

Photostability enhancement of azoic dyes adsorbed and intercalated into Mg–Al-layered double hydroxide



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ABSTRACT

Two azoic dyes 4-aminoazobenzene-4-sulfonic (AS) and ethyl orange (EO) were adsorbed on or intercalated into Mg–Al–CO₃ layered double hydroxide (LDH) for photostability enhancement. Fluorescence analysis results showed that the photostability of two dyes could be greatly improved after being adsorbed on the surface of Mg–Al–CO₃-LDH matrix. Furthermore, photostability of adsorbed dyes was superior to that of intercalated dyes. It was suggested that AS or EO was adsorbed on LDHs surface through a strong chemisorption interaction, resulting in the enhancement of photostability. After the UV irradiation under N₂ atmosphere, the adsorbed dyes not only show great increase of fluorescence intensity but also exhibited high stability against UV irradiation. This work provides a feasible approach to enhance the photostability of azoic dye confined in an inorganic two-dimensional (2D) matrix via changing the microenvironment, which may be considered to be a promising method of improving photostability of solid fluorescent materials.

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1. Introduction

Modern dyes have a multiple variety and attracted much attention owing to their vivid color, broad spectra, strong fluorescence intensity, and high quantum yield [1,2]. Azo dyes are one important class of modern dyes accounting for approximately half of dyes produced annually [3] and thus are extensively used in textile, printing, leather, paper making, drug, food industries and optical devices [4]. However, when these fluorescent materials are applied into the field of solid state self-emission devices [5,6], they are usually restricted due to the relatively poor thermal or optical stability. Moreover, fluorescence quenching induced by aggregation is another primary reason for limiting the application of fluorescent dyes. To overcome these disadvantages, great efforts have been devoted to the design and synthesize new fluorescent molecules. Unfortunately, the time-consuming synthesis process and relatively low yield often prevent their development [7]. Therefore, it is a challenge to synthesize fluorescent materials with both good thermal and high optical stability.

Recently, great interest has been paid to the assembly of two-dimensional (2D) ordered organic–inorganic hybrid composites by complexation of organic dye molecules with solid host matrices, since the inorganic host matrixes could improve thermal- and photo-stability of the dyes after combination with the host

materials [8,9]. In this regard, layered double hydroxides (LDHs), also sometimes termed anionic or hydroxalite clays, are one family of inorganic layered with hydroxide sheets, where a net positive charge is developed on the layer due to partial substitution of trivalent for divalent cations [10]. The empirical formula of LDHs is generally expressed as $[M^{II}_x M^{III}_{1-x}(\text{OH})_2]^{x+} (A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{II} and M^{III} are di- and tri-valent metal cations occupying octahedral positions in hydroxide layers. Aⁿ⁻ is the exchangeable anion between the brucite-like layers to compensate the positive charge [11]. The *x* values (range between 0.2 and 0.4) determine the charge density of the positive layer and the anion exchange capacity [12]. The relatively large surface area, good thermal stability, high sorption and ion-exchange capability of LDHs allow the formation of a wide range of inorganic–organic hybrid nanocomposite materials [13,14]. The rigid and confined space imposed by LDHs layers can inhibit the thermal vibration and rotation of fluorescent dye anions relating to the nonradiative relaxation process of their exciting states, and also form an ordered and regular microenvironment for the interlayer anions [15]. Therefore, stabilization and protection effect from the inorganic host structure could meet the need to improve thermal and photostability of fluorescent dyes for long-term application [16].

In this context, 4-aminoazobenzene-4-sulfonic (AS⁻) and ethyl orange (EO⁻) (Fig. 1) are employed as model water soluble azo dyes [17,18] and adsorbed to the external surface of the host or intercalated into Mg–Al–CO₃-LDH by ion-exchange procedures [19]. The enhancement of stability of these compounds under UV irradiation, thermal and structure stability were confirmed by

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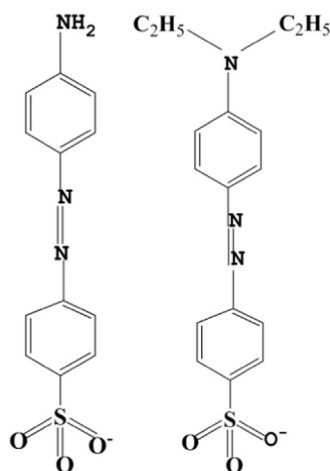


Fig. 1. The structural formula of each guest anion. (1) AS and (2) EO.

fluorescence spectra, thermogravimetry and differential scanning calorimetry (TGA–DSC) and leaching test. The cause of the stabilization was then explored that was seldom reported before. It is found that the stabilization effect is related to the host–guest interactions that affect the distribution and orientation of guests in the host, and the thermal and optical stability of guests can be improved.

2. Experimental section

2.1. Materials

4-Aminoazobenzene-4-sulfonic sodium ($C_{12}H_{10}N_3SO_3Na$, > 90%) and ethyl orange ($C_{16}H_{19}N_3SO_3Na$, > 98%) were purchased from Alfa Aesar Chemical Co. Ltd. NaOH (AR), Na_2CO_3 (AR), $MgSO_4 \cdot 7H_2O$ (AR), $Al_2(SO_4)_3 \cdot 18H_2O$ (AR) were purchased from Beijing Chemical Co. Ltd and used without further purification. All the aqueous solution was prepared with de-ionized and CO_2 -free water.

2.2. Preparation of the intercalation and adsorption compounds

The layered host Mg–Al–LDH in carbonate form was synthesized according to the literature methods [12]. For the sake of higher charge density in the host sheets, the Mg/Al molar ratio was fixed at 2.0. The intercalation and adsorption compounds were prepared by the ion-exchange method previously described [19]. It is well known that carbonate anions are strongly held in the interlayer region and difficult to be replaced by other counter anions at neutral or slightly alkaline pH values. Briefly, 0.6 g of Mg–Al– CO_3 -LDH was dispersed in 50 mL de-ionized water containing 0.7 g AS (or 0.8 g EO) at 90 °C for 10 h, and the samples containing chromophore only on the external surface of the crystals were obtained at pH=7, denoted by Mg–Al– CO_3 -LDH–AS (or EO) [16,19]. Two steps have been followed to intercalate the dye anions into the interlayer region of the layered host. The first step involves the replacement of carbonate anions with chloride at pH=5 to obtain Mg–Al–Cl LDH. So, 0.6 g of Mg–Al– CO_3 -LDH was dispersed in a 0.6 mol L^{-1} NaCl aqueous solution (25 mL) and the solution was controlled at pH value of 5 by adding a 0.5 mol L^{-1} HCl aqueous solution to prevent contamination by atmospheric CO_2 . The mixture was stirred at 70 °C for 4 h. After filtrating and washing, the product was reacted by stirring with 50 mL of 0.7 g AS (or 0.8 g EO) aqueous solution under N_2 atmosphere at 90 °C

for 10 h, and the solid was the intercalated compound, denoted by Mg–Al–AS (or EO)-LDH [19].

2.3. Thermostability analysis

Thermogravimetry and differential scanning calorimetry (TGA–DSC) were conducted in 150 μ L alumina crucibles by using a NETZSCH STA 449C thermoanalyzer at a rate of 10 °C/min under air atmosphere. The TGA and DSC curves were recorded from 25 to 700 °C.

2.4. Leaching test

The leaching amounts of organic dyes for different wash times were determined by treating 10 mg intercalation or adsorption compounds in 10 mL ethylene glycol. The system was stirred slowly, open to the atmosphere at 25 °C, for 5 times, 0.5 h every time, and then the samples were centrifuged at 3000 rpm for 20 min. The leaching percentages of organic dyes for the different wash times were determined by the standard curves of UV–vis absorption spectra [19] by measuring the absorption intensity at 405 nm for AS and 457 nm for EO.

2.5. Photostability analysis

To investigate the light endurance of each sample, AS and EO were irradiated by UV light under ambient temperature and pressure. Irradiation experiments were conducted in the Ultra-violet aging test chamber ($\lambda=365$ nm, $P=250$ W), the powder samples were loaded in a quartz flask and positioned 10 cm away from the UV source. The fluorescence spectra were collected by F-7000 spectrophotometer (Hitachi Limited, Japan) after radiating 1, 2, 3, 4, and 5 h under air and N_2 atmosphere.

3. Results and discussion

3.1. Structural characterization of nanohybrids

X-ray power diffraction (XRD) patterns [19] of Mg–Al– CO_3 -LDH, Mg–Al– CO_3 -LDH–AS (or EO), and Mg–Al–AS (or EO)-LDH are shown in Fig. S1. Fourier Transform infrared (FT-IR) spectra [19] of Mg–Al– CO_3 -LDH, Mg–Al– CO_3 -LDH–AS (or EO), Mg–Al–AS (or EO)-LDH, AS and EO are shown in Fig. S2.

The X-ray diffraction pattern of the Mg–Al– CO_3 -LDH in Fig. S1a exhibits the characteristic diffractions at low 2θ values, which are ascribed to diffractions by planes (003) and (006), corresponding to the basal spacing and its higher order diffractions [20]. The absorption peak at 1360 cm^{-1} in Fig. S2a is the vibration of CO_3^{2-} , which indicates the existence of CO_3^{2-} between the layers [19].

The basal spacing of Mg–Al– CO_3 -LDH–AS (or EO) in Fig. S1b is similar to the original materials, indicating that AS and EO anions have not been intercalated into the layers. However, by comparing Fig. S2b and e with Fig. S2c and f the phenyl group vibration absorption band of AS or EO in Fig. S2c and f can be observed and the vibration absorption peak of CO_3^{2-} in Fig. S2c and f still exists, which indicates that compounds have not been intercalated as anions by replacing the CO_3^{2-} [19].

The X-ray diffraction pattern [19] for the intercalated samples (Fig. S1c) shows out a smaller degree (003) diffraction line as a consequence of the intercalation of dye anions in the LDH. The effective intercalation of anions can also be confirmed by FTIR spectrum. As shown in Fig. S2d and g, the characteristic bands of organic chromophores anions are clearly observed. In addition, the peak characteristic of CO_3^{2-} in Fig. S2d and g is absent, indicating that the ion-exchange process is complete.

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