

Eco-friendly betanin hybrid materials based on palygorskite and halloysite

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ABSTRAC

Eco-friendly betanin/clay minerals hybrid materials with good stability were synthesized combining natural betanin molecules extracted from beetroot with 2:1 type palygorskite (Pal) and 1:1 type halloysite (Hal), respectively. It was found that the adsorption, grinding and heating treatment played a key role to enhance the interaction between betanin and clay minerals during preparation process, which favored improving the thermal stability and solvent resistance of natural betanin. The L^* and a^* values of the betanin/Pal and betanin/Hal hybrid materials were 64.94 and 14.96, 62.55 and 15.48, respectively, indicating that betanin/Hal exhibited the better color performance. The structural characterizations

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confirmed that betanin was mainly adsorbed on the outer surface of Pal or Hal through hydrogen-bond interaction, and part of them also were entered into the inner surface of Hal *via* electrostatic interaction. Therefore, Hal preferred to improve the color properties, heating stability and solvent resistance of natural betanin due to its structural features compared with Pal.

Keywords: Palygorskite; Halloysite; Betanin; Hybrid materials; Stability

1. Introduction

There has been a long history in the applications of natural plant pigments as colorants for use in the fiber, pottery, paints, and murals, even dating back to prehistoric times [1-6]. Several centuries ago, the Mayans in ancient Mesoamerica invented the well-known Maya blue with bright color and excellent stability, which was commonly used in pottery and mural paintings during the late pre-Spanish period [7-9]. With the development of the characterization techniques and deeper cognition about interaction mechanisms of Maya blue, much progress has been made in the preparation of synthetic substitutes for natural pigments. Although man-made pigments bring great commercial benefits, they will produce persistent organic pollutants or carcinogens in the production process.

In recent years, the dye industry has been forced to gradually ban the production of potentially toxic dyes or pigments [10, 11]. After more than a century of decline, natural plant pigments have once again become the focus of attention due to abundance in nature, low toxicity, good biocompatibility and biodegradability, no oncogenic hazard [4, 12, 13].

Betalains are water-soluble natural plant pigment containing nitrogen and responsible for the deep yellow or red color of beetroot [14-17]. Betanin is the main ingredient in betalain, which provides vivid colors for food products, such as ice cream, yogurt and fudge, enhancing the visual effects and promoting consumption [16, 18-20]. However, it has never been found in the same plant as anthocyanin in the plant kingdom. Due to the antioxidants, anti-inflammatory and anticarcinogenic activities, natural betanin pigment has significant curative effect on the chronic diseases including inflammation, diabetes, cancer, neurological health and so on [19, 21, 22]. It is increasingly realizing the importance of natural plant pigments toward human health and the environment, but it is still a challenge to resolve the innate instability and sensitivity against environmental factors (*e.g.* light, oxygen, pH and metal ions), and fast degradation, which can result in a loss of colors and properties of these natural pigments [15, 20, 23-26]. Amjadi *et al.* studied the inclusion of this bioactive compound in liposomal nanocarriers to improve its digestive stability, antioxidant activity and oral bioavailability [20, 27]. However, liposomes have low physical-chemical resistibility and easily degraded at the acidic or high-temperature circumstance [28].

Clay minerals have high specific surface area, cation exchange capacity and excellent adsorption properties [29-32]. In addition, different clay minerals have different morphologies, structures, chemical compositions, and properties [33-35]. Therefore, clay minerals have become the focus of the relevant researches on the loading of natural pigments in the last few years, and the interaction between clay minerals and natural pigments is explored and guide to improve the properties of natural pigments. Among them, palygorskite

(Pal) is a naturally rod-like hydrated magnesium aluminum phyllosilicate clay mineral with a 2:1 ribbon-layer structure composed of two continuous silica-oxygen tetrahedron sheets and one discontinuous metal-oxygen octahedron sheet [36-39]. One of the most classic applications of Pal is to synthesize Maya blue pigments as an inorganic host of the stabilizing natural indigo dyes. By contrast, halloysite (Hal) is a natural hollow tubular clay mineral with the external diameter of 20-60 nm, inner lumen larger than 10 nm, and the relatively low surface hydroxyl group density [40-43]. As a dioctahedral 1:1 clay mineral, Hal is composed of the one tetrahedral SiO_4 sheet and one octahedral gibbsite $\text{Al}(\text{OH})_3$ sheet [44, 45]. Interestingly, the surface charge of Hal is the result of the interaction between the negatively charged outer layer (siloxane groups) and the positively charged inner surface (aluminol groups) in the range of pH 2-8 [46, 47]. At present, our group have successfully synthesized a series of acid/base reversible allochroic anthocyanin/clay minerals hybrid pigments based on anthocyanin natural molecules and clay minerals (Pal, Hal, sepiolite, kaolinite, and montmorillonite) [35, 39]. However, the studies on the natural anionic pigments and clay minerals are rarely reported.

Based on above background, the hybrid materials with the expected stability were obtained by loading betanin using Pal and Hal by adsorption, grinding and heating treatment. The environmental stability and possible stability mechanism between clay minerals and betanin molecules were systematically compared and studied in this paper.

2. Experimental

2.1 Materials

Pal was obtained from Guanshan Mine, Anhui Province, China, and the main chemical compositions are Al_2O_3 (8.28%), Na_2O (2.15%), CaO (1.28%), MgO (12.29%), SiO_2 (58.05%), K_2O (0.92%) and Fe_2O_3 (5.04%). Hal was provided by Zhengzhou Jinyangguang Ceramics Co., Ltd., Zhengzhou, China, and the main chemical compositions included Al_2O_3 (29.49%), Na_2O (0.07%), CaO (0.08%), MgO (0.39%), SiO_2 (42.56%), K_2O (0.85%) and Fe_2O_3 (1.37%). Hal was ground and treated with 4% HCl (wt.%), and then filtered by passing through a 200-mesh sieve and dried. Betanin (red beet extract diluted with dextrin) was provided by Tokyo chemical industry Co., Ltd., Tokyo, Japan.

2.2. Preparation of betanin/clay mineral hybrid materials

At first, 0.75 g of betanin was completely dispersed into 40 mL of distilled water with a pH of 2.0 adjusted by HCl . Then, 1 g of Pal or Hal were slowly added to the above mixture and magnetically stirred for 2 h, respectively, followed by oscillation with 200 rpm at 30 °C for 24 h in a constant temperature shaker (THZ-98A, INESA, Shanghai, China) to reach the adsorption equilibrium. And then, the products were separated by centrifugation at 4000 rpm for 15 min. Subsequently, the wet precipitation was washed with 40 mL of distilled water for 5 min and then centrifuged at 4000 rpm for 15 min. The obtained wet betanin/Pal or betanin/Hal samples were first dried at 40 °C for 5 h in a vacuum drying oven, and then ground in a mortar for 30 min, respectively. After that, the samples were treated at 120 °C for 4 h. Finally, the betanin/Pal and betanin/Hal hybrid materials were obtained after screening through a 100 mesh sieve, respectively. It should be noted that the above operations were carried out in dark conditions.

2.3. Stability tests

The thermal stability of the as-prepared hybrid materials was tested using a STA449F3 simultaneous thermal analyzer (NETZSCH-Gerätebau GmbH, Selb, Germany) in the temperature range from 30 to 550 °C with a heating rate of 10°C/min under nitrogen atmosphere. In order to further evaluate the thermal stability of the two samples, 0.04 g of betanin/Pal and betanin/Hal were successively placed in a blast drying oven at 90, 120, 150 and 180 °C for 60 min to conduct heat resistance test. The thermal stability of the samples was evaluated by comparing the colorimetric values before and after treatment at different heating temperatures.

The stability differences of the betanin/Pal and betanin/Hal hybrid materials dissolved in distilled water, acidic, ethanol and basic solutions also were evaluated, respectively. Typically, 0.04 g of samples were dispersed into 20 mL of distilled water, 0.1 M HCl, and 0.1 M NaOH, respectively, and then vibrated at 120 rpm and 25 °C for 24 h in a constant temperature shaker. After centrifugation at 4000 rpm for 15 min, the wet precipitation was completely dried in a vacuum drying oven at 40 °C, followed by the colorimetric values of the dried samples before and after treatment in the above three solutions were measured to study the chemical stability.

2.4. Characterizations

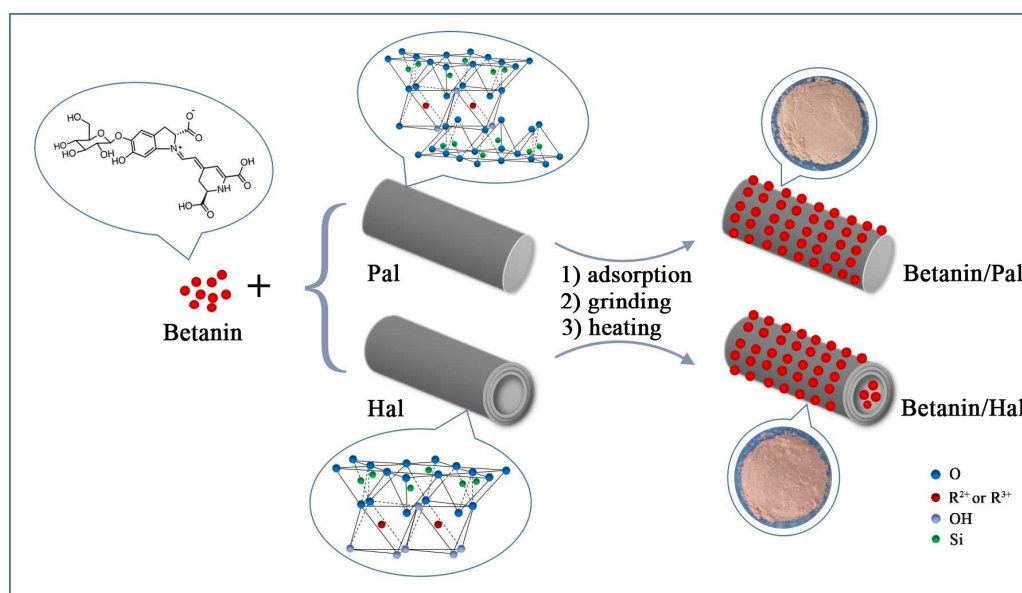
The Fourier transform infrared (FTIR) spectra of samples were measured in the range of 400-4000 cm^{-1} on a Nicolet NEXUS FTIR spectrometer (Nicolet iS50, Thermo Scientific, USA) using KBr pellets. The X-ray diffraction patterns (XRD) were record on an X'pert

PRO diffractometer along with Cu-K α radiation at 40 kV and 30 mA, the diffraction data of samples were obtained from 3 to 80° at a scanning rate of 2°/min. The morphologies were taken using the field emission transmission electron microscopy (TEM, Tecnai G 2 F20 S-TWIN TMP, USA) after the sample was dispersed ultrasonically in anhydrous ethanol and dropped onto a micro grid. The surface area and pore volume of samples were measured at -196°C with N₂ as an adsorbate using the Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP2020, Atlanta, USA). The zeta potentials were measured on a Malvern Zetasizer Nano system (ZEN3600, UK) with a 633nm He-Ne laser irradiated, in which 0.05 g of sample was dispersed into 10 mL of deionized water and sonicated for 20 min before measurement of zeta potential. The XPS spectra were recorded on an X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos Co., Ltd.). Thermal gravimetric analysis (TGA) was obtained on a STA449F3 simultaneous thermal analyzer (NETZSCH-Gerätebau GmbH, Wittelsbacherstrasse, Germany). The colorimetric values and reflectance spectra of all samples were calculate on a Color-Eye automatic differential colorimeter (X-Rite, Ci 7800) according to the Commission International de l'Eclairage (CIE) 1976 $L^*a^*b^*$ colorimetric method, in which L^* was the color lightness ranging from black (0) to white (100), while a^* and b^* represented the hue with positive and negative values mean red to green and yellow to blue, respectively. The chemical composition was collected from E3 X-ray fluorescence spectrometer (PANalytical, Almelo, Netherlands).

3. Results and discussion

3.1 Preparation and characterization of the hybrid materials

The preparation process of betanin/clay mineral hybrid materials are shown in Scheme 1, and the main preparation processes includes adsorption, grinding and heating treatment. Typically, the first step is to load the betanin molecules onto Pal or Hal through a simple 24 h adsorption process [39, 48]. Subsequently, the grinding and heating treatment are applied to promote the physical and chemical interaction between natural pigments and clay minerals strengthening the protective effect of clay minerals on natural pigments [39, 48]. Among them, the application of heating treatment helps to remove the water molecules partially located in the clay minerals, resulted in facilitating the fixation of betanin molecules on clay minerals and improving their stability [1, 8, 9, 35, 39]. The natural Pal and Hal are white and light yellow (Table S1), respectively, and hybrid materials present pink color after incorporation of betanin, which indicates that the hybridization has occurred between natural pigments and clay minerals [13, 35, 39].



Scheme 1. Schematic illustration for preparation of betanin/Pal and (b) betanin/Hal hybrid materials.

TEM micrographs of betanin/Pal and betanin/Hal hybrid materials exhibit the typical morphologies of clay minerals remained after the introduction of betanin molecules (Figure 1a and b) [39, 42, 48-50]. Among them, the surface of Pal with the rod-like morphology becomes rough due to the successful adsorption of betanin. On the contrary, Hal exhibited the hollow tubular morphology with the external diameter of 20-60 nm and inner lumen larger than 10 nm, and the surface roughness of Hal was significantly less than that of Pal when betanin was added. Therefore, it indicates that betanin might be loaded on both the inner and outer surfaces of the Hal nanotubes [51].

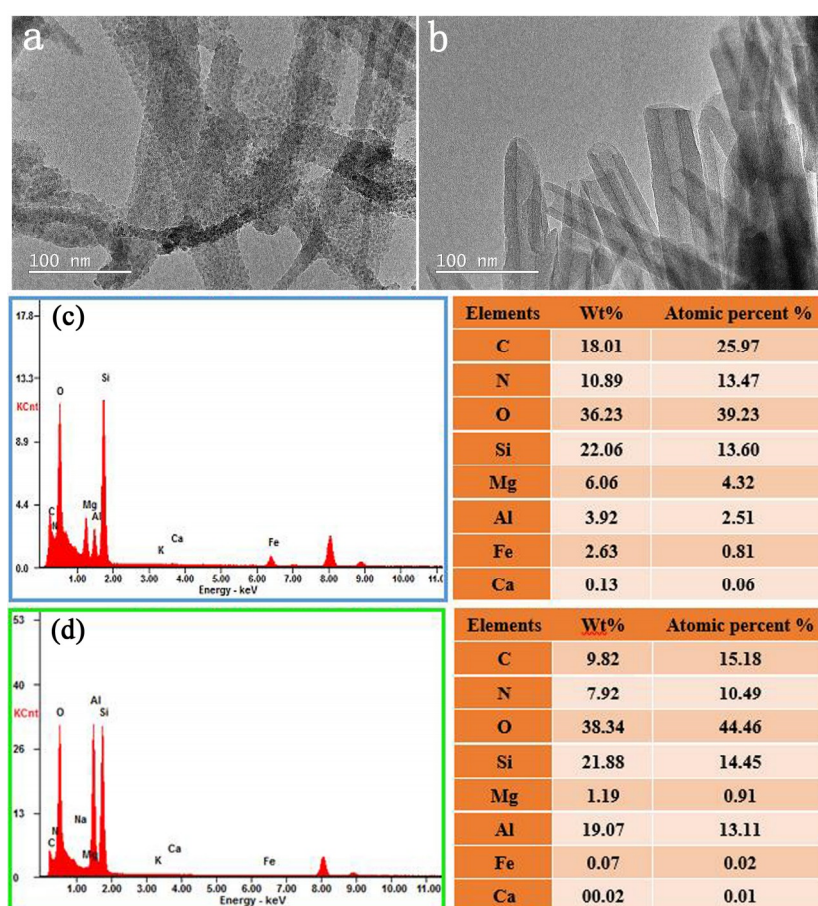


Figure 1. TEM images and EDS spectra of (a) and (c) betanin/Pal, and (b) and (d) betanin/Hal hybrid materials.

EDS analysis is used to reveal the involved chemical compositions of betanin/Pal and betanin/Hal samples (Figure S1), and their atomic percent with different elements is presented in Figure 1c and d, respectively. It is obvious that the O, Si, Mg, Al, Fe, and Ca elements are observed, which are derived from Pal and Hal [34, 52, 53]. Furthermore, the presence of C and N demonstrates the successful loading of betanin pigments on Pal and Hal. Among them, the detectable amounts of C and N on the Pal surface are 18.01% and 10.89%, respectively, which are higher than that of betanin/Hal (9.82% and 7.92%), indicating that the amount of betanin loading on the Pal surface was higher than that on the external surface of Hal.

The pore structure parameters of clay minerals and the corresponding hybrid materials are listed in Table 1. Compared with raw clay minerals, the specific surface areas (S_{BET}) of betanin/Pal sample decreases significantly from 185.85 m²/g to 129.19 m²/g while that of betanin/Hal hybrid materials decreases by only 9.81 m²/g after the addition of betanin, indicating that betanin molecules are mainly loaded on the external surface of clay minerals [39, 48]. In addition, the total pore volume (V_{total}) of betanin/Hal sample also reduces by 0.0312 cm³/g, whereas the V_{total} values of betanin/Pal hybrid materials have no significant change. This fact suggests that some organic molecules might be embedded in the lumen of Hal, and some of the small molecules gathered in the nozzle of the nanotubes, resulting in the reduction of the V_{total} values of Hal. What's more, the larger S_{BET} of Pal compared to Hal might further explain why it had a greater adsorption capacity for betanin molecules.

Table 1. Pore structural parameters of the raw clay minerals and hybrid materials.

Samples	S_{BET} (m ² /g)	S_{micro} (m ² /g)	S_{ext} (m ² /g)	V_{total} (cm ³ /g)
Pal	185.85	26.93	158.93	0.4243
Betanin/Pal	129.19	11.40	117.79	0.4288
Hal	58.10	1.43	56.67	0.2064
Betanin/Hal	48.29	-	52.43	0.1752

As shown in Figure 2, the zeta potentials of betanin at lower pH is -26.43 mV, proving it is an anionic natural plant pigment [54]. After adding betanin, the zeta-potential value of Pal increases slightly from -20.60 mV to -17.80 mV, which was consistent with the results of the stabilization of betacyanins by food grade anionic polysaccharides [54]. Interestingly, the surface charge of Hal is the result of the interaction between the negatively charged external surface (SiO₄) and the positively charged inner surface (AlO₆) in the range of pH 2-8 [13, 42, 46]. Therefore, the anion pigment might enter into the lumen of Hal nanotube during the preparation process, and the electrostatic interactions occurred inside the Hal nanotube, resulting in a reduction in the positive charge of Hal, and thus the zeta potentials of the hybrid material decreases significantly from -21.83 mV to -32.93 mV.

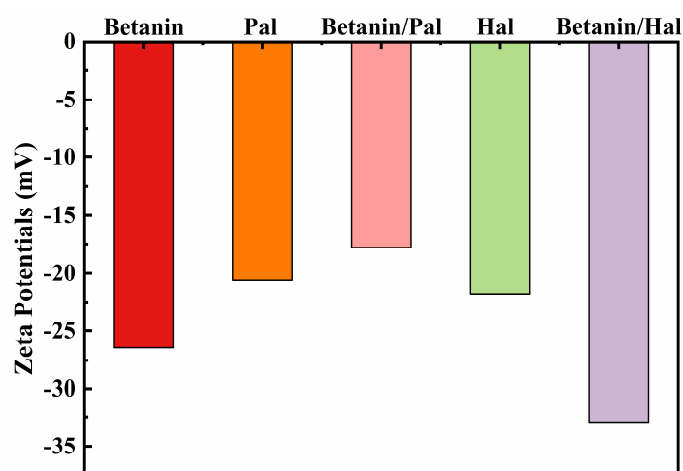


Figure 2. Zeta potentials of betanin, clay minerals and hybrid materials.

As shown in Figure 3a, the XRD patterns of Pal and Hal appear typical characteristic diffraction peaks accompanied by a small amount of impurities such as mica and dolomite [48, 51]. Pal shows three strong reflection peaks in $2\theta = 8.42^\circ$ ($d = 10.49 \text{ \AA}$), 13.79° ($d = 16.42 \text{ \AA}$) and 19.88° ($d = 4.46 \text{ \AA}$), corresponding to (110), (200) and (040) crystal planes [55]. Hal has typical diffraction peaks at $2\theta = 12.04^\circ$ ($d = 7.34 \text{ \AA}$) and 24.72° ($d = 3.60 \text{ \AA}$) corresponding to the (001) and (002) planes [56, 57]. Compared with the XRD patterns of clay minerals and corresponding hybrid materials, it is found that the XRD patterns of hybrid materials are similar to that of the corresponding clay minerals, no emergence of a new diffraction peak and no obvious layer spacing changes of Pal and Hal in (110) and (001), respectively. This indicates that the betanin molecules do not insert into the Pal nano-channels.

The FTIR spectra of clay minerals, hybrid materials and natural betanin molecules are shown in Figure 3b. In case of clay minerals, the characteristic absorption bands are presented in Figure 3b. The absorption bands around $3700\text{-}3500 \text{ cm}^{-1}$ and $3400\text{-}3300 \text{ cm}^{-1}$ are mainly due to the stretching vibration of the O-H group of the structural hydroxyl group and water molecule [57, 58]. In FTIR spectra of Pal, the absorption band at about 1600 cm^{-1} corresponds to the antisymmetric stretching vibration of zeolite water and adsorbed water [48, 59, 60]. The absorption band of $791\text{-}1198 \text{ cm}^{-1}$ was the anti-symmetric stretching vibration peak of Si-O bond [59, 61]. The bands at 508 and 497 cm^{-1} were tetrahedral Si-O deformation and bending vibration, respectively [62]. In FTIR spectrum of Hal, 1637 and 911 cm^{-1} represented the bending vibrations of H_2O and the deformation of -OH [51, 57],

while 1097 and 1032 cm^{-1} was attributed to the bending vibration peaks of Si-O and Si-O-Si, respectively [51, 56]. In the FTIR spectrum of betanin, the absorption band at 3400 cm^{-1} is attributed to the stretching vibration of -OH, the absorption band at 2926 cm^{-1} belongs to the stretching vibration of C-H, and two vibration peaks at 1638 cm^{-1} and 1422 cm^{-1} are ascribed to the -COOH group and the aromatic -CH group, respectively [63]. The symmetric stretching vibration of C-O-C appears at 1024 cm^{-1} [64], while the absorption peak at 707 cm^{-1} confirms the existence of N-H [65]. In the FTIR spectrum of hybrid materials, the absorption peaks of the stretching vibration peaks of O-H bonds in Pal and Hal migrates from 3415 cm^{-1} to 3399 cm^{-1} and from 3459 cm^{-1} to 3481 cm^{-1} , respectively, which may be due to the hydrogen bond interaction between betanin and clay minerals [27].

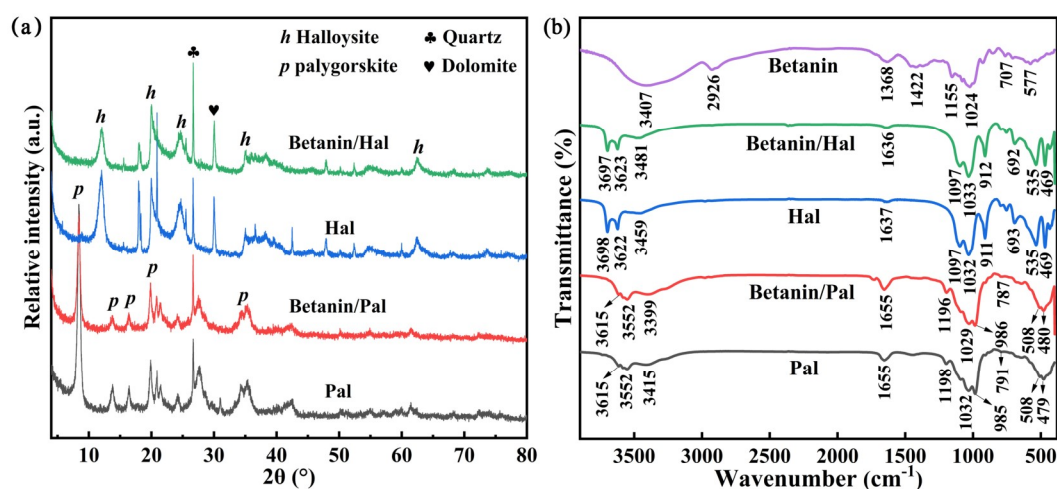


Figure 3. (a) XRD patterns and (b) FTIR spectra of betanin, the natural clay minerals and hybrid materials.

In order to further analyze the existence of surface elements and their chemical states of betanin/Pal and betanin/Hal hybrid materials, the XPS characterization is performed. The XPS survey spectra of betanin/Pal and betanin/Hal samples are shown in Figure S2 and

Figure S3, while XPS spectra of N1s, C1s, Si2p, Al2p and Mg1s are depicted in Figure 4, respectively. As shown in Figure S2, C and N atoms for betanin/Pal and betanin/Hal samples are detected at 284.85 eV (C1s) and 408.08 eV (N1s), 284.83 eV (C1s) and 409.28 eV (N1s), respectively. In addition, the C1s spectra of the betanin/Pal and betanin/Hal samples consists of the C-C(C-H), sp^2 -C, sp^3 -C and with the binding energy at about 285.0 eV, 284.5 eV, and 285.2 eV, respectively (Figure 4a). It indicated that hybrid materials are successfully prepared.

In the case of the high-resolution spectra of Si2p, there are the surface silanol groups (103.15 eV for Pal and 103.28 eV for betanin/Pal; 103.29 eV for Hal and 103.19 eV for betanin/Hal) and Si-O bonds (102.48 eV for Pal and 102.37 eV for betanin/Pal; 102.72 eV for Hal and 102.75 eV for betanin/Hal) (Figure 4b and c) [34, 66, 67]. The peak areas of Si-OH and Si-O in betanin/Pal are less than that in Pal, but the peak areas of these two groups in betanin/Hal are larger than that in Hal, indicating that Si-O-Al and Si-O-Mg of betanin/Pal reduces. On the contrary, more Si-OH and Si-O appear after incorporation of betanin pigment into Hal. The Al2p of Pal exhibits two peaks at 74.95 (Al-OH) and 74.53 eV (Al-O), which shifts to 75.17 eV and 74.47 eV, respectively (Figure 4d). In case of the Al2p of Hal and betanin/Hal, the peaks of Al-OH (75.13 eV for Hal, 75.07 eV for betanin/Hal) and Al-O (74.24 eV for Hal, 74.47 eV for betanin/Hal) appear in the Al2p spectra (Figure 4e). Clearly, it is found that the peak areas of Al-OH and Al-O in the both hybrid materials are all larger than that in Pal and Hal, indicating that more Al-OH and Al-O are produced after introducing small molecules. It indicates that more hydroxyl groups and more the adsorption

sites are provided for betanin under acidic conditions, forming chemical interactions such as hydrogen bonding between betanin pigments and aluminum silicate with abundant hydroxyls, especially Hal [66, 68]. In the case of Pal and corresponding hybrid materials, the binding energy of the Mg element on the surface of betanin/Pal (1304.21 eV) has no obvious change compared with that of Pal (1304.24 eV) (Figure 4f). However, the intensity of Mg1s peak decreases significantly, indicating that some Mg elements are leached from Pal [66].

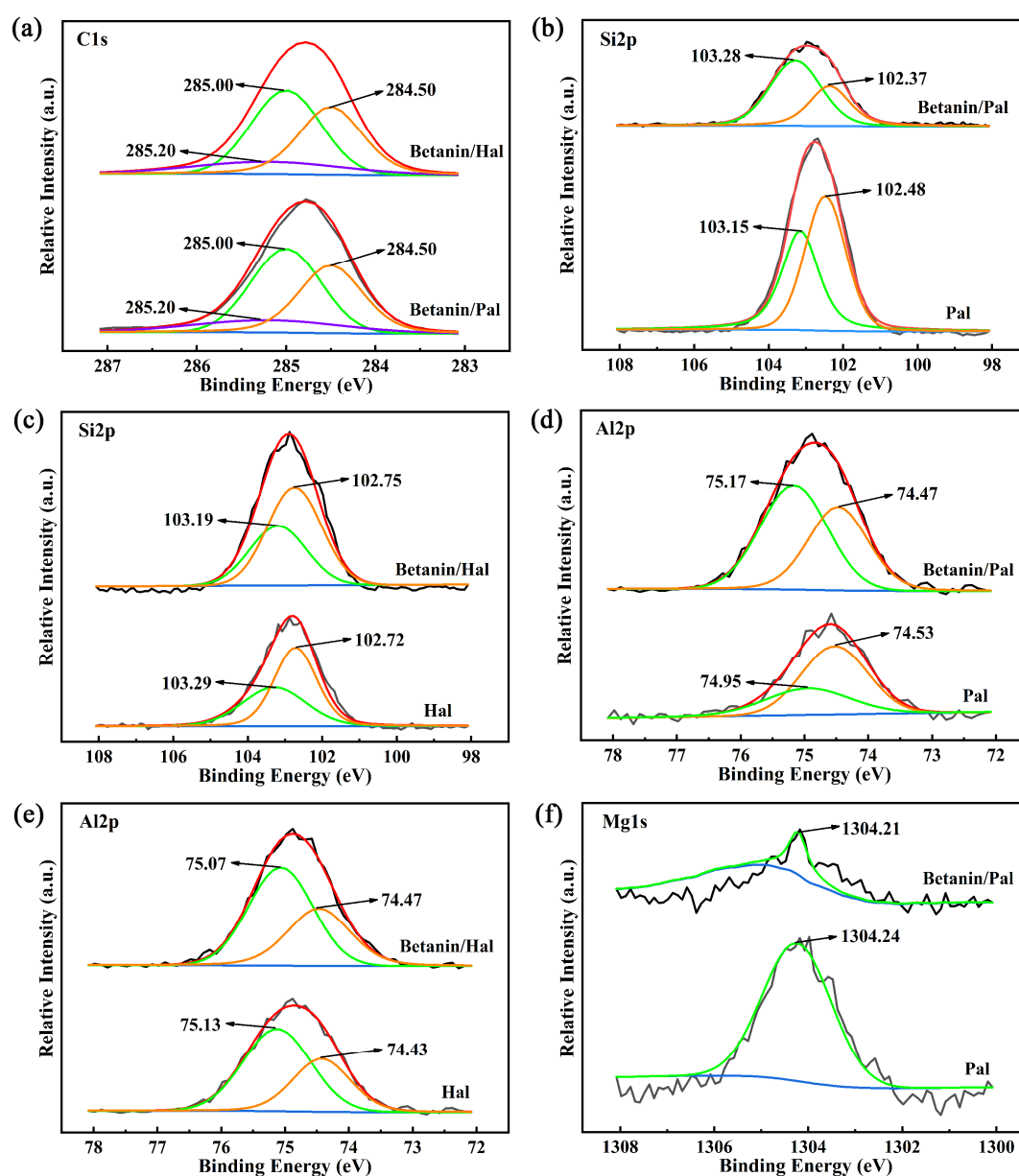


Figure 4. XPS high-resolution scanning spectra of Pal, betanin/Pal, Hal, betanin/Hal: (a) C1s, (b) and (c) Si2p, (d) and (e) Al2p, (f) Mg1s.

3.2 Thermal and chemical stability of the hybrid materials

The DSC-TGA curves of clay minerals, hybrid materials and betanin are shown in Figure 5. As depicted in Figure 5a, clay minerals, hybrid materials and betanin have obvious Endothermic peaks in the DSC curves. As can be seen from Figure 5b, natural betanin begins to degrade at room temperature and rapidly lost the weight at about 200 °C, and it presents a maximum loss at 350 °C suggesting that the degradation of natural pigments basically completes. At 550 °C, the residual mass of betanin is only 25.57%, indicating that natural pigments have poor high temperature resistance. In case of raw Pal, the degradation process occurs in the three stages of 30-550°C, which are related to the removal of the adsorbed water, zeolitic H₂O, the bound OH₂, and part of structural OH, respectively [39, 48, 60, 62]. As for raw Hal, it shows an initial slight mass loss from room temperature, which is attributed to the evaporation of surface physically adsorbed water and the interlayer H₂O. In addition, the bands from 400 °C to 550 °C is a loss of hydroxyl groups of Hal [13, 69, 70]. Obviously, the hybrid material exhibits different degradation behavior to the corresponding clay minerals, which is due to the addition of betanin. The mass loss step of both hybrid materials presents at 30 °C with the weight loss of 2.00% and 2.19% was associated with the evaporation of surface water molecules of clay minerals. Therefore, the betanin in betanin/Pal and betanin/Hal sample exhibits the obviously low weight loss rate of 1.17% and 0.31% at 200 °C, respectively. It is worth noting that the final mass loss of betanin in

betanin/Hal (1.03%) is significantly lower than that of in betanin/Pal (5.61%). Therefore, the results demonstrate that betanin/Hal presents much better thermal stability than betanin/Pal at higher temperatures. It is possibly due to the stronger physical and chemical interactions between Hal and betanin molecules, and the fact that the small molecules partly enters into the lumen of Hal nanotube, resulting in more superior shielding effect.

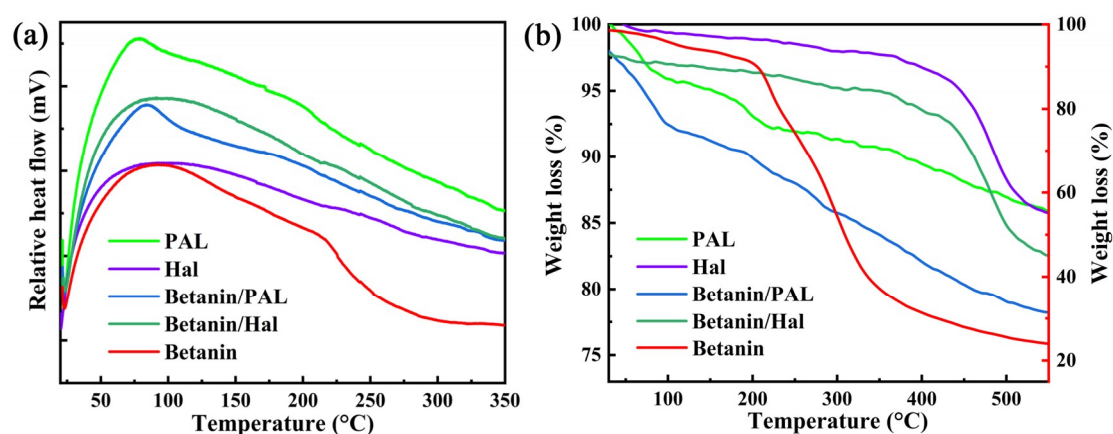


Figure 5. DSC and TGA curves of the raw clay minerals and hybrid materials.

The chromaticity values of betanin and hybrid materials after being successively treated at 90, 120, 150 and 180 °C for 60 min are applied to further evaluate the thermal stability of samples. As shown in Figure 6a, the changes of L^* , a^* and b^* of betanin at lower heating temperature are very obvious, indicating that the thermal stability of betaine is poor. After incorporation of clay minerals, the chromaticity values of the hybrid material changes little within 90 °C (Figure 6b and c). As the temperature continues to rise, the L^* and b^* values of betanin /Pal increase gradually, while the a^* values decreases gradually. Compared with betanin and betanin/Pal, betanin/Hal has a smaller change in chromaticity value exhibiting the better thermal stability, as evidenced by digital images of samples at different heating temperatures (Figure S4). It might be due to the fact that betanin is not only adsorbed on the

external surface of Hal, but also confined in the inner surface [51].

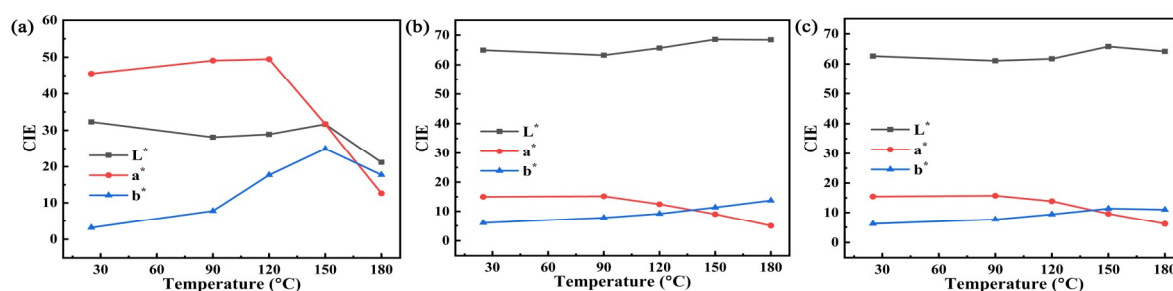


Figure 6. The CIE of (a) betanin, (b) betanin/Pal and (c) betanin/Hal at different temperatures.

Table 2. Color parameters of betanin/Pal and betanin/Hal before and after being treated by distilled water, 0.1 M HCl and 0.1 M NaOH for 24 h.

Different medium	Betanin/Pal			Betanin/Hal		
	L^*	a^*	b^*	L^*	a^*	b^*
Before	64.94	14.98	5.99	62.55	15.48	6.20
Distilled water	69.59	5.13	8.34	55.62	11.97	5.86
0.1 M HCl	73.13	1.89	13.00	59.23	6.32	11.80
0.1 M NaOH	70.47	1.48	9.98	64.60	6.85	13.91

In addition, the solvent resistance of hybrid material is also evaluated. The colorimetric parameters of hybrid materials before and after being immersed into distilled water, 0.1 M hydrochloric acid and sodium hydroxide for 24 h are listed in Table 2. As shown in Table 2, the color parameters of betanin/Pal samples before and after immersion in the three solutions are significantly different. After being treated with hydrochloric acid and sodium hydroxide, the a^* value decreases significantly to 1.89 and 1.48, while b^* increases from 5.99 to 13.00 and 9.98. It suggests that the chromaticity parameters of hybrid materials change little after betanin/Hal is treated by different solutions. Combined with the images of the supernatants

after attack of the above three solutions (Figure S5), it can be concluded that the introduction of Hal is more helpful to improve the stability of natural pigments in distilled water, acid and alkaline solutions.

Clearly, the color of betanin/Hal after being treated by distilled water, 0.1 M HCl and 0.1 M NaOH for 24 h is much closer to the red area than that of hybrid materials under the same treatment condition (Figure 7a). Furthermore, the characteristic absorption bands in the range of 450-600 nm representing red are attributed to the existence of betanin in the diffuse reflectance spectra (Figure 7b and c). The intensity of absorption bands of betanin/Hal samples is larger than that of betanin/Pal samples after being treated using different solvents for 24 h (Figure 7b and c). This further confirms that Hal has a better shielding effect on natural pigments.

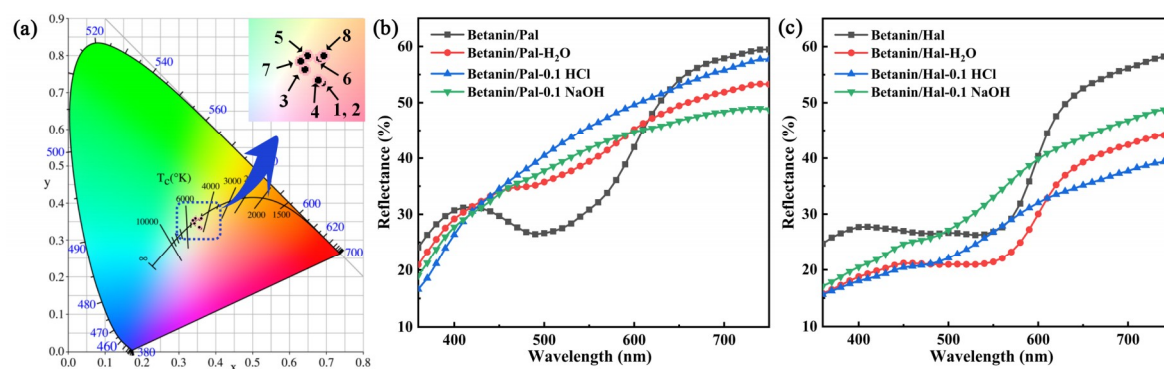


Figure 7. (a) Chromatic CIE coordinates and (b) UV-vis diffuse reflectance spectra of hybrid materials after being treated by distilled water, 0.1 M HCl and 0.1 M NaOH for 24 h (1: Betanin/Pal; 2: Betanin/Hal; 3: Betanin/Pal-H₂O; 4: Betanin/Hal-H₂O; 5: Betanin/Pal-HCl; 6: Betanin/Hal-HCl; 7: Betanin/Pal-NaOH; 8: Betanin/Hal-NaOH).

4. Conclusions

The betanin/clay mineral hybrid materials were successfully prepared by combining the

natural betanin molecules with Pal or Hal. It was found that the betanin/Hal hybrid materials presented the better color performance ($L^* = 62.55$, $a^* = 15.48$, $b^* = 6.20$) than betanin/Pal samples ($L^* = 64.94$, $a^* = 14.96$, $b^* = 5.99$). What's more, the thermal and chemical stability of the betanin molecule was also obviously improved by the physical and chemical interaction between the organic guests and the clay minerals. The results indicated that the betanin molecules were mainly loaded on the surface of Pal, but part of betanin also entered into the internal surface of Hal besides the external surface adsorption due to the electrostatic interaction with Hal, exhibiting the better color property and stability against the external environmental factors. Furthermore, the as-prepared stable hybrid materials may be a potential candidate as eco-friendly antibacterial pigments to be applied in relevant fields combining with the inherent antibacterial and nontoxic components.

Supplementary Materials: Table S1: Color parameters of pure betanin, Pal and Hal; Figure S1: The element mapping images of (A) betanin/Pal and (B) betanin/Hal: (a) C, (b) N, (c) O, (d) Si, (e) Mg, (f), Al (g) Fe, (h) Ca; Figure S2: X-ray photoelectron spectra of Pal, betanin/Pal, Hal and betanin/Hal; Figure S3: XPS high-resolution scanning spectra of betanin/Pal and betanin/Hal: N1s; Figure S4: Digital images of the pure betanin, betanin/Pal and betanin/Hal at different heating temperatures; Figure S5: Digital images of the pure betanin and betanin desorbed from the betanin/Pal and betanin/Hal hybrid materials after being immersed for 24 h in (a) distilled water, (b) 0.1 M HCl and (c) 0.1 M NaOH, respectively.

Author Contributions: A.W. and S.L. designed the experiments; S.L. performed the experiments and characterization analysis; B.M., X.W., and Y.K. assisted with the experimental work; S.L. wrote the original draft manuscript; A.W. and B.M. reviewed and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare no competing financial interest.

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