



## Tunable and rapid crystallisation of phase pure $\text{Bi}_2\text{MoO}_6$ (koechlinite) and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ via continuous hydrothermal synthesis

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### ABSTRACT

Herein, we report the rapid single step hydrothermal synthesis of phase pure  $\text{Bi}_2\text{MoO}_6$  (koechlinite) and  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ , via a continuous hydrothermal flow synthesis (CHFS) reactor, which uses supercritical water of 375–450 °C at a pressure of 24.1 MPa as a crystallising medium. The product being obtained as highly crystalline nano-materials with high surface area. Simple variation in synthesis condition and appropriate solution stoichiometry were shown to be sufficient to select the phase of the product. The materials synthesised showed significant photocatalytic activity towards the decolourisation of methylene blue in comparison to a commercial gold standard photocatalyst.

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### 1. Introduction

The controlled synthesis of nanomaterials (particles <100 nm in diameter) has attracted attention because of the relationship between properties and the dimensionality of materials [1,2]. The use of nanomaterials on an industrial scale is in its infancy, often being hindered by the limitations of current production methods [3]. Growing complexity and optimisation in synthesis methods has allowed for the controlled syntheses of high quality nano and bulk materials, especially in relation to heterometallic oxide systems [4,5]. Multi-component mixed metal oxide systems such as the bismuth molybdates, vanadates and tungstanates are of interest for catalytic processes including: amoxidation, oxidation and photocatalytic reactions [6].

Among the several multi-component mixed metal oxide systems, three phases of bismuth molybdate, namely  $\text{Bi}_2\text{MoO}_6$ ,  $\text{Bi}_2\text{Mo}_2\text{O}_9$  and  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ , have attracted considerable attention as catalysts, for which a number of synthetic protocols have been developed [7–11]. These methods typically involve post synthesis

treatment at elevated temperatures which can make it difficult to control particle morphology and size in the products.

Conventional batch hydrothermal methods offer relatively low temperatures, i.e. “softer” routes for the direct syntheses of many of these solids; relatively large amounts of material can be produced without large capital investment or complex synthesis procedures. Batch hydrothermal reactions of bismuth molybdates have been studied through both *ex situ* and *in situ* X-ray techniques, and recently through Raman spectroscopy [12–16]. This method generates high purity crystalline products with narrow particle size distribution. Typically, synthesis temperatures in the range 140–280 °C and reaction times in the range 3–12 h are used. In addition, judicious choice of reaction temperature, time, stoichiometry and pH are important for the controlled synthesis of specific phases.

Although batch processing methods are used widely both in academia and industry, it could be advantageous to produce bismuth molybdates via continuous methods which may allow generation of smaller particles (with higher surface areas) and perhaps greater control over particle size and shape. Continuous hydrothermal flow synthesis (CHFS) technology has recently gained interest as a direct, fast and controllable route to nanoceramic oxides as developed by the authors and others [17–22]. In the CHFS process, solutions of metal salts are typically pumped to

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meet a pH or chemical modifier feed (or another precursor feed) which is then brought into intimate contact with a supercritical water feed (typically at  $\leq 450$  °C and 24.1 MPa) in an engineered mixer [17]. As a result of the sudden change in conditions experienced by the metal salt feed (lower solubility and a hydrolysing and dehydrating environment), extensive nucleation occurs within fractions of a second and minimal particle growth occurs, with formation of crystalline nanomaterials, Fig. 1 [23]. The nanoparticles are continuously produced (after cooling) from the exit of the reactor as aqueous slurry. The potential for reaction parameters to be independently controlled within a CHFS reactor (flow rate, concentration, pH, co-solvent, temperature, pressure, etc.) offers a distinct advantage over conventional batch hydrothermal methods. The authors recently exploited the rapid crystallising nature of CHFS by developing high throughput CHFS methods (manual and automated) which can generate many different composition nanoceramics in a short time [21,24,25].

In this communication, we describe the rapid and direct synthesis of phase pure  $\text{Bi}_2\text{MoO}_6$  (koechlinite) and  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  nanoparticles in a CHFS reactor. The products were synthesised using solutions of acidified bismuth nitrate and a basic solution of molybdic acid, each of which were pumped at  $10 \text{ mL min}^{-1}$  in the reactor and had been diluted to achieve the desired metal stoichiometries (i.e. either a 2:1 or 2:3 atomic ratio of Bi:Mo). The slurries obtained from the CHFS process were cleaned and freeze-dried prior to analysis. The materials were obtained as yellow powders in yields of ca. 82% and 86% for the attempted synthesis of  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  and  $\text{Bi}_2\text{MoO}_6$  (koechlinite), respectively.

## 2. Experimental

### 2.1. Materials synthesis

Bismuth nitrate [ $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 98.3%] and molybdic acid [ $\text{H}_2\text{MoO}_4$  (80%  $\text{MoO}_3$  by weight), 99.0%] were supplied by Sigma–Aldrich Chemical Company (UK). Ammonium hydroxide solution ( $\text{NH}_4\text{OH}$ , 30% w/w) supplied by VWR was used to adjust the pH of the  $\text{H}_2\text{MoO}_4$  solution prior to reaction. 0.014 M  $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution

and 0.014 M molybdic acid solution or 0.014 M  $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution and 0.028 M molybdic acid solution were used (for Bi:Mo molar ratio: 2:1 or 2:3, respectively). Both reagent solutions were pumped at  $10 \text{ mL min}^{-1}$  and water was pumped through the heater at  $20 \text{ mL min}^{-1}$  and preheated to 450 or 375 °C in a CHFS system described previously (Fig. 1) [17]. A T-piece was used to premix the bismuth and molybdenum sources before meeting the superheated water feed (T in Fig. 1). An initial precipitate is formed *in situ* at pH 4 once the solutions are mixed. This precipitate was then brought into contact with a supercritical water feed being pumped at  $20 \text{ mL min}^{-1}$  at  $\leq 450$  °C and 24.1 MPa in an engineered mixer (R in Fig. 1), resulting in rapid crystallisation of the respective products. Nanoparticulate suspensions of bismuth molybdate were collected at the exit of a back-pressure regulator after cooling and filtration (via a  $7 \mu\text{m}$  inline filter to remove any large agglomerates). The flow of cooling water was set to  $30 \text{ g h}^{-1}$  with an inlet temperature of 10 °C, the capacity of the external jacket was  $141.7 \text{ cm}^3$ . The tubing and fittings were all 316SS Swagelok. After collection, the particles were centrifuged at  $4500 \text{ rev s}^{-1}$  for 30 min several times. The solids were freeze-dried for 22 h at  $1.3 \times 10^{-7}$  MPa after first freezing the slurry at  $-40$  °C.

### 2.2. Materials characterisation

Freeze–drying was performed using a Virtis freeze dryer. BET surface area measurements (using  $\text{N}_2$  gas), were performed on a Micromeritics ASAP 2420 analyser; powders were degassed at 150 °C overnight prior to analysis. A JEOL 3000F Transmission Electron Microscope (300 kV accelerating voltage) was used for generating images of particles, particles were suspended on carbon coated copper grids (Holey Carbon Film, 300 mesh Cu, Agar Scientific, UK). The suspension procedure involved dispersing the dried powders in methanol and ultrasonication for 10 min. XRD patterns were collected on a Bruker D4 diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) over the  $2\theta$  range  $10$ – $80^\circ$  with a step size of  $0.02^\circ$  and a count time of 1 s. The applied Raman microscope system (Renishaw In Viva™) consisted of a light microscope (Leica DL-LM; Olympus BX) coupled to a Raman spectrometer with a laser excitation wavelength of 785 nm. The microscope was equipped with a  $50\times$  objective (N-Plan). The microscope optics were used to focus the laser beam onto the sample and to collect the scattered light to a focus of approximately  $10 \mu\text{m}^2$ . The Rayleigh scattering component was removed using a notch filter. The instrument was calibrated against the Stokes Raman signal of pure Si at  $520 \text{ cm}^{-1}$ .

### 2.3. Photocatalytic activity testing

The photocatalytic activities of the bismuth molybdates were evaluated by degradation of methylene blue (MB) under a mixture of UV and visible light (400 W high pressure Hg discharge lamp). A frosted glass screen (First Mirrors, Bow, London, UK) which was 23 cm in diameter and 0.4 cm thickness was used as a light diffuser. The light energy entering the samples was measured using a photon meter (Photon Control, Cambridge, UK) which indicated a total irradiance of  $20 \text{ mW cm}^{-2}$  [26]. The reaction cell (Duran 50 ml beakers) was wrapped by tinfoil and the diffuser was placed on the top to provide uniform irradiation. In each experiment, 0.1 g of the powder products were added into 50 mL MB solution ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ). Prior to irradiation, the suspensions were magnetically stirred in the dark for 8 h to achieve absorption–desorption equilibrium. The suspensions were then exposed to visible light irradiation and aliquots of 5.0 ml were removed at hourly time intervals for 5 h. Analogous control experiments were performed without catalysts (MB alone). The suspension including the product powders were centrifuged and the absorption spectra of the samples were recorded using an Ocean Optics

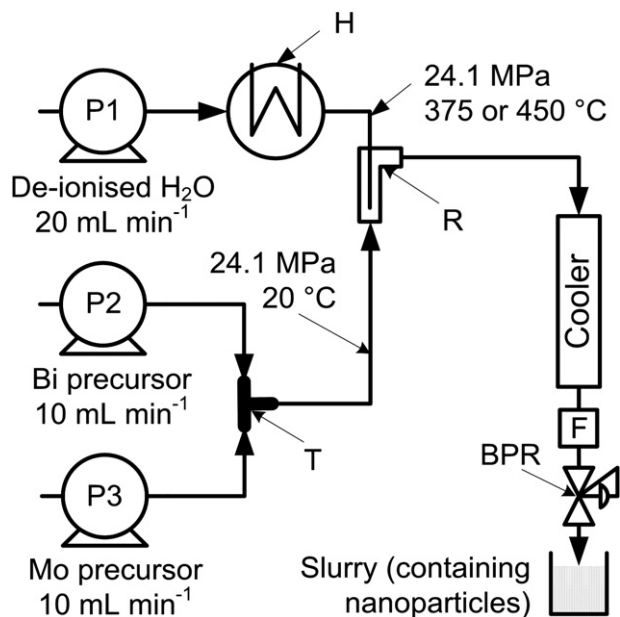


Fig. 1. Schematic of the three pump continuous hydrothermal system used for the synthesis of bismuth molybdate. Key: P = pump, H = heater, BPR = back-pressure regulator, R = counter-current mixer, T = T-piece mixer and F =  $7 \mu\text{m}$  filter.

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