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Continuous-flow laser synthesis of large quantities of iron oxide nanowires in solution

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Abstract

Large quantities of iron oxide nanowires are rapidly synthesized at room temperature by pulsed-laser (248 nm) ablation of iron powder under methanol. By introducing a stream of methanol, a continuous flow of nanoscale products is collected. Through control of the flow rate, and hence the residence time of the products within the growth vessel, their morphology can be controlled. At high collection rates a lamellate 'nanobelt' morphology is observed, whereas at low collection rates nanowires dominate. Chemical and structural characterization suggests that the as-synthesized products have the stoichiometry of the goethite [FeO(OH)] phase. Annealing at temperatures above 400 °C crystallizes the products as hematite (α-Fe₂O₃).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanostructures such as nanoparticles, nanowires and nanobelts have been shown to possess different magnetic, optical, electronic, mechanical and chemical properties in comparison to those exhibited by the same materials in bulk form [1]. This dependence on morphology is especially clear for the magnetic properties of nanostructures, where the size and dimensionality are critical [2–4].

Different oxides of iron are used extensively in the fields of high density magnetic storage, semiconductor devices and as photocatalysts [5–7]. Goethite [α-FeO(OH)] is a common form of iron oxide, which is produced through the weathering of other iron-rich minerals. It is generally yellowish in color and well known since prehistoric times for its use as a pigment. It has an open channel structure, which accounts for its extraordinary capability to incorporate and fix ions from migrating solutions [8, 9]. Hematite (α-Fe₂O₃) is one of the most commonly studied phases, due to its interesting chemical and physical properties. It has been demonstrated as an anode for photo-assisted electrolysis of water, as an active component of gas sensors, and as a photocatalyst as well as an ordinary catalyst [10–13].

1D iron oxide nanostructures, such as nanowires and nanotubes, are of particular interest. For example, hematite 1D nanostructures have applications in lithium ion battery electrodes, gas sensors, field-effect transistors and field emission cathodes [4, 14, 15]. Hematite nanowires have been synthesized by many different techniques including surface oxidation, thermal oxidation and electrochemical deposition [16–19]. These are generally complex processes taking considerable time (1.5–120 h), needing different gas flows and high temperatures (400–800°C). Also, these processes typically produce nanowires that are attached to a metallic substrate, and thus subsequent collection for device integration can be challenging. Therefore, there is need for a synthesis route that is rapid, and that can be run continuously, to collect solutions of nanowires such that they can be readily processed. In this paper, a laser synthesis route for producing goethite/hematite nanowires, which can be operated in continuous flow, is demonstrated.

2. Experimental details

Solutions of iron oxide nanostructures were synthesized by an ultraviolet pulsed-laser ablation [20] technique, using the laser pulses from a Lambda-Physik LPX 210i excimer laser.
operating at 248 nm, with a pulse duration of 25 ns. A schematic diagram of the experimental set-up is shown in figure 1. Iron powder (Goodfellow Cambridge Ltd, purity >99% and maximum particle size of 60 μm) was used as the starting material. It was placed in an open vessel mounted on a computer-controlled X–Y translation stage. Sufficient powder was used to produce a thin layer (∼5 mm deep) on the bottom of the vessel, which was then filled with methanol (AR grade, Fisher Scientific UK Ltd) up to a depth of ∼2 cm. 120 mJ laser pulses were focused to produce a fluence of ∼11 J cm$^{-2}$ at the surface of the iron. The laser spot was raster scanned over the entire bottom area of the vessel. A laser shot repetition rate of 20 Hz was used throughout the experiments. Due to the high temperatures and pressures induced at the laser focal spot, the surrounding solvent was observed to boil locally, violently ejecting iron powder away from the focal point (figure 1). These ejected particles were rapidly heated by subsequent laser shots, a process which was observed as bright flashes of light. Initially, the laser was run for five minutes until a yellowish coloration to the methanol was observed. At this point a continuous flow of methanol was introduced into the vessel at a rate of 360 ml h$^{-1}$. The solution of products, overflowing down a tube, was subsequently collected. As this tube was near the top of the vessel, little or no iron powder was found to contaminate the products. The nanostructure of the products was investigated using a FEI Quanta 200 scanning electron microscope (SEM) and a Philips CM200 high-resolution transmission electron microscope (TEM) operating at 200 kV. Drops of each solution were dried (at 70 °C) onto silicon substrates and holey carbon grids for SEM and TEM investigation, respectively.

3. Results and discussion

Figure 2 shows an SEM image of the product collected after 5 min of laser ablation i.e. just before starting the flowing methanol. It demonstrates clearly a mixture of lamellate ‘nanobelts’ (width 1.5–2.0 μm, length 14–16 μm, of nanometric thickness) and nanowires (diameter 20–300 nm, length 2–8 μm). An SEM image of the product collected after the methanol had been flowing for a period sufficient to have completely replaced the initial volume of methanol present in the growth vessel is displayed in figure 3(a). This sample consisted mainly of nanobelts and very few nanowires. This difference in morphology, with and without the flow of methanol, we attribute to the effect of the prolonged irradiation of the products in solution, after they have been created. To explain this more fully, a set of mechanisms leading to the growth of the nanobelts and nanowires is introduced as follows.

Typically during ablation under liquid media, nanoparticles are observed to form as the high density of ablated...
Figure 4. Schematic diagram showing the proposed mechanism for formation of nanowires. (a) Nanobelts grow in solution by a photochemical or photothermally assisted reaction between methanol and the ablation products. (b) The interaction between the laser and the nanobelts initiates fragmentation of the nanobelts. (c) After sufficient exposure only nanowires remain in solution.

species condenses. Here nanoparticles are not observed to form, thus suggesting that a rapid chemical reaction is occurring between the ablated iron species and the methanol or OH$^-$ radicals. This reaction may be enhanced, or induced, by the UV irradiation of the solvent. The absence of nanoparticles also suggests that the products of this reaction stay in solution for long enough that rapid condensation into nanoparticles does not occur. As the reaction products slowly come out of solution, larger, extended nanocrystallites could form. The experiment was repeated using distilled water as the liquid and here only hematite nanoparticles were formed. Hematite is insoluble in water, so a rapid formation of nanoparticles would be expected. We suggest that the morphology of the nanobelts is a consequence of the crystal habit of the iron oxyhydroxide formed. Once nanobelts grow, it is suggested that the nanowires form by laser-induced fragmentation of the nanobelts into nanowires. To test this hypothesis, another growth run was performed where the methanol flow was not started until after 20 min of ablation. Here, the initial flow of product consisted entirely of nanowires similar to those shown in figure 3(b) (yield $\sim 1$ g l$^{-1}$, dry weight). A similar result could be obtained by taking a solution containing mainly nanobelts, and irradiating it with the laser for 10 min (without the iron powder being present). The nanobelts in solution were then converted into nanowires, as shown in the SEM image of figure 3(b). The inset in this figure is a TEM image showing the morphology of individual nanowires. This fragmentation mechanism is supported by the observation (from figure 2) that the ends of the nanobelts appear jagged, where sections have broken away. A schematic representation of this fragmentation mechanism is shown in figure 4. It is also possible that iron oxide fragments, produced by the laser-induced destruction of the nanobelts, act as nucleation sites for the growth of nanowires. The source of Fe, O and H atoms for this growth are the vaporization products of the nanobelts and residual Fe atoms dissolved in the methanol.

Optimum flow rates can now be determined to grow products consisting entirely of nanowires or nanobelts. The critical parameter controlling the morphology appears to be the residence time of the products within the growth vessel. The mean residence time of an object in the solution is estimated as the volume of methanol in the vessel divided by the flow rate. This is a suitable and appropriate assumption, as ablation-induced convection currents ensure constant mixing. At high collection rates (when the flow of methanol results in a residence time significantly less than $\sim 20$ min) a ‘nanobelt’ morphology is expected, whereas at lower collection rates (residence time of the products more than $\sim 20$ min) mainly nanowires should result. These figures would be expected to depend on the precise experimental configuration (laser repetition rate, laser scanning rate and the vessel volume and configuration).

Having demonstrated control over the morphology of the products, the type of oxide synthesized was investigated by Raman spectroscopy (Reinshaw Ramanscope, 782 nm excitation). An as-produced nanowire solution was drop-cast onto a silicon substrate and the methanol allowed to evaporate. In addition, samples were annealed in air in a tube furnace at different temperatures (100–800 °C) for 6–8 h. It was found that the structure and morphology of the wires do not change up to a temperature of 300 °C. As the annealing temperature was increased, the color of the dried products changed from yellow to rust-colored. Figure 5(a) shows the Raman spectra for the unannealed material and samples annealed at 400 and 800 °C. Peaks corresponding to $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeO(OH) and the silicon substrate are observed [4, 16, 21, 22]. The as-prepared sample showed only one peak, which corresponds to $\alpha$-FeO(OH) (the strongest for this structure). However, without
additional peaks, complete assignment to this stoichiometry is not possible but the yellow color of the product, and the fact that it was synthesized in a medium containing OH, would support assignment as an iron oxyhydroxide. By increasing the annealing temperature above 300 °C the goethite peak disappeared and peaks corresponding to α-Fe₂O₃, hematite appeared consistent with the literature [8] according to the reaction below:

\[
2\text{FeO(OH)} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}. \tag{1}
\]

TEM images of the unannealed material and the samples annealed at 400 and 800 °C are shown in figures 5(b)–(d), respectively. The inset of figure 5(b) displays the selected-area electron diffraction (SAED) pattern of the unannealed sample showing only diffuse rings, indicative of poor crystallinity, or a nearly amorphous structure of the sample. From figures 5(c) and (d) it can be seen that the wires become nanocrystalline at 400 °C and single crystals by 800 °C.

4. Summary and conclusion

In conclusion, we have shown that pulsed-laser ablation of iron powder in methanol produces solutions of iron oxide nanostructures. By controlling the flow rate of methanol into the growth vessel, the morphology of the product can be controlled, producing nanobelts and nanowires at high and low flow rates, respectively. Chemical and structural characterization suggest that the as-synthesized products have the stoichiometry of the goethite phase. Annealing at temperatures above 400 °C crystallizes the products as hematite (α-Fe₂O₃). This approach is relatively simple, can be run continuously and has many advantages over traditional surface oxidation methods.

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