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Synthesis and characterisation of cobalt hydroxy carbonate $Co_2CO_3(OH)_2$ nanomaterials

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ABSTRACT

In an attempt to make nanofibres based upon cobalt oxides, a novel compound hydrated cobalt hydroxy carbonate was formed. This compound is related to the minerals of the rosasite mineral group. X-ray diffraction (XRD) showed that the formed compound was a cobalt hydroxy carbonate, and scanning electron microscopy (SEM) displayed bundles of fibres on the micron scale in length and nanoscale in width. The morphology was compared with that of the rosasite mineral group. X-ray photoelectron spectroscopy (XPS) proved two bond energies for cobalt and three for oxygen in the compound. The compound was characterised by vibrational spectroscopy and the spectra related to minerals of the rosasite mineral group. The stability of the synthetic mineral was limited to temperatures below 200 °C.

1. Introduction

In recent years, synthesis of inorganic nanoscale materials with special morphologies has been of great interest in material science [1,2]. The intrinsic properties of nanoscale materials are mainly determined by their composition, structure, crystallinity, size and morphology [3]. In particular, one dimensional (1D) nanoscale inorganic materials including nanofibres, nanowires and nanotubes have attracted intensive interest due to their distinctive geometries, novel physical and chemical properties and potential applications in numerous areas [4]. Because of their high surface area, chemical and thermally stability and mesoporous properties, metal oxides have been extensively used as carrier and support for a variety of industrial catalysts at high temperature as well as low temperature. The oxides of cobalt can be employed as catalysts [5], adsorbents [6,7], composite materials [8,9] and ceramics [10–12].

Transition metal oxides are widely used in the field of heterogeneous catalysis. Cobalt oxide and its derived compounds are especially interesting due to their exceptional physical and chemical properties, which make them promising materials widely applied in rechargeable Li-ion batteries [13,14], gas sensing [15], catalysis [16,17], ionic exchangers [18], magnetic materials [19], etc. Cobalt oxide (Co_3O_4) is an important magnetic p-type semiconductor with an indirect bandgap of 1.5 eV [20]. Li et al. [21] reported in 2005 that Co_3O_4 nanotubes, nanorods, and nanoparticles can be used as the anode materials of lithium-ion batteries. Especially the Co_3O_4 nanotubes prepared with template displayed high discharge capacity and superior cycling reversibility and excellent sensitivity to hydrogen and alcohol. Cobalt oxyhydroxide (CoOOH) is considered as a nonstoichiometric oxyhydroxide and has more oxidation state (Co^{3+}) than Co_3O_4. In recent years, CoOOH has been applied as an alternative material for CO detection, to improve a Co_3O_4-based gas sensor. Geng et al. [22] synthesised the hierarchical dumbbell like CoOOH nanostructures, which have large active surface area and exhibited a superior sensitivity to CO at room temperature, as well as good reproducibility and short response/recovery time. These as-prepared CoOOH nanostructures could be potential nanosensors.

It is well known that intrinsic properties of inorganic materials are mainly determined by their composition, structure, crystallinity, size and morphology; great efforts have been devoted to investigation of different cobalt oxyhydroxide and cobalt oxides materials synthesis. It is reported that after 4-h calcination at 400 °C, one dimensional hierarchical Co_3O_4 nanocolumns were obtained from $Co(OH)_2$ prepared through one-step hydrothermal synthesis with hydrazine hydrate and Na_3PO_4 as morphology directing agents [23]. Yang and Sasaki [24] successfully synthesised CoOOH hierarchically hollow spheres by nanorods self-assembly through bubble templating. Cobalt oxides with novel structure can be controlled synthesised from suitable precursors. The present

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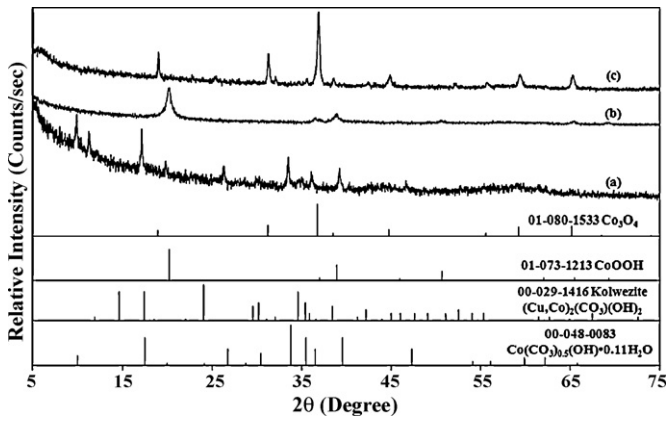

Fig. 1. XRD patterns of (a) synthesised cobalt hydroxy carbonate, (b) the oxidized product from cobalt hydroxy carbonate, and (c) the sample after thermal analysis up to 1000 °C; and their corresponding reference XRD patterns.

of carbonate in the synthesis process of cobalt hydroxide precursors can result unique morphology of the products. 3D sisal-like, dandelion-like and rose-like architectures of cobalt hydroxide carbonate were synthesised through a selected-control hydrothermal process [25]. As a precursor of Co_3O_4 nanorods for CO oxidation catalyst, nanorod-shaped cobalt hydroxide carbonate was obtained by the precipitation of cobalt acetate with sodium carbonate incorporating ethylene glycol [17]. Xu and Zeng [26] reported a detailed investigation on formation of cobalt basic carbonate compounds with dimensional and morphological controls. In this work, cobalt hydroxide carbonate with fibrous morphology was synthesised in the assistance of urea and Na_3PO_4.

The oxides of cobalt are also a crucial precursor in sol–gel technique for preparing high-purity and high-strength monolithic cobalt oxide ceramics for use as substrates for electronic circuits, abrasive grains, high-temperature refractory materials, fibres and thin films [27]. Since the resulting cobalt oxide prepared from a number of common chemicals can keep the original size and morphology after calcination, great efforts have been devoted to the investigation of nanoscale materials, especially 1D nanostructures, such as nanofibres and nanotubes [28,29]. In this work, attempts were made at synthesising nanofibres based upon the compounds of cobalt including cobalt oxides and cobalt carbonate. We report the synthesis and characterisation of nanofibres based upon cobalt hydroxy carbonate.

2. Experimental

Analytical grade $Co(NO_3)_2{\cdot}6H_2O$, $Na_3PO_4{\cdot}12H_2O$ and urea were used as precursors to prepare the cobalt hydrate carbonate precipitate. 2 mmol of $Co(NO_3)_2{\cdot}6H_2O$ and 19 mg $Na_3PO_4{\cdot}12H_2O$ were dissolved in 140 mL deionised water. The solution was kept stirring at the room temperature for 0.5 h, then 0.6 g urea was added in. After stirred for another 1 h, the mixture was transferred into an autoclave maintained at 100 °C for 18 h. The resultant light purple precipitate was washed with deionised water by filtrating. Dried at 65 °C for 2 days, half of the product was collected as sample (a), another half of the resultant sample was mixed with 30 mL deionised water, stirred to be suspension. After 4 mL of 8 M NaOH solution was added in, the suspension was then treated by adding 4 mL 30% H_2O_2 solution, keeping stirring at room temperature. Thirty minutes later, the mixture was transferred into an autoclave, which was then kept at 45 °C for 16 h. Finally, the treated precipitate was washed and dried at 65 °C for 2 days, collected as sample (b).

3. Characterisation

3.1. X-ray diffraction (XRD)

X-ray diffraction patterns were collected using a PANalytical X'Pert PRO X-ray diffractometer (radius: 240.0 mm). Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 40 kV and 40 mA, with Cu Kα radiation of 1.540596 Å. The incident beam passed through a 0.04 rad soller slit, a 1/2° divergence slit, a 15 mm fixed mask, and a 1° fixed antiscatter slit.

3.2. Scanning electron microscopy (SEM)

The specimens were mounted on SEM mounts with carbon tape and sputter-coated with a thin layer of gold. The scanning electron microscopy (SEM) images were taken with a FEI Quanta 200 operating at 30 kV (FEI Quanta 200 SEM, FEI Company, Hillsboro, OR, USA).

3.3. X-ray photoelectron spectroscopy (XPS)

Data were acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was Monochromatic Al Kα X-rays (1486.6 eV) at 150 W (15 kV, 10 mA) and at 45° to the sample surface. Photoelectron data were collected at take off angle of theta = 90°. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0×10^{-9} Torr and during sample analysis 1.0×10^{-8} Torr.

A small amount of each finely powdered sample was carefully applied to double sided adhesive tape on a standard Kratos Axis Ultra sample bar. This was attached to the sample rod of the Load Lock system for initial evacuation to $\sim 1 \times 10^{-6}$ Torr. The sample bar was then transferred to the UHV Sample Analysis Chamber (SAC) for collection of X-ray Photoemission spectra. All the spectra were referenced to the adventitious carbon of binding energy (BE) 285.0 eV. Spectra were subjected to a Shirley baseline. Various data handling procedures were carried out using the CasaXPS version 2.3.14 software.

3.4. Raman spectroscopy

Raman spectra were collected using an Olympus BHSM microscope, equipped with 10 and 50× objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge coupled device (CCD). Raman spectra were excited by a 633 nm laser at a resolution of 4 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

3.5. Infrared spectroscopy (IR)

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be