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Preparation of Environmentally Friendly BiVO$_4$@SiO$_2$ Encapsulated Yellow Pigment with Remarkable Thermal and Chemical Stability

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Abstract: The preparation of environmentally friendly inorganic encapsulated pigments with a bright color and sufficient stability provides an effective strategy for expanding their applications in plastic, paint, glass, and ceramic decoration. The challenges facing the use of such pigments include the formation of a dense protective coating with the required endurance, the relatively weak color of the encapsulated pigments, and the preferable inclusion particle size. Environmentally friendly BiVO$_4$ is regarded as a very promising pigment for multiple coloring applications due to its brilliant yellow color with high saturation. However, its poor thermal and chemical stability greatly limit the application of BiVO$_4$. Herein, we report a sol–gel method to synthesize inorganic BiVO$_4$@SiO$_2$ yellow pigment with a core–shell structure. By controlling the synthesis conditions, including the particle size and dispersion of BiVO$_4$ and the calcination temperature, a BiVO$_4$@SiO$_2$ encapsulated pigment with excellent chromatic properties was achieved. The obtained environmentally friendly BiVO$_4$@SiO$_2$ pigment with encapsulation modification has a comparable color-rendering performance to BiVO$_4$, and it has a high thermal stability at 700 °C, excellent acid resistance, and good compatibility in plastics. The present research is expected to expand the application of yellow BiVO$_4$ pigment in harsh environments.

Keywords: encapsulated pigment; BiVO$_4$@SiO$_2$; yellow color; thermal stability; resistance to chemical erosion

1. Introduction

Inorganic pigments have been applied in various products such as ceramics, enamels, paints/coatings, plastics, and glasses due to their high hiding power, weather resistance, UV stability, and thermal stability [1–7]. Among them, yellow pigments are particularly interesting because of their great applicability in many industries, such as the building, automotive, decorative paints, and plastics industries [7–10]. In particular, inorganic yellow pigments, with their striking color, are in great demand due to their usefulness in many applications. However, conventional industrial pigments such as chrome yellow (PbCrO$_4$) and cadmium yellow (CdS$_{1-x}$Se$_x$) contain toxic elements (Pb, Cr, Cd, Se, etc.), which have adverse effects on animals, plants, and the environment. Therefore, the development of novel environmentally friendly yellow pigments is especially important. Bismuth vanadate (BiVO$_4$), an eco-friendly type of yellow pigment, has attracted much attention due to its bright color, nontoxicity, and high hiding power [10–14]. This environmentally friendly inorganic yellow pigment has the potential to replace iron yellow, chrome yellow, cadmium yellow, nickel titanium yellow, and chromium titanium yellow pigments [7,15]. Simultaneously, because green or yellow is an eye-catching color, greenish-yellow BiVO$_4$ pigments can be used as

traffic marks and building coatings, indicating that greenish-yellow $BiVO_4$ pigments seem to be promising candidates in terms of pigment safety and environmental friendliness [10,14,16].

Many studies on the doping modification of yellow $BiVO_4$ pigment via different synthesis methods have been carried out to tailor its phase structure, particle size, chromatic performance, and spectral characteristics [1,11–14,16–21]. For example, Sameera et al. synthesized V-site Nb-doped $BiVO_4$ via the citrate complexation route [19]. The resulting pigment exhibits excellent color characteristics that are comparable to those of commercial $BiVO_4$ and has a high NIR reflectivity. Wendusu et al. synthesized Bi-site La-doped $BiVO_4$ via a hydrothermal method [20]. The yellowness of the doped pigments ($b^* > 80$) was higher than that of a commercially available $BiVO_4$ pigment. Ca/Zn codoped $BiVO_4$ was also synthesized via the evaporation-to-dryness method by Toshiyuki et al. [1], and the most vivid greenish-yellow hue was obtained for $BiVO_4$ with a high yellowness. It can be concluded from the above-mentioned studies that the doping process is effective in tailoring the properties of $BiVO_4$ pigments, such as the NIR reflectance and color, but it needs to be emphasized that this has no obvious positive effect on improving the thermal and chemical stability of $BiVO_4$. Furthermore, most of the doped pigments show a reddish-yellow color with a depressed b^* value instead of the more striking greenish-yellow color for pure $BiVO_4$. Even when applied in plastic coloring, both pure and doped $BiVO_4$ pigments often suffer from discoloration due to the erosion of the plastic melt above 150 °C.

Interestingly, the formation of a core–shell structure can improve the thermal stability of these pigments through the modification of the encapsulation with more stable materials, such as $ZrSiO_4$, SiO_2, and Al_2O_3 [22–25]. For instance, the working temperature of $ZrSiO_4$-encapsulated carbon black via sol–gel-spraying could be effectively increased to 900 °C [22]. Although $ZrSiO_4$ is usually selected as a coating layer to protect the colorant, the synthesis temperature of the dense $ZrSiO_4$ layer is not less than 950 °C [24]. The too-high temperature required for the formation of a dense protective coating is extremely unfavorable for $BiVO_4$ due to its poor thermal stability; at these temperatures, the volatilization of V and thus the alteration of the phase structure and color of the pigment would be unavoidable. Furthermore, the V ions in $BiVO_4$ can react easily with zirconium hydroxide, one of the precursors for synthesizing $ZrSiO_4$ or ZrO_2, which brings about a significant color change in the pigment [26,27]. Thus, in the present work, SiO_2 was selected to encapsulate $BiVO_4$ pigments due to the lower temperature to form a dense surface protective coating. The thermal stability of yellow $BiVO_4$ pigments is similar to that of red γ-Ce_2S_3 pigment. Li and co-workers prepared core–shell γ-Ce_2S_3@SiO_2 red pigment via the Stober method, and the thickness of the dense SiO_2 layer was as thick as 140 nm after multiple coating [25,28]. The oxidization-resistant temperature was enhanced from 300 to 550 °C after coating with a dense SiO_2 layer for γ-Ce_2S_3 pigments. Similarly, the synthesized α-Fe_2O_3@SiO_2 composite revealed greatly incremented thermal stability, less color variation, and strong acid–alkali resistance compared with Fe_2O_3 [29].

In this study, we developed a sol–gel method to construct an environmentally friendly $BiVO_4$@SiO_2 encapsulated pigment. The pretreatment and dispersion of $BiVO_4$ powder, and the effect of calcination temperature on the phase composition, morphology, and color-rendering properties, were systematically studied to achieve bright-color and high-thermal-stability yellow $BiVO_4$@SiO_2 pigment. The spectroscopic properties and resistance to acidic solution and high-temperature plastic melt for the obtained $BiVO_4$@SiO_2 pigment were also investigated. It was found that the encapsulation did not weaken the chromatic performance of $BiVO_4$, while the thermal and chemical stability could be significantly enhanced. This present work opens up a vast space for expanding the application of brilliant yellow $BiVO_4$-based pigments in paints, coatings, plastics, and even ceramic, enamel, and glass decorations.

2. Results and Discussion

2.1. Pretreatment and Dispersion of BiVO₄ Pigment

Typically, a suitable particle size is preferred to improve the coating effect of a pigment. Therefore, a ball-milling process was used to optimize the particle size of the as-received $BiVO_4$ pigment powder. As displayed in Figure 1, the median diameter (D_{50}) of $BiVO_4$ decreased from 0.51 to 0.17 μm as the milling time increased from 0 to 4 h. When a pigment powder has a larger particle size, its specific surface area is smaller, and the wrapping rate is lower. In contrast, if the pigment particles are too small, which is equivalent to the particle size of SiO_2 synthesized via the sol–gel method, it causes electrostatic repulsion, resulting in a decrease in the encapsulation rate. In this study, after the milling time was increased up to 4 h, the particle size did not obviously reduce. As such, the $BiVO_4$ ball-milled for 4 h was selected for the following coating.
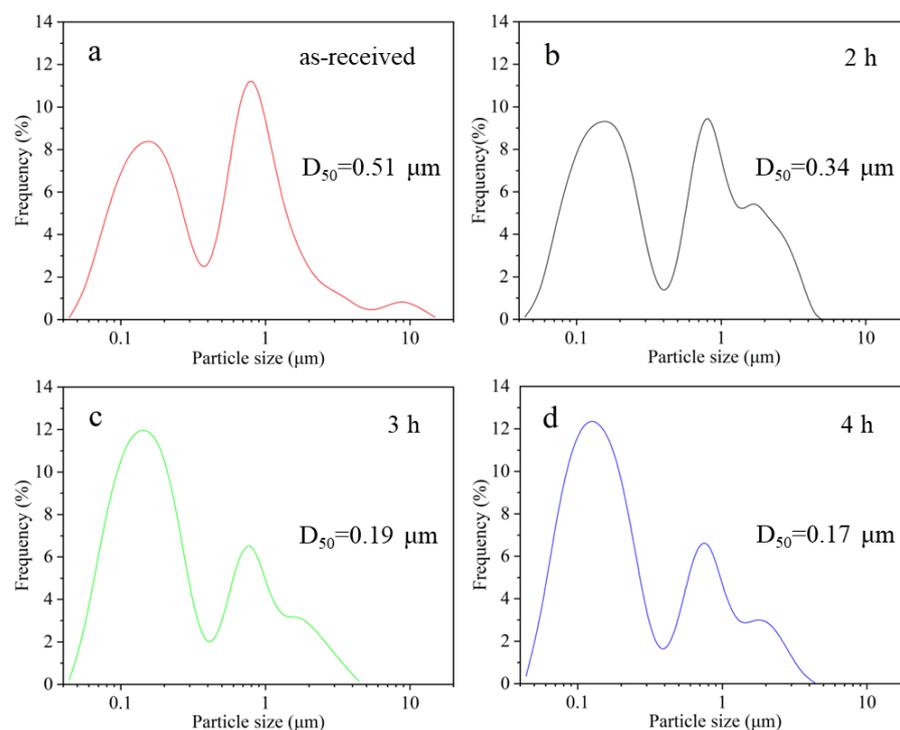

Figure 1. Particle size distributions of $BiVO_4$ (**a**) as-received or treated with ball milling for (**b**) 2 h, (**c**) 3 h, or (**d**) 4 h.

On the other hand, the dispersion of $BiVO_4$ in the reaction system could directly affect the encapsulation effect. Therefore, we used the dilute HCl and NaOH aqueous solutions to adjust the pH value of the $BiVO_4$ suspension and tested the corresponding zeta potentials. The isoelectric point of $BiVO_4$ particles in an aqueous solution was around pH = 6.5 (Figure 2). Under acidic conditions, the surface of $BiVO_4$ is positive, and the zeta potential is relatively low (<20 mV), which indicate the poor stability of the particles in aqueous solutions. Under alkaline conditions, the surface of $BiVO_4$ is negative; especially when the pH value is above 8, the zeta potential is around −40 mV. The much higher zeta potential under alkaline conditions is beneficial for achieving the stable dispersion of $BiVO_4$ particles to improve the encapsulation rate. In addition, OH^- nucleophilic catalysis under alkaline conditions is conducive to the condensation of hydrolytic TEOS, contributing to a dense SiO_2 layer [30]. In contrast, H^+ catalysis under acidic conditions tend to form a linear connection of SiO_2 precipitate with many hydroxyl groups on its surface, which can be easily combined with H_2O and other solvents in the system via intermolecular H bonds, resulting in a loose and porous SiO_2 layer. In addition, the resistance of $BiVO_4$ powder to alkaline conditions is much better

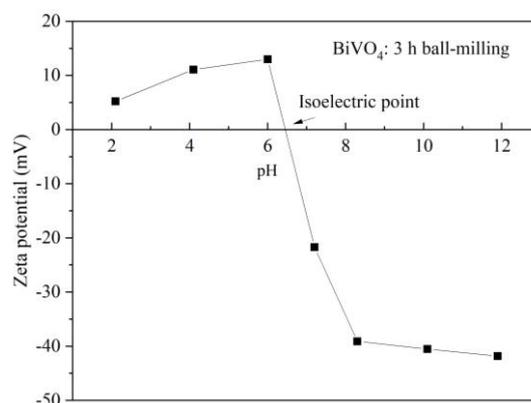than to acid. Therefore, this work carried out the SiO_2 coating process in an alkaline environment (pH ≈ 9.5).

Figure 2. Zeta potentials of $BiVO_4$ at different pH values.

2.2. Phase Composition and Morphology of BiVO₄@SiO₂ Pigment

Figure 3a and 3b present the XRD results of the synthesized $BiVO_4@SiO_2$ pigments prepared at different calcination temperatures with a TEOS concentration of 0.5 mol/L. Only the monoclinic $BiVO_4$ (m-$BiVO_4$, PDF#14-0688) with high crystallinity could be observed for the samples calcinated at 350–750 °C. It is thought that the synthesized SiO_2 was in an amorphous state and could not be detected with XRD. Thus, the process to synthesize SiO_2 from TEOS in alkaline solutions had a negligible effect on the phase structure of $BiVO_4$. As the calcination temperature was further increased to above 800 °C, minor tetragonal SiO_2 (t-SiO_2, 2θ = 21.94°, PDF#71-0785) was detected (Figure 3b). Meanwhile, an additional weak diffraction peak at 2θ = 18.7° appeared, which could be ascribed to tetragonal $BiVO_4$ (t-$BiVO_4$, PDF#14-0133) [18]. It is proposed that the scheelite m-$BiVO_4$ consists of isolated VO_4 tetrahedra, which are corner-connected by BiO_8 dodecahedra. At higher temperatures, m-$BiVO_4$ tends to transform to t-$BiVO_4$ due to the volatilization of some V ions, resulting from the defective SiO_2 coating of the encapsulated pigment calcined at 800 °C, as shown in the TEM image (Figure 4i). In t-$BiVO_4$, Bi^{3+} cations are located at the centrosymmetric site of the BiO_8 polyhedra, whereas m-$BiVO_4$ exhibits a distorted BiO_8 dodecahedron due to Bi^{3+} off-centering [31]. Table 1 lists the corresponding lattice parameters of the m-$BiVO_4$ phase for the as-received $BiVO_4$ and $BiVO_4@SiO_2$ prepared at 800 °C, which were calculated from the XRD results using MDI jade software (v6.5). It can be seen that although the monoclinic structure was maintained, tiny lattice distortion occurred after high-temperature calcination, along with a small increase in the lattice size, probably due to the loss of trace amounts of V ions. Particularly, a small reduction in the β angle was also observed, indicating the cell symmetry was slightly improved. These results also suggest that m-$BiVO_4$ undergoes a greenish-to-reddish tone transition at high temperatures due to the generation of cation vacancy defects and thus lattice distortion and/or phase transition. Figure 3c,d show the SEM morphology of the encapsulated $BiVO_4$ pigment. The SiO_2-coated primary particles had a near-spherical or elliptic structure, and a certain degree of particle agglomeration was unavoidable for the encapsulated pigment due to the bonding effect of the amorphous SiO_2.

Table 1. Lattice parameters of m-$BiVO_4$ for the as-received $BiVO_4$ and $BiVO_4@SiO_2$ prepared at 800 °C.

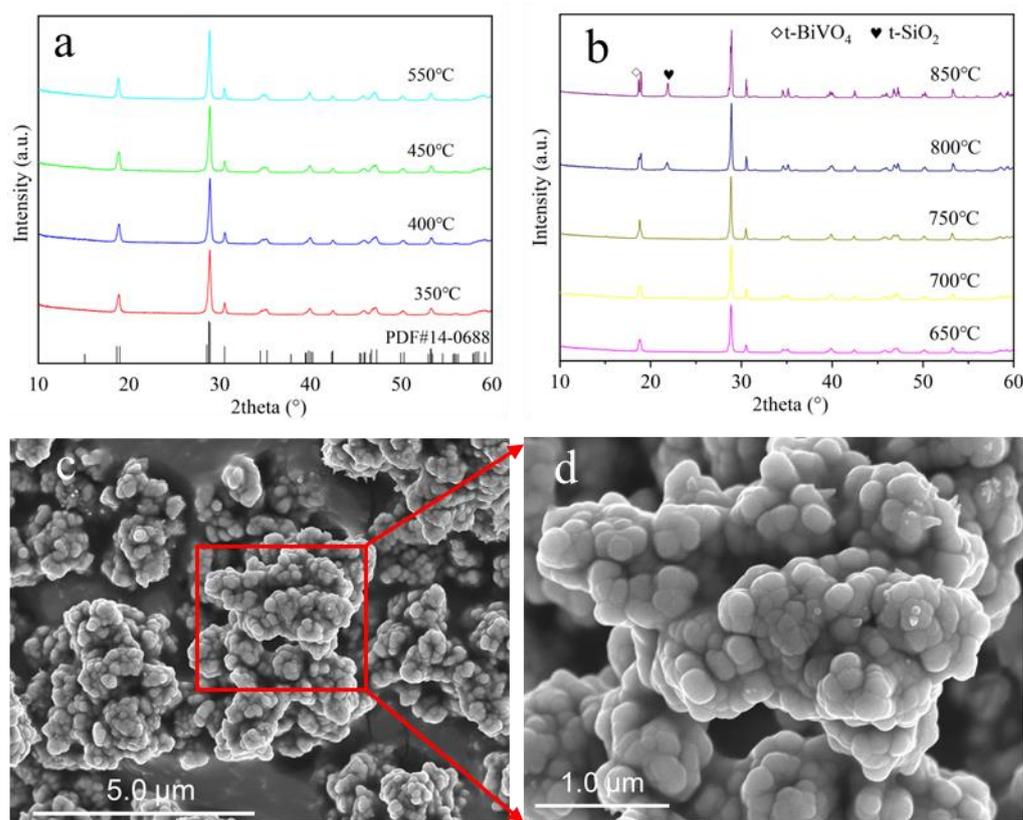| Sample	Lattice Parameter					
	a/Å	b/Å	c/Å	α/°	β/°	γ/°
$BiVO_4$	5.186	11.698	5.101	90.000	90.287	90.000
$BiVO_4@SiO_2$	5.192	11.717	5.116	90.000	90.184	90.000

Figure 3. XRD patterns of BiVO₄@SiO₂ (**a**,**b**) calcined at different temperatures for 6 h. (**c**) SEM images of BiVO₄@SiO₂ encapsulated pigment calcined at 500 °C and (**d**) corresponding enlarged view of the selected area.

TEM and EDS analyses were further conducted to characterize in detail the morphology and size of the BiVO₄@SiO₂ pigments prepared with a TEOS content of 20 g and calcined at different temperatures (Figure 4). As shown in Figure 4a–e, a dense and uniform SiO₂ layer around the BiVO₄ particles was successfully achieved, forming a core–shell structure with a coating thickness of about 60~100 nm. Bi and V were located in the center, and Si and O were dispersed throughout the coating layer. The inner BiVO₄ particles of the encapsulated pigment exhibited a diameter of 100~200 nm when calcined at 500 °C, as shown in Figure 4f, and their size gradually increased with increasing calcination temperature. In particular, significant grain growth happened as the temperature increased from 700 to 800 °C (300~400 nm, in Figure 4i). This could mostly be ascribed to the coalescence of small BiVO₄ particles, since their fusing point was close to 800 °C. On the whole, the agglomerated particle size of the BiVO₄@SiO₂ pigments was 1~2 μm, which is much smaller than those of the traditional encapsulated ceramic pigments, such as red or yellow $CdS_{1-x}Se_x@ZrSiO_4$ (>10 μm) [32]. This ensures the colorimetric properties of the pigment and its wide applications, especially in inkjet print decoration for ceramics and glasses. However, when calcined at 800 °C, the SiO₂ coating surrounding the BiVO₄ particles became discontinuous and tended to separate from the particle surface, resulting in partial exposure of the pigment (Figure 4i). This could be ascribed to the shrinkage of the coating resulting from the crystallization and structural rearrangement of SiO₂, which is consistent with the XRD results in Figure 3b. The observed phenomenon suggested that the thickness of the SiO₂ layer was insufficient to effectively improve the thermal stability and chromatic performance of BiVO₄ at temperatures higher than 800 °C. To solve this problem, it is necessary to increase the coating thickness with a higher TEOS content and optimize the preparation process in future work.
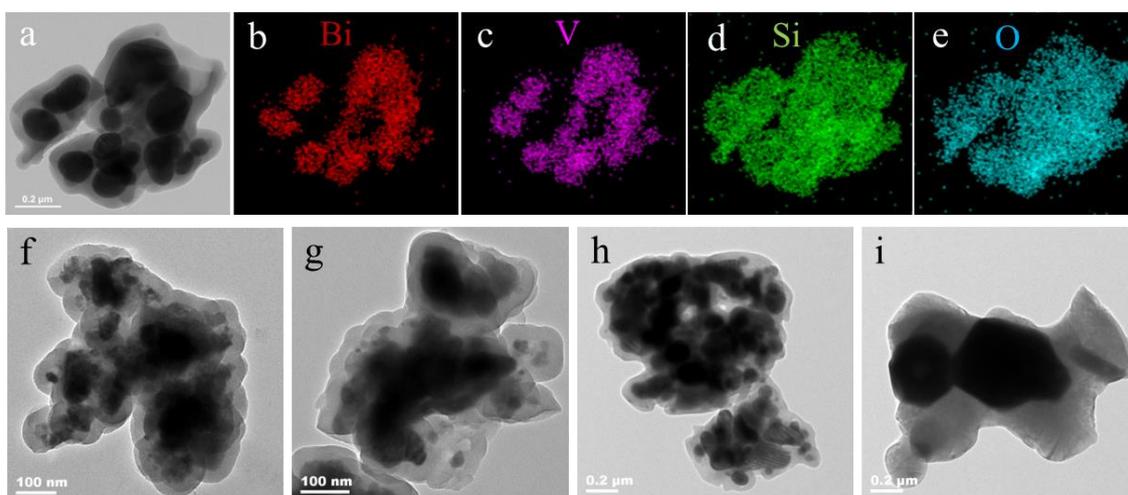
Figure 4. (**a**) TEM image and (**b–e**) corresponding EDS elemental mapping of BiVO$_4$@SiO$_2$ with 20 g of TEOS added and calcination at 500 °C. TEM images of BiVO$_4$@SiO$_2$ at different calcination temperatures of (**f**) 500 °C, (**g**) 600 °C, (**h**) 700 °C, and (**i**) 800 °C.

2.3. Chromatic and Spectroscopic Properties of BiVO$_4$@SiO$_2$ Pigments

The CIE-L*a*b* color parameters (L*, a*, b*, C*, h°, ΔE*) of the BiVO$_4$@SiO$_2$ pigments calcined at different temperatures are listed in Table 2. For comparison, the corresponding parameters for the as-received BiVO$_4$ pigment are also provided. It was found that the yellowness (b*) and color saturation (C*) of BiVO$_4$@SiO$_2$ pigment improved to some extent when calcined at 500–700 °C. In particular, the encapsulated sample at 600 °C exhibited the highest b* and C* values, which were comparable to those of Ca/Zn-co-doped BiVO$_4$ and higher than those of most of BiVO$_4$ pigments when doped with other transition metals or rare earth metal ions [1,11,12,20,21]. These obtained results indicate that the introduction of SiO$_2$ (37.5% in mass content) does not affect the chromatic properties of BiVO$_4$ pigment. A similar phenomenon was also found for the synthesis of hybrid SiO$_2$/BiVO$_4$ pigments, with SiO$_2$ as the core, by He et al. [33]. The addition of SiO$_2$ is expected to decrease the use cost of yellow pigment greatly since BiVO$_4$ is much more costly than SiO$_2$. However, when the calcination temperature was further increased to 800 °C, the L*, b*, and C* values of the encapsulated pigment became slightly lower than those of BiVO$_4$. Importantly, as shown in Table 2, the a* value changed from negative to positive, indicating that BiVO$_4$@SiO$_2$ pigment underwent a transition from a greenish to a reddish-yellow color. Corresponding to this, the resulting pigment presented a relatively large chromatic aberration (ΔE* = 8.73) relative to BiVO$_4$. Generally, a greenish-yellow color is preferable to reddish since the former looks brighter and more striking. The degradation of the chromatic properties of BiVO$_4$@SiO$_2$ prepared at 800 °C was probably caused by the incomplete encapsulation of the SiO$_2$ coating and thus the generated defects of the cation vacancies and lattice distortion, and even the formation of a small amount of the t-BiVO$_4$ phase, as determined via TEM observation (Figure 4i) and the XRD results (Figure 3b and Table 1). In this case, the volatilization of some V ions at high temperatures would be inevitable in consideration of the poor thermal stability of BiVO$_4$, which led to the formation of lattice defects, the changes in structure, and thus the spectral characteristics. Despite this, the hue angle (h°) values for all BiVO$_4$@SiO$_2$ encapsulated pigments were around 87, indicating an intense yellow color.

Table 2. CIE-L*a*b* chromatic parameters of BiVO$_4$ and BiVO$_4$@SiO$_2$ pigments calcined at different temperatures.

Calcination Temperature	Color Parameter					
	L*	a*	b*	C*	h° (°)	ΔE* [1]
BiVO$_4$	88.94	−3.93	80.09	80.19	87.19	/

500 °C	90.29	−4.24	80.38	80.49	86.98	2.00
600 °C	88.69	−4.42	83.83	83.95	86.99	3.78
700 °C	88.26	−2.57	81.52	81.56	88.20	2.06
800 °C	87.60	4.63	79.03	79.17	86.65	8.73

[1] Chromatic aberration $\Delta E^* = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{0.5}$.

To display the colors of all the samples more intuitively, the corresponding chromatic coordinates of the BiVO$_4$@SiO$_2$ pigments are plotted in the L*a*b* color space (Figure 5). The colors of BiVO$_4$@SiO$_2$ calcined at 500 °C, 600 °C, and 700 °C were quite similar. In addition, the coordinate location of BiVO$_4$@SiO$_2$ pigment calcined at 500–700 °C was closer to the green region than that prepared at 800 °C, which could be ascribed to the decreased thermal stability resulting from the defective SiO$_2$ coating at 800 °C.
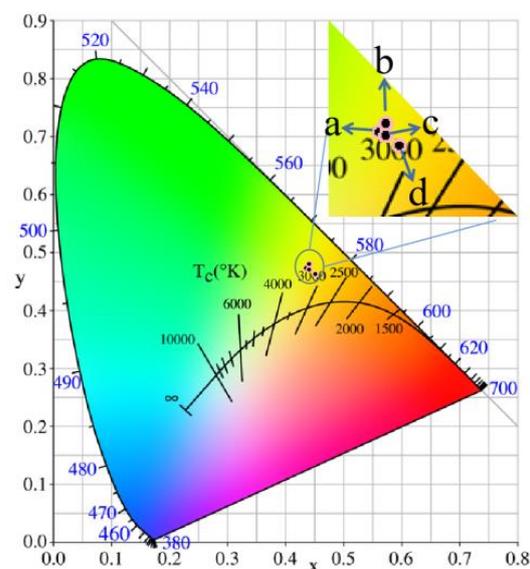

Figure 5. Chromatic coordinates of BiVO$_4$@SiO$_2$ at different calcination temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C.

To further elucidate the effect of SiO$_2$ encapsulation on the color-rendering performance of the BiVO$_4$ pigment, the UV–Vis diffuse reflectance properties were also investigated, as shown in Figure 6a. The BiVO$_4$ and BiVO$_4$@SiO$_2$ pigments show a very close high reflectance (>90%) from the yellow to red bands in the wavelength range of 550–780 nm but a relatively low reflectance from blue to purple light in the wavelength range of 380–490 nm. Furthermore, the reflectance of BiVO$_4$@SiO$_2$ in the 380–490 nm wavelength range is slightly lower than that of BiVO$_4$, which contributes to a little higher yellowness (b*) for the former [19]. In addition, the two samples had the same reflectance/absorption edge of about 500 nm in the green band, since BiVO$_4$ is the main color-rendering substance, and thus they were endowed with a greenish tone (negative a* value). On the whole, the measured visible spectrum characteristics are consistent with the chromatic performance shown in Table 2 and Figure 5. The effect of SiO$_2$ coating on the NIR reflectance performance of the BiVO$_4$ pigment was also investigated, with results displayed in Figure 6b. Only a minor reduction in the NIR reflectance within the 780–2500 nm wavelengths could be observed when SiO$_2$ coating with a high mass percentage of about 37.5% was introduced. Both samples possessed an overall sunlight NIR reflectance of more than 90%. The retained high NIR reflectivity of the BiVO$_4$@SiO$_2$ encapsulated pigment means that it has good prospects for being applied as a cold pigment for energy-saving applications such as architectural coatings, vehicle paints, exterior wall tiles, and other building decoration materials, since NIR radiation accounts for 52% of the energy from sunlight [14,16,34–36]. Furthermore, the preparation cost of BiVO$_4$@SiO$_2$ is much lower than that of BiVO$_4$ considering the ~37.5% SiO$_2$ content.

Therefore, from the perspectives of colorimetric performance, thermal stability, near-infrared reflectance, and cost, the obtained $BiVO_4@SiO_2$ pigment is an excellent candidate for "cool" roofs and energy-saving coating materials, having excellent weather resistance and thermal stability.
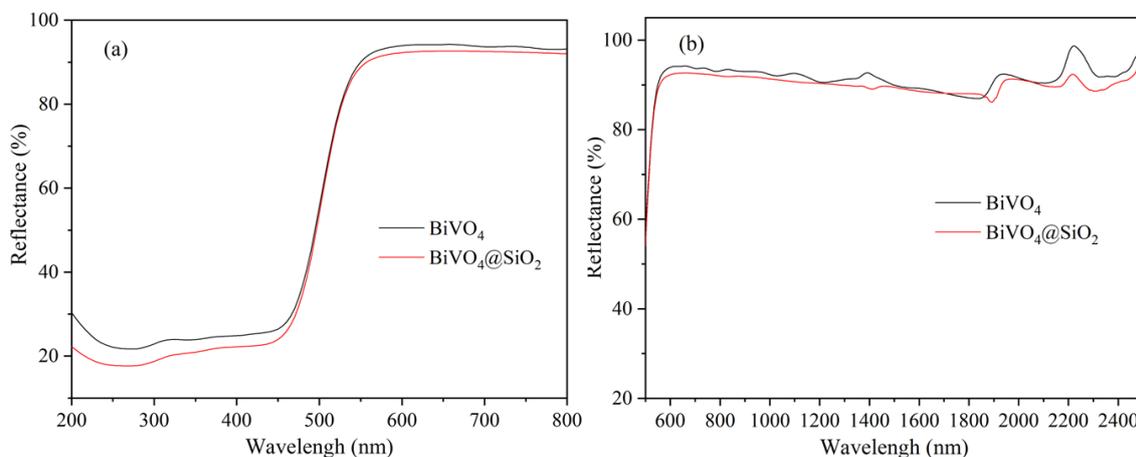

Figure 6. (**a**) UV–Vis and (**b**) NIR reflectance spectra of $BiVO_4$ and $BiVO_4@SiO_2$ calcined at 700 °C.

### 2.4. Evaluation of Thermal and Chemical Stability of $BiVO_4@SiO_2$ Pigment

In order to verify the effect of coating modification on the thermal stability of $BiVO_4$, the 600 °C-encapsulated and as-received $BiVO_4$ pigments were heat-treated at 500 and 700 °C for 24 h, respectively, and then their color-rendering performance were evaluated. The colors of post-test $BiVO_4$ and $BiVO_4@SiO_2$ are shown in Figure 7, and the corresponding L*, a*, and b* values are listed in Table 3. At 500 °C, $BiVO_4$ showed a more reddish-yellow color compared with $BiVO_4@SiO_2$. Compared with the as-received $BiVO_4$ pigment (Table 2), the brightness (L*) and yellowness (b*) showed no significant change, while the a* value changed from positive to negative, suggesting that the pigment transformed from greenish to reddish-yellow. This clearly shows that even at 500 °C, the $BiVO_4$ pigment does not have a sufficient thermal stability due to the loss of V ions. In sharp contrast, no obvious change in chromatic performance occurred for the $BiVO_4@SiO_2$ pigment at 500 °C compared to the as-prepared counterpart (Table 2). It is noted that even with treatment at 500 °C for 24 h, $BiVO_4@SiO_2$ still exhibited color-rendering performance superior to that of uncoated $BiVO_4$. When treated at 700 °C, the color of $BiVO_4$ turned brown due to the greatly increased a* and decreased b* values. However, the $BiVO_4@SiO_2$ pigment still possessed a brilliant yellow color at 700 °C. Compared with the $BiVO_4@SiO_2$ pigments, the L* (from 87.72 to 78.48) and b* (from 80.89 to 62.31) values of $BiVO_4$ were greatly reduced, while the a* value (from 2.73 to 11.28) was greatly enhanced. It is worth noting that despite heat treatment at 700 °C for 24 h, the color-rendering performance of $BiVO_4@SiO_2$ was still better than those of some ion-doped $BiVO_4$, such as $(BiV)_{1-x}(YNb)_xO_4$- and $(LiLa)_{1/2}MoO_4$-doped $BiVO_4$ with a yellowness b* of < 77 [11,12]. As a result, the temperature resistance of $BiVO_4@SiO_2$ pigment is remarkably better than that of $BiVO_4$ pigment, and the silica layer can significantly improve the thermal stability of $BiVO_4$ pigment.

Table 3. CIE L*, a*, b* values of BiVO₄ and BiVO₄@SiO₂ after heat treatment at 500 °C and 700 °C.

Temperature (°C)	Sample	Chromatic Parameter				
		L*	a*	b*	C*	h° (°)
500	BiVO₄	88.21	0.21	79.91	79.91	89.85
	BiVO₄@SiO₂	89.71	−4.28	82.43	82.54	87.03
700	BiVO₄	78.48	11.28	62.31	63.32	79.74
	BiVO₄@SiO₂	87.72	2.73	80.89	80.93	88.07
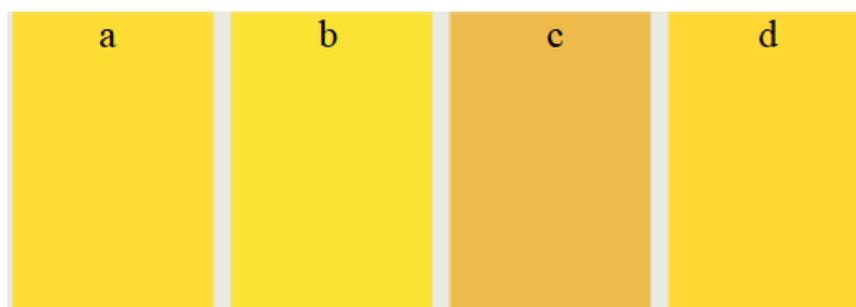
Figure 7. Photographs of BiVO₄ at (**a**) 500 °C and (**c**) 700 °C for 24 h; BiVO₄@SiO₂ at (**b**) 500 °C and (**d**) 700 °C for 24 h.

Generally, BiVO₄ has a poor resistance to acid corrosion. Thus, to test the effectiveness of SiO₂ encapsulation in improving its acid corrosion resistance, SiO₂-coated and uncoated BiVO₄ pigments were treated with a 5 wt.% HCl solution for different durations. As shown in Figure 8, the as-received BiVO₄ dissolved almost completely and lost its yellow color after placement in the HCl solution for only 1 min, while BiVO₄@SiO₂ showed no obvious change after 90 min under the same condition, retaining its vivid yellow color. Further, the UV–Vis reflectance spectra of the BiVO₄@SiO₂ pigment from before and after the acidic corrosion test are compared in Figure 9. No obvious change in reflectance spectral characteristics was found for the two samples. These findings clearly indicate that excellent acid corrosion resistance was achieved successfully for BiVO₄ pigment through the modification with a silica coating. The obtained result also further suggests that the prepared amorphous SiO₂ coating is sufficiently dense to prevent the penetration of acidic solutions. Considering that BiVO₄ has good alkaline resistance, the prepared BiVO₄@SiO₂ pigment would have good application prospects in both acidic and alkaline coatings or paints.
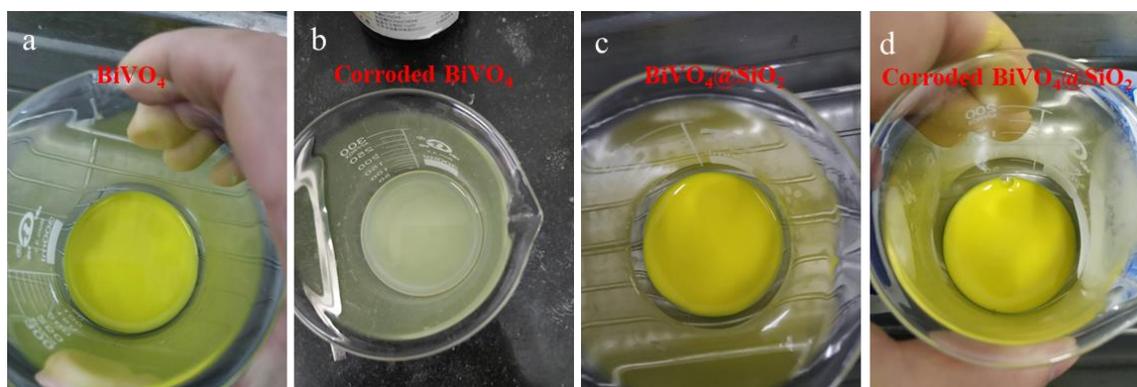
Figure 8. Photographs displaying the acid resistance of the pigments: BiVO₄ (**a**) in water and (**b**) treated for 1 min in HCl solution; BiVO₄@ SiO₂ (**c**) in water and (**d**) treated for 90 min in HCl solution.

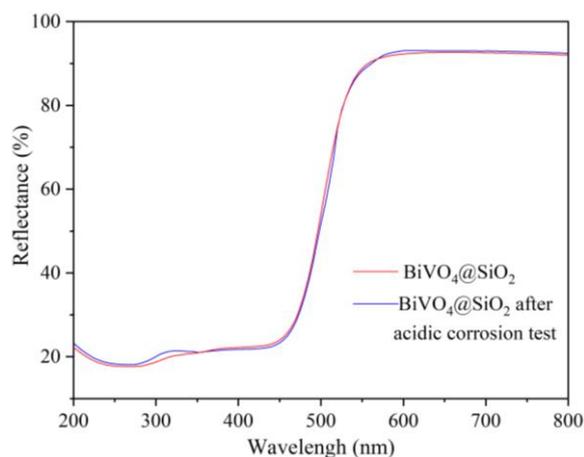**Figure 9.** UV–Vis reflectance spectra of BiVO₄@SiO₂ before and after acidic corrosion test.

The environmentally friendly and nontoxic BiVO₄ pigment is considered to be one of the most promising materials in plastic coloring applications [1,13]. However, in practical applications, it was found that pure BiVO₄ pigment is vulnerable to the erosion by some plastic melts, resulting in degraded color-rendering performance. To investigate the influence of SiO₂ encapsulation on the resistance to plastic melt of yellow BiVO₄ pigment, the prepared BiVO₄@SiO₂ was well mixed into white polypropylene (PP) in a mass ratio of 5:1000, and then injection-molded into plastic plates at 240 °C. For comparison, the BiVO₄-colored plastic sample was also prepared under the same conditions. It can be seen from Figure 10 that the BiVO₄@SiO₂-colored plastic plate exhibited a bright greenish-yellow color, while the color of the sample with BiVO₄ was dull and pale yellow. Accordingly, the former possessed much higher L* and b* values. These results indicate that the SiO₂ coating successfully enhanced the erosion resistance of BiVO₄ pigment to high-temperature plastic melt, and the obtained BiVO₄@SiO₂ encapsulated pigment had a very strong tinting strength, even though the actual content of BiVO₄ was only 0.32 wt.%. In short, the thermal and chemical stability, as well as the color performances, of the BiVO₄ pigment can be effectively enhanced via SiO₂ encapsulation modification, which is expected to greatly promote the application of this pigment in plastics, coatings, or paints, and even ceramics and glass surface decorations.
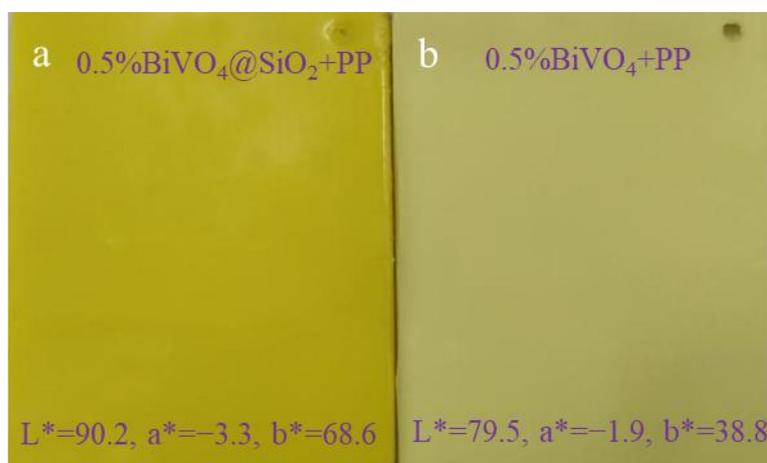

Figure 10. Photographs of PP plastics colored with (**a**) 0.5% BiVO₄@SiO₂ and (**b**) 0.5% BiVO₄ pigment.

3. Experimental Section

3.1. Preparation of Encapsulated Pigments

$BiVO_4@SiO_2$ pigment was prepared via a sol–gel method (Figure 11). The bismuth vanadate ($BiVO_4$) pigment with a primary grain size of about 100 nm was synthesized at 350~400 °C and provided by Jiangxi Jinhuan Pigments Co., Ltd., Yichun China. Before use, the pigment powder was treated with ball milling to ensure good dispersity. The reagents of AR-grade tetraethoxysilane (TEOS) and sodium dodecyl benzene sulfonate (SDBS) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. In a typical synthesis, 10 g of $BiVO_4$, 0.2 g of SDBS, and a certain amount of ethanol were mixed and ball-milled for 3 h to obtain the pigment suspension. Then, an ethanol solution of 20 g TEOS was added, and the mixture with a TEOS content of ~0.5 mol/L was mechanically stirred for 2 h. Subsequently, ammonium hydroxide ($NH_3 \cdot H_2O$, 28 wt.%, 20 g) was slowly added and stirred for 10 h. Finally, the mixture was dried at 75 °C for 12 h and then annealed at a certain temperature (400~850 °C) for 6 h under an air atmosphere to obtain $BiVO_4@SiO_2$ pigment.
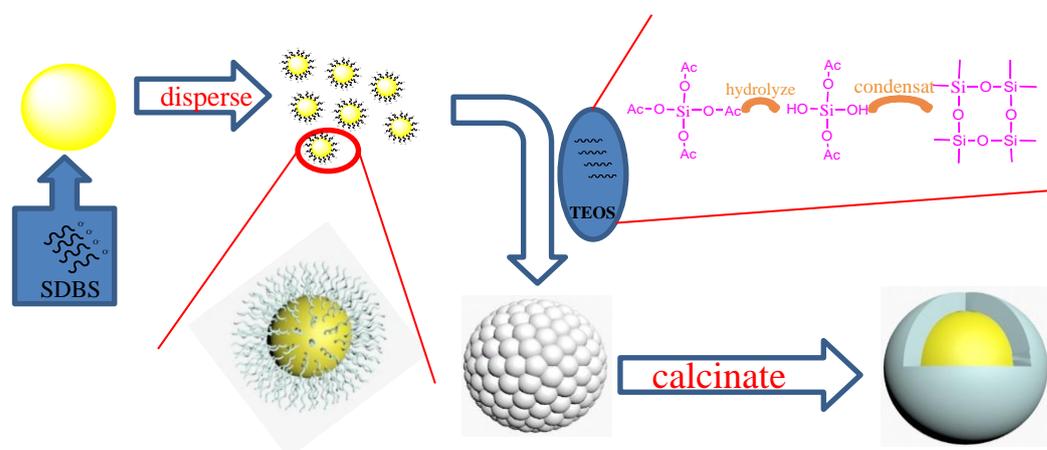

Figure 11. Schematic diagram for the synthesis of $BiVO_4@SiO_2$ pigment via the sol–gel method.

3.2. Materials' Characterization

Particle size distribution of the $BiVO_4$ pigment was analyzed with a laser diffraction particle analyzer (Bettersize2600, Bettersize Instruments, Dandong, China). Zeta potential measurements at different pH values were conducted using a Nanosizer (Nano ZS90, Malven, Worcestershire, UK). Phase composition of the encapsulated pigments was recognized with an X-ray diffractometer (XRD, D8-Advance, Bruker, Mannheim, Germany), using Cu Kα radiation (40 kV, 40 mA) at a step width of 0.02 °min^{-1}. Field-emission scanning electron microscopy (FE–SEM, SU–8010, Hitachi, Tokyo, Japan) analysis was performed to obtain the morphology of pigment powder. Transmission electron microscope (TEM) and energy-dispersive spectroscopy (EDS) investigations were carried out on a JEOL JEM–2010 (Tokyo, Japan). Ultraviolet–visible (UV–vis) and near-infrared (NIR) spectra were obtained with an ultraviolet–visible–near infrared (UV–Vis–NIR) spectrophotometer (UV–3600, Shimadzu, Kyoto, Japan) using $BaSO_4$ as a reference.

3.3. Colorimetric Measurements

The color-rendering performance of the pigment was quantified using the CIE-L*a*b* chromaticity coordinate value of the International Commission on Illumination, where L* is the brightness of the color (L* = 0 means black, L* = 100 means white), a* represents green (−)/red (+) value, and b* represents blue (−)/yellow (+) value. The values of a* and b* range from −100 to 100. The color density, $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$, represents the color saturation. h° (h° = arctan (b*/a*)) is the color angle (for yellow, h° ranges from 70~105°). The L*a*b* chromaticity parameter and the tristimulus values of X, Y, and Z for the pigment were

determined using a desktop colorimetric spectrophotometer (Ci7600, X-rite, Grand Rapids, American).

3.4. Stability Tests

To evaluate the high-temperature stability of BiVO$_4$@SiO$_2$ pigment, the pigments before and after the SiO$_2$ encapsulation were incubated at a constant temperature (500 °C, 700 °C) for 24 h, and then the chromaticity properties of the pigments were analyzed. To test the acid corrosion resistance, the SiO$_2$-coated and as-received BiVO$_4$ pigments were ultrasonically dispersed in a 30 mL of diluted hydrochloric acid solution (5 wt.% HCl), separately, and the dissolutive state of pigments over time was observed. The stability of pigments subjected to the erosion of plastic melt was also investigated in order to evaluate the application feasibility of BiVO$_4$@SiO$_2$ pigment in plastic coloring. For this purpose, the pigment (0.5 wt.%) was mixed with white polypropylene (PP) granules, followed by shaping into plastic plates via the injection molding technique at 240 °C, and the appearance of the BiVO$_4$@SiO$_2$- and BiVO$_4$-colored plastics was compared.

4. Conclusions

BiVO$_4$@SiO$_2$ encapsulated pigment, with its brilliant yellow color and strong tinting strength, was developed via the sol–gel method. The prepared BiVO$_4$@SiO$_2$ pigments were mostly composed of monoclinic BiVO$_4$ and amorphous SiO$_2$ calcined 350–800 °C. A core–shell-structured BiVO$_4$@SiO$_2$ encapsulated pigment was successfully obtained when calcined at 500–700 °C, with a dense SiO$_2$ coating thickness of 60~100 nm and an inclusion particle size of 1~2 μm. The BiVO$_4$@SiO$_2$ encapsulated pigment showed comparable chromatic parameters to pure BiVO$_4$, and the encapsulation of SiO$_2$ coating did not weaken the color-rendering performance of BiVO$_4$. In particular, chromatic parameters of L* = 88.69, a* = −4.42, and b* = 83.83 were achieved for BiVO$_4$@SiO$_2$ prepared at 600 °C, which are superior to those of pure BiVO$_4$ in yellowness. The obtained BiVO$_4$@SiO$_2$ pigments also possessed a high NIR reflectivity of more than 90%, though a high content of amorphous SiO$_2$ phase was introduced.

The thermal stability was effectively increased from ≤350 °C for BiVO$_4$ to at least 700 °C for yellow BiVO$_4$@SiO$_2$ pigment. Furthermore, the chemical corrosion resistance of the BiVO$_4$ pigment could be remarkably enhanced by the encapsulation of dense SiO$_2$ coating. The polypropylene plastic colored with only 0.5% BiVO$_4$@SiO$_2$ pigment at 240 °C displayed an obvious brilliant yellow color, indicating the good erosion resistance to plastic melt and the strong tinting strength of the encapsulated pigment.

In summary, the thermal and chemical stability, as well as the color performance, of BiVO$_4$ pigment can be effectively enhanced via SiO$_2$ encapsulation modification. Thus, this research provides a cost-effective strategy for realizing applications of environmentally friendly BiVO$_4$ pigment under high temperatures or corrosive environments, such as in plastics, energy-saving coatings, or paints, and even in ceramics and glass surface decoration.

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