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Highly porous hematite nanorods prepared via direct spray precipitation method

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ABSTRACT

Hematite nanoparticles can be formed through a variety of synthesis routes, each of which can substantially affect the properties of the resulting product. In this article we report the use of a facile synthesis route, direct spray precipitation, and compare the performance of these α -Fe₂O₃ products with those obtained through standard precipitation method. Through this new method, we obtain a nanocrystalline α -FeO(OH) precursor material, while an amorphous material is obtained from precipitation route. The highly efficient, low temperature (300 °C) calcination of this nanocrystalline precursor results in the formation of hematite nanorods with a diameter between 20 and 30 nm. These nanorods exhibit an extremely high surface area (up to 166 m² g⁻¹) attributed to their morphology and apparent nanoporosity. This very high surface area coupled with higher attenuation in the ultraviolet-visible with a low temperature synthesis give this material potential for further investigation as photocatalyst or energy storage material.

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1. Introduction

Nanoparticles of hematite (α -Fe₂O₃) are an example of a nanomaterial that can be tailored to exhibit favourable magnetic [1,2], optical [3–5] electrochemical [6–8] and photocatalytic [9,10] properties for a variety of applications [11]. Hematite nanoparticles have been reported to be produced from many different routes available such as hydrothermal [2,7,12,13], high-energy ball milling [14], spray pyrolysis [15], precipitation [3,5], thermal decomposition [4] along with more advanced techniques [1,8,9,16,17]. However, some of these methods required a long time to achieve the desired size and properties (hydrothermal, ball-milling) or very high temperatures (spray pyrolysis). In this article we introduce an efficient method of synthesising very high specific surface area α -Fe₂O₃ nanoparticles namely, direct spray precipitation, which involves the rapid delivery of a Fe³⁺ solution into a solution of strong base via two-fluid spray nozzle. This has the advantages of combining the high-yield and possibility for thermally efficient (low temperature, 300 °C) nature of traditional α -Fe₂O₃ precipitation with the smaller droplet size and kinetic effects associated with the increased velocity of these droplets, such as is featured in spray pyrolysis. This results in the formation of nanorods of crystalline α -FeO(OH) in a significantly more efficient process that previously reported [18], which after undergoing low temperature decomposition results in α -Fe₂O₃ nanorods that initially exhibit extremely high surface area and ultravioletvisible optical absorbance as compared to traditionally precipitated α -Fe₂O₃. However this high porosity is lost upon heating and unlike traditionally precipitated material this further heating does not result in a significant blue shift of absorption spectra.

2. Experimental

2.1. Synthesis

Iron(III) nitrate hexahydrate (Fe(NO₃)₃ · 9H₂O, Sigma–Aldrich 99%) and sodium hydroxide (NaOH, Sigma–Aldrich \geq 97%) were dissolved into deionized water to create 0.15 M Fe(NO₃)₃ and 1.5 M NaOH solutions. Under the influence of magnetic stirrer bar, NaOH solution was added to the Fe(NO₃)₃ solution drop-wise via Pasteur pipette. In the direct spray precipitation method, solutions of the same concentration were used, except a spray nozzle and peristaltic pump were used to spray the Fe³⁺ solution into the basic





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Fig. 1. Diagram of reaction set-up for direct spray precipitation method.

NaOH solution (Fig. 1). Both methods resulted in a red-brown precipitate which were allowed to rest overnight, resulting in the partial separation of the solid and liquid phases. The spray precipitation precursor underwent ageing, changing in colour from brown-red to yellow. After decanting the upper liquid layer, the precipitants were separated, washed and resuspended multiple times at 11,000 RPM for 5 min via centrifugation. The resulting solid precursor materials were then dried in an oven for 3 h at 90 °C. This precursor material was then annealed at 300 °C, 400 °C and 500 °C in a tube furnace (Thermotech, Haugesund, Norway) for 4 h.

2.2. X-ray diffraction

Powder diffraction data was obtained for all samples on a Enhanced Mini-Materials Analyser (EMMA) X-ray Diffractometer (XRD) (GBC Scientific Equipment, Melbourne, Australia) between 20 and 90 ° at 2.000° min⁻¹ and a step size of 0.020° . Mean crystalline size was calculated using Scherrer's Formula, while lattice parameters were calculated using MAUD software.

2.3. Brunauer–Emmett–Teller analysis

The specific surface area of all samples was investigated using a NOVA 1000 (Quantachrome, Boynton Beach, Florida, USA) high speed gas sorption analyser. N₂ gas was used as the adsorbate at the temperature of liquid nitrogen on samples previously degassed at 130 $^\circ$ C overnight.

2.4. Scanning transmission electron microscopy

TED (transmitted electron detector) images were then taken using a JSM-7500FA cold Field Emission Gun Scanning Electron Microscope (FEGSEM) (JEOL, Tokyo, Japan). The operating parameters include an accelerating voltage between 17 and 25 kV at a working distance of 8 mm, a beam current of 10 μ A and a spot size setting of 8. Carbon film coated copper grids were dipped into suspensions of each sample in ethanol.

2.5. Ultraviolet-visible absorption spectroscopy

Suspensions of $\sim 0.05 \text{ mg.mL}^{-1}$ of nanoparticles in ethanol were sonicated for 2–3 h after which the absorbance between 250 and 1000 nm was obtained using a UV-1800 Spectrophotometer (Shimadzu, Kyoto, Japan). Direct-transition optical

bandgaps were determined from constructing Tauc plots [19], plotting $(\alpha h\nu)^n = K(h\nu - E_g)$, where $n = \frac{1}{2}$ for indirect and n=2 for direct transitions, while α [3]:

$$\alpha = \frac{2.303 \times 10^3 A \rho}{c\ell} \tag{1}$$

and ρ , the density of hematite is set to 5.25 g cm⁻³, *c* is the concentration of the suspension in g mL⁻¹ and ℓ is the path length in cm.

Band gap E_g values quoted in this study refer to those of direct band gap n=2 transitions, as this featured a better linear fit.

3. Results and discussion

The diffraction patterns obtained for traditionally precipitated samples (Fig. 2(a)) show that while an amorphous phase with no strong peaks was obtained as the precursor material (black pattern), α -Fe₂O₃ was confirmed as the primary phase of all other samples. The yellow precursor obtained though the direct spray method exhibited nanoscale crystallinity with a number of very broad peaks corresponding to a primary goethite phase (α -FeO (OH)), PDF card no. 00-003-0249) with lattice parameters $a = 4.6139 \pm 0.0009 \text{ Å}, \quad b = 9.941 \pm 0.001 \text{ Å} \quad \text{and} \quad c = 3.0224 \pm 1.0001 \text{ Å}$ 0.0004 Å. Hematite nanoparticles produced through this direct spray precipitation initially exhibit a larger degree of peak broadening (Fig. 2 and Table 1) and as such values obtained for mean crystalline size for this method give smaller values than those calculated for standard precipitated samples (calculated using (104) peak) for the same calcination temperature. Both preparation methods also show a decrease in lattice parameters *a* with increasing calcination temperature above 500 °C (Fig. 2(d)), while c shows a steady decrease with increasing temperature for the samples prepared though standard precipitation. Lattice parameter *c* stays roughly constant for samples obtained through spray precipitation.

Table 1 shows that at low sintering temperature, the use of direct spray precipitation results in particles with a much higher specific surface area, which is $166 \text{ m}^2 \text{ g}^{-1}$ for a mean crystalline size of 10 nm, compared to $55 \text{ m}^2 \text{ g}^{-1}$ and 21 nm size for traditionally precipitated hematite nanoparticles. This is due to this temperature being sufficiently high enough to drive off entrapped water within the goethite structure [20]. As the annealing temperature increased, this property is quickly lost as thermally driven crystal growth engulfs the apparent nanoporosity, which can be seen through the inverse proportionality in Fig. 2 (c). This same porosity is not evident in the α -Fe₂O₃ nanoparticles formed through traditional precipitation. Scanning transmission images show that the mean crystalline size of nanoparticles formed through the precipitation method (Fig. 3(a) and (b)) is in good agreement with values calculated from the X-ray diffraction patterns. They also depict a reasonably uniform particle size distribution, with the morphology of these particles being spherical. However, precursor and calcinated samples formed through direct spray precipitation method (Fig. 3(c)-(f)) have the morphology of nanorods, a particle geometry which has been previously obtained through other methods of synthesis [21-23]. These nanorods have a diameter which agrees with the calculated mean particles sizes obtained through the use of Scherrer's formula on the (1 0 4) peak, while they have a length that is greater than 100 nm.

The large values obtained for specific surface area obtained from BET analysis for the 300 °C sample (Fig. 3(d)) can be explained from this morphology and the evident nanoporosity can be seen in the STEM images (Fig. 3(d)), which can be seen to become less apparent with an increase in firing temperature. It is a Download English Version:

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