Dyes and Pigments 104 (2014) 131–136

Contents lists available at ScienceDirect

Dyes and Pigments

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

Facile synthesis of multicolor organic–inorganic hybrid pigments based on layered double hydroxides

Pinggui Tang, Yongjun Feng, Dianqing Li*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 30 August 2013
Received in revised form
4 December 2013
Accepted 9 December 2013
Available online 18 December 2013

Keywords:
Intercalation
Hybrid pigments
Multicolor
Supramolecule
Layered double hydroxides
Thermostability

ABSTRACT

C.I. Acid Yellow 25 and C.I. Acid Blue 25 have been co-intercalated into the interlayer galleries of ZnAl layered double hydroxides by co-precipitation method to produce multicolor organic–inorganic hybrid pigments. The obtained pigments are characterized by X-ray diffraction, scanning electron microscopy, fourier transform infrared spectroscopy, thermogravimetric-differential thermogravimetric-differential thermal analysis, ultraviolet–visible spectroscopy, chemical composition and CIE 1976 $L^*a^*b^*$ color scales. The results suggest that there exist host–guest interactions between host sheets and guest dye anions and guest–guest interactions between the dye anions. The intercalation into the interlayer region of layered double hydroxides significantly improves the thermostability of the two dyes. The color of the organic–inorganic hybrid pigments can be easily tuned from orange yellow to yellow green, yellowish green, green, bluish green and blue by adjusting the molar ratio of dye anions in the interlayer room of layered double hydroxides.

1. Introduction

Organic–inorganic hybrids have attracted wide attention because they have the advantages of both organic (light weight, flexibility, versatility, etc.) and inorganic materials (high thermal and mechanical resistance) [1]. Hybrid materials with extraordinary new properties and multifunctional character do not only represent a new field of basic research but also provide prospects for many new applications in various areas, such as optics, solid electrolytes, catalysis, biomaterials and biomedical applications [2]. Moreover, the synergistic effect between the organic and inorganic parts is expected. On account of their swelling and soft-matter-related properties, clays have always been utilized as inorganic matrices to combine with organic components to generate multifunctional hybrid materials [2].

Layered double hydroxides (LDH) is a class of anionic layered clays with a general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH^{-})_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} stand for various divalent and trivalent metal cations, respectively, and A^{n-} represents the interlayer anions in the hydrated interlayer galleries [3]. In the past two decades, LDHs have received considerable attention due to their large versatility in terms of chemical composition, charge density and anion exchange, ability to build up 2D-organized structures, good thermal stability, and widely potential applications in catalysis [4,5], adsorption [6,7], sensors [8,9], electrochemistry [10,11], polymer additives [12–14] and drug delivery [15].

Recently, considerable interest has been focused on the fabrication of chromophore–inorganic composite materials, because they may show novel functionalities that are not present in the individual components alone [1,16,17]. The composites of inorganic matrices and the organic chromophores offer a number of synergistic effects. The inorganic host structure gives stabilization and protection by making the sandwich structure with the organic chromophores which contribute the optical function, color, fluorescence, and nonlinear optical properties [1,18]. Several organic chromophore–LDH composites have been reported in recent years [17,19–23]. However, the color of these hybrid compounds is monotone, which greatly restricts their application as pigment. Here, we reported a strategy to prepare multicolor organic chromophore–LDH hybrid pigments. C.I. Acid Yellow 25 (AY25) and C.I. Acid Blue 25 (AB25) were selected as the organic chromophores due to their bright color and high color strength. Both of the chemical structures are illustrated in Fig. 1. Multicolor organic–inorganic hybrid pigments were prepared by co-intercalating AY25 and AB25 into the interlayer galleries of ZnAl LDH via co-precipitation method. The color of the new hybrids can be easily tuned from orange yellow to yellow green, yellowish green, green, bluish green and blue by modulating the molar ratio of AB25/AY25

* Corresponding author. Tel.: +86 10 64436992; fax: +86 10 64425385.
E-mail address: lidq@mail.buct.edu.cn (D. Li).

0143-7208/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2013.12.012

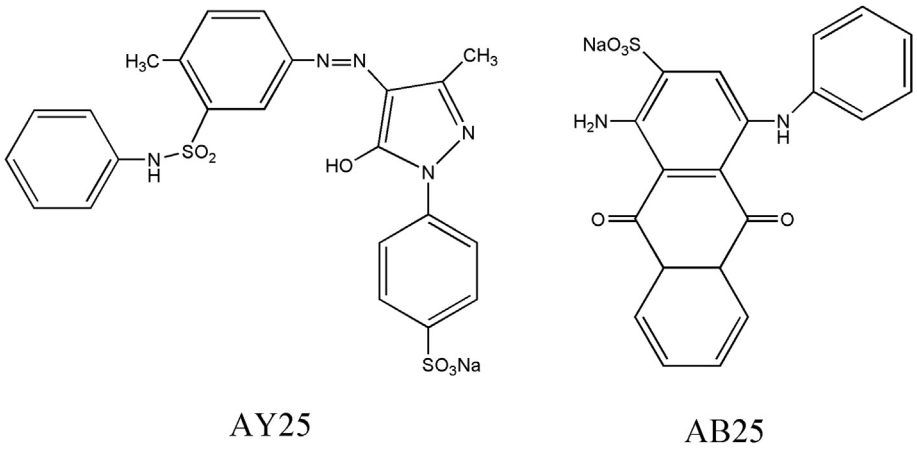

Fig. 1. The chemical structures of AY25 and AB25.

in the interlayer region of LDHs. Meanwhile, the intercalation significantly enhances the thermal stability of AY25 and AB25.

2. Experimental section

2.1. Materials

NaOH, $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, ethylene glycol and ethanol were A.R. grade reagents. Deionized water with the conductivity less than 10^{-6} S cm^{-1} was freshly decarbonated by boiling before use in the synthesis and washing steps. AY25 and AB25 were commercial products (Hangzhou Aronda Chemicals Co. Ltd.) with a purity of 94% and were recrystallized three times in water before use.

2.2. Synthesis of ZnAl–YB–LDHs

AY25 and AB25 anions co-intercalated LDHs (ZnAl–YB–LDHs) were synthesized through co-precipitation method. The mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.01 mol), $Al(NO_3)_3 \cdot 9H_2O$ (0.005 mol), AY25 and AB25 were dissolved in a mixture of water and ethylene glycol (150 mL, the volume ratio of water to ethylene glycol is 2:1). The total molar amounts of AY25 and AB25 were fixed to be 0.0055 mol where the molar percentage of AB25 was set to be 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 100 percent, respectively. NaOH (0.03 mol) was dissolved in water (80 mL) and then added dropwise into the above mixed solution with vigorous stirring under N_2 atmosphere at 50 °C. The resulting precipitate was then aged at 100 °C with violent agitation under a N_2 stream for 24 h. The product cake was collected after six repetitive centrifugation and dispersion cycles in hot deionized water and two centrifugation and dispersion cycles in ethanol. Finally, the obtained product was dried at 100 °C to constant weight. The obtained LDHs were denoted as LDH-*n*, where *n* represents the molar percentage of AB25.

The physical mixtures of LDH-0 and LDH-100 were obtained by vigorous stirring their cakes in ethanol solvent until forming a uniform mixture, centrifuging and drying at 100 °C to constant weight. The molar ratios of AB25/AY25 for the physical mixtures are equal to those for LDH-40, LDH-50 and LDH-60, respectively, and the physical mixtures were correspondingly denoted as M-40, M-50 and M-60.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer with monochromatic Cu K_α radiation ($\lambda = 0.15406$ nm) operating at 40 kV and 30 mA. Fourier transform infrared spectroscopy (FT-IR) spectra were collected on a Bruker Vector 22 infrared spectrophotometer by employing the KBr disk method with a weight ratio of sample/KBr of 1:100. Thermogravimetric-differential thermogravimetric-differential thermal analysis (TG–DTG–DTA) were performed on a PCT–IA instrument in the temperature range of 30–800 °C with a heating rate of 10 °C min^{-1} under air atmosphere. The acid dyes were dissolved in ethanol and the new hybrid pigments were dispersed in ethanol through ultrasonic treatments and then their Ultraviolet–visible (UV–vis) absorbance spectra were recorded on a Shimadzu UV-2501PC instrument. Elemental analyses for metal elements in the LDHs powder were performed on an ICPS-7500 inductively coupled plasma emission spectrometer (ICP–ES). Carbon, nitrogen and hydrogen analyses were carried out on Elementar vario EL Analyzer. Scanning electron microscope (SEM) images were obtained with a Hitachi S-4700 scanning electron microscope operating at 20 kV. The $L^*a^*b^*$ values and color coordinates of the obtained products were determined in terms of CIE 1976 $L^*a^*b^*$ with a TC-P2A automatic colorimeter (Xinao Yike Optic-Electronic Co., Beijing). 0.20 g of the new hybrid pigment was put into a sample cell and then tightly squashed with a glass rod. Before color measurement, the colorimeter was calibrated with a standard black cylinder and a white $BaSO_4$ plate.

3. Results and discussion

3.1. Structure and morphology of the samples

Fig. 2A shows the powder XRD patterns of the prepared ZnAl–YB–LDHs with typical Bragg reflections of LDH and only one series of *00l* reflections, suggesting that AY25 and AB25 were co-intercalated into the interlayer galleries of LDHs and uniformly dispersed in the galleries to form a homogeneous phase. The *00l* reflections become stronger and more symmetrical as the content of AB25 increases, indicating the enhancement of the crystallinity. The 003 reflections for LDH-0 and LDH-100 give an interlayer distance of 2.94 and 2.42 nm, respectively, in good agreement with those values reported in the literature [24,25]. Given that the thickness of a LDH layer is 0.48 nm, the gallery height is 2.46 nm for LDH-0 and 1.94 nm for LDH-100, which is larger than the length of the corresponding dye anion but smaller than double times of the length. The dye anions would form a monolayer with interdigitated arrangement in the LDH channel for LDH-0 and LDH-100 [22]. The 003 reflections for AY25 and AB25 co-intercalated LDHs show that