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Research paper

In situ self-assembled preparation of the hybrid nanopigment from raw sepiolite with excellent stability and optical performance

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ABSTRACT

A novel nanopigment with excellent stability and optical performance was prepared by installing rhodamine B (Rhb) onto the hexagonally ordered mesoporous silica (Al-MCM-41) using in situ self-assembled method (Rhb@SSA). The Rhb molecules were assembled and enriched in special microenvironment between the template and silica walls by the reconstructed process. Raw sepiolite (Sep) was used as effective and environmentally-friendly source of silicon and aluminum in the synthesis of Al-MCM-41. The structure and performance of nanopigments obtained by different supports and preparation methods were characterized by XRD, BET, SEM-EDX, TEM, FT-IR, TGA, UV–Vis, the excitation spectrum and emission spectrum and colorimetric tests. The cetyl-trimethyl ammonium bromide (CTAB) with dual functions of templating-photosensitizer plays an important role in formation of the Al-MCM-41 and the colour performance enhancement. 0.5% Rhb@SSA prepared via impregnation method shows better performance than those of 0.5% Rhb/Sep and 0.5% Rhb/Al-MCM-41.

1. Introduction

A particularly attractive property of the organic/inorganic hybrid nanopigments is that it doesn't fade despite in the environment of harsh humidity and high temperature. Thus, the stable pigments have attracted much attention of researchers in the fields of chemistry, material and archaeology.

Incorporation of small dye molecules by impregnation in meso- and micro-porous material is a frequently employed strategy to fabricate the organic/inorganic hybrid nanopigments (Ruiz-Hitzky, 2001; Calzaferri et al., 2003; Raha et al., 2009; Beltrán et al., 2014; Siwińska-Stefańska et al., 2017). Among various porous compounds, interlayered clays have been highly attractive due to their controllable pore dimensions and cheapness (Zhuang et al., 2018). The dye molecules may penetrate into the tunnels of clays (Chiari et al., 2003; Fois et al., 2003; Giustetto et al., 2005; Chiari et al., 2008; Río et al., 2009), or be adsorbed onto the grooves (Tilocca and Fois, 2009), or block the entrances of the channels (Hubbard et al., 2003). It has shown that the interaction between dye molecules and clays is complex, including hydrogen bonding between C═O and N—H of the dye molecules with the edge silanols of clays (Hubbard et al., 2003), hydrogen bonding between carbonyls of dye molecules and structural water of clays (Giustetto et al., 2005). In addition, some researchers claimed that the Fe^{3+}, Al^{3+} and Mg^{2+} of clays should have influences on the interaction between dye molecules and clays (Nagasawa et al., 2004). In order to improve the stability of the hybrid nanopigments, researchers have tried to prepare the hybrid pigments by dry-grinding clay with dye molecules. And a proper rotation speed, milling time and heating temperature would effectively promote the interactions between dye molecules and clays (Wu et al., 2017). Moreover, some researchers reported fabrication of stable hybrid pigments by adsorption of cation dye molecules onto modified clays, which is followed by hydrolysis and polycondensation of tetraethoxysilane (TEOS) via a modified Stöber method to form a layer of SiO_2. The obtained pigments have excellent stability against acid, alkali, organic solvent, thermal aging (Fan et al., 2014; Zhang et al., 2015; Wu et al., 2017).

However, a common impregnation method can easily result in aggregation of dye molecules on the surface of the carrier. As a consequence of the high tendency of dye molecules easily to form H-type sandwich aggregates (H-aggregates) without luminescence ability and with activity as an efficient quencher for the monomer fluorescence (Chen et al., 2002; Sasai et al., 2004). In situ self-assembled method is a new synthetic route with superiority that the active particles can be assembled and enriched in nearly microporous environment by the reconstructed process and extremely dispersed in the diffused channel. Yang et al. (2017) fabricated a special catalyst incorporated with highly-dispersed copper oxides. Dispersed CuO species were in situ produced and encapsulated in the channels of mesoporous silica. Guan

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et al. (2017) had prepared a novel material, which was incorporated with highly-dispersed silver compound using in situ self-assembled method. The stability and performance of the material prepared by in situ self-assembled method is obviously higher than that prepared by common impregnation method. The hybrid nanopigments prepared via an in situ self-assembled method has seldom been reported.

The aim of this work is to find a new route to prepare stable hybrid fluorescent nanopigments. The Rhb@SSA with excellent stability and dispersion was prepared by installing Rhb molecules onto the Al-MCM-41 obtained from raw sepiolite using in situ self-assembled method. Sepiolite was used as an effective and environmentally-friendly source of silicon and aluminum in the synthesis of Al-MCM-41 (Jin et al., 2012; Yang et al., 2015; Yang et al., 2010a, 2010b). To study the influences of different carriers and preparation methods on the performance, Rhb/Sep and Rhb/Al-MCM-41 were also prepared via impregnation method. The structure and performance of 0.5% Rhb@SSA, 0.5% Rhb/Sep and 0.5% Rhb/Al-MCM-41 were discussed.

2. Materials and experimental

2.1. Materials

The sepiolite (Sep, effective substance > 70 mass %) was obtained from Xiangtan Yuanyuan Sepiolite New Materials Company Limited (China). CTAB and Rhodamine B (Rhb) were purchased from Gelest Incorporated. HCl (37%), NaOH, HNO_3 (69%), and ethanol (A.R.) were provided by China National Medicines Corporation Ltd.

2.2. Experimental

2.2.1. Preparation and characterization

2.2.1.1. 0.5% Rhb@SSA. The sepiolite was treated with the HNO_3 of 0.5 M at 25 °C for 1 h to remove the impurities. The mixture of acid treated Sep (10 g) and NaOH (10 g) was ball-milled together and calcined in air at 550 °C for 5 h. The mixture was added into deionized water (100 mL) to obtain silicon aluminum source. Then the extracted solution was separated from the dispersion by filtration. At the same time, a certain amount of CTAB and Rhb were added into 100 mL of deionized water (marked as solution A). The extracted solution was slowly added to the solution A with magnetic stirring. After stirring for 1 h, 2 mol/L of HNO_3 was added to adjust pH value to 7 and continuously stirred for 2 h. The mixture was filtered, washed repeatedly with deionized water, and then the filter cakes were dried in an oven at 60 °C for 4 h.

2.2.1.2. Al-MCM-41. Compared with the above procedure, the difference lies in the following two points, one is that the final mixture was calcined at 540 °C for 5 h in air at a heating rate of 3 °C/min to obtain mesoporous Al-MCM-41 material, the other is that the solution A does not contain Rhb.

2.2.1.3. 0.5% Rhb/Sep and 0.5% Rhb/Al-MCM-41. To study the influences of different carriers and preparation methods on the stability and optical performance, the 0.5% Rhb/Sep and 0.5% Rhb/Al-MCM-41 were prepared via impregnation method. Briefly, the same amount of Rhb was supported on Sep and Al-MCM-41, respectively. Then, they were dried at 60 °C and labeled as 0.5% Rhb/Sep and 0.5% Rhb/Al-MCM-41.

The X-ray diffraction pattern was scanned on a D/max 2500 TC diffractometer using Cu Kα radiation (λ = 1.542 Å). The tube voltage was 40 kV, the current was 30 mA, and the 2 theta range of 1–4.5°. and 5–80°. The unit cell parameter a_0 was calculated according to the formula (1), and the wall thickness value d_w was calculated by the formula (2). Specific surface area and pore parameters of the samples were measured by N_2 adsorption on Quantachrome NOVA2200e. Specific surface area and pore diameters were calculated by using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) method. The micrographs of the samples were obtained using a field emission scanning electron microscope (SEM, JSM-6701F, JEOL). The microstructures of the samples were observed by transmission electron microscopy (TEM) on a Tecnai G2 20 ST electron microscope operating at 200 kV. The instrumental magnification ranged from 2×10^4 to 10×10^6. The sample was deposited on a copper grid and coated with a holey carbon film. FT-IR spectra of the samples were collected on a Thermo Nicolet NEXUS TM spectrometer (Thermo, Madison, USA) in the range of 4000–400 cm^{-1} using KBr pellets. UV–Vis spectra were obtained on a UV-2550 spectrophotometer with a scan range of 200–500 nm by using 1 cm quartz cuvette. About 3 mL of the supernatant was put into a cuvette to record the UV–Vis spectra. Thermogravimetry (TG) analysis of the samples were carried out on a Netzsch STA 449C (German) coupled to mass spectrometer with a heating rate of 10 °C/min under N_2 atmosphere.

$$a_0 = 2d_{100}/\sqrt{3} \quad (1)$$

$$d_w = a_0 - D_{BJH} \quad (2)$$

Where D_{BJH} denotes pore diameter obtained by BJH method and d_{100} is the interlayer space of (100) face of the samples (Yang et al., 2010a, 2010b).

2.3. Performance tests

2.3.1. Thermal stability tests

To compare the thermal stability, the hybrid nanopigments were analyzed over a temperature from 30 to 800 °C at a rate of 10 °C/min under nitrogen atmosphere by using thermal analyzer. Besides, the thermal stability of the nanopigments was also evaluated according to the following procedures: the nanopigments were calcined at 60 °C, 120 °C, 180 °C, 210 °C and 240 °C for 2 h in a muffle furnace, respectively.

2.3.2. Chemical stability tests

In order to compare the resistance of the prepared nanopigments to acid, alkali and organic solvent, 0.2 g of 0.5% Rhb/Sep, 0.5% Rhb/Al-MCM-41 and 0.5% Rhb@SSA were dispersed in 8 mL 1 mol/L HCl, 1 mol/L NaOH or anhydrous ethanol, respectively. And then, the mixtures were shaken in a thermostatic shaker at 30 °C and 150 rpm for 24 h, 48 h, 72 h. Afterwards, the supernatants were separated from the mixtures by centrifugation at 8000 rpm for 10 min and analyzed by using a UV–Vis spectrophotometer to confirm the amount of the released dyes from nanopigments.

2.3.3. Colorimetric tests

A Minolta CR-300 colorimeter was used to measure the CIE $L^*a^*b^*$ colour scale (using 2° observer/D65 standard). Lightness (L^*) represents the brightness or darkness of the colour, i.e., how the colour approaches to the black (low values of L^*) or to the white (high values of L^*). And a^* and b^* are colour coordinates, where $+a^*$ is the red direction, $-a^*$ the green direction, $+b^*$ the yellow direction, and -b^* the blue direction. Moreover, the changes in individual components enabled calculation of the total change in colour ΔE^*. The colour difference ΔE^* (CIE 1976) was calculated using the relation $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$. The symbol c^* stands for chrome and h^* for hue.

2.3.4. Optical tests

The fluorescence excitation spectra of Rhb, Sep, Al-MCM-41, 0.5% Rhb/Sep, 0.5% Rhb/Al-MCM-41, 0.5% Rhb@SSA were measured at room temperature by a fluorescence spectrophotometer (LS55).