Process Intensification Strategies for the Synthesis of Superparamagnetic Nanoparticles and Fabrication of Nano-Hybrid

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ABSTRACT

Continuous flow spinning disc processing (SDP), which has extremely rapid mixing under plug flow conditions, effective heat and mass transfer, allowing high throughput with low wastage solvent efficiency, is effective in gaining access to superparamagnetic Fe_3O_4 nanoparticles at room temperature. These are formed by passing ammonia gas over a thin aqueous film of $Fe^{2+/3+}$ which is introduced through a jet feed close to the centre of a rapidly rotating disc (500 to 2500 rpm), the particle size being controlled with a narrow size distribution over the range 5 nm to 10 nm, and the material having very high saturation magnetizations, in the range 68–78 emu g^{-1}. SDP also shown to be effective for fabrication of superparamagnetic carbon nanotubes composite. Ultra fine (2-3 nm) magnetite (Fe_3O_4) nanoparticles were uniformly deposited on single-walled carbon nanotubes (SWCNTs) _in situ_ by modified chemical precipitation method using SDP in aqueous media at room temperature under continuous flow condition

Keywords: Spinning disc processor , superparamagnetic, continuous flow technology, magnetic nanoparticles, carbon nanutubes

1   INTRODUCTION

Traditional fluid based synthesis techniques for the production of nanoparticles have inherent limitations such as poor particle size distribution and reproducibility, and difficulties in scalability for commercial production. Process intensification, by means of spinning disc processing (SDP), potentially offers an avenue for the production of monodisperse nanoparticles with tuneable and controllable properties. SDP, Figure 1, is a rapid flash nano-fabrication technique with all reagents being treated in the same way, and is in contrast to traditional batch technology where conditions can vary across the dimensions of the vessel.[1] The reagents are directed towards the centre of the disc, which is rotated rapidly (300 and 3000 rpm) resulting in the generation of a very thin fluid film (1 to 200 μm). The thinness of the fluid layer and the large contact area between it and the disc surface facilitates very effective heat and mass transfer. The drag forces between the moving fluid layer and the disc surface enable very efficient and rapid mixing. The greatest strength of SDP synthesis is the broad range of control possible over all the operating parameters involved in nanoparticle formation, enabling the simultaneous and individual optimization of many interdependent operating mechanisms, with the ultimate goal of achieving very narrow particle size distributions.[2] Another feature of SDP is that it is continuous flow, readily allowing scale-up of the ensuing product formation.
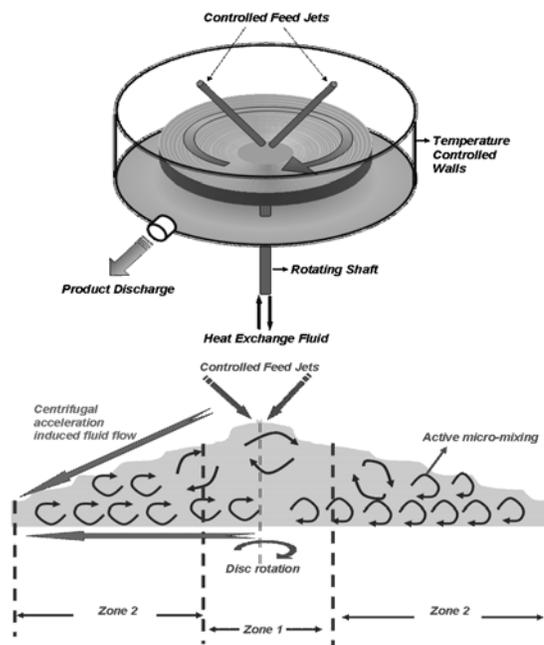
Figure 1. (a) Schematic representation of a SDP, (b) Hydrodynamics of the fluid flow over a spinning surface.

The most common cost effective and convenient way to synthesize Fe_3O_4 nanoparticles is by co-precipitating ferrous and ferric salt solutions with a base, such as

aqueous NaOH or NH$_4$OH. [3] However, the size distribution of the Fe$_3$O$_4$ nanoparticles produced using this method is normally very broad. Consequently, the downstream purification and isolation process is more expensive and is time and energy intensive. Furthermore, scale-up of this method using conventional reactors can be problematic given the inhomogeneous agitation and areas of localized pH variations, resulting in the precipitation of non-magnetic iron oxides.[4] Herein we demonstrate the successful synthesis of Fe$_3$O$_4$ nanoparticles via co-precipitation using NH$_3$ gas as a base source using spinning disc processing (SDP) under scalable and continuous flow conditions. To our knowledge, this is the first use of NH$_3$ gas as a precipitating agent to make Fe$_3$O$_4$ nanoparticles in a thin fluid film. The technology offers a realistic route towards large scale synthesis of Fe$_3$O$_4$ nanoparticles with precise control within the 10 nm size range.

The efficient SDP capability of fabricating magnetic nanoparticles decorated single wall carbon nano-tubes (SWCNTs) were also demonstrated. A novel yet simple method to coat superparamagnetic Fe$_3$O$_4$ nano-particles of narrow size distribution on SWCNTs *in situ* by modified chemical precipitation method using SDP in aqueous media at room temperature under continuous flow conditions was reported in this paper.

2   EXPERIMENTAL

2.1   Synthesis of Fe$_3$O$_4$ nanoparticles

In a typical synthesis, aqueous solutions of Fe$^{2+/3+}$ precursors were prepared by dissolving FeCl$_2$.4H$_2$O (10 mM) and (20 mM) FeCl$_3$.6H$_2$O (1:2 molar ratios) in deoxygenated ultrapure Mili-Q water. The SDP was a Protensive 100 series with integrated feed pumps to direct the reactants onto the rotating disc. The above solutions were delivered onto the disc surface using one feed jet at 1.0 mls^{-1}, using continuous flow gear pumps (MicroPumps). Grooved and smooth stainless steel discs with 100 mm diameter were used which were manufactured from 316 stainless steel with the grooved disc having 80 concentric engineered grooves equally spaced at 0.6 mm depth.

The reactor chamber was purged with argon gas before the reaction to remove oxygen. Ammonia gas was then fed into the sealed reactor chamber at a constant flow rate. Black suspensions of Fe$_3$O$_4$ nanoparticles were collected from beneath the disc through an exit port.

The samples collected were immobilized with a permanent magnet and supernatant solutions were decanted. Samples were re-dispersed in deoxygenated ultrapure Mili-Q water.

2.2   Fabrication of Fe$_3$O$_4$ decorated Carbon Nanotubes (CNT)

For purification and functionalization of SWCNTs, 10 mg of SWCNTs were dispersed in 5 ml of 1: 1 mixture of 70% HNO$_3$ and 98% H$_2$SO$_4$ aqueous solutions in the reaction chamber. The reaction was carried out in a CEM Focused Microwave Synthesis System, Discover Model. The microwave power was set at 300 W, and the pressure was 12 bar, and the temperature was set at 130 ^{o}C for 30 minutes. After the reaction, the SWCNTs were filtered, washed and re-dispersed in 100 mL of ultra pure Milli-Q water and sonicated for 15 minutes. The functionalized SWCNTs were dispersed in water and the container purged with N$_2$ gas to remove oxygen then 10 mM of FeCl$_2$.4H$_2$O and 20 mM of FeCl$_3$.6H$_2$O (1:2 molar ratios) was added and the mixture stirred for 1 hour. After that, the solution was filtered to remove excess Fe$^{2+/3+}$ and the resulting carbon nano-tube and Fe$^{2+/3+}$ complex was re-dispersed in deoxygenated Mili-Q water.

Solutions/suspensions of CNTs and Fe$^{2+/3+}$ were fed from one feed and the deoxygenated NH$_4$OH aqueous solution was fed from the other under an atmosphere of high purity (99.9%, BOC Gasses) argon gas, within the sealed reactor chamber. The disc surface was manufactured from 316 stainless steel. The 10 cm grooved disc was used for the current study, with 80 concentric engineered grooves equally spaced approximately 0.6 mm in height. Samples were collected from beneath the disc through an exit port.

3   RESULTS AND DISCUSSION
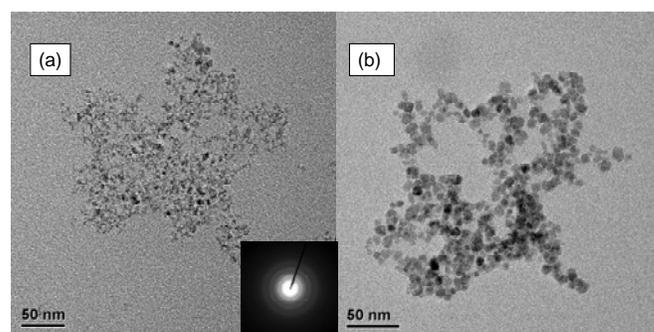
Figure 2. TEM images of Fe$_3$O$_4$ nanoparticles (10 mM Fe^{2+}) synthesized at 25 ^{o}C on grooved disc with disc rotating speed: (a) 2500 rpm and (b) 500 rpm

The operating parameters of the SDP were effective in controlling the size, size distribution and shape of the Fe$_3$O$_4$ nanoparticles in the presence of NH$_3$ gas feed as the base

rather than NH_4OH aqueous solution. In a typical synthesis, the samples were synthesized using 10 mM of Fe^{2+} and 20 mM of Fe^{3+} aqueous solution and were fed at $1mls^{-1}$ onto the rotating grooved disc. A high rotation speed of 2500 rpm resulted in ultrafine (3-5 nm) particles with asymmetrical shape. A lower speed of 500 rpm, resulted in spherical nanoparticles of around 10 nm in size, Figure 2.

The fluid layer of the SDP has a plug flow characteristic, where the particles produced are constantly being removed from the nucleation and growth zones by radial propagation across the disc. At high rotation speeds the non-linear wave regime is dominant in the fluid film, which in turn ensures greater gas adsorption into the thin film. Consequently the nucleation process becomes dominant, thereby resulting in a number of ultra-small magnetic nanoparticles. At lower spin speeds the wave regime is no longer predominant, and the velocity of the traversing waves are highly reduced, and so is the absorption of the corresponding NH_3 gas into the flowing film. The number of nucleation sites is thereby decreased and the growth process becomes dominant at lower speeds resulting in the formation of larger particles.
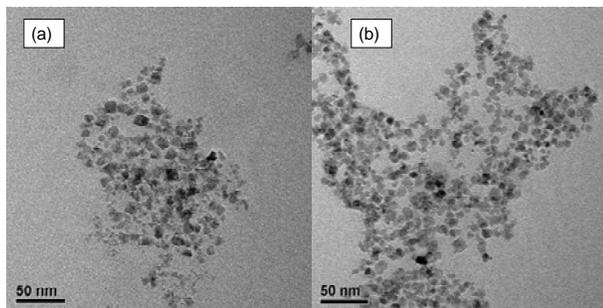
Figure 3. TEM images of Fe_3O_4 nanoparticles (10 mM Fe^{2+}) synthesized on smooth disc with disc rotating speed of 500 rpm, at (a) 25 ^{o}C and (b) 120 ^{o}C.

At constant speed, samples synthesized using the grooved disc had a narrower particle size distribution compared to the smooth disc. The particle size for the samples synthesized on the grooved disc ranged from 3-5 nm (Figure 2a), whereas the particle size distribution of a sample prepared using the smooth disc ranged from 3 -12 nm (Figure 3a). When using the grooved disc, the shear forces and viscous drag between the moving fluid layer and the periodic grooved surface give rise to more efficient turbulent mixing within the fluid layer and this in turn results in homogeneous reaction conditions in the thin film. The grooves on the disc also result in the formation of waves on the flowing film, thereby amplifying the amount of the NH_3 gas adsorbed. However, on a smooth disc the micro-mixing is not as efficient resulting in a broader size

distribution. Increasing the temperature of the disc offers scope to overcome the aforementioned size distribution issues associated with the smooth disc. At higher temperature the absorption efficiency of the gas is reduced in the flowing fluids, however the growth conditions become highly amplified [5]. As a result, the size distribution of the samples prepared on the smooth disc became very narrow with particle sizes in the range 8-10 nm for the reactions at 120 ^{o}C, Figure 3(b).
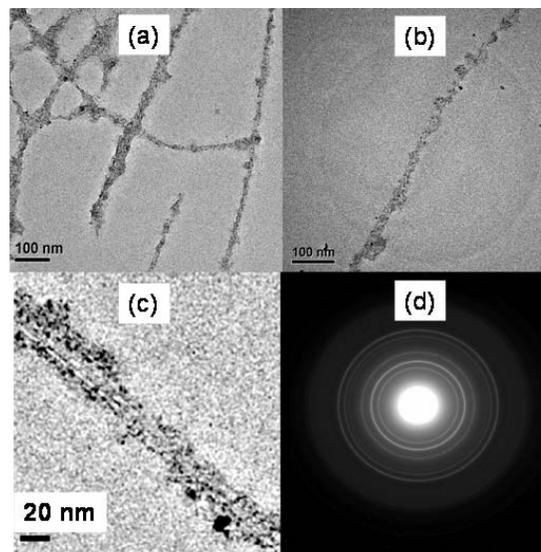
Figure 4. TEMs of Fe_3O_4–SWCNT composite at (a and b) low resolution; (c) high resolution and (d) associated SAED pattern for material synthesized using SDP

For the fabrication of Fe_3O_4-SWCNT composite, ultrafine (2-3nm) of Fe_3O_4 nano-particles with very narrow size distribution were observed to be uniformly coated onto the CNTs surface, Fig 4 (a), (b) and (c). As can be seen from the TEM images, the distribution of Fe_3O_4 nano-particles on the SMWNTs surface is very uniform and no local aggregation is observed with a very high coverage density. The ability to effectively decorate the SWCNTs with Fe_3O_4 nano-particles relates to the functionalisation of the nano-tubes with COO^- moieties that can bind directly to $Fe^{2+/3+}$ ions. [6] The use of this simple yet strategic approach reduces the down-stream processing dramatically. This is associated with purification/separation steps to remove excess nanoparticles that grow independently in solution and are not associated with the CNTs.

4   CONCLUSION

In conclusion, the particle size of Fe_3O_4 nanoparticles

can be controlled by judicious choice of the operating parameters of SDP technology. The capabilities of SDP in controlling particle size and stability have been clearly demonstrated with the ability to produce ultra-small superparamagnetic magnetite nanoparticles with high saturation magnetizations, and with narrow size distributions. We have also developed a novel, simple, rapid, cost effective and scalable method to decorate CNTs with 2-3 nm Fe_3O_4 nano-particles using SDP. The resulting CNTs show high coverage density. The apporach also avoids the need for subsequent purification and separation of the composite material from excess Fe_3O_4 nano-particles formed in solution, unlike in the case of using batch reactions. Futhermore the ability of SDP to fabricate superparamagnetic SWCNT composites under continuous flow in scalable quantities is significant in any down stream applications.

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