inset)) as purchased is a black powder consisting of bacillary crystallites. It is a macrocyclic compound having an alternating nitrogen–carbon aromatic ring structure coordinating a central iron atom. Figure 1(a) shows such crystals dispersed on a silicon surface out of a dried ethanolic suspension. Such samples were heated in a furnace for 30 min at 500 °C at a base pressure of <2 × 10\textsuperscript{−5} mbar. During heating the pressure increased due to sublimation of FePc molecules, and evaporation of nitrogen and hydrogen from decomposed FePc molecules. SEM micrographs show that the crystals transform into skeleton-like structures (figure 1(b)). A closer look at the structures reveals a capillary network which probably consists of tubular or flaky carbon (figure 1(b) (inset)). TEM allows...
the investigation of the internal structure. Heating of FePc crystals on SiO₂-covered TEM grids in a furnace shows that nanoparticles form in the crystals with elapsing time. Figure 2 demonstrates this transformation: after 2 min heating in a furnace at 500 °C almost no change is observed, but after 3 min the TEM images already show cleft structures. After 10 min the nanoparticles become clearly visible and after 30 min they coarsen to bigger clusters. TEM diffraction measurements after the heat treatment show that the nanoclusters consist of fcc-Fe at room temperature. A statistical analysis of 130 particles after a heat treatment of 10 min at 500 °C (figure 2(c)) reveals a reasonably narrow size distribution peaking at 8.1 nm with a standard deviation of 2.15 nm (figure 3).

In situ heating of the samples in a TEM unveils that the transition starts around 400 °C, and all individual crystals transform into iron/carbon structures. In this case, the samples were not observed during the whole process but just sporadically during heating. In other experiments, the samples were heated from ambient temperature up to 700 °C under constant observation. In this case, the transition was directly observed between 600 and 700 °C.5 In this temperature range the crystals transform in a few minutes. Figure 4 shows a series of video images of the development of an individual crystal. In this case the formation of the metal particles starts at 622 °C, then at 662 °C they are getting bigger, and at 701 °C they begin to move in the matrix, absorbing material on their way. The nanoparticles move randomly in the Fe/C structure of the original FePc crystal, leaving empty space behind. This migration gives rise to the characteristic final structure (see also the video streams in the Supporting Information available at stacks.iop.org/Nano/18/215601). The particle movement corresponds to a self-avoiding random walk and can be simulated by a simple algorithm: in the simulations the FePc crystals are represented by a two-dimensional (2D) matrix. The matrix positions are “filled” with pseudo particles with a size of

Figure 2. TEM micrographs of a time series of FePc heated at 500 °C in a vacuum furnace for (a) 2 min, (b) 3 min, (c) 10 min, (d) 30 min.
about 3 nm, the ‘nutrition’ units. Then, a random distribution of germs is spread in the matrix. The migration algorithm assumes that each germ picks up a random neighbour unit and moves to its location, leaving behind a void location where it has been before. In principle, each location is equal as long as there is ‘food’; empty locations are disregarded. Additionally to the random walk we implemented a slight anisotropy in a way that the absorption in vertical direction is favoured in order to mimic the crystal structure of FePc. Proceeding with this algorithm for each germ leads to a final structure similar to the transformed FePc crystals. The germs stop their movement when there is no direct neighbouring nutrition unit left. Figure 5 shows a comparison of an in situ transformed FePc crystallite and a simulated self-avoiding random walk of pseudo particles with a size of about 3 nm (green: pristine material; red-black: pseudo particles with increasing amount of absorbed material).

Diffusion, ripening, and surface (energy) minimization enables the iron to form bigger roundish aggregates. Additionally, the surface energy can be lowered when the iron aggregates are surrounded by carbon. This leads to a ‘hiding’ of particles in the pockets. The particles must avoid free surface facets (capillary forces). In turn, this leads to a growth of the particles into the material, out of the holes into the self-created cavities. Since the particles, by undergoing this process, always stay in contact with non-transformed material, they can absorb more and more iron (from the stock). The movement stops and leaves the final characteristic structure behind when there is no more iron left in the direct proximity. In the long run, particles can diffuse over large distances and form extended aggregates. As larger particles move more slowly, a relatively narrow size distribution can be obtained at intermediate stages. Further optimization of the process parameters might lead to an even sharper size distribution.

The iron/carbon powder obtained after heating of macroscopic amounts of FePc for 10 min at 500 °C shows ferromagnetic hysteresis. SQUID measurements reveal that both the coercive field and the remanent magnetization increase as the temperature decreases. Furthermore, the iron/carbon structures are active catalysts for the chemical vapour deposition (CVD) growth of carbon nanotubes. In an experiment using a tube furnace at 650 °C, multi-wall nanotubes grow nicely using acetylene as carbon source. They are of similar quality as the CVD tubes obtained using iron-containing solutions as catalyst [19]. As other groups have shown, carbon nanotubes can also be produced directly by pyrolysis of iron phthalocyanine [20–22].
To conclude, under heating in vacuum FePc crystallites decompose into iron nanoparticles embedded in a carbon matrix. By means of in situ TEM investigations we observed the remarkable formation mechanism of these structures. A classical nucleation, growth and ripening phase is succeeded at higher temperature by a gluttony phase, during which the particles move in the carbon matrix, acquiring further material. The synthesis method is very appealing due to its simplicity. It involves only one precursor and only one heating step. The method was demonstrated for the fabrication of iron nanoparticles but can easily be generalized to other systems since there are over 70 ions known which can be accommodated by phthalocyanine [23].

Experimental methods

Iron phthalocyanine (FePc) was suspended in ethanol, sonicated for 5 min, and dried on silicon oxide surfaces. The samples were then submitted to a tubular vacuum furnace at 500 °C and <2×10⁻⁵ mbar for different time periods by means of a transfer rod.

SEM characterizations were performed to analyse the structures in plan view. A Philips XL 30 microscope equipped with a field-emission gun operating at an acceleration voltage between 3 and 5 kV, a working distance of typically 10 mm, and in secondary electron image mode, was used.

The internal structure of the samples was controlled by TEM. For this purpose a Philips EM 430 microscope equipped with a Gatan image plate operating at 300 kV was used. The FePc crystallites were dispensed on TEM grids covered with a thin SiO₂ film. The transformation of FePc crystals as a function of temperature to a carbon matrix with embedded iron particles was directly observed and video-taped in situ in a TEM equipped with a resistively heatable sample holder.

The magnetic properties of the obtained Fe/C powder were measured with a quantum design SQUID magnetometer (MPMS7). This apparatus, which has a sensitivity of <10⁻⁶ emu (corresponding to 1 μg of powder), is equipped with a cryogenic sample stage which permits control of the temperature between 1.8 and 340 K. The applied field varied between ±45 kOe.

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