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Growth of $BiVO_4$ particles in cellulosic fibres by in situ reaction

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Abstract

Cellulosic fibres were used to obtain well-defined $BiVO_4$ particles using a simple controlled precipitation method; microscopy analysis suggests that the $BiVO_4$ particles grow from nucleation sites located in the cell wall structure and inside the lumen of fibres.

Keywords: Bismuth vanadate; Pigments; Cellulosic fibres

1. Introduction

The development of synthetic strategies to grow crystalline particles of controllable structure and morphology is an important goal in inorganic chemistry with important implications in mineral pigments and fillers technology [1]. For example, the size and morphology of inorganic fillers used in the papermaking process has a strong impact on the microstructure and optical properties of paper [2]. We have recently reported a chemical method which allows the synthesis of morphologically well-defined $BiVO_4$ particles on glass substrates, at mild temperatures [3]. We show in this study that the method is advantageous and can be adopted to produce $BiVO_4$ particles of well-defined morphology using cellulosic fibres as substrates.

For some applications, $BiVO_4$ pigments have been used as an interesting alternative to cadmium and lead pigments which have been associated with potential toxicity issues. To the best of our knowledge, $BiVO_4$ pigments have not been investigated as colorants in paper materials. One of the reasons may be due to the fact that this pigment is expensive compared to traditional yellow pigments. However, it is a high performance brilliant pigment with good gloss and hiding power. The simple synthetic method described here shows that cellulosic fibres can be coloured in situ with a yellow pigment which has a very good chemical resistance. The method is easily scaled up. Moreover, the results presented here suggest that the cellulosic fibres are capable of influencing the nucleation and crystal growth of $BiVO_4$ microparticles. This opens up the possibility to use this approach to exercise control in the crystallization of particles of other inorganic compounds.

2. Experimental

2.1. Synthesis

All chemicals, except celluloses, were supplied by Aldrich and used as received. Wood cellulose fibres (*Eucalyptus globulus*, ECF bleached kraft pulp, composed essentially of cellulose (~85%) and glucuronoxylan (~15%)) supplied by Portucel (Portugal) were disintegrated and washed with distilled water before use. Cellulose powder (for thin layer chromatography applications) was supplied by Riedel-de Haën. A typical chemical bath to grow $BiVO_4$ particles in cellulosic

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fibres was prepared as follows. To a buffer phosphate solution (7.5 cm^3) was added 1.25 mmol of $Bi(NO_3)3\cdot 5H_2O$ and 2.50 mmol of EDTA. This mixture was stirred during 5 min and then 2.50 mmol of $NaVO_3$ and 0.25 g of cellulosic fibres were added to the suspension. The pH was adjusted to 7 using an aqueous solution of NaOH 1 mol dm^{-3}. The mixture was then refluxed over 8 h. The fibres are collected by filtering and are thoroughly washed with distilled water. A laboratory sheet of paper was prepared with cellulosic fibres containing $BiVO_4$ particles, using a conventional sheet former (vacuum filtration of an aqueous suspension of fibres through a forming wire of 70 μm size, followed by mechanical pressing and air drying).

2.2. Characterization

The visible diffuse reflectance spectra of the materials were recorded on a Jasco V-560 UV/vis spectrophotometer, using MgO as the reference. FT-IR spectra were measured from KBr disks (Aldrich, 99%+, FT-IR grade) on a Matson 700 FTIR spectrometer. Raman spectra were recorded using a Bruker RFS100/S FT-Raman spectrometer (Nd:YAG laser, 1064 nm excitation). Thermogravimetric analyses (TGA) were carried out using a Shimadzu TGA-50, with a heating rate of 10 °C/min. X-ray powder diffraction (XRD) was performed, using a Philips X'Pert instrument operating with Cu-K$_\alpha$ radiation ($\lambda = 1.54178$ Å) at 40 kV/50 mA. Scanning electron microscopy (SEM) images were obtained using a FEG-SEM Hitachi S4100 microscope operating at 25 kV.

3. Results and discussion

The thermal treatment (85 °C) of an aqueous solution containing $Bi(NO_3)_3$, $NaVO_3$ and ethylenediaminetetraacetate (EDTA) yields the solid $BiVO_4$. EDTA acts as a chelating agent to avoid spontaneous formation of $BiVO_4$ at room temperature. The thermal treatment of a chemical bath with a similar composition in which cellulosic fibres have been previously introduced produces a fibrous composite of $BiVO_4$/cellulose. The resulting fibres have sufficient strength to be processed into a sheet of paper. An aqueous suspension of the composite fibres was prepared under vigorous mechanical agitation, followed by vacuum filtration to obtain a coloured sheet of paper containing 38.5% (w/w) of $BiVO_4$. The paper showed a visible reflectance spectrum typical of monoclinic-$BiVO_4$ prepared by conventional procedures (Fig. 1). After the fibres have been processed into a sheet, the remaining aqueous solution was colourless, showing that the $BiVO_4$ particles have been strongly retained by the fibres.

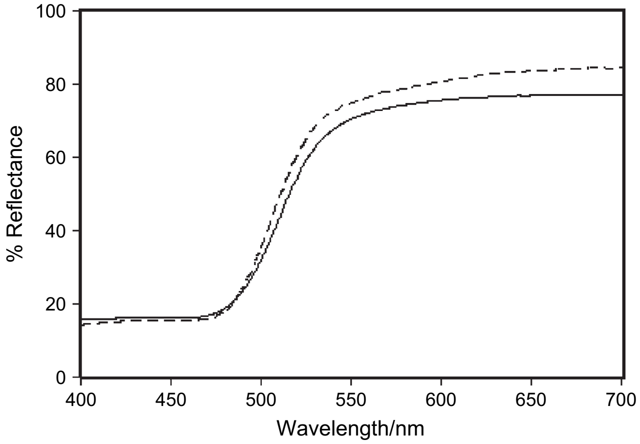

Fig. 1. Visible reflectance of a sheet of paper containing $BiVO_4$ particles (full line) and monoclinic $BiVO_4$ pigment (dashed line).

The $BiVO_4$ monoclinic phase in the composite was identified by X-ray powder diffraction and Raman spectroscopy [4]. The infrared spectra of both the composite and cellulosic fibres were identical showing that no chemical degradation of the cellulose had occurred. The $BiVO_4$ content could be varied by changing the relative amounts of $Bi(NO_3)_3$ and $NaVO_3$ used in the synthesis.

In a control experiment, in which chemical microcrystalline cellulose was used in the synthesis, instead of wood cellulose fibres, optical microscope images showed that the $BiVO_4$ particles did not attach to the cellulose. This suggests that the structure and composition of the cellulosic substrate is determinant in the synthesis efficiency. Several optical microscope images of the composite material showed an even distribution of $BiVO_4$ particles on the cellulosic fibres, revealing a rather uniform composite material. A typical microscope image showing cellulosic fibres covered with $BiVO_4$ particles with a detail on a vessel cell is shown in Fig. 2. It is unlikely that this microstructure homogeneity

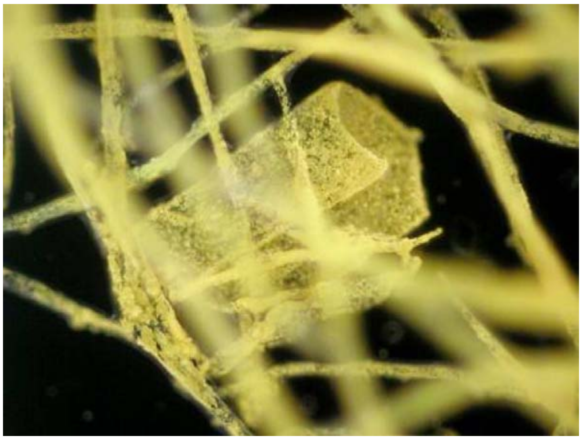

Fig. 2. Optical microscope image of cellulosic fibres/$BiVO_4$ showing a vessel cell in the centre (20×).

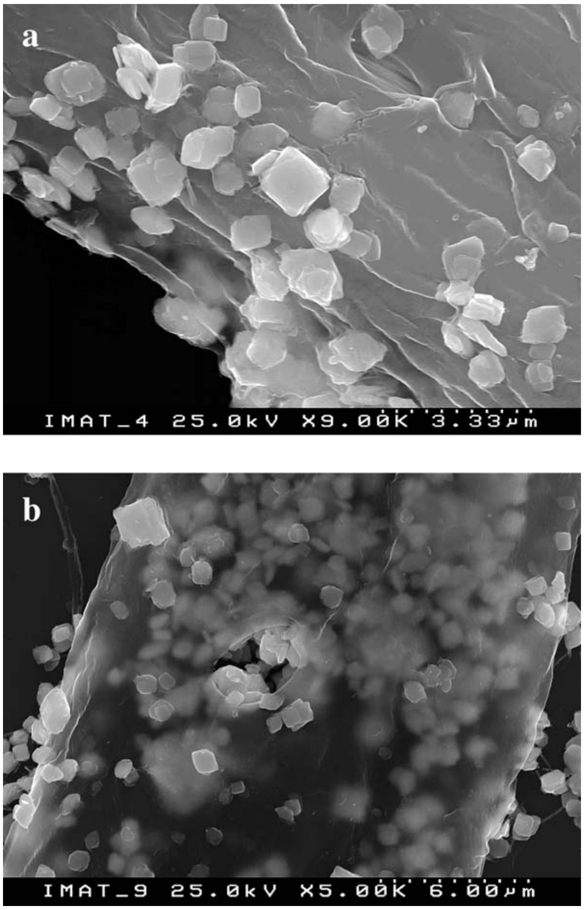

Fig. 3. SEM images of cellulosic fibres containing $BiVO_4$ particles.

would be attained without the cellulosic fibres acting as nucleation substrates. This means that the $BiVO_4$ particles were generated in the reaction mixture via a heterogeneous nucleation process. In fact, the scanning electron microscopy images of the fibres show plate-like micron sized $BiVO_4$ particles attached not only to the surfaces of the cellulosic fibres, but also in their internal structure (Fig. 3). SEM images suggest that this internal deposition is occurring in the lamellar structure of the fibrous cell wall [5], probably between the thin outer secondary cell wall (S1) and the inner secondary cell wall (S2 + S3) (Fig. 3a). It may be suggested that the presence of a fraction of amorphous glucuronoxylan [6] in the wood fibre cell walls may play a key role in the process: carboxyl groups in glucuronic acid moieties, by complexing Bi^{3+} species, could function as nucleation sites of $BiVO_4$. This hypothesis will be checked in our future investigations. The precipitation may also occur in void lumen of fibres, as shown in the case of thin walled parenchyma cells (Fig. 3b). Energy dispersive X-ray mapping of individual particles in Fig. 3 confirmed that they consisted of bismuth vanadate.

It is well known that dyeing of cellulosic fibres has been accomplished using several organic colorants. The use of inorganic pigments for this purpose has been less investigated and, in principle, can open up other possibilities in the application of coloured cellulosic fibres. From these results, it can be anticipated that $BiVO_4$/cellulose fibres may find interesting applications in painting and coating applications, the cellulose fibres acting as support and dispersing agent for the pigment and, simultaneously, modifying the rheology of the product. Other applications for $BiVO_4$ containing fibres may include pigment carriers in the production of coloured papers and fillers for fibrous polymer composites.

Acknowledgements

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