



Biomimetic Superhydrophobic Cobalt Blue/Clay Mineral Hybrid Pigments with Self-cleaning Property and Different Colors

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Abstract. Inspired by self-cleaning and water-repellent properties of the lotus leaf, biomimetic superhydrophobic cobalt blue/clay mineral hybrid pigments were facilely fabricated based on the rough surface of hybrid pigments and the modification with various organosilanes. The obtained hybrid pigments were characterized using various analytical techniques. Due to the difference in the compositions and morphologies of clay minerals, the obtained cobalt blue/clay mineral hybrid pigments exhibited different color properties. Superhydrophobicity of hybrid pigments was mainly regulated by the types of organosilanes instead of the morphologies of hybrid pigments. The sprayed coating of the superhydrophobic hybrid pigments exhibited the excellent self-cleaning performance with high water contact angle and low sliding angle. The coatings also presented excellent environmental and chemical durability even under harsh conditions. Therefore, the obtained biomimetic superhydrophobic cobalt blue/clay mineral hybrid pigments may be applied in various fields, such as anticorrosion, self-cleaning coating, etc.

Keywords: Biomimetic · Superhydrophobic · Cobalt blue · Clay minerals · Self-cleaning

1 Introduction

Cobalt blue (cobalt aluminate, CoAl_2O_4) pigment is a typical eco-friendly blue inorganic pigment. Due to high refractive index, excellent chemical and thermal stability, it can be widely applied in ceramics, paints, engineering plastics, etc. However, the high cost of CoAl_2O_4 pigment severely restrains their relevant applications due to the high price of cobalt compounds and the disadvantages of the traditional solid phase method

(Armijo 1969). In addition, most of the common application fields of CoAl_2O_4 pigment are hydrophilic, which may be easily contaminated by dark liquid, oil stains, blot in our daily life. Therefore, it is very necessary to develop low-cost CoAl_2O_4 pigment with self-cleaning ability.

Inspired by the unique water-repellent surfaces of the lotus leaf in the natural world (Barthlott and Neinhuis 1997), the design of superhydrophobic surfaces has become the focus in both fundamental research and industrial applications by construction of rough surface structure and modification using materials with low surface free energy. Recently, substrate-based inorganic hybrid pigments composed of an inorganic substrate coated with inorganic pigment nanoparticles have attracted increasingly attention. Our groups successfully prepared CoAl_2O_4 hybrid pigment after incorporation of different clay minerals (Mu et al. 2015; Zhang et al. 2017). Incorporation of clay minerals greatly decreased the production cost and calcining temperature for formation of spinel CoAl_2O_4 , as well as preventing from the aggregation of CoAl_2O_4 nanoparticles after being uniformly anchored on the surface of clay minerals. Based on the rough surface of the hybrid pigments, it could realize the superhydrophobic modification of hybrid pigments using materials with low surface free energy. In this study, different CoAl_2O_4 hybrid pigments derived from kaoline (Kaol), palygorskite (Pal), halloysite (Hal) and montmorillonite (Mt) were prepared and modified using different organosilanes including octyl triethoxysilane (OTES), dodecyl trimethoxysilane (DTMS), hexadecyltriethoxysilane (HTES) and perfluorooctyl trimethoxysilane (PFOTMS), and the effect of the types organosilanes and the morphologies of hybrid pigments on the superhydrophobic properties was comparatively studied.

2 Methods and Approaches

Cobalt blue/hybrid pigments were prepared according to the similar procedure reported in our previous study (Zhang et al. 2017). Typically, 2.91 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 7.50 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.09 g of clay minerals were added to 50 mL of water under magnetic stirring at 150 rpm for 30 min, and then 3 M NaOH was added dropwise into above mixture until the pH was reached to 10. The suspension was continuously stirred for 2 h at room temperature, and then the solid products were collected by centrifugation, washed with water and directly calcined at 1100 °C for 2 h with a rate of 10 °C/min. Next, the superhydrophobic modification of hybrid pigments was conducted in the ammonia saturated ethanol solution (Zhang et al. 2018). 0.54 g of organosilanes and 1.5 g of hybrid pigments with different weight ratios were firstly added into 45 mL above ethanol solution and stirred for 1 h at room temperature, and then 4.00 g of water was injected quickly into the solution and stirred for 24 h at room temperature. The solid products were finally washed with ethanol for three times and dried in an oven at 60 °C. The obtained samples were labeled as clay mineral-HP-organosilanes according to the involved clay minerals and organosilanes.

3 Results and Discussion

Table 1. Color parameters, water contact angle (CA) and sliding angle (SA) of superhydrophobic hybrid pigments before and after being treated at various conditions

Samples	Conditions	L*	a*	b*	CA/°	SA/°
Kal-HP-HTES	-	38.1	2.6	-63.8	164.2	1.0
	98% H ₂ SO ₄	37.4	2.6	-63.6	163.8	1.2
	3 M NaOH	38.1	2.6	-63.8	163.3	1.3
	UV for 3 days	38.0	2.6	-63.9	164.0	1.1
Pal-HP-HTES	-	16.2	-21.1	-23.5	148.1	2.4
	98% H ₂ SO ₄	15.8	-20.8	-26.2	148.2	2.3
	3 M NaOH	16.7	-21.3	-24.8	147.5	2.4
	UV for 3 days	16.9	-22.2	-23.3	148.3	2.4
Hal-HP-HTES	-	55.8	-2.3	-55.0	151.2	1.2
	98% H ₂ SO ₄	55.6	-2.4	-54.6	151.6	1.5
	3 M NaOH	55.8	-2.8	-53.7	151.8	1.8
	UV for 3 days	55.2	-2.6	-54.2	150.8	1.2
Mt-HP-HTES	-	24.5	-21.2	-32.3	156.4	3.7
	98% H ₂ SO ₄	23.2	-21.3	-33.2	155.6	3.4
	3 M NaOH	24.6	-21.4	-32.7	157.5	3.1
	UV for 3 days	21.2	-20.4	-30.5	154.8	3.3
Kal-HP-OTES	-	38.1	2.5	-63.8	135.1	4.0
Kal-HP-DTES	-	38.1	2.6	-63.8	151.2	3.0
Kal-HP-PFOTMS	-	38.0	2.5	-63.7	165.2	2.0

The color parameters, CA and SA of superhydrophobic hybrid pigments before and after being treated at various conditions were summarized in Table 1. It was found that superhydrophobic hybrid pigments derived from different clay minerals presented different color properties (Fig. 1), which might be attributed to the difference in the compositions of clay minerals, especially Fe element. Among the employed clay minerals, the higher content of Fe element was observed in Pal and Mt than Kal and Hal, which decreased the color parameters of hybrid pigments. By contrast, hybrid pigment prepared using Hal exhibited the optimum color properties, and hybrid pigments obtained from Kal came second. In addition, the water contact angle and sliding angle of different hybrid pigments derived from different clay minerals had no obvious difference after being modified using HTES (Fig. 1). Except for Pal-HP-HTES, the values of CA and SA of them were higher than 150° and below 5°, respectively. Although the hybrid pigments were treated at various conditions, the color properties, CA and SA almost kept stable, indicating the excellent environmental and chemical durability. Furthermore, superhydrophobic Kal-HP modified with various organosilanes presented different CA and SA. With the increase in the carbon chain length, the values of CA increased while the SA values decreased. Meanwhile, the incorporation of

fluorine atom in organosilanes also favored enhancing the superhydrophobic properties of hybrid pigments.

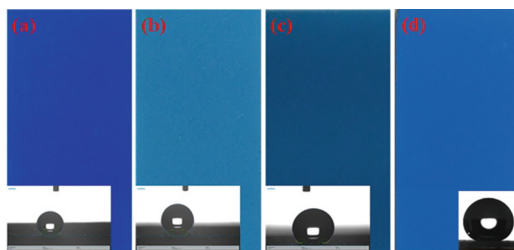


Fig. 1. Digital photos of (a) Hal-HP-HTES, (b) Mt-HP-HTES, (c) APT-HP-HTES and (d) Kal-HP-HTES

4 Conclusions

Superhydrophobic cobalt blue/clay mineral hybrid pigments with self-cleaning property and different colors were successfully prepared by modifying using organosilanes based on the rough surface. The color and superhydrophobicity were closely related to the compositions of clay minerals and the types of organosilanes.

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References

- Armijo JS (1969) The kinetics and mechanism of solid-state spinel formation—a review and critique. *Oxid Met* 1:171–198
- Barthlott W, Neinhuis C (1997) Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* 202:1–8
- Mu B, Wang Q, Wang AQ (2015) Effect of different clay minerals and calcination temperature on the morphology and color of clay/ CoAl_2O_4 hybrid pigments. *RSC Adv* 5:102674–102681
- Zhang AJ, Mu B, Luo ZH, Wang AQ (2017) Bright blue halloysite/ CoAl_2O_4 hybrid pigments: preparation, characterization and application in water-based painting. *Dyes Pigm* 139:473–481
- Zhang AJ, Mu B, Hui AP, Wang AQ (2018) A facile approach to fabricate bright blue heat-resisting paint with self-cleaning ability based on CoAl_2O_4 /kaoline hybrid pigment. *Appl Clay Sci* 160:153–161

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