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Design of microreactors for tuneable core-shell nanoparticles synthesis

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Highlights

- Innovative microreactors configurations are designed for synthesis of complex structures.
- Continuous synthesis of Fe@Fe_3O_4 core/shell nanoparticles
- Independent control of the core size and shell thickeness of Fe@Fe_3O_4 nanoparticles

1. Introduction

Nanoparticles (NPs) have attracted the scientific interest during the last decades and are currently being used and explored for a large number of applications, such as catalysis [1] and biomedical drug delivery [2]. Despite their potential, their deployment in large scale application requires overcoming of a number of hurdles related to complicated scale-up of multi-stage batch methods. Furthermore, a tight control on their size distribution is necessary as their properties are highly size-dependent. In this context, microreactors are presented as an attractive alternative where continuous NPs synthesis can be carried out in a repeatable, robust and accurate manner, desirable for industrial production. Moreover, their inherent laminar flow can be used to tune the size of the NPs without employing surfactants.

2. Methods

Fe@Fe_3O_4 core/shell nanoparticles were synthesized by thermal decomposition of $Fe(CO)_5$ precursor in a high boiling point octadecene solvent at 170°C in the presence of oleic acid and oleylamine. In a typical flow nanoparticle synthesis, a solution of the metal precursor was pumped into a microreactor submerged inside an oil bath at the desired temperature.
Different reactor materials including fluoropolymer tubing, stainless steel tubing and glass capillaries were used to evaluate the fouling of the reactors. The geometry of the reactors was carefully controlled using 3D printing supports to ensure the onset of transitional flows (Dean vortixes) within the channels.

3. Results and discussion

The aim of this work is the production of core-shell Fe@Fe_3O_4 in microreactors to tune the core size and the shell thickness. For this, we have adapted a well-known batch synthesis method that produces iron nanoparticles [3], which are then been converted into Fe@Fe_3O_4 core/shell NPs upon exposure to oxygen.

The continuous synthesis of Fe@Fe_3O_4 core/shell NPs in flow reactors, in the presence of oleic acid and oleylamine surfactants leads to a homogeneous size distribution of particles of 8 nm diameter with a 4 nm Fe core. These are similar results to those obtained in batch processes (Figure 1). Despite the obvious advantages associated to the presence of capping ligands regarding size control, size tuneability is very limited.

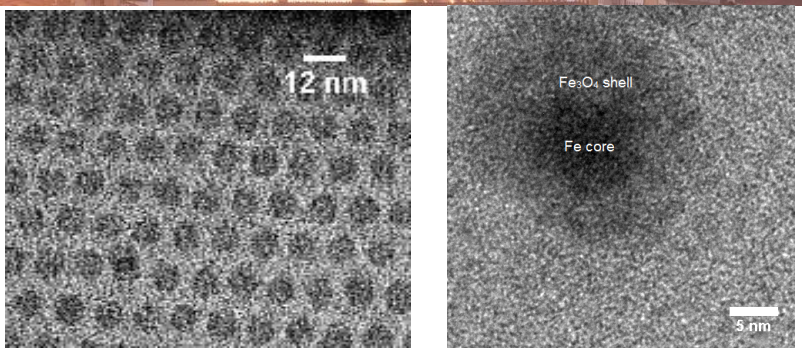

Figure 1. Core/Shell Fe@Fe_3O_4 nanoparticle synthesized in batch and flow reactors respectively

Microreactors offer the opportunity to separate core synthesis from shell growth by using reactors in series. In addition, their inherent laminar flow regime enables the synthesis of nanoparticles in the absence of surfactants, while the high mass and heat transfers allow a rapid change of reaction conditions [4]. Using these characteristics, Fe@Fe_3O_4 core/shell NPs are synthesized in two reactors in series. In the first step, seeds are grown to the desired core size in the absence of surfactants. In conventional batch synthesis, this would lead to quick agglomeration of iron seeds. The growth of the seeds can then be stopped by surfactant addition, effectively capping the particle surface. This leads to an efficient nucleation and growth separation as well as precise growth control by tuning the particle residence time. During the second step, the shell is formed around the seeds by further $Fe(CO)_5$ decomposition, resulting in an interlayer of trapped carbon between the core and the shell [5]. Once the nanoparticles are exposed to air, the outer shell oxidizes to Fe_3O_4 while the core remains metallic, stabilized by the trapped carbon interlayer.

In addition, this study will also present the effect of reactor material on the final iron yield and fouling. We have demonstrated that diffusion of the metal precursor across the reactor walls (e.g. polytetrafluoroethylene (PTFE) tubes) lead to a considerable decrease on yield and consequently fouling of the reactor.

4. Conclusions

In this paper, we demonstrated the design of multi-stage microreactor systems for the synthesis of complex materials such as core-shell nanoparticles. Deep understanding of the chemical steps taking place during the synthesis, their kinetics and the opportunities offered by the laminar flow regime leads to very precise size control without the need of surfactants. This opens a new range of possibilities for the engineering of unique nanostructures.

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Keywords
Microreactors; continuous synthesis; nanoparticles; surfactant-free