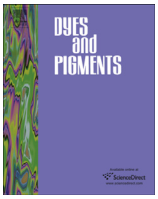
Dyes and Pigments 128 (2016) 49–53

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Facile preparation of highly cost-effective $BaSO_4@BiVO_4$ core-shell structured brilliant yellow pigment

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ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form
12 November 2015
Accepted 4 January 2016
Available online 15 January 2016

Keywords:
Core-shell architecture
Yellow pigment
Color coordinate
Sol–gel method
Reflectance spectra
Bismuth vanadate

ABSTRACT

$BiVO_4$ as an environmentally-friendly yellow pigment has been received increasing attention over the past two decades. Unfortunately, the relatively high cost hinders its large-scale applications. Herein, core-shell structured $BaSO_4@BiVO_4$ yellow pigments with a mean particle size of 193 nm were successfully synthesized, in which the $BiVO_4$ coating has a pure monoclinic scheelite structure and a thickness of ~5 nm. It is found that the appropriate particle size and monoclinic scheelite $BiVO_4$ coating give this pigment a brilliant greenish-yellow color. For the $BaSO_4@BiVO_4$ micro-composite loaded with 16.3 wt.% $BiVO_4$, its color coordinate L^* and b^* values can reach up to 76.53 and 75.46, much higher than the corresponding values 64.50 and 60.11 of pure $BiVO_4$. Consequently, our strategy can save at least 83.7 wt.% $BiVO_4$ without any detriments to color properties and also shows great potential in cutting down the cost of other expensive pigments.

1. Introduction

Pigments could be classified into two categories: inorganic pigments and organic pigments [1]. Inorganic pigments have a lot of applications in manufacturing porcelains, ceramic tiles, enamels, paints, rubber, imitation leather, varnishes, building materials, and floor coverings, owing to their superior acidic-alkali resistance, weather resistance, thermal stability and hiding power [2–5]. Specifically, yellow pigments are of particular importance and widely used for road markings due to their high visibility [1]. However, the most popular and excellent conventional yellow pigments such as chrome yellow ($PbCrO_4$) and cadmium yellow (CdS) contain toxic elements Pb, Cr and Cd, which have negative effects on people's health and the environment [6]. For maintaining socially sustainable development, more and more countries and international organizations have released laws to strictly confine the utilization of Pb, Cr and Cd, especially in products that have direct contact with human body. Therefore, a number of countries have invested considerable manpower and financial resources into the study of new environmentally-friendly yellow pigments [2,7–11].

$BiVO_4$ (BVO) with greenish-yellow hue is a relatively new non-toxic yellow pigment that has drawn increasing attention over the past two decades and is capable of substituting iron yellow, chrome yellow, cadmium yellow, nickel titanium yellow and chromium titanium yellow [2,4,12]. It should be noted that the photophysical properties and visible light absorption of BVO are strongly influenced by its crystal structure. There are three polymorphs for BVO: tetragonal zircon (*t-z*), monoclinic scheelite (*m-s*), and tetragonal scheelite (*t-s*), among which the *m-s* phase has the highest color intensity and exhibits vivid yellow. In the meantime, *m-s* BVO with a narrower direct bandgap of ~2.4 eV is also one of the most promising photocatalysts for toxic organic degradation, which gives BVO based yellow pigments potential ability to relieve air pollution [13–15]. In addition, *m-s* BVO based yellow pigments usually exhibit excellent near-infrared radiation (NIR) reflectance (>90%), which is able to reduce the IR-induced heat build-up effectively and thus conserve the source of energy [3,4]. Therefore, BVO with *m-s* structure is of particular importance as one yellow pigment and is also the most extensively studied one.

Up to date, a lot of work has been done to improve the color properties, weather resistance, NIR reflectance, chemical resistance and irradiation stability of BVO [2–4,16–18]. For example, N. Imanaka et al. introduced Ca, Zn and La elements into BVO to pursue yellow pigments with higher yellow chromaticity and richer yellow

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http://dx.doi.org/10.1016/j.dyepig.2016.01.013
0143-7208/

hue so as to replace other toxic pigments (i.e. $PbCrO_4$, CdS) [2,16,17]. P. Rao et al. developed high NIR reflecting “cool yellow pigment” by adding Y/Nb and Ta/P to BVO [3,4]. S. E. Pratsinis et al. reported the coating of SiO_2 on BVO to achieve thermally stable yellow pigments for coloring plastics [18]. As a result, a sequence of lead-free and chromate-free BVO based compounds had been developed and used to manufacture brilliant yellow pigments with good gloss and hiding power. However, there is still a big obstacle on the way of the large-scale application of these BVO based yellow pigments, which is the high cost, and very few researches ever focused on this aspect.

According to the core-shell doctrines, the pigment particles can be divided into two parts, the kernel layer and the shell layer. It is well-known that the color properties of pigments are mainly determined by the shell part instead of the core part [19–21]. Therefore, the application of core-shell structure will be a promising way to reduce the high cost of BVO based yellow pigments if it does not bring any detrimental effect or even bring good effect on the color performances. This strategy has been successfully used in cutting down the cost of TiO_2 white pigment by replacing the core part with cheaper $BaSO_4$ (BSO) [22–24]. Hence, it is quite valuable to develop BVO coated BSO yellow pigments and investigate their color properties.

In this work, BSO as one common, stable and much cheaper raw material is employed to be the core component of our pigments. BSO@BVO core-shell structured yellow pigments were successfully synthesized with a facile sol-gel method followed by one-step sintering. The morphology, elements distribution, crystal structure and particle size distribution were characterized in detail. The color properties of the as-prepared BSO@BVO yellow pigments were analyzed systematically using CIE $L^*a^*b^*$ system. It is found that nearly all color parameters for BSO@BVO samples are enhanced compared with those of pure BVO.

2. Experimental

2.1. Synthesis of $BaSO_4$@$BiVO_4$ core-shell yellow pigments

All chemicals are of analytical grade and used as received without further purification. A typical synthesis procedure of BSO@BVO core-shell composite yellow pigments is made up of two steps, one is BVO precursor preparation and the other one is BVO and BSO incorporation. In the preparation of 0.2 M BVO precursor, 20 mmol $Bi(NO_3)_3\cdot 5H_2O$ and threefold citric acid (60 mmol) were mixed and dissolved in 80 ml N,N-dimethylformamide under continuous stirring. After the solution was limpid, 20 mmol NH_4VO_3 was slowly added into the solution under vigorous stirring until the color of the suspension became green. Subsequently, 20 ml concentrated nitric acid was added drop by drop to make the suspension become a limpidly mazarine solution by constant stirring and 0.2 M BVO precursor solution was formed in the end. Likewise, 0.4 M, 0.6 M and 0.8 M BVO precursor solutions could be obtained simply by changing the amount of chemicals with the same process. In the second step, 100 g BSO together with ethanol were ball-milled using planetary ball mill for 12 h to obtain uniform and smaller sized BSO particles. Then 100 ml BVO precursors with various concentration were added into the dried BSO particles. The as-obtained mixture was mechanically stirred for 4 h to form a homogeneous slurry. The slurry was then kept at 120 °C for 0.5 h and 180 °C for 12 h to get BSO@BVO xerogel. Afterwards, the claybank BSO@BVO xerogels were sintered in a muffle furnace at 500 °C for 2 h with an increasing rate of 10 °C/min and cooled down to room temperature naturally. After another 2 h ball-milling, BSO@BVO core-shell structured yellow pigments loaded with different amount of BVO were finally obtained and were denoted hereafter as BSO@BVO-1 (0.2 M), BSO@BVO-2 (0.4 M), BSO@BVO-3 (0.6 M) and BSO@BVO-4 (0.8 M).

2.2. Characterization

Morphologies of BSO@BVO pigments were observed with a field emission transition electron microscope (JEM 2100F) with an acceleration voltage of 200 kV. Phase structure were determined by powder X-ray diffraction (XRD) analysis (Rigaku D/MAX255ovl/84, Cu K_α radiation) from 15° to 60° (2θ) at a scan rate of 4°/min under 35 kV and 200 mA. The color properties of all the prepared samples were evaluated in terms of the CIE 1976 $L^*a^*b^*$ system using a colorimeter (Data Color 600S). In this system, L^* represents the lightness axis ranges from 0 (black) to 100 (white), a^* is the red-green axis and b^* means the yellow-blue axis. C_{ab} (chroma) stands for saturation of color and h_{ab} represents the hue angle. The chroma is defined as $C_{ab} = [(a^*)^2 + (b^*)^2]^{1/2}$ while the hue angle can be calculated via $h_{ab} = \arctan(b^*/a^*)$. It should be noted that h_{ab} is expressed in degrees and ranges from 0 to 360° [25]. Reflectance spectra was also recorded with Data Color 600S. The band gap energies of the samples were determined from the absorption edge of the absorbance spectra represented by the Kubelka–Munk function, $f(R)=(1-R)^2/2R$, where R was reflectance [26]. The particle size distribution of the composite pigments is measured using Mastersizer 2000E Laser Diffraction Particle Size Analyzer in water medium with calgon as the dispersant.

3. Results and discussion

It is well-known that for pure BVO yellow pigment, *m-s* phase is the most desired phase, so is for the BVO shell of BSO@BVO composite yellow pigments. Therefore, XRD characterization was carried out to make sure whether *m-s* BVO has been attached to BSO core successfully. Fig. 1 summarizes the XRD patterns of pristine BSO powders, pure BVO and BSO@BVO-3 yellow pigments. All the diffraction peaks detected in pure BVO could be well assigned to *m-s* phase with a space group of *I2/a* (JCPDS card no. 140688) and no signals of impurities are observed. From the comparison of the XRD pattern of BSO@BVO-3 with those of pure BVO and pure BSO, it is found that only *m-s* phase BVO and pristine BSO are detected in BSO@BVO-3 pigment. Green blocks in Fig. 1 are used to mark the diffraction peaks of BVO out of those of BSO. It is worth noting that the intensity of (121) diffraction peak of BVO shell in BSO@BVO-3 yellow pigment is almost equivalent to the corresponding peak of

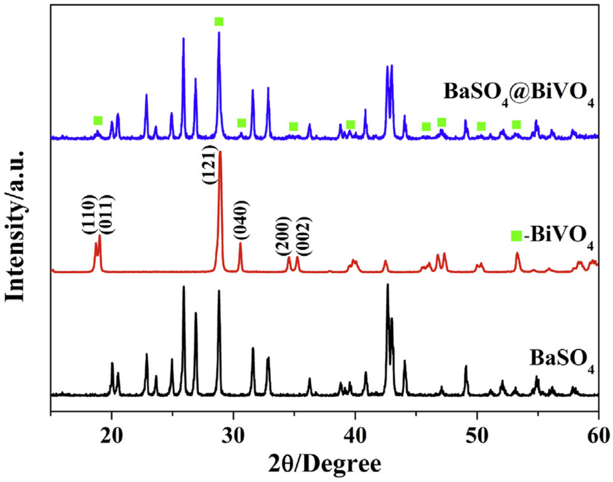

Fig. 1. XRD patterns of pristine $BaSO_4$ (black line), pure $BiVO_4$ (red line) and $BaSO_4$@$BiVO_4$-3 core-shell structured yellow pigment. The $BiVO_4$ peaks in the composite yellow pigment is indexed with blue square. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)