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

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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 characterisation suggests that the as-synthesised products have the stoichiometry of the goethite [FeO(OH)] phase. Annealing at temperatures above 400 °C crystallizes the products as hematite (α -Fe₂O₃).

Nanostructures such as nanoparticles, nanowires and nanobelts have been shown to possess different magnetic, optical, electronic, mechanical, and chemical properties compared to those exhibited by the same composition 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

The different oxides of iron are used extensively in the fields of high density magnetic storage, semiconductor devices and as photo-catalysts.⁵⁻⁷ Goethite [α -FeO(OH)] is a common iron oxide, which forms through the weathering of other iron-rich minerals. It is generally yellowish in color and well known, since pre-historic 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 photoassisted electrolysis of water, as an active component of gas sensors and as a photocatalyst as well as an ordinary catalyst.¹⁰⁻¹³ The conversion of goethite to hematite also has many technological applications.¹⁴

1D iron oxide nanostructures 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.^{4,15-16}

Hematite nanowires have been synthesized by many different techniques including surface oxidation, thermal oxidation and electrochemical deposition.^{23,17-19} 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, so 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 letter, a laser-synthesis route for producing goethite/hematite nanowires, which can be operated in continuous flow, is discussed.

Solutions of iron oxide nanostructures were synthesized by an ultraviolet pulsed laser ablation²⁰ 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 setup is shown in Fig. 1(a). 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 $\sim 11 \text{ J/cm}^2$. The laser spot was raster scanned over the whole 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 focus (Fig.1a). These ejected particles could then be rapidly heated by subsequent laser shots, a process which could be 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/hour. The solution of products, overflowing down a tube, was collected.

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). Drops of each solution were dried (at 70 °C) onto silicon substrates and holey-carbon grids for SEM and TEM investigation, respectively. Figure 1(b) shows an SEM image of the product collected after 5 minutes 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 , 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 long enough to have completely replaced the initial volume of methanol present in the growth vessel is displayed in Fig. 2 (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. Specifically, we propose that the nanobelts grow in the solution by a photo-chemically induced reaction between the ablation products (mainly atomic iron) and the methanol. The precise reaction pathways are currently under investigation, but the complex photo-chemistry is beyond the scope of this letter. 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. However, in this case the methanol flow was not started until after 20 minutes of ablation. Here, the initial flow of product consisted entirely of nanowires (yield ~1 g/litre, dry weight.) A similar result could be obtained by taking a solution containing mainly nanobelts, and irradiating it with the laser for 10 mins (without the iron powder being present.) The nanobelts in solution were then converted into nanowires, as shown in the SEM image of Fig 2 (b). Inset in this figure is a TEM image showing the morphology of individual nanowires. This fragmentation

mechanism is supported by the observation that (from figure 1(b).) that the ends of the nanobelts appear jagged, sections have broken away.

Optimum flow rates can now be suggested to grow entirely 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. A good 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 ~20 minutes) a “nanobelt” morphology is expected, whereas at lower collection rates (residence time of the products more than ~ 20 minutes) mainly nanowires should result. Of course, these figures would depend on the precise experimental configuration (laser repetition rate, laser scanning rate and the vessel volume.)

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 dropped on a silicon substrate and the methanol was 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 is increased, the color of the dried products changed from yellow to rust-colored. Figure 3(a) shows the Raman spectra for the unannealed material and samples annealed at 400 °C and 800 °C. Peaks corresponding to α -FeO(OH), α -Fe₂O₃, and the silicon substrate are observed.^{4,21-23} The as-prepared sample evidenced only one peak, which corresponds to α -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 appeared corresponding to α -Fe₂O₃, hematite, consistent with the literature.^{8,24} TEM images of the unannealed material and the samples annealed at 400 and 800 °C are shown in Fig.3 (b), (c) and (d), respectively. The inset of Fig. 3(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 nature. From Fig. 3(c) it can be seen that the wires clearly become nanocrystalline at 400 °C and appear as single crystals by 800 °C.

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 could be controlled, producing nanobelts and nanowires at high and low flow rates, respectively. Chemical and structural characterisation suggested that the as-synthesised products have the stoichiometry of the goethite phase. Annealing at temperatures above 400 °C crystallizes the products as hematite (α -Fe₂O₃). Other transformations, such as reducing to magnetite or iron may also be possible from this starting material. This approach is relatively simple, can be run continuously and has many advantages over traditional surface oxidation methods.

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FIG. 1: (Color online) (a) Schematic diagram of the experimental setup. (b) SEM image of iron oxide nanobelts and nanowires obtained after 5 min of laser irradiation just before the starting the methanol flow.

FIG. 2: SEM image of the iron oxide (a) nanobelts achieved after a sufficient time of methanol flow (b) nanowires synthesized by laser irradiation of the collected solution for 10 min. The inset of (b) is the TEM image individual nanowires.

FIG. 3: (a) Raman spectra of unannealed and annealed (at 400 and 800 °C) iron oxide nanowires. TEM image of the samples are displayed for unannealed (b) as well as annealed at 400 °C (c) and 800 °C (d). The inset of (b) shows the selected area electron diffraction (SAED) pattern of the unannealed sample.