Processing and Application of Ceramics 16 [4] (2022) 335–340

https://doi.org/10.2298/PAC2204335Z

Facile synthesis of high colour rendering $BiVO_4$ yellow pigment via self-propagating combustion method

Xiaojun Zhang[1,*], Wen Li[2], Weihui Jiang[1,2,*], Yanqiao Xu[1], Jian Liang[1], Qian Wu[1], Lifeng Miao[1]

[1]*National Engineering Research Center for Domestic & Building Ceramics, Jingdezhen Ceramic Institute, Jingdezhen 333000, China*

[2]*School of Material Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333000, China*

Received 10 May 2022; Received in revised form 20 September 2022; Accepted 10 October 2022

Abstract

High colour rendering bismuth vanadate ($BiVO_4$) pigments were successfully synthesized by self-propagating combustion method at low temperature (200 °C). Interestingly, the addition of citric acid as a fuel was beneficial to the formation of well-dispersed olive-like $BiVO_4$ particles with the size around 730 nm. Furthermore, the as-prepared pigments also exhibited high purity m-$BiVO_4$ phase and brilliant yellow hue (b = 78.12), which is better than that of previously reported in literature and commercially available $BiVO_4$ yellow pigments. Importantly, the pigments were applied in various substrates (PMMA, glass and ceramics), and showed excellent colour rendering, dispersion properties, thermal and chemical stability, indicating its potential application in the high-grade plastic, glass and ceramic-ware decoration.*

Keywords: *pigment, yellow, bismuth vanadate, self-propagating combustion method, colouration mechanism*

I. Introduction

Owing to their high covering power, excellent weather resistance and thermal stability, inorganic pigments consisting of complex metal oxides have been widely utilized in plastics, glass, ceramic tiles, paints, rubber, vehicles and inks [1,2]. Specially yellow as a caution colour is employed to be served as the background colour of traffic and road markings due to its brilliant hues and high level of visibility [3,4]. Unfortunately, most conventional yellow pigments contain toxic heavy metals (Pb, Cd, Cr and Sb), such as cadmium yellow (CdS), chrome yellow ($PbCrO_4$, $BaCrO_4$) and Naples yellow ($Sb_2Pb_3O_8$), which severely limits their application because they are hazardous to environment and health [5]. Thus, it is necessary to develop environmentally friendly and less toxic inorganic yellow pigments [6].

Bismuth vanadate ($BiVO_4$), as a chromate- and lead-free inorganic yellow pigment, has been widely applied in plastics, coatings, food, traffic signs and inks due to its brilliant yellow hue and gloss, excellent weather resistance and environmental benignity [7]. Among three crystalline structures of $BiVO_4$, monoclinic scheelite-type $BiVO_4$ (m-$BiVO_4$) presents vivid yellow colour, which also has been recognized as a promising photocatalyst under visible light with a narrow band gap of 2.4–2.5 eV [8]. Hence, m-$BiVO_4$ has become one of the most popular and common yellow pigments on the market, which increasingly attracts much attention of researchers [9]. At present, several methods have been used to synthesize $BiVO_4$ pigment, such as solid-state reaction [10,11], hydrothermal method [12,13], chemical bath deposition method (CBD) [14], sol-gel method [15], non-hydrolytic sol-gel method (NHSG) [16], etc. Sameera *et al.* [11] prepared $BiVO_4$ yellow pigment by a solid-state reaction of Bi_2O_3 and V_2O_5 calcined at 800 °C for 6 h, which showed the reddish-yellow hue, as $L^* = 65.79$, $a^* = 14.29$, $b^* = 52.57$. Zhang *et al.* [12] also synthesized the m-$BiVO_4$ pigment via a hydrothermal method heated at 200 °C for 1.5 h, which exhibited a greenish-yellow hue, as $L^* = 91.64$, $a^* = -2.45$, $b^* = 63.07$. In our previous work [16], we prepared $BiVO_4$ pigment via a facile NHSG process in alcohol/dibasic

*Corresponding author: tel: +86 0798 8499162
e-mail: *zhangxiaojun@jci.edu.cn* (X. Zhang)
jiangweihui@jci.edu.cn (W. Jiang)

esters system at 400 °C, which exhibited brilliant yellow hue, as L^* = 74.83, a^* = −0.34, b^* = 71.18. Nevertheless, the high synthesis temperature, complicated procedure, low purity, easy agglomeration and impure colour severely restricted the large scale industry application of $BiVO_4$ yellow pigments.

Particularly, the self-propagating combustion (SPC) method has been widely used to synthesize homogeneous and fine crystalline composite oxides, because it requires only simple equipment, low process temperature and short time consumption. This method was also applied to synthesize some inorganic pigments, such as nanosized $CaAl_{12}O_{19}$ green pigment, $CoAl_2O_4$ and $Zn_{0.9}Co_{0.1}Al_2O_4$ blue pigments [17–19]. To date, there are little studies about the synthesis of $BiVO_4$ yellow pigment via SPC method. Therefore, a template-free SPC method was proposed to synthesize well-dispersed olive-like m-$BiVO_4$ pigment with high colour intensity at low temperature. The phase composition, morphology and colouristic properties of $BiVO_4$ pigment were studied, and the corresponding synthesis mechanism was also proposed. Moreover, the colour stability of the synthesized $BiVO_4$ pigment for application in polymethyl methacrylate (PMMA) plastic, glass and ceramic tiles was also investigated.

II. Experimental

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5\,H_2O$, 99%, Shanghai Aladdin Co. Ltd, China) and ammonium metavanadate (NH_4VO_3, 99%, Shanghai Aladdin Co. Ltd, China) were used as starting materials without further purification. Citric acid ($C_6H_8O_7 \cdot H_2O$, 99.5%, Shanghai Aladdin Co. Ltd, China) was used as a fuel. The high colour rendering $BiVO_4$ yellow pigments were synthesized using SPC method. In the first step two solutions were prepared. The solution A by dissolving $Bi(NO_3)_3 \cdot 5\,H_2O$ and $C_6H_8O_7 \cdot H_2O$ in 30 ml of 1 M HNO_3 solution and the solution B by dissolving NH_4VO_3 also in 1 M HNO_3 solution. Then the V^{5+} containing solution B was added into the solution A, while adjusting molar ratios n(citric acid) : $n(Bi^{3+})$: $n(V^{5+})$ = 1 : 1 : 1, and magnetically stirred for 15 min. $NH_3 \cdot H_2O$ as pH regulator was employed to adjust pH value of mixture solution to 7. After stirring for about 30 min, the $BiVO_4$ precursor solution was heated to 90 °C to evaporate the water, followed by combustion at 200 °C. As a consequence, nanosized $BiVO_4$ yellow pigments were successfully obtained.

The crystalline phases of the pigments were characterized by X-ray diffraction (XRD, Bruker D8 Advance) and Raman spectrometer (inVia, Renishaw, UK). The morphology and size of the samples were observed by scanning electron microscope (SEM, JSM-6700F) and high-resolution transmission electron microscopy (HRTEM, JEM-2010). UV-Vis diffuse reflectance spectra were measured on a UV-Vis spectrophotometer (Lambda 850) in the wavelength range of 380–900 nm. The colour properties of pigments were measured with a colorimeter (WSD-3C, L^*, lightness, 0 for black and 100 for white; a^*, red (+)/green (−) axis; b^*, yellow (+)/blue (−) axis).

III. Results and discussion

Figure 1a presents XRD patterns of the $BiVO_4$ pigments prepared with and without citric acid as a fuel. It can be seen that all of the diffractions in each XRD pattern could be well indexed to monoclinic scheelite $BiVO_4$ (JCPDS 14-0688) with characteristic diffraction peaks at 19.02, 28.90, 30.46, 34.42, 35.11, 40.16, 42.43, 46.64, 47.23 and 53.26°, which are assigned to (011), (121), (040), (200), (002), ($\bar{1}$12), (051), (240), (042) and (161) planes, respectively. It indicates that the addition of the fuel citric acid does not change the monoclinic structure of $BiVO_4$. It is worth noting that the relative diffraction intensities ratios between 040 and 121 peaks (I_{040}/I_{121}) reduce gradually with the addition of

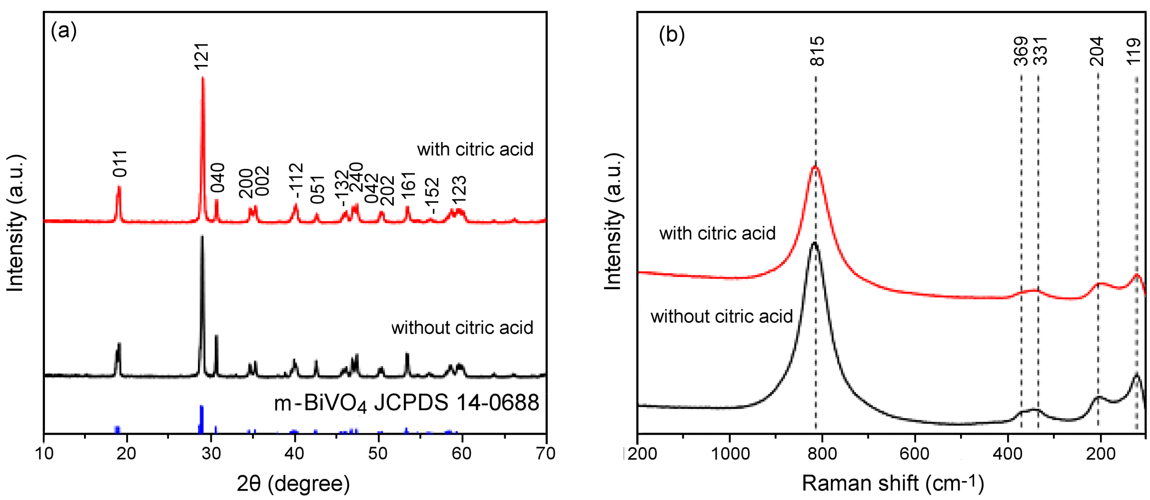

Figure 1. XRD patterns (a) and Raman spectra (b) of the $BiVO_4$ pigments prepared by SPC method with and without the addition of citric acid

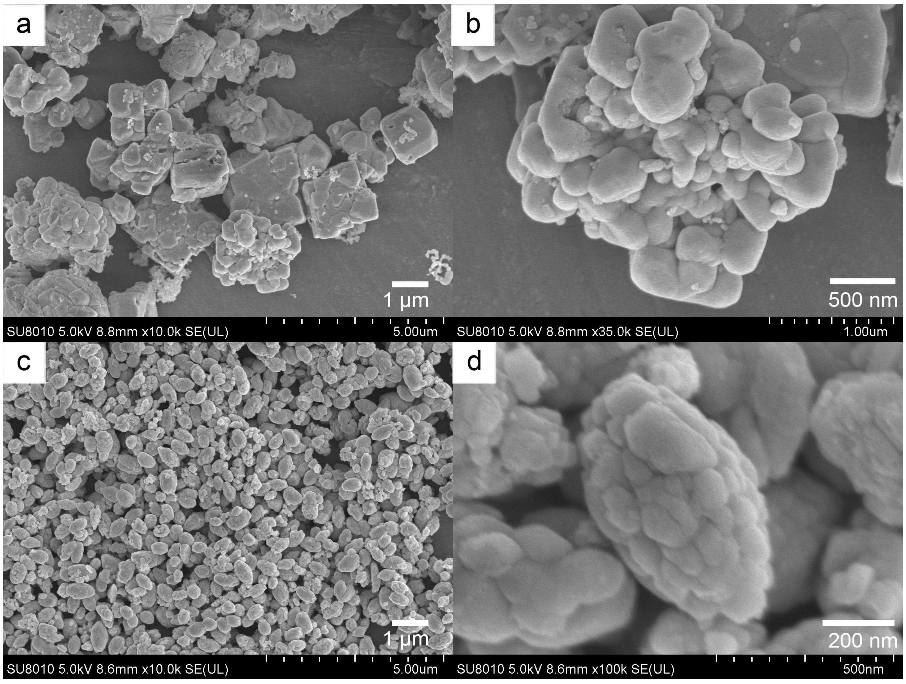

Figure 2. SEM images of the $BiVO_4$ pigments prepared by SPC method: without (a,b) and with (c,d) the addition of citric acid

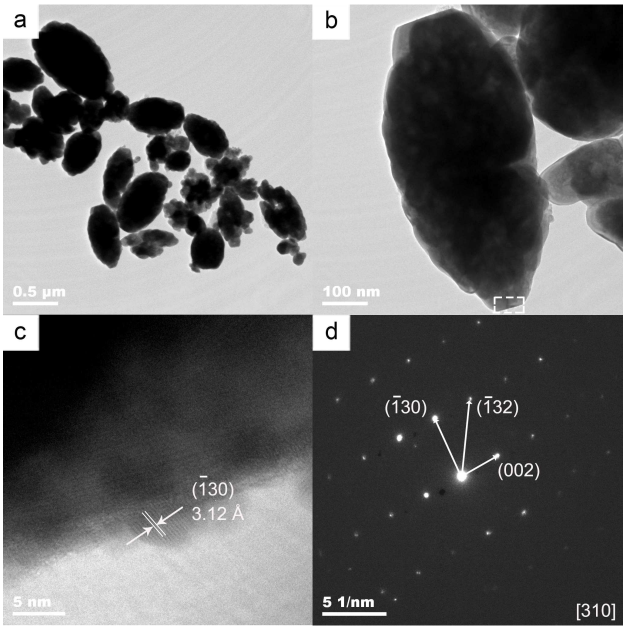

Figure 3. TEM images (a,b), HRTEM image (c) and SAED pattern (d) of the $BiVO_4$ pigments prepared by SPC method

citric acid, indicating the limitation of the preferential orientation along the (040) facets [20]. Therefore, it reveals that citric acid as the fuel can influence the preferential growth of $BiVO_4$ crystal, which plays a role of structure-directing agent [21]. It is well known that the Raman band position is specific to particular chemical group, and it is extra sensitive in the short range, which has been used to distinguish similar allotropes of $BiVO_4$ [22]. Figure 1b presents the Raman spectra of $BiVO_4$ pigment with and without the addition of citric acid. The typical vibrational bands of m-$BiVO_4$ appeared at 815, 369, 331, 201 and 119 cm^{-1}. The band at 815 cm^{-1} was assigned to the ν_1 symmetric stretching mode of VO_4, and those peaks at 369 and 331 cm^{-1} were attributed to the ν_1 bending modes of VO_4 units [23]. The bands at 201 and 127 cm^{-1} represented the external mode of $BiVO_4$ [6]. Combined with XRD results, it is proved that m-$BiVO_4$ pigment with high purity can be easily obtained through our synthetic route.

The surface morphologies of the $BiVO_4$ pigments prepared with and without citric acid were investigated by SEM, as shown in Fig. 2. It can be seen that the morphology of the prepared $BiVO_4$ pigments highly depends on whether citric acid is added. Figures 2a,b present that the sample prepared without adding citric acid has irregular shape with the average size of 2.4 μm. This could be attributed to the fact that the Bi^{3+} and VO_3^- in solution can react with each other directly to form $BiVO_4$ in the absence of citric acid, resulting in the random stacking of crystals and formation of irregular particles. However, well-dispersed and uniform olive-like $BiVO_4$ particles with the size around 730 nm composed of nanoparticles can be obtained after introducing citric acid as a fuel in SPC process, as shown in Figs. 2c,d. Therefore, it can be speculated that the fuel citric acid also acts as structural directing agent during the formation of $BiVO_4$, which has a great influence on the growth of $BiVO_4$ crystals.

Figure 3 illustrates TEM images of the $BiVO_4$ pigment synthesized by SPC method. It can be observed that the pigment exhibits olive-like $BiVO_4$ nanostructure, which is composed of small nanocrystals. HRTEM image shows the interplanar spacing of 3.12 Å, corresponding well to the $(\bar{1}30)$ plane of m-$BiVO_4$ (Fig. 3c). The corresponding selected-area electron diffraction (SAED) pattern can be indexed as the (002), $(\bar{1}30)$ and $(\bar{1}32)$ reflections of m-$BiVO_4$ (JCPDS 14-0688).

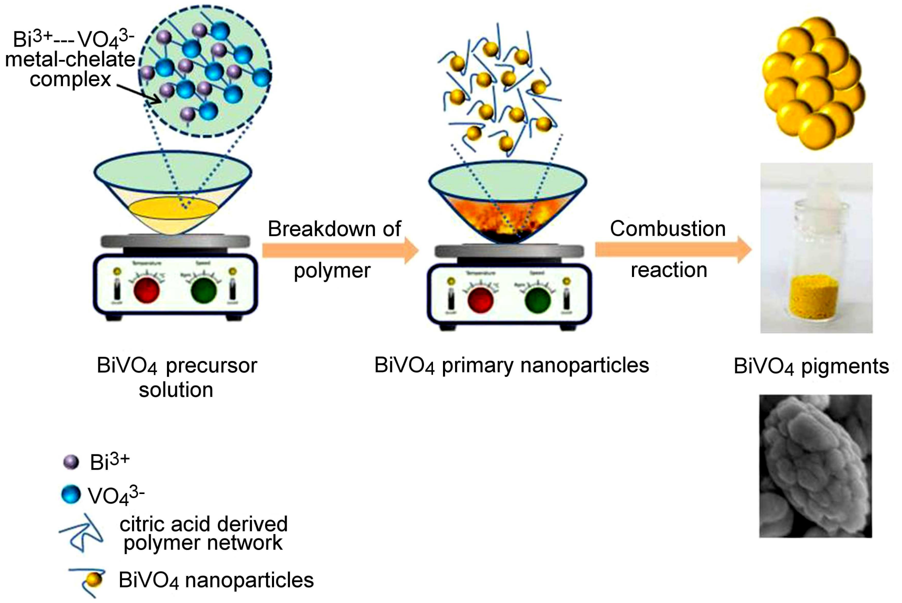

Figure 4. Schematic illustration of the formation mechanism of $BiVO_4$ olive-like pigment prepared by SPC method

The schematic illustration of the formation mechanism of olive-like $BiVO_4$ pigment prepared by SPC method is shown in Fig. 4. Firstly, citric acid as a kind of chelating agent can react with metal ions to form metal-chelate complexes, followed by the formation of a polymer chain net, which contributes to the uniformity of metal ions. Then, the polymer chains entrapped with cations and solvents break down to short chains after increase of temperature [24]. Subsequently, the short polymer chains twist and tangle together to form olive-like aggregated polymer particles, which further transform to the olive-like $BiVO_4$ yellow pigment consisting of nanoparticles after the combustion process. This is in accordance with the observations in Figs. 2 and 3. Moreover, the well-dispersed olive-like $BiVO_4$ pigment is beneficial to their potential applications in different substrates, such as ceramic, glass and plastic.

For a more intuitive comparison of the effects of citric acid on the chromaticity of pigment, the colour coordinates of $BiVO_4$ pigments prepared with and without citric acid were shown in Fig. 5a. The CIE-$L^*a^*b^*$ coordination values of the samples were presented in Table 1. More positive b^* values relate to more deep yellowish hues, and higher C_{ab} values correspond to more in-

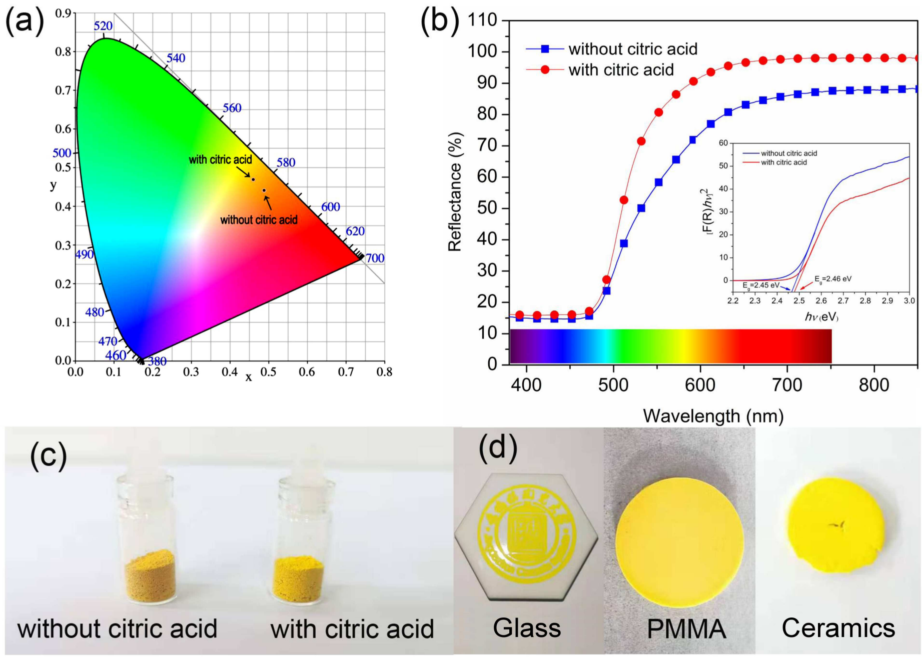

Figure 5. Chromatic coordinates of $BiVO_4$ pigments (a), reflectance curves (insert image is the plots of $(F(R)h\nu)^2$ vs $h\nu$) (b), digital photographs of $BiVO_4$ pigments (c) and photographs of $BiVO_4$ based PMMA composite/glass/ceramics (d)

Table 1. Comparison of synthesis temperature, colour parameters, morphology and crystallite size of $BiVO_4$ pigments obtained by several methods

Synthesis methods	Temperature [°C]	Colour coordinates					E_a [eV]	Morphology	Particle size [μm]	Ref.
		L^*	a^*	b^*	C_{ab}	h_{ab}				
Solid-state method	800	65.79	14.29	52.57	54.47	74.78	2.29	spherical	16	[11]
Hydrothermal-method	200	91.64	−2.45	63.07	63.12	87.78	-	nanosheets	0.01–0.04	[12]
CBD method	<100	68.08	16.52	42.32	45.43	68.68	-	-	13	[14]
sol-gel method	500	77.18	−0.53	71.19	71.19	90.44	2.45	spherical	0.4	[15]
NHSG method	400							spherical	0.74	[16]
Commercial $BiVO_4$	-	94.4	−16.7	76.9	78.7	77.8	2.51	-		[7,24]
Commercial CdS	-	90.4	−6.0	95.10	95.29	93.61	-	-		[25]
Commercial $PbCrO_4$	-	87.9	3.8	98.40	98.47	87.79	-	-		[25]
SPC method#	200	78.41	4.25	78.12	78.24	86.89	2.46	olive-like	0.73	This work
SPC method##	200	58.94	17.13	60.56	62.94	74.21	2.15	irregular	2.4	This work

SPC method with citric acid
SPC method without citric acid
$C_{ab} = (a^{*2} + b^{*2})^{1/2}$, purity of hue (0–100) and $h_{ab} = \arctan(b^*/a^*)$, hue angle (0–360°, pure yellow = 90°)

tense chromatic. The results indicate that the pigment prepared by SPC method with addition of the citric acid as a fuel exhibits an ideal colouristic attributes, and its CIE coordination is L^* = 78.41, a^* = 4.25, b^* = 78.12. The synthesis temperature, colour parameters, morphology and crystallite size comparisons for the prepared samples, commercially available and previously reported $BiVO_4$ yellow pigments were listed in Table 1 [11,12,15,25]. It is worth noting that the colour property of the prepared $BiVO_4$ is comparable to that of the well-known commercial inorganic pigments (i.e. CdS, $PbCrO_4$) [26]. Moreover, the synthesis temperature of the pigment prepared via the facile SPC route can be lowered to 200 °C, which is favourable to obtain well-dispersed olive-like $BiVO_4$ particles without the assistance of template. Figure 5b depicts the UV-Vis diffuse reflectance spectra of the prepared $BiVO_4$ pigments. It can be seen that the pigments show strong optical absorption behaviour at wavelengths shorter than 500 nm, covering the blue light region (435–480 nm). As a result, the pigments present yellow colour, due to complementary colour to yellow. The reflectance of the pigment prepared with adding citric acid is stronger than the control sample, suggesting higher yellow hue (b^*). This result is consistent with data obtained in CIE-$L^*a^*b^*$ system and the digital photographs of the $BiVO_4$ pigments (Fig. 5c). The bandgap of the $BiVO_4$ pigments prepared with and without citric acid was estimated from DRS, demonstrating a value of 2.46 and 2.45 eV, respectively, which is close to 2.4 eV for the $BiVO_4$ materials reported in the literature [7]. To study the potential of the pigments as colourants for various applications, the colour characteristics on various substrates were further investigated, e.g. ceramics, glass, and polymethyl methacrylate (PMMA), as shown in Fig. 5d. The samples exhibit a brilliant yellow hue, suggesting that the $BiVO_4$ pigment has good thermal and chemical stability in various substrates, suggesting that the prepared $BiVO_4$ pigments present great application potential in the decoration of various ceramics, glass and plastic materials.

IV. Conclusions

In conclusion, nanosized monoclinic $BiVO_4$ pigments with uniform olive-like morphology were fabricated by a template-free SPC process at low temperature (200 °C). The fuel citric acid played a key role in the formation of olive-like $BiVO_4$ particles. The as-prepared $BiVO_4$ pigments exhibit high purity and an excellent tinting strength, as L^* = 78.41, a^* = 4.25, b^* = 78.12 (C_{ab} = 78.24, h_{ab} = 86.89). Furthermore, the prepared pigments were introduced into glass and ceramics, in which the prepared samples present smooth surface and brilliant yellow hue. This demonstrates that the low-cost and high-grade $BiVO_4$ pigments are ideal alternatives for traditional and toxic yellow inorganic pigments for the application in various fields (e.g. PMMA, glass and ceramics).

Acknowledgments: This work was kindly supported by Jiangxi Provincial Natural Science Foundation (20202BABL214013), the Science Foundation of Jiangxi Provincial Department of Education (GJJ211343, GJJ211315, GJJ201345, GJJ190736), Jingdezhen Science and Technology Bureau Planning Project (20212GYZD009-06).

References

1. X.W. Wang, B. Mu, J. Xu, A.Q. Wang, "Reversibe thermochromic superhydrophobic $BiVO_4$ hybrid pigments coatings with self-cleaning performance and environmental stability based on kaolinite", *ACS Appl. Mater. Inter.*, **13** [2] (2021) 3228–3236.
2. B. Huang, Y. Xiao, H.Y. Zhou, J.Q. Chen, X.Q. Sun, "Synthesis and characterization of yellow pigments of $Bi_{1.7}RE_{0.3}W_{0.7}Mo_{0.3}O_6$ (RE = Y, Yb, Gd, Lu) with high NIR reflectance", *ACS Sustain. Chem. Eng.*, **6** [8] (2018) 10735–10741.
3. X.W. Wang, B. Mu, W.B. Wang, Q. Wang, A.Q. Wang, "A comparative study on color properties of different clay minerals/$BiVO_4$ hybrid pigments with excellent thermal stability", *Appl. Clay. Sci.*, **181** [15] (2019) 105221–105230.

4. A. Mahmoodi, Z. Jiryaei, A. Dadras, M. Khorasani, X. Shi, "A hybrid yellow nanopigment as an environmentally sound alternative to lead chromate pigment for pavement markings", *J. Clean. Prod.*, **319** (2021) 128733–128745.
5. L.Y. Cao, X.N. Fei, H.B. Zhao, "Environmental substitution for $PbCrO_4$ pigment with inorganic-organic hybrid pigment", *Dyes Pigments*, **142** (2017) 100–107.
6. X.W. Wang, B. Mu, A.P. Hui, Q. Wang, A.Q. Wang, "Low-cost bismuth yellow hybrid pigments derived from attapulgite", *Dyes Pigments*, **149** (2018) 521–530.
7. L. Guan, J.L. Fan, Y.Y. Zhang, Y.P. Guo, H.N. Duan, Y.J. Chen, H. Li, H.Z. Liu, "Facile preparation of highly cost-effective $BaSO_4$@$BiVO_4$ core-shell structured brilliant yellow pigment", *Dyes Pigments*, **128** (2016) 49–53.
8. G.J. Partl, I. Hackl, T. Götsch, S. Penner, M. Tribus, N. Weinberger, L.L. Petschning, D. Schildhammer, G.L. Fuhrmann, H. Huppertz, H. Schottenberger, "High temperature stable bismuth vanadate composite pigments via vanadyl-exchanged zeolite precursors", *Dyes Pigments*, **147** (2017) 106–112.
9. S. Sameera, P.P. Rao, S. Divya, A.K.V. Raj, "Brilliant IR reflecting yellow colorants in rare earth double molybdate substituted $BiVO_4$ solid solutions for energy saving applications", *ACS Sustain. Chem. Eng.*, **3** [6] (2015) 1227–1233.
10. S. Sameera, P.P. Rao, V. James, A.K.V. Raj, "Influence of $(LiLa)_{1/2}MoO_4$ substitution on the pigmentary properties of $BiVO_4$", *Dyes Pigments*, **104** (2014) 41–47.
11. S. Sameera, P.P. Rao, S. Divya, A.K.V. Raj, T.R.A. Thara, "High IR reflecting $BiVO_4$-$CaMoO_4$ based yellow pigments for cool roof applications", *Energ. Buildings*, **154** (2017) 491–498.
12. L. Zhang, D.R. Chen, X.L. Jiao, "Monoclinic structured $BiVO_4$ nanosheets: Hydrothermal preparation, formation mechanism, and coloristic and photocatalytic properties", *J. Phys. Chem. B*, **110** [6] (2006) 2668–2673.
13. Wendusu, I. Ken-ichi, M. Toshiyuki, I. Nobuhito, "Novel environment-friendly yellow pigments based on $(Bi,La)VO_4$", *Chem. Lett.*, **40** [8] (2011) 792–794.
14. M.C. Neves, M. Lehocky, R. Soares, L. Lapcik Jr., T. Trindade, "Chemical bath deposition of cerium doped $BiVO_4$", *Dyes Pigments*, **59** [2] (2003) 181–184.
15. S.S. Fathimah, P.P. Rao, V. James, A.K.V. Raj, G.R. Chitradevi, S. Leela, "Probing structural variation and multifunctionality in niobium doped bismuth vanadate materials", *Dalton T.*, **43** [42] (2014) 15851–15860.
16. X.J. Zhang, T. Chen, Y.Q. Xu, W.H. Jiang, J.M. Liu, Z.X. Xie, "Synthesis and characterization of environmentally friendly $BiVO_4$ yellow pigment by non-hydrolytic sol-gel route", *J. Sol-Gel Sci. Technol.*, **91** (2019) 127–137.
17. M. Ardit, S. Borcănescu, G. Cruciani, M. Dondi, L. Lazău, C. Păcurariu, C. Zanelli, "Ni-Ti codoped hibonite ceramic pigments by combustion synthesis: crystal structure and optical properties", *J. Am. Ceram. Soc.*, **99** [5] (2016) 1749–1760.
18. Q. Tang, H. Zhu, C. Chen, Y.X. Wang, Z.G. Zhu, J.Q. Wu, W.H. Shih, "Preparation and characterization of nanoscale cobalt blue pigment for ceramic inkjet printing by sol-gel self-propagating combustion", *Mater. Res.*, **20** (2017) 1340–1344.
19. R. Ianoş, E. Muntean, C. Păcurariu, R. Lazău, C. Bandas, G. Delinescu, "Combustion synthesis of a blue Co-doped zinc aluminate near-infrared reflective pigment", *Dyes Pigments*, **142** (2017) 24–31.
20. S.M. Thalluri, M. Hussain, G. Saracco, J. Barber, N. Russo, "Green-synthesized $BiVO_4$ oriented along {040} facets for visible-light-driven ethylene degradation", *Ind. Eng. Chem. Res.*, **53** [7] (2014) 2640–2646.
21. Z.X. Hao, X.W. Lv, W.X. Hou, X. Liu, "Facile synthesis of BiOCl single-crystal photocatalyst with high exposed (001) facets and its application in photocatalytic degradation", *Inorg. Chem. Commun.*, **134** (2021) 109038–109044.
22. X.W. Wang, B. Mu, J. Xu, A.Q. Wang, "Preparation of high-performance bismuth yellow hybrid pigments by doping with inorganic oxides", *Powder Technol.*, **373** (2020) 411–420.
23. T. Masui, T. Honda, W.N. Imanaka, "Novel and environmentally friendly $(Bi,Ca,Zn)VO_4$ yellow pigments", *Dyes Pigments*, **99** [30] (2013) 636–641.
24. H.Q. Jiang, H. Endo, H. Natori, M. Nagai, K. Kobayashi, "Fabrication and photoactivities of spherical-shaped $BiVO_4$ photocatalysts through solution combustion synthesis method", *J. Eur. Ceram. Soc.*, **28** (2008) 2955–2962.
25. A.K. Bhattacharya, K.K. Mallick, A. Hartridge, "Phase transition in $BiVO_4$", *Mater. Lett.*, **30** [1] (1997) 7–13.
26. G. Gauthier, S. Jobic, M. Evain, H.J. Koo, M.H. Whangbo, C. Fouassier, R. Brec, "Syntheses, structures, and optical properties of yellow Ce_2SiS_5, $Ce_6Si_4S_{17}$, and $Ce_4Si_3S_{12}$ materials", *Chem. Mater.*, **15** [4] (2003) 828–837.