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Dye-interleaved nanocomposite: Evan's Blue in the lamella of Mg–Al-layered double hydroxide

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Abstract

Layered organic–inorganic hybrid nanocomposite, containing an organic dye in an inorganic interlayer was prepared using Evan's Blue (EB) as a guest in Mg–Al layered double hydroxide inorganic host by a self-assembly technique, with the Mg–Al ratio of 4 in the mother liquor at pH = 7.5. Powder X-ray diffractogram shows that the basal spacing of the Mg–Al layered double hydroxide with nitrate as the intergallery anion expanded from 8 to about 20 Å to accommodate the EB anion, for the formation of the Mg–Al layered double hydroxide–EB layered organic–inorganic hybrid nanocomposite (MAEN). Formation of such a material is useful, for example for controlled release purposes of dye for slow dyeing process.

Keywords: Hydrotalcite; Layered double hydroxide; Evan's Blue; Intercalation; Nanocomposite; Layered material

1. Introduction

The development of new organic–inorganic hybrid type materials opens promising prospects for applications in various areas of science and technology. This is because these types of material have better or improved properties than their counterparts, or the property can be tailor-made to a specific application such as in photochemical reaction [1], selective optical transmission [2], photochromic coating [3], controlled release [4], and gene reservoir [5], to name a few.

Hydrotalcite-like material or layered double hydroxide (LDHs) is one of the popular inorganic hosts for the formation of an organic–inorganic hybrid type nanolayered composite, or the so-called nanocomposite materials [6]. The LDH can be regarded as a layered inorganic host with a lamella thickness of about 8 Å if nitrate is present as a counter anion, and this lamella can be interleaved with an organic moiety, especially of anionic type to replace the nitrate to balance the net charge of the LDH sheets. Due to a bigger size

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and the orientation of the organic moiety which was intercalated inside the organic–inorganic hybrid lamella structure, an expansion of basal spacing could usually be observed [7].

This type of material can be synthesised directly by co-precipitation or the so-called spontaneous self-assembly method [8], in which the host and the guest species are included in the mother liquor, followed by aging process to form a well-ordered layered nanocomposite. Alternatively, the host has to be prepared first, followed by modification or further treatment of the host and finally insertion of the guest molecule inside the interlayers [9,10].

Attempts have been made to intercalate various dye molecules, in particular organic dyes inside layered inorganic lamella, especially anionic clays for various purposes and applications. For example, work on the formation of nanocomposite layered inorganic LDH containing intercalated dye was done by several researchers. The dye used included naphthol blue black [11], indigo carmine and cocaine [12] and water soluble dye which is useful for ink jet technology [13].

In the present study, intercalation of an anionic dye, Evan's Blue into the Mg–Al LDH to form an organic–inorganic nanohybrid composite material (MAEN) is reported and discussed. In this study, the Mg–Al LDH was chosen as a host and EB as a guest molecule or intergallery anion. Spontaneous self-assembly of organic and inorganic component molecules was adopted in this study. Due to color bearing materials of EB, formation of its nanocomposite is expected to inherit the same property. This property is useful for slow coloring or staining agents. In addition, if the loading percentage of the guest is high, then such a property can be exploited as a route for slow release of dyes.

2. Experimental

All the chemicals used in this synthesis were obtained from Sigma and used without further purification.

The synthesis of Mg–Al–EB nanocomposite (MAEN) was done by spontaneous self-assembly method. A solution containing $\mathrm{Mg/Al}(R) = 4$ and EB was prepared and the pH of the solution was adjusted to about 7.5. Various concentrations of EB were used, from 0.00625 to 0.025 M. Dropwise addition of EB into the mother liquor in a reaction vessel was carried out under nitrogen atmosphere. The solution was aged for 18 h in an oil bath shaker at 70 °C. The resulting precipitate was centrifuged, thoroughly washed and dried in an oven at 120 °C, overnight and kept in a sample bottle for further use and characterisation. A similar method was adopted to synthesise the nanocomposite material at pH 10 and for the preparation of Mg–Al LDH with nitrate as the intergallery anion (MANL). However, the addition of EB solution into the mother liquor was omitted for the synthesis of the latter.

Powder X-ray diffraction (PXRD) patterns of the samples were obtained by using filtered CuK_α radiation in a Shimadzu Diffractometer D-6000. FTIR spectra were recorded by a Perkin–Elmer 1750X spectrophotometer. KBr pellet of 1% sample was used to obtain the FTIR spectra.

3. Results and discussion

Evan's Blue (EB) is an organic dye (C.I. 23860) and has a formula, $C_{34}H_{24}N_6Na_4S_4O_{14}$. The molecular structure is given in Fig. 1. This organic dye is also called Direct Blue 53 and is used in staining procedure [14] and has other purposes.

3.1. X-ray diffraction patterns

Fig. 2 shows powder X-ray diffraction (PXRD) patterns for MAEN synthesised using various

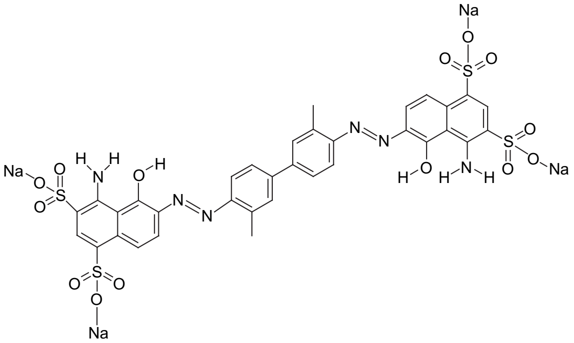

Fig. 1. Molecular structure of Evan's Blue.

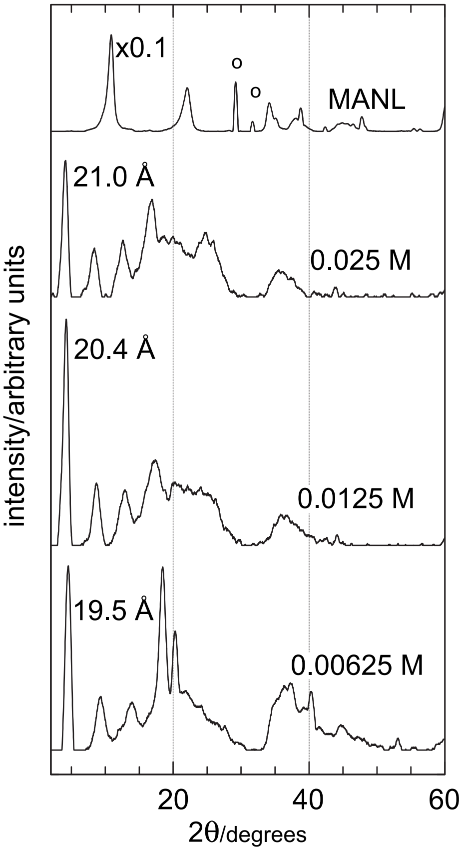

Fig. 2. PXRD patterns for MANL (×0.1) and MAENs prepared at various concentrations of Evan's Blue at pH 7.5 (o = unknown phase).

concentrations of EB. Also given in the figure is the PXRD of MANL, an LDH with nitrate as a counter anion, for comparison. As shown in the figure, the basal spacing for MAENs increased from 19.5 to 21.0 Å when the concentration of the EB used in the synthesis was increased from 0.00625 to 0.025 M. A large expansion of the basal spacing from 8.2 Å in the MANL indicated that the expansion is to accommodate the EB moiety with an orientation that warrants the expansion of the basal spacing.

The PXRD patterns in Fig. 2 shows that EB could be intercalated into the Mg–Al double layer lamella at various concentrations. However, the resulting well-ordered nanocomposite could be best obtained if 0.0125 M EB was included in the mother liquor containing magnesium and aluminium nitrate with Mg/Al molar ratio of 4 at pH 7.5, resulting in the nanocomposite with a basal spacing of 20.4 Å.

Attempts were made to intercalate EB at lower concentration, but no expansion of the basal spacing could be observed if <6.25 mM of EB was used. On the other hand, an expansion was observed if >6.25 mM of EB was used, and the basal spacing increased with the concentration of EB, but mixed phases with LDH were obtained. This indicates that the expansion of basal spacing is due to the inclusion of EB, and relatively pure nanocomposite phase can be obtained if 0.0125 M EB is available in the mother liquor, under our experimental conditions stated earlier (Table 1).

The synthesis of the nanocomposite materials was also done at pH 10, at two different concentrations, 0.0125 and 0.025 M. These two concentrations were chosen because they gave relatively good PXRD patterns of the resulting nanocomposite when it was synthesised at pH 7.5, as shown in Fig. 2.

However, the PXRD diffractograms (Fig. 3) show a mixed phase (Table 1); LDH together with the nanocomposite phase was present in the as-synthesised compound. Therefore, we concluded that the same conditions as previously adopted for the formation of the nanocomposite at pH 7.5 were not suitable for the formation of a well-ordered nanolayered structure of the inorganic layers containing the organic dye, EB at pH 10.

3.2. FTIR

As a result of successful intercalation of EB, we subsequently used 0.0125 M EB to repeat the

Table 1
Properties of the nanocomposites synthesised using various EB concentrations at pH 7.5 and 10

[EB]	pH = 7.5		pH = 10	
	d/Å	Phase observed	*d*/Å	Phase observed
0.00625	19.5	NC	–	–
0.0125	20.4	NC	20.3	NC + LDH
0.025	21.0	NC	20.5	NC + LDH

d = basal spacing.

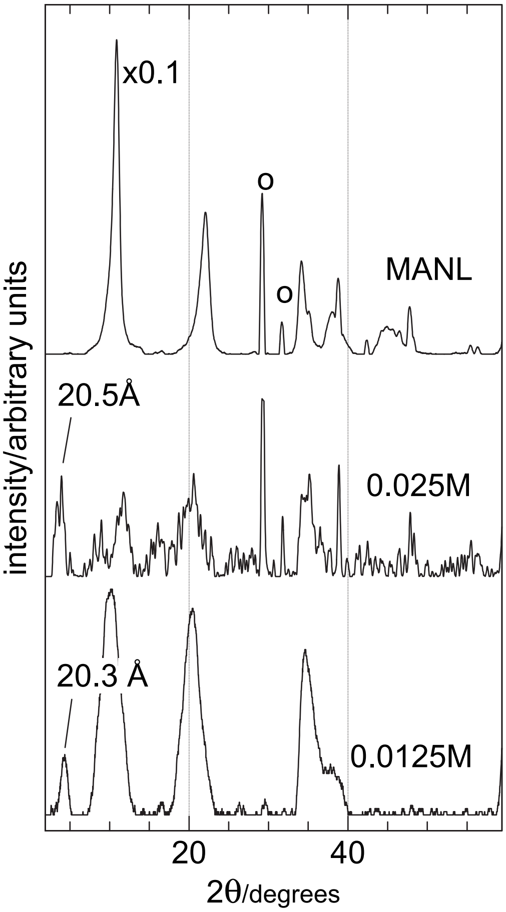

Fig. 3. PXRD patterns for MANL (×0.1) for intensity comparison and MAENs prepared at various concentrations of Evan's Blue at pH 10 (o = unknown phase).

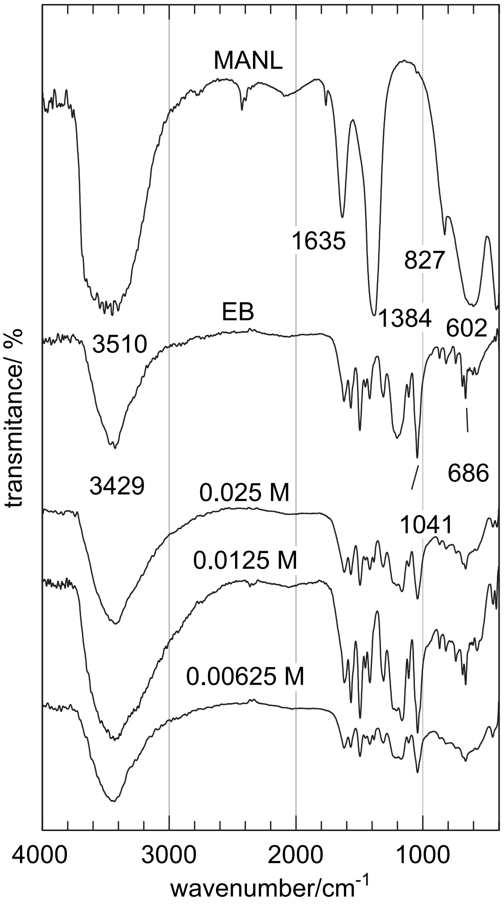

Fig. 4. FTIR spectra for MANL, EB, and MAENs prepared at various concentrations of Evan's Blue at pH 7.

synthesis of MAEN. It was found that the formation of the nanocomposite is reproducible with similar basal spacing. We subsequently used this sample for further characterisation.

Fig. 4 shows the FTIR spectra of LDH, EB and the nanocomposites synthesised using various concentrations of EB at pH 7.5.

As shown in the figure, the LDH spectrum is dominated by a broad absorption band at around 3510 cm^{-1}. This band is attributed to the OH stretching, due to the presence of hydroxyl group of LDH and/or physically adsorbed water molecule. The appearance of a weak band at 827 cm^{-1}, and another strong absorption band at around 1384 cm^{-1} can be attributed to the presence of nitrate group, the intergallery anion in the Mg–Al LDH. The band at 1635 cm^{-1} is due to $\nu_{\text{H–O–H bend}}$ vibration. As shown in the figure, the as-synthesised LDH is relatively free from carbonate anion, due to the absence of any sharp absorption band at around 1400 cm^{-1}, which can be attributed to the carbonate ν_3-vibration [15]. Bands at around 600–400 cm^{-1} can be attributed to the Al–OH and Mg–Al–OH bending vibration [16].

By comparing the FTIR spectra of EB with MANLs, it is clear that the FTIR absorption bands of the nanocomposite are dominated by the EB absorption character. In addition, the absence of absorption band at around 1384 cm^{-1} indicates the absence of the nitrate in the resulting nanocomposite. This is a good sign to indicate that EB actually occupied the inorganic interlamellar, and at the same time negating the nitrate anion to be co-intercalated, and resulting in a pure nanocomposite phase.

A close look at the absorption bands of the nanocomposite shows that a broad band at 3429 cm^{-1} can be attributed to the OH stretching of the molecule, together with the absorption of moisture during the preparation of the KBr pallet. Band at around 1050 cm^{-1} is attributed to sulphonate salts [12]. In addition, the H–O–H bending vibration ($\nu_{\text{H–O–H bend}}$) and O–H symmetric stretching vibration ($\nu_{\text{O–H sym}}$) in these nanocomposites appear in the ranges of 1619 and 3429 cm^{-1}, respectively. The lower values of $\nu_{\text{O–H sym}}$ in these nanocomposites compared to that of free OH groups (>3650 cm^{-1}) indicate that all the OH groups are involved in hydrogen bonding with EB and the Mg–Al double metal hydroxide interlayer [16].

Fig. 5 shows the FTIR spectra of the nanocomposites synthesised under similar conditions but at pH 10. The characteristic of this spectrum is the presence of a strong, sharp absorption band at 1385 cm^{-1}, which is due to nitrate functional group. This is parallel with the observation of the LDH phase in the PXRD diffractogram shown in Fig. 3, indicating impure nanocomposite phase of the resulting materials as a result of co-intercalation of nitrate anion into the LDH inorganic interlayer during the formation of the nanocomposite.

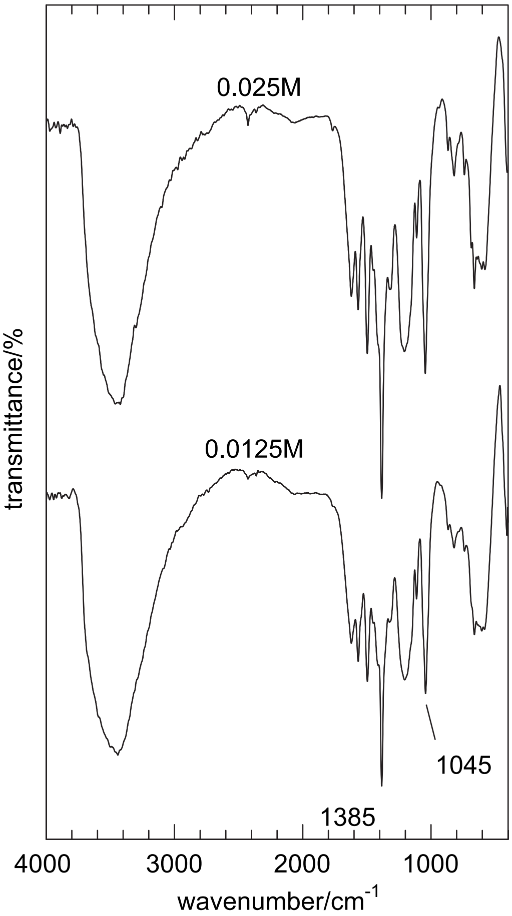

Fig. 5. FTIR spectra for MAENs prepared at various concentrations of Evan's Blue at pH 10.

4. Conclusion

This study shows that layered organic–inorganic hybrid nanocomposite, containing an organic dye in an inorganic interlayer can be prepared by using Evan's Blue as a guest in the Mg–Al layered double hydroxide inorganic host by a self-assembly technique, with the Mg–Al ratio of the mother liquor of 4 and pH = 7.5. Powder X-ray diffractogram shows that the basal spacing of the Mg–Al layered double hydroxide with nitrate as the intergallery anion expanded from 8.2 to 20.4 Å to accommodate the EB anion and gives a well-ordered nanolayered structure. The expansion is attributed to a bigger size of the organic moiety than nitrate with a specific orientation that warrants the expansion of the basal spacing which can be observed by PXRD technique, for the formation of the Mg–Al layered double hydroxide–EB layered organic–inorganic hybrid nanocomposite. Formation of such a material is useful, for example for controlled release purposes of dye for slow dyeing process.

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