

SPONTANEOUS SELF-AGGLOMERATION OF MAGNETIC NANOPARTICLES INTO NANOWIRES

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Abstract. A newly developed method for the formation of nanowires by self-aggregation of nanoparticles is presented in this paper. Co₃C, Co-rich, and Ni nanoparticles dispersed on holey carbon grids are inserted in a vacuum oven and are co-annealed with PolyChloroTriFluoroEthylene (PCTFE) at 375 °C. No external electric or magnetic fields were applied. High resolution electron microscopy (HREM) was extensively used to determine the shape, size distribution and crystallographic phase of the starting and produced materials. Interestingly, after an annealing cycle of 72 hours, the nanoparticles seem to self-agglomerate into nanowires which have diameters in the 5-20 nm range and lengths exceeding at cases 1 micron. The diameter of the produced wires is in the same range as the diameter of the initial nanoparticles, further supporting the notion that the nanowires have formed out of nanoparticle agglomeration. Close inspection of nanowire HREM images shows that the core structure of nanowires wider than approximately 11 nm resembles linked nanoparticles. Phase identification performed using the HREM images reveals the core is of the same phase/material as the starting nanoparticles.

Since nanowires appear to form over holes on the holey carbon grid, a base growth mechanism is proposed. The fluorocarbon vapour decomposes over the transitional metal nanoparticles and carbon tubules start growing. The nanoparticles appear to be trapped inside the tubules where their close proximity enhances their fusion into a continuous core. At the studied temperature, the nanoparticle fusion is seen to be limited by the size of the nanoparticles manifested by continuous cores only in the thin nanowires. The process presented here shows that nanoparticles can spontaneously self-align into nanowires in a way and to an extent never reported before. Therefore there is certainly scope for studying this method further to reveal more information about the catalytic action of transitional metals on hydrocarbons and the exact nanowire formation mechanism. Although it is currently a matter of speculation, this process might lead to the effortless growth of nanowires at particular places when building miniature circuits.

1. INTRODUCTION

Recently many methods have emerged for the formation of nanoparticles with control over their size. In their own merit such nanoparticles have significant technological importance [1]. Even more impressive is however the manipulation of such nanoparticles to form new structures [2,3] and shapes [4] leading to the prediction that new artificial optical and electrical materials can occur [5].

The most popular/frequently used method for 'fusing' nanoparticles together is 'oriented attachment' where two adjacent nanoparticles merge either after they have fully aligned [2,6,7], or with a lattice mismatch to form complex structures [8,9]. When building nanoscale devices, nanowires are very desired building blocks since one can use them to connect device's components or take advantage of their 1-D structure to extract novel properties [10]. Nanowires

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can be formed by oriented attachment of nanoparticles brought together in solution [4, 11–15], by filling the voids of pre-conditioned templates [16–21] or by a catalytic process [22, 23]. A common feature of all methods based on oriented attachment is that the nanoparticles initially seem to be assembled into a line via the help of surfactants or ligands encapsulating the nanoparticles in the solution, with oriented attachment taking over to ensure the particles' fusion with crystallographic alignment. In the second and third mechanisms, the nanowires are formed because lateral growth is restricted by a rigid template or favourable kinetics, respectively. Even though practical applications in photonics [11] and electrical circuits [24] have been shown, it seems likely that nanowires will have their most profound effect on magnetic applications; e.g. spintronics [17, 20, 25]. The reason is that nanowires of a magnetic material can, due to their shape, be permanently magnetised even if their diameter is close to or below the superparamagnetic limit [26, 27]. This makes ferromagnetic nanowires distinctively advantageous over any other ferromagnetic nanostructures, even though alternatives for use of ferromagnetic nanoparticles have been proposed [28].

Oriented attachment seems to be the best candidate method for forming ferromagnetic nanowires because it allows control over their size and can be used to form extremely thin nanowires. However, in the initial steps required to align the nanoparticles into lines an organic layer surrounding them is often used. The presence of an organic coating might lead to a reaction with the ferromagnetic core since such materials are known catalysts for the decomposition of organic molecules. In addition, bare ferromagnetic cores exposed to air are susceptible to oxidation which would greatly affect their magnetic properties.

In this paper we report the formation of Co_3C , Co, and Ni nanowires on holey carbon grids through the self-assembly of nanoparticles which need not be pre-arranged into lines. The nanowires are encapsulated in carbon, the latter presenting a natural barrier to oxidation of the core. Depending on the material of the initial nanoparticles, nanowires of up to 1 μm long can be formed. Using atomic resolution electron microscopy images, the formed nanowires are seen to be of the same material as the initial nanoparticles, suggesting that it is possible to form nanowires of various materials via simply varying the initial nanoparticles. This concept is proved here for Co_3C , Co, and Ni. The presence of the fluorocarbon vapour is proved necessary for the

formation of nanowires. The single-crystal nature of the core of thin wires suggests that nanoparticle fusion depends strongly on nanoparticle size.

2. EXPERIMENTAL

The annealed samples were prepared by sprinkling the nanoparticles from a toluene solution onto holey carbon grids. The sample was placed inside a quartz beaker and a piece of PolyChloroTriFluoroEthylene (PCTFE) was placed inside a second beaker next to it as shown in Fig. 1. In order to keep our vacuum chamber clean from the deposition of PCTFE vapour, we placed both beakers inside a stainless steel cylinder and capped its ends with Al foil. Before starting the annealing cycle, the chamber was evacuated to a base pressure of $8 \cdot 10^{-6}$ mbar. All HREM work was carried out using a JEOL 4000EX II microscope with a resolution limit of 1.4 \AA . Phase identification was carried out using the HREM images: the images were scanned directly from the negative and their digital diffraction patterns (DDPs) were obtained as the fast Fourier transform of the image. The DDPs were used to measure the lattice spacings and angles with high accuracy and the obtained values were compared to well documented crystallographic data of known materials obtained from the EPSRC's Chemical Database Service at Daresbury [29]. The Co_3C particles were formed by cathodic arc discharge between a graphitic rod anode and a cathode made of compressed Co and graphite powders (Co : Graphite = 1:1, weight) in a high gas pressure region. A more detailed description of the method can be found elsewhere [30]. The Co mate-

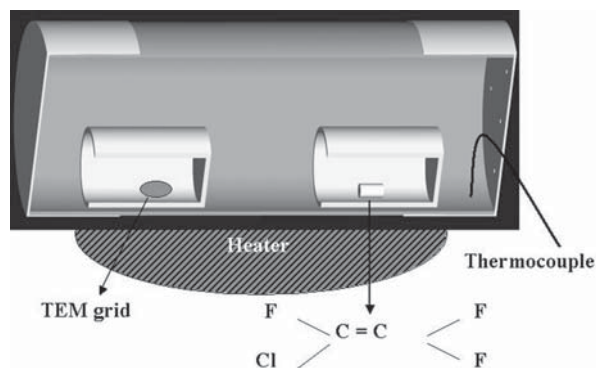


Fig. 1. Schematic of the experimental setup showing the two beakers inside the stainless steel chamber and the chemical formula of PCTFE. The two ends of the cylinder are capped with Al foil with holes on one side for the vapour to escape.

rial was produced from Co_3C by annealing it in inert environment at $375\text{ }^\circ\text{C}$ for several days (more details in the next section). The Ni nanoparticles were produced from an organometallic precursor.

3. RESULTS AND DISCUSSION

Contrary to the regular arrangement of particles in 2-D patterns reported by other researchers [31], our nanoparticles, especially the Co_3C ones, were seen to form single layer agglomerates without any evident arrangement. Fig. 2a shows an area of a sample of Co_3C nanoparticles after co-annealing with

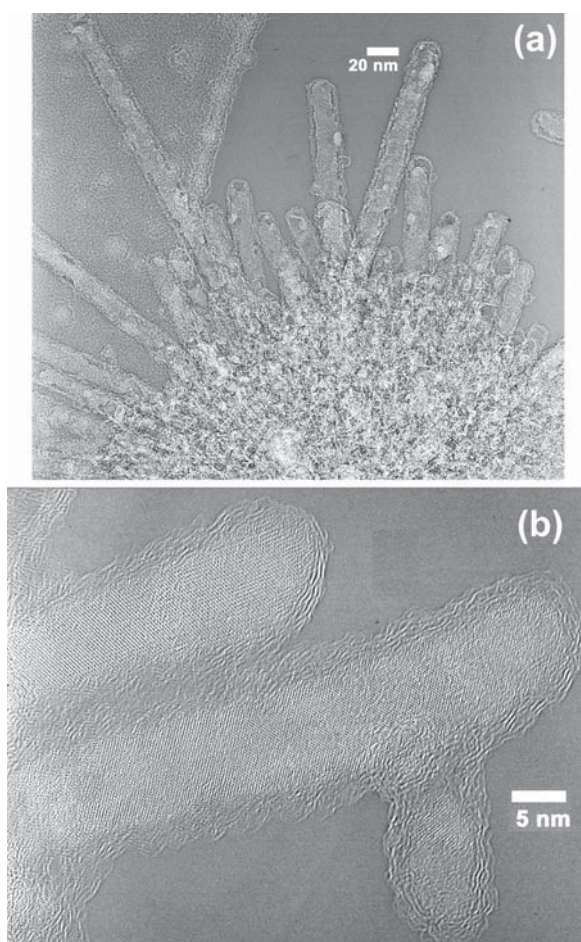


Fig. 2. Co-annealing of Co_3C nanoparticles and fluorocarbon: (a) Low magnification TEM image showing carbon tubules filled to a great extent with a metallic phase, (b) HREM lattice fringe image of two nanowires with apparently single crystal metallic cores, encapsulated by 4-6 disordered graphitic layers. Phase identification showed that the metallic phase of the core is Co_3C . The diameter of metallic single crystal wires like those shown here is between 4.4 and 11.2 nm as measured from several HREM images.

PCTFE. Metallic nanowires encapsulated by carbon tubules are seen emerging radially out of Co_3C particle clusters. Fig. 2b shows an HREM image of the single crystal core of two nanowires. A continuous crystal core is typical for nanowires with diameter between 4.4 and 11.2 nm. On the other hand, the core of wider tubes consists of nanoparticles simply assembled together with evident boundaries between them. Short range nanoparticle merging is evident in many cases as is discussed in more detail later. Images like 2b were used for phase identification of the filled core, always consistent with a projection of Co_3C .

The evident formation of metallic nanowire structures of the same material as the starting particles is an exciting prospect since this could allow control over the nanowire material by simply controlling the phase of the initial particles. In order to explore the prospect of phase customization and to verify the process itself, we applied the same process using Co-rich nanoparticles produced in the following way: a TEM grid containing Co_3C particles was annealed in a pre-evacuated chamber at exactly the same conditions used for the growth of the nanowires ($375\text{ }^\circ\text{C}$, 72 hours) under a flow of N_2 gas in the absence of fluorocarbon vapour. Phase identification revealed that carbon had almost entirely segregated out of the Co_3C lattice, creating effectively carbon encapsulated Co-rich nanoparticles. Importantly, independent magnetisation measurements on bulk powder samples of this material verified the weak magnetisation of the initial Co_3C material and a subsequent 190 times increase in magnetisation when the Co_3C particles were annealed in N_2 gas flow at $375\text{ }^\circ\text{C}$ for 72 hours. The magnetic measurements are consistent with carbon segregation out of the weakly magnetic Co_3C phase. After this process, the particles were still arranged in agglomerates and no nanowires could be detected by TEM. This actually proved that the carbon encapsulated Co_3C nanowires shown in Fig. 1 were formed through the interaction between the Co_3C particles and the fluorocarbon.

In turn, a TEM grid with dispersed Co-rich nanoparticles was co-annealed with PCTFE at $375\text{ }^\circ\text{C}$ for 72 hours. Fig. 3a shows a low magnification TEM image of the resulting material. In this case impressively long nanowires (up to $1\text{ }\mu\text{m}$) could be seen in abundance. Similar to previous observation, the nanowires that are thicker than 11 nm appear [see Fig. 3b] to form by merging nanoparticles without a continuous crystal lattice being formed throughout the volume of the core. Phase identification us-

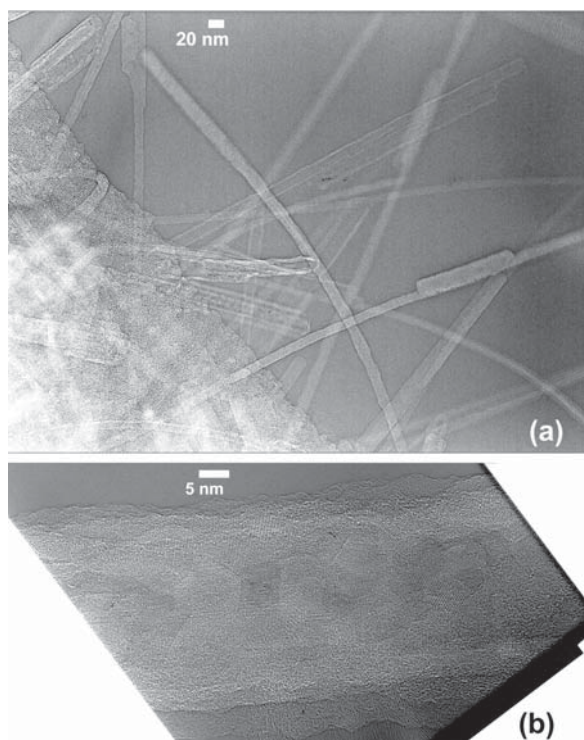


Fig. 3. Co-annealing of Co-rich nanoparticles with fluorocarbon: (a) Low magnification TEM image of the resulting nanowires growing up to 1 μm long, (b) HREM image of a nanowire like those in (a) showing convincingly that the metallic core is made of assembled nanoparticles. The single crystal Co wires are typically around 10 nm wide while the imperfect core can have a diameter of up to 32 nm. The core is always encapsulated by an amorphous carbon layer.

ing HREM images like the one shown in Fig. 3b revealed that the core of the nanowires consists of α -Co encapsulated by an amorphous carbon (a-C) layer. Ni particles showed similar behaviour to Co ones. Fig. 4a shows a low magnification image of Ni particles dispersed on the TEM grid from a toluene solution. Using such images and X-Ray peak broadening, the average particle size was estimated to be 22 nm. Image 4b shows long nanowires extending out of nanoparticle agglomerates. Nanowire length exceeded 1 μm at cases. Fig. 4(c) shows a high magnification image of the continuous core of a Ni nanowire with evident encapsulation by an a-C layer.

The formation of carbon tubules with walls made of amorphous-like carbon is a common feature at low growth temperatures [32]. The appearance of the crystalline walls when the fluorocarbon decomposition took place over Co_3C particles suggests a

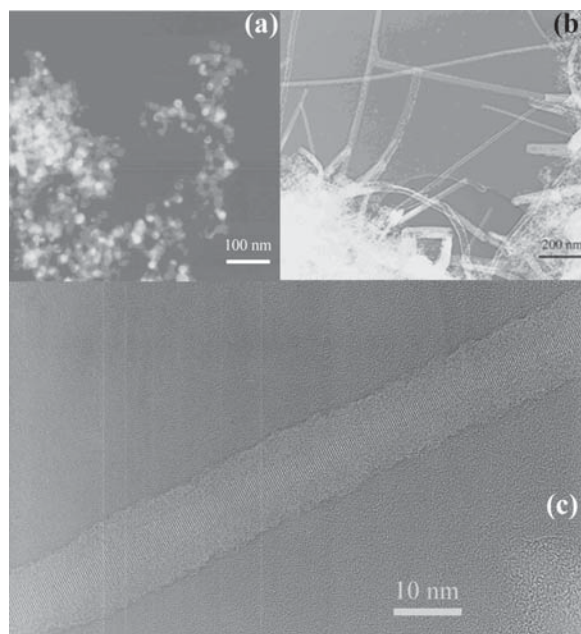


Fig. 4. Co-annealing of Ni nanoparticles with PCTFE. Similar to Co particles, the resulting nanowires length exceeds at cases 1 mm. (a) and (b) Low magnification TEM image of the starting Ni particles and the resulting nanowires, respectively. (c) High resolution image of part of a 10 nm wide Ni nanowire laying on the a-C film.

more efficient catalysis of the PCTFE vapour by Co_3C . This is in agreement with previously observed Ni_3C catalytic particles at the tips of nanotubes with highly crystalline walls [33]. However, the improved catalysis seems to come at the expense of the growth rate since nanowires formed using Co-rich or Ni nanoparticles are much longer than Co_3C wires.

Images such as 3b are the strongest proof so far that the formed nanowires result from the self-assembly of the respective nanoparticles. Continuous crystalline cores such as those shown in image 2b and 4c are mainly seen for wires with a diameter less than 11 nm (4.4–11.2 nm). The core structure of our thin and thick nanowires is similar to that previously reported for materials formed via perfect [11, 12] and imperfect oriented attachment [8, 9], respectively. This similarity suggests the nanoparticles merge following the same mechanism.

However, there is little information of how the carbon tubules grow to encapsulate and assemble the nanoparticles out of their aggregates. The decomposed PCTFE certainly plays an important role

because in the absence of its vapour nanowires are not formed. The catalytic action of the nanoparticles on PCTFE vapour is evident by the availability of carbon for the formation of carbon walls around the nanowires. The carbon walls formed are structurally similar to the ones grown by chemical vapour deposition (CVD) over a catalyst. However, in our method we are not aware of the existence of strong carbon etchants like ammonia and hydrogen, used during the catalytic growth of nanotubes by CVD. Therefore there is no mechanism that would keep the surface of the nanoparticles clean for the reaction to continue and grow the carbon walls via the tip growth mechanism proposed for CVD nanotubes. Therefore, we anticipate that once the side of any given nanoparticle exposed to the fluorocarbon vapour is covered with carbon, additional carbon for building the carbon walls is provided by the decomposition of fluorocarbon over neighbouring nanoparticles. It is the eventual joining of the carbon walls from one nanoparticle to the next, we propose, that gives rise to a base growth mechanism for the carbon tubules. The poor crystallinity of the carbon walls is likely to be due to their growth in separate events.

The joining of the carbon walls actually drives the nanoparticles into assembly inside the carbon tubule, with the wall growth and particle merging happening concurrently. Since carbon walls have formed mainly on the side of the particle exposed to the fluorocarbon, there still clean surface for nanoparticle merging. The most eligible mechanisms for particle merging are oriented attachment and surface diffusion. These two processes are not independent and both seem to depend on the size of the particle. In oriented attachment, smaller particles would align easier as it would be easier for them to rotate amid their surroundings. Similarly, the lower temperature limit for surface diffusion is decreased with the size of the particles. During nanowire formation, if the joining carbon comes from individual nanoparticles (involving only two particles at a time) the result is a thin carbon tubule containing one particle along its diameter. The merging of these particles is made easier by their small size. On the other hand, carbon might merge across the surface of more than one nanoparticles which are exposed to the fluorocarbon vapour simultaneously. In this case, more than one particles will be fitted across the wire's diameter. As particles start merging their size increases which makes oriented attachment and surface diffusion less likely. Since the size distribution of our initial Co_3C and Co-rich particles ranges from 4 to 15 nm with a maximum

around 10 nm, it is expected that single core nanowires will have diameters in the same range while those with imperfect cores will have a larger diameter (typically 9-30 nm), in agreement with our observations.

In this article we have demonstrated that nanowires encapsulated in carbon can be formed via the decomposition of a fluorocarbon over Co_3C Co and Ni nanoparticles at relatively low temperatures. This is the first time that self-assembly of nanoparticles out of their agglomerates is reported without re-dispersion or the use of external fields to guide the motion of the nanoparticles. Combination of this method with advances in the arrangement of nanoparticles from solution can result in magnetic nanowires that are safely protected inside carbon walls against oxidation; a crucial detail for the lifetime of the formed devices. The most attractive aspects of the invented technology are its simplicity and scalability.

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