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Decoration of Multiwalled Carbon Nanotubes with Protected Iron Nanoparticles

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Abstract

A method to simultaneously synthesize carbon-encapsulated magnetic iron nanoparticles (Fe-NPs) and attach these particles to multi-walled carbon nanotubes (MWCNT) is presented. Thermal decomposition of cyclopentadienyliron dicarbonyl dimer $[(C_5H_5)_2Fe_2(CO)_4]$, over a range of temperatures from 250° C to 1200° C, results in the formation of Fe-NPs attached to MWCNT. At the same time, a protective carbon shell is produced and surrounds the Fe-NPs, covalently attaching the particles to the MWCNT and leading to resistance to acid dissolution. The carbon coating varies in degree of graphitisation, with higher synthesis temperatures leading to a higher degree of graphitisation. The growth model of the nanoparticles and subsequent mechanism of MWCNT attachment is discussed. Adsorption potential of the hybrid material towards organic dyes (Rhodamine B) has been displayed, an indication of potential uses as material for water treatment. The material has also been electrospun in to aligned nanocomposite

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fibres to produce a soft magnetic composite (SMC) with future applications in sensors and fast switching solenoids.

1. Introduction

Iron and iron oxide nanoparticles have received significant interest in recent years[1] for applications such as: anodes for lithium-ion batteries[2,3], magnetic resonance imaging[4], magnetic fluid hyperthermia[5] and cancer diagnosis[6]. The synthesis method should be simple, cheap and scalable, as well as ideally being able to provide a means of protecting the nanoparticles.

A number of synthesis routes have been proposed for iron and iron oxide nanostructures[7]. Methods include: decomposition[8], microwave-hydrothermal[9], ultra-sonication assisted[10], hydrolysis of iron chloride[11], gas-liquid interfacial synthesis[12], the reverse micelle method[13], laser pyrolysis[14], laser ablation[15] and liquid-solid-solution[16]. They are also a result of high iron loading in carbon nanotube (CNT) synthesis[17] and similar results can be achieved by filling CNTs[18,19]. Here we demonstrate a one-step thermal synthesis method to simultaneously grow and encapsulate iron nanoparticles (FeNP) and attach them to preformed carbon nanotubes, to form a nanoparticle-multiwalled carbon nanotube (FeNP-MWCNT) hybrid material. The resultant composite is both magnetic and oleophilic, allowing for possible applications in oil recovery[20]. A carbon coating has been shown to encapsulate the nanoparticles, leading to stability in air and protection of the nanoparticles from dissolution in acidic media (hydrochloric and nitric acids have been tested). Effective encapsulation results in the ability of the hybrid to be introduced into harsh environments and allow for chemical processing to occur. MWCNT and FeNP functionalisation can be carried out in the same manner owing to the graphitic coating[21]. Functionalisation has the potential to improve biocompatibility, improve selectivity[22] and enhance functionality[3]. The relatively low synthesis temperature (250° C) to produce encapsulated nanoparticles has only been seen in a handful of journals[9,12,23–25] and none using a one-step synthesis route. The system introduced in this study avoids complex synthesis routes and provides a low cost, simple route for protecting iron rich nanoparticles.

Typically, coatings are used to protect the material from wear and oxidative damage[26] and to improve properties such as electronic conductivity[27] and biocompatibility *in vivo*[28]. Protective coatings have been produced using a variety of materials, such as alumina[25], silica[29], and a variety of polymers, such as polyethylene glycol (PEG)[22] and PEG-polyisoprene block copolymers[30]. Amorphous carbon coated magnetic iron nanoparticles have been synthesized using a polymer-templated method[31] and has been shown to be stable in air[32,33]. The same method has also produced graphitic carbon coatings[34], other method of producing graphitic carbon coatings include evaporation of metals with a hydrocarbon flow[35] and decomposition of iron nitrate in the presence of starch[36]. However, no resistance to acidic media is shown, where acid resistance is shown[37], multiple synthesis steps are required. Simultaneous nanoparticle growth and protection is beneficial, as it negates the need for further processing steps, which increase cost, and can lead to increased loss of product and contamination of the material. Graphitic carbon coatings are expected to exhibit beneficial properties over other coatings, such as electron conductivity and potential for biocompatibility.

Synthesizing a carbon coating around the iron nanostructures has benefits over other coatings, as the chemistry is well known and functionalisation can be used to attach useful moieties, such as anti-cancer drugs (e.g. doxorubicin) for targeted cancer treatment[38,39] or selective groups, such as those used for enzyme immobilization[40]. Nanoparticle formation and subsequent carbon coating in a one-step synthesis route can be achieved by the choice of precursor used.

The decomposition of iron pentacarbonyl in the presence of oleic acid is a well known method for Fe-NP formation[23]. Ferrocene has also been shown to decompose and form a carbon shell around the iron nanoparticles and has shown to exhibit novel structures[41].

Cyclopentadienyliron dicarbonyl dimer $[(C_5H_5)_2Fe_2(CO)_4]$, was chosen in this work because, unlike other precursors, it can form free radicals during decomposition, due to the dimeric nature of the molecule[42]. Studies have shown it to be a useful radical initiator in free radical photopolymerisation[43] and has been shown to act as a catalyst for MWCNT growth[44]. The presence of free radicals is likely to aid the attachment of the nanoparticles to carbon nanotubes during the nucleation process. The reaction mechanism for radical formation is shown in Figure 1, where the μ -bonded carbonyl groups (CO bonded to both iron atoms) break a bond with one

of the iron atoms, forming the intermediate species. This species can then break down into two identical radicals, as the iron-iron bond is broken and one electron from the sigma bond goes to each of the iron species.

Figure 1: Schematic of radical formation from cyclopentadienyliron dicarbonyl dimer upon the addition of heat.

Radicals are extremely reactive species and are short lived; these species could react with nearby MWCNT material and form chemical bonds. The iron-containing bonding sites will then act as fixed nucleation sites for nanoparticle formation. In this work a mechanism for nanoparticle formation on MWCNT samples is proposed and the properties of the resultant composite material are investigated.

2. Experimental

Cyclopentadienyl iron(II) dicarbonyl dimer $[(C_5H_5)_2Fe_2(CO)_4]$ (99%, Sigma Aldrich) was combined with commercially available MWCNTs (Arkema Graphistrength) a ratio of 10:1. This was achieved by dispersing the nanotubes in chloroform ($\geq 99\%$, Sigma Aldrich) and adding the precursor before sonicating (225W) for 1 hour. The resultant homogenous solution was dried under air. The solid was collected and placed in a ceramic boat before being introduced in to a tube furnace. All experiments were carried out at atmospheric pressure in nitrogen gas. The final temperature, temperature rate and holding time were varied across experiments in order to ascertain the optimum synthesis conditions. All experiments were left to cool to below $70^\circ C$ before the sample was removed from the tube furnace chamber.

Adsorption of rhodamine B dye (Sigma Aldrich) was demonstrated by diluting the dye solution to a concentration of 10 nmol dm^{-3} using de-ionised water. The solution was placed in a quartz

cuvette and a small amount of the composite material was added. The solution was analyzed by UV/visible spectroscopy (Varian Cary 5000) before and 5 minutes after the addition of the composite material.

Electrospinning the material in to aligned sheets was achieved by dispersing the magnetic hybrid material in water under ultra-sonication (300 W, for 30 minutes using a fine tip probe) using sodium dodecylbenzene sulfonate (SDBS) as a surfactant. Once dispersed, the solution was blended with polyethylene oxide (2,000,000 M_v) (PEO) to give it desired viscoelastic properties, allowing it to then be electrospun onto a high speed rotation surface (+15 kV, at a distance of 22 cm).

3. Results and Discussion

The iron nanoparticle decorated MWCNT material was found to be magnetic both as a solid and in solution. In order to determine if the magnetic material was protected, it was soaked in a 2M solution of hydrochloric acid (Sigma Aldrich) and tested with a magnet. The effect of synthesis temperature on the protective ability of carbon shell that encapsulates the nanoparticles was also investigated.

The carbon shell has the ability to protect the internal nanoparticle, provided that the carbon layer fully encapsulates the particle. Hydrochloric acid was chosen as, unlike other mineral acids (HNO₃ and H₂SO₄), it is not expected to oxidise the carbon shell[37]. Resistance to an external environment is required for medical applications, such as cancer treatment[1]. A fraction of the hybrid material was added to 2M HCl_(aq) for 24 hours and then filtered, before being washed with water and re-dispersed in methanol. To determine if the synthesis temperature had an effect on shielding ability, the acid test was carried out on samples produced at low (250° C) and high (1000° C) temperatures. Temperatures below 250° C have not, so far, produced protected nanoparticles using a one-step synthesis method. Nanoparticle formation is not expected much below 250° C when using this precursor, which exhibits a decomposition point of 194° C.

Higher synthesis temperatures are expected to produce larger nanoparticles due to increased coagulation and Ostwald ripening. Samples synthesised over a range of temperatures (250° C, 550° C, 1000° C and 1200° C) were analysed by STEM using a HAADF detector. From the images collected, the diameters of 100 nanoparticles were measured for each synthesis temperature, histograms showing the range of measured nanoparticle sizes and average size can be found in the supplementary information. Results confirm that nanoparticles are larger with increased synthesis temperature.

Figure 2: NP-MWCNT hybrid material showing a) magnetic properties as a solid and after soaking in $\text{HCl}_{(\text{aq})}$, b) the topography of the hybrid using SE mode STEM imaging and c) the same image in ZC imaging mode depicting the positions of the iron nanoparticles on the CNT network.

Figure 2a shows that the hybrid material is magnetic and remains so after acid soaking, indicating that a significant number of nanoparticles are well protected from acid dissolution. During the acid treatment process, the materials synthesized at low temperature gained a slight green colour, whilst the high temperature analogue remained clear. This indicates that high temperature synthesis conditions result in a more efficient protection for iron nanoparticles from $\text{HCl}_{(\text{aq})}$. After acid soaking, materials synthesized at higher temperatures were removed from solution when in close proximity to a magnet more quickly than those synthesized at low temperature. This supports the observed colour change in proving that more nanoparticles synthesized at low temperature were dissolved after soaking in $\text{HCl}_{(\text{aq})}$ as a result of less protection around the nanoparticles.

Figure 3: a) a single nanoparticle attached to a MWCNT (synthesized at 1200° C), showing the line across which Electron Energy-Loss spectra was acquired, to measure the carbon (C), oxygen (O) and iron (Fe) relative composition within the nanoparticle. b) The relative intensity of the C, O and Fe signals across the nanoparticle shows that the core of the particle is iron rich, with an iron oxide shell which in turn is surrounded by a carbon coating. The small difference in peak maxima position for O and C confirm separate shells are present. The discontinuities in the spectra are related to errors in the spatial drift corrections during Electron Energy-Loss Spectroscopy (EELS) (indicated by the arrows).

In Figure 2c the majority of particles are between 10-40 nm with the smallest being less than 10nm and the largest above 90nm. The nanoparticles are anchored at specific sites, such as MWCNT defects or where crossover points. Particles have a uniform coating of carbon,

suggesting that this step occurs after the nanoparticle has been synthesized, i.e. carbon coating occurs in the cooling process, confirming the mechanism proposed in Figure 5. Using the internal carbon source provided by the iron precursor allows for a high iron to carbon ratio, which is desired for many applications where protected magnetic particles are used. Overall there is a significant quantity of iron present in the sample, as can be seen in Figure 2c.

The elemental profile in Figure 3b across the nanostructure indicates that the nanoparticle is predominantly made of iron, comprising of an iron rich core of about 50 nm diameter. It can be deduced that as the iron precursor decomposes to form mainly metallic iron particles and that the nitrogen gas used in synthesis avoids significant oxidation. However, partial oxidation does occur. This leads to the presence of an iron oxide shell, approximately 5 nm in thickness. This is indicated in the EELS spectra by an increase in the oxygen content around the nanoparticle. The large peak of carbon at the periphery of the nanoparticle proves that it is coated in a carbon layer. The coating is mostly amorphous, determined by the low level of organization, compared to the highly ordered planes seen in the nanotube walls, as shown in Figure 4c.

In Figure 4a, the nanoparticle appears to be attached to the carbon nanotube using amorphous carbon as “molecular glue”. The initiation of the attachment is proposed to be a result from radical formation during the decomposition of the precursor (Figure 1). The radicals formed could attack the MWCNTs and form a bond between an iron atom and a MWCNT before the radical further decomposes to form the beginning of a FeNP. The Fe-NP grows in size following the mechanism in Figure 5 and subsequently exudes carbon from the nanoparticle upon cooling. In this case the carbon layer has remained amorphous; it encapsulates the iron-rich nanoparticle and supports the attachment of the nanoparticle to the MWCNT.

Figure 4: High resolution STEM images in TE mode of single iron rich nanoparticles. a) attached to a MWCNT (synthesized at 1200°C) with an iron-oxide (5 nm), amorphous carbon (6 nm) shells and amorphous carbon provides the binding to the MWCNT. **b)** Showing encapsulating shells of iron oxide and graphitic carbon (synthesized at 250°C) and **c)** encapsulating shells of graphitic carbon with no iron oxide layer (synthesized at 1200°C).

As the carbon shell is predominantly an amorphous coating (see Figure 4a), it is hypothesised that the majority of the carbon present was not absorbed in to the iron nanoparticles to form an iron carbide phase. However, a graphitic carbon coating can be resolved for the low (Figure 4b) and the high (Figure 4c) temperature synthesis routes, indicating that this can occur even at low synthesis temperatures. Many particles imaged by STEM show the same shell, it has been concluded that the carbon shell is a result of nanoparticle synthesis and not overlap of a near-by carbon nanotube. STEM has been used to characterise degree of graphitisation unambiguously, although Raman spectroscopy and XRD would assess a larger amount of sample the majority of signal obtained in both of these techniques would be due to the MWCNT material and not the graphitic shell surrounding the nanoparticles. To graphitize at relatively low temperature the nanoparticle must act as a catalyst for this transformation. Iron oxide nanoparticles have been

shown to be catalytically active at temperatures as low as 110° C[45], it is therefore feasible that the nanoparticles can act as a catalyst for graphitizing carbon.

Iron oxide has been shown to be present in the product at high (Figure 3) and low (Figure 4b) temperatures. The iron oxide shell is only present in some of the material, with less iron oxide seen at higher synthesis temperatures. The presence of iron oxide can be described with two competing explanations: as a result of oxygen from the precursor or oxidation in air after synthesis. There is appreciable oxygen content in the organometallic compound used, from the CO ligands, which could lead to the oxidation of synthesised nanoparticles, depending on the decomposition mechanism of these groups. The disproportionation reaction of carbon monoxide has been shown to form CNTs and onion-like particles[46], meaning that free carbon and free oxygen are present in the system. At high temperatures, these oxygen containing groups do not lead to as many nanoparticles containing iron oxide; this could be explained by the carbon present reducing iron oxide to iron during synthesis[3].

At low temperature, the system does not have enough energy to initiate this process and therefore the oxide remains. If this were the only mechanism of iron oxide formation, the carbon adsorbed by the particle would be exuded after oxidation had occurred. Subsequently, the carbon layer would remain as an amorphous coating. However, particles with graphitic shells and iron oxide surrounding the FeNP have been also observed at these low temperatures (Figure 4b). Therefore, the oxidation of the FeNP by the oxygen contained in the precursor is not the only mechanism.

Another potential explanation is that oxidation occurs after nanoparticle formation. This could be explained by the FeNP exuding the carbon as a discontinuous layer that does not fully encapsulate and protect the internal nanoparticle. The nanoparticle is then subject to oxidative attack, leading to an iron oxide layer surrounding the iron rich centre. In this explanation, amorphous carbon with a thickness of 6nm (Figure 3) does not sufficiently protect the nanoparticle from oxidation. Similarly, the graphitized layer seen in Figure 4b is not sufficient to protect the encapsulated nanoparticle from oxidation. This would require the carbon shell to expand, which seems unlikely. Although if many graphitic planes are seen, rather than one

continuous sheet, this may be possible but would leave areas of the nanoparticle surface completely unprotected.

Graphitisation of the carbon layer is seen at both low and high temperature synthesis (Figure 4b and 4c). Carbon will be absorbed and subsequently exuded from the nanoparticle as graphitic layers, if enough energy is present to overcome the energy barrier associated with the phase transformation. At the low synthesis temperatures seen in this study (250° C), graphitic carbon is not expected to be formed from iron nanoparticles. It could be that the presence of an iron oxide layer provides an alternative low energy pathway for graphitisation and analysis of the produced graphitic layers appears to show a highly defective structure. This would support the argument for iron oxide being present before the carbon coating is formed rather than oxidising post synthesis. At higher synthesis temperatures, metallic iron nanoparticles catalyse graphitic shell formation with less defective structure, appearing as a continuous sheet. It can be deduced that higher temperature synthesis leads to a higher percentage of the nanoparticles formed having a graphitic shell capable of protecting the encapsulated particles from acid dissolution. However, a recent paper studying CNT synthesis *in situ* (via TEM) confirmed that iron oxide nanoparticles must be reduced to iron carbide (Fe_3C) before CNT growth is possible, after carbon is exuded as graphitic sheets, a metallic iron particle remains[47]. Therefore, iron oxide could cause graphitisation but would not be present as iron oxide after synthesis, casting doubt on the mechanism proposed above.

To summarise, iron nanoparticles have been synthesised and attached to carbon nanotubes. The nanoparticles exhibit an encapsulating carbon shell, which has been shown to vary in graphitic content, depending on synthesis temperature. However, the presence of graphitic planes at low synthesis temperatures (250° C) and iron oxide confuses the mechanism by which carbon is known to graphitise.

A mechanism was proposed by Weatherup *et al.* has shown a low temperature synthesis route for graphitic structures (in this case for graphene synthesis)[48]. This mechanism has been applied to this research to shed light on the production of graphitic carbon encapsulated nanoparticles at low temperatures. According to the iron-carbon phase diagram, iron and carbon can alloy, with

carbon penetrating the sub-surface to form iron carbide, the highest concentration of which is at the surface. Such nanoparticles containing a metal carbide phase have been shown to provide a low energy pathway for carbon nanotube formation [49]. In this instance, the necessary carbon source is not present to synthesize nanotubes, instead only a small amount of carbon is present from the decomposition of the precursor. Upon cooling, the carbon is exuded from the nanoparticle as separate phases of iron and graphitic carbon phases.

Nyamori *et al.* propose that carbon species derived from C_5H_5 or CO ligands, such as those present in $(C_5H_5)_2Fe_2(CO)_4$, will break down into free carbon (C_1) or similar small carbon radicals ($C\cdot$)[50]. Other studies have shown that carbonyl groups will be lost in the through decomposition, shown for iron pentacarbonyl [51]. In this work, this would lead to most of the carbon used to form the shell coming from the cyclic carbon ring. Assuming that the precursor does break down into small species, such as C_1 and $C\cdot$, a mechanism can be proposed for the formation of encapsulated nanoparticles (Figure 5), following the steps outlined by Moisala *et al.* for SWCNT synthesis using nickel acetylacetonate[52]. The precursor (1) decomposes into a metal vapour (2), which coalesces into nanoparticles (3). Carbon-containing groups (CO and C_5H_5) are broken down (4) carbon is dissolved into the nanoparticle, providing enough energy is present (5), until the saturation point is reached (6), or the carbon source is removed. Carbon is exuded from the nanoparticle as the material is cooled (7) the nanoparticle is encapsulated by a carbonaceous layer (8).

Figure 5: 1) Iron precursor ($(C_5H_5)_2Fe_2(CO)_4$) decomposes to form 2) Iron vapour; Agglomeration occurs, to form 3) Iron nanoparticles. 4) carbon-containing groups are broken down on surface leading to free carbon that 5) adsorbs in to iron nanoparticle forming iron carbide species and 6) becomes saturated. Upon cooling 7) the trapped carbon diffuses to the surface forming separate iron and carbon phases, 8) as carbon deposits build up on the surface the nanoparticle is completely encapsulated.

As carbon is adsorbed in to the Fe-NP carbon-containing iron phases are produced, these are austenite (γ -Fe) and cementite (Fe_3C). An iron phase of ferrite (α -Fe) and a separate carbon layer are thermodynamically favourable, when compared to γ -Fe and Fe_3C , at room temperature[53]. Yu *et al.* also propose a metal-carbon fused phase during the formation of carbon encapsulated nanoparticles of cobalt and nickel[54] as well as iron[36]. This supports the proposed model in Figure 5, that the carbon is exuded upon cooling.

The carbon shell has shown to produce both amorphous (Figure 3) and graphitic (Figure 4b and 4c) carbon phases. As described above, carbon is exuded from the nanoparticle upon cooling (Figure 5, stage 7), which is true for graphitic carbon formation. When the energy present in the system is greater than the activation energy required to form an iron carbide phase, carbon will be dissolved in to the iron nanoparticle, upon cooling this carbide phase is exuded from the nanoparticle as graphitic planes. The graphitic planes form uniformly over the surface of the nanoparticle, producing carbon shells that encapsulate the inner nanoparticle.

If amorphous carbon surrounds the nanoparticle, it can be concluded that insufficient energy was present to form an iron carbide phase. The process would therefore stop at stage 4 of Figure 5, with carbonaceous groups being broken down at the surface of the nanoparticle but not absorbed. Amorphous carbon may still encapsulate the nanoparticles and even provide some degree of protection to the internal particle, however rigid bonding structure of graphitic sheets and increased resistance to oxidative attack is expected to provide improved protective ability to the internal nanoparticle.

Figure 6: UV/visible spectroscopy of rhodamine dye solutions before (black) and after (red) the removal by a small amount of magentic composite material. Results show that rhodamine ($P_{\max}$ at 550 nm) is adsorbed on to the surface of the composite material and can be removed from solution using a magnet. The presence of the composite in solution has increased the background signal measured.

A small amount (20 mg) of the magnetic nanohybrid was added to a weak solution of rhodamine dye (10 nmol dm^{-3}), and within 5 minutes the solution underwent a colour change from pink to clear. To demonstrate the adsorption of the dye on to the composite material, UV/visible spectroscopy was undertaken on a solution of the dye before and after the removal by the composite material. Five minutes after the composite was added, a magnet pulled the composite and adsorbed dye to the bottom of the cuvette, in order for the after removal measurement to be taken.

The rhodamine was adsorbed by MWCNT surfaces through a number of interactive forces, such as aromatic stacking of the sp^2 hybridised carbon. This is a result of electron orbital overlap between the nanotube and the aromatic ring of the dye molecule[55]. For aromatic stacking to occur, there must be low levels of amorphous carbon contamination present. The material produced in this study is expected to be a superior candidate for adsorption of organic dyes because of the combination of high surface area MWCNT graphitic surfaces, with low amorphous carbon content, high iron to carbon ratio, and importantly magnetic nanoparticles the can draw the MWCNT material out of solution with a magnet.

Figure 7 – The electrospun soft magnetic composite (SMC) containing the magnetic hybrid material. The coupon seen here was approximately 5 cm by 8 cm; the SMC remains magnetic after electrospinning despite a low hybrid material content.

In order to further demonstrate the application versatility of this new magnetic CNT nano-hybrid, a soft magnetic composite (SMC) was also produced revealing further applications for SMC items such as rotating machinery, fast switching solenoids [56] “intelligent fibres” for military

clothing[57] and magnetic sensors[58]. SMC materials are commonly produced using iron powder and resin, using magnetic nanoparticle loaded CNTs as opposed to iron has the added benefit of improved mechanical performance [59]. Electrospinning this solution resulted in a large area of highly aligned nano-fibres loaded with magnetic CNTs. Magnetism in the SMC is demonstrated (despite the low CNT content), confirming that the magnetic nano-hybrid material can have further applications in advanced SMCs.

4. Conclusions

A one-step thermal synthesis method of producing carbon encapsulated magnetic iron nanoparticles attached to MWCNTs has been outlined. The relatively low temperatures used have only been reported in a handful of journals and none which encapsulate the nanoparticle in parallel. The choice of precursor, cyclopentadienyl iron dicarbonyl dimer, is paramount to the successful synthesis of the composite material by providing an iron and carbon source with a favourable decomposition route to produce nanoparticles, as has not previously been studied in this manner. A mechanism for nanoparticle formation has been outlined and the structures of the nanoparticles have been investigated. Higher synthesis temperatures increase the protective ability of the carbon coating.

By synthesizing protected magnetic nanoparticles on to carbon nanotubes the scope for functionalisation and the attachment of linking molecules opens up new possibilities of research in the fields of energy management, chemical processing and biotechnology. The hybrid material has also been electrospun to form a light weight and aligned CNT composite that can be manipulated with a magnet, highlighting how the material may find applications as a soft magnetic composite. Producing high surface area solids like this could help to overcome the hurdles of nanoparticle contamination for future applications.

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