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Synthesis and characterization of $NiFe_2O_4$@Co_3O_4 core-shell nanoparticles

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ABSTRACT

Premade nickel ferrite ($NiFe_2O_4$) nanoparticles were used as a core around which cobalt (II, III) oxide (Co_3O_4) was grown. In an attempt to vary the shell thickness, the concentration of Co used was varied. It was found that the concentration of Co did dictate whether Co_3O_4 formed on the surface but not its thickness. Additionally, it was established that a two-step synthesis route was needed to synthesize the core-shell material. Concentrations below 11.0 wt.% Co yielded a partial shell whilst a concentration of 7.6 wt.% Co yielded a uniform shell layer around most $NiFe_2O_4$ nanoparticles. All particles with a Co_3O_4 shell was obtained by following a two-step synthesis where 3.8 wt.% Co was used in each step to target a final loading of 7.7 wt.% Co. Whilst a concentration of 11.0 wt.% Co yielded a partial shell, the presence of Co_3O_4 nanoparticles was also evidenced. A concentration of 19.1 wt.% Co resulted in the formation of separate Co_3O_4 nanoparticles amongst the $NiFe_2O_4$ nanoparticles.

1. Introduction

Cobalt catalysts based on Co_3O_4 have intriguing properties and thus find application in a variety of catalytic reactions, such as oxidation reactions in environmental applications [1–5], NO decomposition [6], electro-catalytic applications [7,8], and after reduction in hydrogenation reactions [9–11], such as the Fischer-Tropsch synthesis [10,11]. Despite the high activity typically gained with these catalysts, the cost of cobalt can significantly increase the cost associated with the catalytic process. This would mean that routes to lower the cost of cobalt-based catalysts are constantly being sought. One such way would be to replace the catalytically unavailable cobalt oxide in the catalyst with a cheaper alternative.

In an industrial catalyst, only a small percentage of cobalt oxide is on the surface. Subsurface cobalt oxide is not directly involved in the reaction, and can thus be replaced by a less expensive material. This would result in the formation of a core-shell catalyst, in which the shell of cobalt oxide is combined with a core of a less expensive material. Core-shell materials can be described as nanoparticles that comprise of a core and a shell (outer layer material) with the active-phase topology tailored to have a specific structure and composition at the nanoscale level but in a manner that allows for scale up [12,13]. The core can vary in size and shape and the shell can have different thicknesses and surface morphologies [13–20]. These materials may have different electronic and geometric properties around the catalytically active center resulting in novel catalytic properties [11,13,21–23].

The main attraction of core-shell catalysts is the reduction in costs that can be obtained. For instance, replacing cobalt oxide with another metal oxide core-shell catalyst may result in a catalyst cost saving of up to 50% if the core is composed of oxides of Fe, Zn, Ti or Si [11]. Calderone et al. [11] state that achieving a particular cobalt shell thickness for a certain crystallite size whilst maintaining an overall cost saving and achieving a high performance material does require a cheap, simple and scalable method. This means that the shell should be epitaxially grown onto the core material [24] thus requiring minimal lattice mismatch between the core and the shell.

$NiFe_2O_4$ is a suitable candidate that fits this criterion due to the similarity of its crystal structure with that of Co_3O_4. Using $NiFe_2O_4$ as a core would allow for the preparation of a cheaper nanoparticle than one containing only cobalt oxide as the cost of nickel and iron is low by comparison. In this present work, a simple precipitation route [13] using $CoCO_3$, $(NH_4)_2CO_3$ and NH_3/NH_4OH solution as reactants was followed to produce a Co_3O_4 shell around a $NiFe_2O_4$ core. A one-step and two-step preparation (targeting 7.6 wt.% Co) was compared to determine if the number of preparation steps would influence the Co_3O_4 shell formation

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around the core nanoparticle. Since various shell thicknesses can alter the core-shell nanoparticle's properties [18], it was necessary to determine whether this synthesis route could yield core-shell nanoparticles with varying shell thicknesses. It is known that the concentration of the metal precursor that forms the shell is proportional to the thickness [25]. Therefore, the influence of the cobalt concentration (wt.% Co) was investigated in an attempt to establish whether increases thereof would yield a thicker Co_3O_4 shell.

2. Materials and methods

2.1. Preparation of $NiFe_2O_4$

An excess of $Fe(NO_3)_3 \cdot 9H_2O$ (Fe/Ni mole ratio = 2.3) was used to avoid the formation of nickel oxide (NiO) as a side product. In a typical synthesis, $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich) (0.08077 mol) was dissolved in absolute ethanol (Sigma Aldrich) (30 mL). Similarly, $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) (0.03515 mol) was dissolved in absolute ethanol (30 mL). Then, citric acid (Sigma Aldrich) (0.1159 mol) was dissolved in absolute ethanol (30 mL) and placed in a water bath at 303 K and allowed to stir until it dissolved. Thereafter, the $Fe(NO_3)_3 \cdot 9H_2O$ solution was added to the citric acid solution followed by the addition of the $Ni(NO_3)_2 \cdot 6H_2O$ solution. The metal nitrate-citric acid solution was allowed to stir for 95 min before the temperature of the water bath was increased to 333 K. The metal nitrate-citric acid solution was kept at this temperature for 2 h under stirring. After this time, a brown gel formed which was then oven-dried at 383 K for 24 h. The as-formed resin was then calcined in a muffle furnace at 723 K for 5 h.

2.2. Preparation of $NiFe_2O_4$@Co_3O_4

The synthesis procedure used was based on the work done by Calderone et al. [13] however higher synthesis temperatures were used in this present study to drive the formation of Co_3O_4 within the 24 h period. In a typical synthesis, $(NH_4)_2CO_3$ (Sigma Aldrich) (5 · 10 mmol) was dissolved in deionized water and 25 wt.% ammonia aqueous solution (Sigma Aldrich) was added. $CoCO_3$ (Sigma Aldrich) (0.58 mmol) was then added (pH = 11.5). This suspension was then stirred at 318 K for 2 h, during which the cobalt carbonate formed the cobalt hexamine precursor. This was evidenced when the pink suspension turned a clear violet colour. The solution was then filtered. This filtrate (pH = 10.8) was added to a round bottom flask containing $NiFe_2O_4$ and was stirred at 358 K for 6 h. The temperature was then increased to 368 K and allowed to stir for 24 h. The solvent was removed under vacuum and the dried solid was rinsed with water and dried under vacuum. The solid obtained was oven-dried at 383 K, overnight. The synthesis procedure should result in the formation of Co_3O_4, since the cobalt hexamine precursor decomposes below 373 K to yield $Co(OH)_2$ [26] which by further heating in air is transformed into Co_3O_4 [27].

In order to keep the concentration of Co in the synthesis low and to minimize self-nucleation, a two-step synthesis was also done. This multi-step synthesis procedure was also used in an attempt to improve the coverage of the core nanoparticle by the shell. For the two-step synthesis, the above procedure was followed for step 1 using the reactant quantities indicated in Table 1. In step 2, the cobalt precursor solution was made as per step 1; however, the suspension was added to the dried solid from step 1. The synthesis then followed the process outlined above.

In order to investigate whether the Co_3O_4 shell thickness can be varied, the concentration of Co in the synthesis solution was varied (Table 1) by increasing the mass of the $CoCO_3$ whilst keeping the mass of $NiFe_2O_4$ the same. The quantities of $(NH_4)_2CO_3$ and aqueous NH_3 solution were adjusted stoichiometrically.

Table 1
Summary of masses used for the synthesis of the various $NiFe_2O_4$@Co_3O_4 nanoparticles.

Sample	Mass $CoCO_3$/g	Mass $(NH_4)_2CO_3$/g	Volume $NH_{3(aq)}$/mL	Concentration/wt.% Co
1	0.0693	0.4866	3.0	6.3
2	0.0847	0.5872	3.6	7.6
3	0.1263	0.9663	6.0	11.0
4	0.2429	1.9384	10.4	19.1
5 Step 1	0.0408	0.3239	1.8	3.8
5 Step 2	0.0408	0.3239	1.8	3.8

2.3. Characterization methods

X-ray powder diffraction (XRPD) patterns were collected on a Bruker D8 Advance X-ray diffractometer equipped with a Co-Kα X-ray source (λ = 1.78897 Å). Phase identification of the diffraction data was done using Bruker DIFFRAC.EVA Version 2 software while average crystallite sizes and relative phase abundances were obtained from Rietveld refinements using Bruker AXS Topas Version 4.1.

Mössbauer spectroscopy (MS) experiments were performed at room temperature (RT) using a conventional constant acceleration spectrometer operating in absorption mode and equipped with a $^{57}Co/Rh$ source. Low temperature experiments were performed at 4.2 K in zero applied field (LT) and in a 10 T applied magnetic field (AF) using an Oxford Instruments Spectromag SM4000-10 cryomagnet. The MS spectra were analysed by means of a least squares programme Normos that models them using sextet subspectra based on a Lorentzian line-shape profile. Identification of the spectral components was based on the comparison of their isomeric shift (δ), quadruple splitting (ΔE_Q) and hyperfine magnetic field (B_{hf}) values with those reported in the literature. All isomer shift and magnetic hyperfine field values are reported relative to metallic iron (α-Fe).

For the TEM analysis, the sample was prepared by crushing and mixing with ethanol to form a suspension. The suspension was placed in an ultrasonic bath to disperse the particles into fine particulates. After ultrasonication, a small amount of sample was transferred onto a copper TEM grid (SPI Supplies, 300 mesh) using a pipette. The copper grid was placed in a single-tilt TEM specimen holder and transferred into the TEM for analysis. An FEI Technai Osiris Electron Microscope was used for low magnification TEM analysis. The instrument has a field emission gun as an electron source. Bright field (BF) images were acquired on a Gatan CCD camera that was controlled by Gatan Digital Micrograph software. Scanning Transmission Electron Microscopy (STEM) images were captured by a High angle annular dark field (HAADF)-STEM detector that was controlled by FEI TIA software. Energy Dispersive X-ray Spectroscopy (EDS) elemental mapping was performed using ChemiSTEM EDX detector system controlled by Bruker Espirit software. A double Cs corrected JEOL ARM 200F transmission electron microscope operated at 200 kV was also used in the present study. HAADF STEM) as well as bright field (BF) STEM imaging at atomic resolution was used. Electron energy loss spectroscopy (EELS) Spectrum Imaging (SI) was performed using the DualEELS™ mode on the Gatan GIF Quantum ERS™ spectrometer. This allows for acquisition of the intense zero loss peak (ZLP) and the elemental edges at virtually the same time. The convergence semi-angle of 21.4 mrad was used for the STEM probe and the collection semi-angle of the spectrometer was 54.3 mrad at a camera length of 1 cm.

For Raman spectroscopy, the powders were placed on a microscope slide and measured using an inVia Raman system, utilising the 785 nm line of a solid-state diode laser. The beam was focussed with a Leica microscope using a ×20 objective. Data were collected for the region 50–2000 cm^{-1} for 10 s, scanned 20 times using a laser power of 0.1%. Wire Version 4.1 software was used for data capturing and instrument control. The Raman band of pure Si was measured before data accumulation commenced for calibration purposes.