Modified layered double hydroxides nanocomposites with the polyoxyethylene sulfate

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Recently there has been considerable interest in the bio-molecule/LDHs' nanocomposites, which often exhibit extraordinarily high synergetic and complementary behavior between two component materials. In particular, the combination of two-dimensional layered materials and intercalation technique offers new areas for developing new composites with desired functionality [1–6]. One of the layered materials, LDHs, also called "anionic clays", have received considerable attention due to their technological importance in catalysis, adsorption, ion-exchange, optics, medical science, and nanocomposite materials engineering [7–12]. LDHs' can be represented by the general formula: $[M^{\alpha}_{1-x}M^{\beta}_{x}(OH)_2]^{x+}\ [A^{m-}_{x/m}\cdot nH_2O]^{x-}$, abbreviated as: $[M^{\alpha}$-M^{β}-X] [13]. LDHs' possess a positive charged hydroxide basal layer due to substitution of trivalent cation for part of the divalent cation and are electrically balanced by the interlayer anions. LDHs are layered nanocomposite materials with ion-exchange ability and biocompatibility, and the cell activity experiment indicates that it is noncytotoxic on cells [14]. Based on these findings, it is proved that LDHs can act as a new inorganic carrier for encapsulating functional biomolecules which can be incorporated between hydroxide layers due to the electrostatic interaction between cationic brucite layers and anionic biomolecules to form steady bio-LDHs nanocomposites. These nanocomposites can prevent biomolecules from degradation of enzyme and other substances. When the nanocomposites are introduced into cells where the pH is slightly acidic, LDHs' layers will be dissolved, and the biomolecules can be released. It is also found that the charge neutralization through hybridization between LDHs and biomolecules would greatly enhance the transfer efficiency of biomolecules into cells through endocytosis, since it greatly reduces the electrostatic repulsive interaction between cell membranes and biomolecules [15]. If we can modify the surface of the nanocomposites properly and make them combine with single-cloned antibody, the composites can assemble in cells and the property of selecting recognition of a target can be greatly enhanced. However, macro biomolecules such as peptides, proteins and nucleic acids cannot be intercalated or adsorbed easily, so LDHs need surface modification to enhance the selective recognition of medicine. Biomolecules can interact with modified LDHs and be intercalated into or adsorbed on LDHs through hydrogen bond or electrostatic interaction. The common organic modifier is sodium dodecylsulfate (SDS) [16, 17], but it may result in the protein denaturation, so we need to choose new organic modifier and do more research on the surface modification of LDHs.

In the present study, we modified the surfaces of LDHs with a long chain polymer PEG's derivative polyoxyethylene sulfate and synthesized relevant intercalated nanocomposites. We briefly discussed the preparation, characterization, and properties of the modified PEGS/LDHs and SDS/LDHs nanocomposites.

All the chemicals used in this work were of analytical grade and used without any further purification. Polyoxyethylene sulfate $NaSO_3(OCH_2CH_2)_nOSO_3Na$ (PEGS-400 $n = 9$, PEGS-600 $n = 13$, PEGS-1000 $n = 22$) was synthesized by our laboratory.

The preparation of [Mg-Al-NO_3] was done by a non-steady coprecipitation [18]. Under a N_2 atmosphere, a mixed solution of magnesium and aluminum nitrate was prepared in the molar ratio of 2:1. A given amount of $NaNO_3$ was added. Then diluted ammonia water (6%) was added to the solution at a speed of 20 ml/min. The final pH value was 9.5. The precipitate was aged for 1 hr. at room temperature, and then washed with deionized water. After that, the filter cake was peptized at 60 °C, forming the positive sol. It was dried at 65 °C to get [Mg-Al-NO_3].

The intercalation of the LDH with PEGS and SDS. Dense suspensions of LDHs were diluted to 0.5 wt% solid content. To 0.02 mol/L of PEGS aqueous solutions (100 ml) added 100 ml of LDHs suspension. The pH values of the mixtures were adjusted to 9.0 with sodium hydroxide. Suspensions were aged at 60 °C for 4 days. The resulting precipitate was centrifuged, washed twice with methyl alcohol and separated by centrifugation. The resulting white solid was thoroughly washed with deionized water, centrifuged and dried in vacuum at 60 °C. The synthesis of [Mg-Al-SDS] nanocomposite was done by an ion-exchange method described above.

X-ray diffraction (XRD) used was a D/max-γ B diffractometer with Cu Kα radiation. Data were collected over the 2 θ range from 2 to 40 °C in the increments of 0.02 °C /s at room temperature. Thermogravimetric (TG) analysis was performed under a N_2 atmosphere using a Schimadzu TGA-40 Thermogravimetric Analyzer. Fourier transform infrared (FTIR) analysis were recorded on a Nicolet 50X spectrophotometer,

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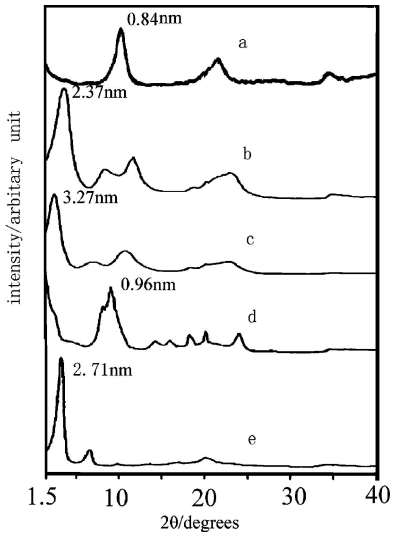

Figure 1 XRD patterns for (a) [Mg-Al-NO_3], (b) [Mg-Al-(PEGS-400)], (c) [Mg-Al-(PEGS-600)], (d) [Mg-Al-(PEGS-1000)], (e) [Mg-Al-SDS].

in the range of 400–4000 cm^{-1}. Transmission electron microscopy (TEM) analysis was performed using a JEM-100CX II electron microscope. TEM samples were prepared by dipping amorphous carbon coated copper TEM grids into dilute aqueous suspensions of the samples powder, which was washed only by deionized water. The electrophoretic mobility (μ) of samples was measured using a DXD-I microelectrophoresis instrument with a flow through sample cell. Samples were prepared by dispersing 0.05 vol.% of each samples powder.

The X-ray diffraction patterns for the pristine LDH, SDS/LDH and PEGS/LDHs nanocomposites are shown in Fig. 1. It is seen that the basal spacing (d_{003}) of the [Mg-Al-NO_3] is 0.84 nm, and the basal spacing of [Mg-Al-(PEGS)] are 2.37, 3.27 and 0.96 nm, respectively, indicating that the basal spacing of LDHs has been expanded because of the intercalation of PEGS into the LDHs galleries. The length of PEGS molecule was calculated according paper [17], the relevant molecular length of PEGS (with different molecular weight $n = 9$, 13, 22), were 3.99, 5.51 and 8.94 nm, respectively. Since the brucite-like LDHs sheet is 0.48 nm, the space occupied by PEGS-400 and PEGS-600 would be approximately 1.89 and 2.79 nm the ratios of the length of molecule and basal spacing are 2.1 and 2.0, so the orientations of PEGS in the gallery of LDHs may be monolayer, the PEGS lie inclined with the two -OSO_3^- groups linking with the adjacent layer of LDHs. As to PEGS-1000 ($n = 22$), the ratio of the length of molecule and basal spacing is 18.6, so the orientations of PEGS in the gallery of LDHs may also be monolayer, the PEGS lie horizontally as zigzag type or helix state. The PEGS possible arrangements are showed in Fig. 2.

As to PEGS-400 and PEGS-600, the bilayer or trimolecular layer is impossible because PEGS molecule has two anion groups which would exclude each other. And if it arranges as that, the mol number of molecule would increase which the TG data do not support. For the [Mg-Al-SDS], it's basal spacing is 2.71 nm, and close to reported data [17]. The alkyl chain of the SDS is nearly perpendicular to the layer of the LDHs.

Fig. 3 shows the FTIR spectra of [Mg-Al-NO_3], SDS/LDH and PEGS/LDHs respectively, in the 4000–400 cm^{-1} wave number range. Besides the vibration band characteristics of the LDHs (OH stretching of [Mg-Al-NO_3]) 3456 cm^{-1}; (absorption band of nitrates) 1383 cm^{-1}; (OH stretching of water) 1640 cm^{-1},

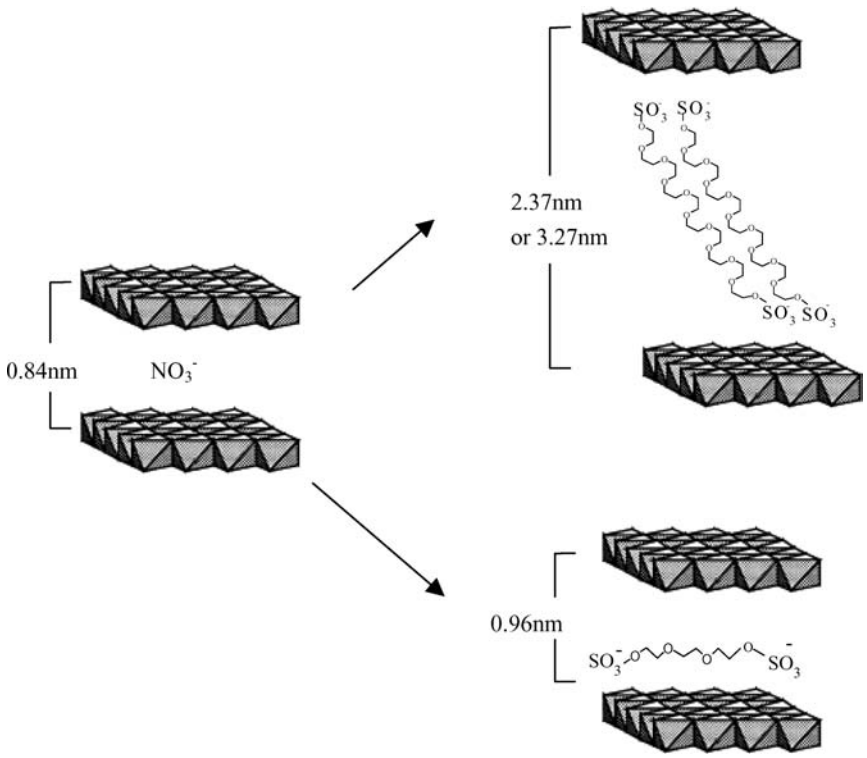

Figure 2 Schematic illustration of each anion structure intercalated in the LDHs inorganic layer (a) [Mg-Al-NO_3], (b) incline monolayer [Mg-Al-(PEGS-400)] and [Mg-Al-(PEGS-600)], (c) horizontal [Mg-Al- (PEGS-1000)].

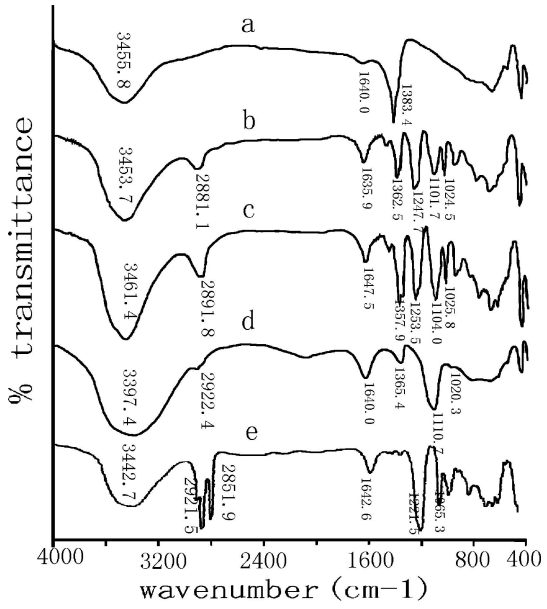

Figure 3 IR spectra of the [Mg-Al-NO_3] (a), [Mg-Al-(PEGS-400)] (b), [Mg-Al-(PEGS-600)] (c), [Mg-Al-(PEGS-1000)] (d), [Mg-Al-SDS] (e).

the band attributed to the intercalated PEGS are also observed in the spectra of the three nanocomposites (Fig. 3b, c and d). The presence of PEGS in intercalated compound is evidenced by the characteristic C-H stretching bands of methylene groups over the 2850–2925 cm^{-1}. The presence of C—O stretching vibrations can be implied by the observation of bands at 1110 cm^{-1}. The OSO_3^- asymmetric stretches at 1250 cm^{-1}[19]. There is little PEGS-1000 molecule in layers because the organic molecule lie parallelly in monolayer arrange, which result in weak absorption in the IR spectrum. So, we can not find the band of the OSO_3^- asymmetric stretches in Fig. 3d. The absorption band at 1383 cm^{-1} disappearing in Fig. 3b, c and d, show that PEGS molecules have been intercalated into the gallery of LDHs, and substituted the nitrate, which was consistent with the result of XRD. Fig. 3e is the FTIR spectra of [Mg-Al-SDS]. As expected the presence of CH stretching vibrations of methyl groups could be implied by the observation of triplet bands at 2800–3000 cm^{-1}. Moreover, the band at around 1222 cm^{-1} is due to sulfonate salts.

TEM micrographs for sample [Mg-Al-NO_3], SDS/LDHs and PEGS/LDHs are shown in Fig. 4. [Mg-Al-NO_3] consisted of hexagonal particles with the length about 100–120 nm, Compared to [Mg-Al-NO_3], the [Mg-Al-PEGS-400] is spherical particles (Fig. 4b), and the increasing of the basal spaces indicates that the PEGS-400 have intercalated into LDHs. For the PEGS-600, after interacting with LDHs, the increasing of the basal spaces indicates the intercalation reaction also has happened, and the nanocomposites observed are irregular spherical particles whose diameter is about 200–350 nm. When PEGS-1000 was mixed with LDHs for half an hour, we can observe that the length of the hexagonal particles became longer and rhombus particles with the length about 100–200 nm can be observed at the same time. With the interaction time increasing, the process continues. After PEGS-1000 interacts with LDHs for 4 days, intercalation reaction can be proved through XRD. However, the obtained nanoparticles are stick particles with the length about 300–500 nm (Fig. 4d). Because the $-CH_2CH_2O-$ chains of PEGS ($n = 9, 13$) were short, it was easy to tie LDHs layers tightly. The solid liquid interface energy made LDHs become intercalated composite sphere as the formation of water droplet on the surface of solid. When the $-CH_2CH_2O-$ chains in the polymer increased to a certain extent, PEGS molecules could not lie inclined but lie horizontally as zigzag or helix state between LDHs layers. LDHs layers modified with the polymer linking with each other made the particles of LDHs turn to stick particles with the length about 300–500 nm

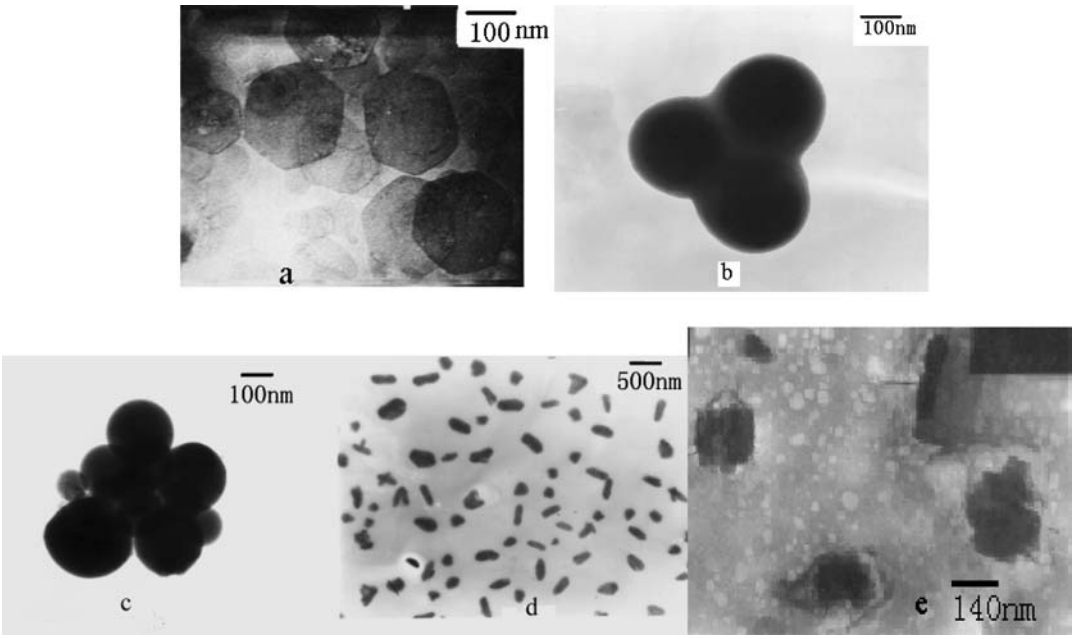

Figure 4 TEM photographs for LDH, samples (a) [Mg-Al-NO_3], (b) [Mg-Al-(PEGS-400)], (c) [Mg-Al-(PEGS-600)], (d) [Mg-Al-(PEGS-1000)], (e) [Mg-Al-SDS].

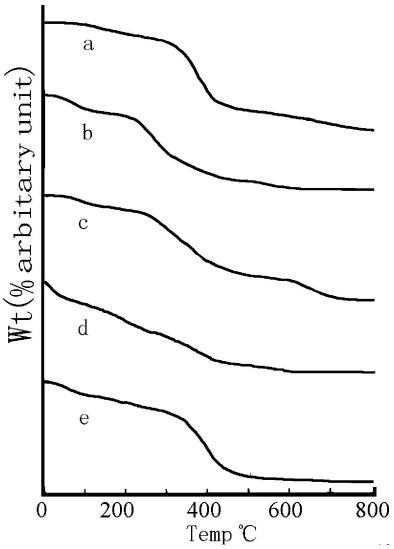

Figure 5 TG data for LDHs samples (a) [Mg-Al-NO_3], (b) [Mg-Al-(PEGS-400)], (c) [Mg-Al-(PEGS-600)], (d) [Mg-Al-(PEGS-1000)], (e) [Mg-Al-SDS].

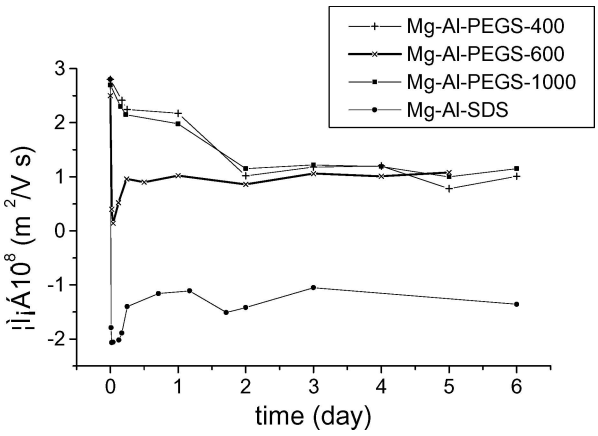

Figure 6 Electrophoretic mobility (μ) vs. reaction time data for [Mg-Al-(PEGS)] and [Mg-Al-SDS] samples.

(Fig. 3). The lamellar structure of the [Mg-Al-(PEGS-1000)] was preserved upon intercalation, this made it a suitable precursor to prepare bio-molecule/LDHs.

For the [Mg-Al-SDS], the nanocomposites observed are irregular slices approximately 150–200 nm in length. It is shown that many molecules are adsorbed in the outer surface of nanoparticals particles, which was consistent with the result of the electrophoretic mobility, these molecules adsorbed in the outer surface denatured macro biomolecules such as peptides, proteins and nucleic acids.

TG weight loss profile for samples [Mg-Al-NO_3], [Mg-Al-(SDS)] and [Mg-Al-(PEGS)] are displayed in Fig. 5. [Mg-Al-NO_3] showed characteristic weight loss regions that correspond to the loss of surface and interlayer water (50–150 °C) and nitrate decomposition and dehydroxylation of the LDHs sheets (300–800 °C). The total weight loss for this region (70-800 °C) was 49.0% [21]. The sample [Mg-Al-(SDS)] displayed features due to the removal of adsorbed and interlayer water (50–230 °C) and surfactant degradation and dehydroxylation of the LDHs layer (230–800 °C). The total weight loss for this region (70–800 °C) was about 60%, which was 11% higher than the weight loss for the [Mg-Al-NO_3] because of the existing of SDS. For the [Mg-Al-(PEGS-400)] and [Mg-Al-(PEGS-600)] (Fig. 5b and c), there are three steps of weight loss on the TG diagram. The total weight loss for these two samples (70–800 °C) were about 62% which was 13% higher than the weight loss for the [Mg-Al-NO_3] because of the existing of polymer. In the TG curve of [Mg-Al-(PEGS-1000)] (Fig. 5d), there are four steps. The total weight loss for this sample (70–800 °C) was 41.7%, which was lower than the total weight loss for the [Mg-Al-NO_3]. The reason is that PEGS-1000 molecules lie parallel in layers, and substituted NO_3^- of pristine LDHs. The polymer located within the galleries attached to surfaces of the platelets, which made water not lie in galleries. So, the whole loss of weight is lowered which was consistent with the first steps of the [Mg-Al-(PEGS-1000)] (Fig. 5d). However, the X-ray data in Fig. 1 indicated that the PEGS-1000 has intercalated into layer of LDHs since the basal spacing of the [Mg-Al-(PEGS-1000)] is expanded to 0.96 nm. For the PEGS-400 and PEGS-600, the polymer intercalated in the gallery of LDHs layers is in the perpendicularly arrange, which made the nanocomposite have big free space between the galleries, so that water can stay in layers. Because of the lying of polymer, the total weight loss for these two samples is higher than pristine LDHs.

The electrophoretic mobility of [Mg-Al-NO_3] particle was $+2.80 \times 10^{-8}$ m^2 v^{-1} s^{-1}. With the aging time increasing, the electrophoretic mobility curve of [Mg-Al-SDS] showed a different behavior. There was a sharp decay of μ value up to the region near the 3 hr, followed by a slight increase with the aging time, which produced a valley. Since then the μ value became nearly constant at a value slightly higher than the minimum observed. The electrophoretic mobility measurements are based on the sample adsorption on the outer surface of LDHs layers. The reaction of SDS with [Mg-Al-NO_3] probably included two parts: adsorption and intercalation. At the beginning, most SDS were adsorbed on the outer surface of LDHs layers, which resulted in the sharp decreasing of μ value because of the effect of negative charge of sulfonate groups in SDS. The intercalation started almost at the same time at a slow rate compared with the adsorption. So a small portion of SDS was probably removed from the outer surface to the interlayer of LDHs, which leaded to the decrease of total negative charge and μ value increased slightly. Moreover, when the system reached an equilibrium between adsorption and intercalation, the μ value became nearly constant. Because there were still many sodium dodecylsulfate adsorbing on the surface of the composite, and dissociating in the solution through unadsorption. So the μ value of [Mg-Al-SDS] was -1.74×10^{-8} m^2 v^{-1} s^{-1}. It may result in the protein denaturation, which made it not become LDHs modifier. There were some reports about the intercalation of LDHs layers by polymer to get the polymer/LDHs nanopartical [20]. Because of the positive zeta potential of LDHs, the polymer which was selected to intercalate into LDHs layer were all anionic polymers. And the polymer/LDHs nanoparticals exhibited a negative μ value because the

polymer adsorption occurred on the outer surface of nanoparticals. However, in this experiment condition, the μ value of [Mg-Al-(PEGS-400)], [Mg-Al-(PEGS-600)] and [Mg-Al-(PEGS-1000)] still was positive, and was 0.98, 1.08 and 1.05×10^{-8} m^2 v^{-1} s^{-1}, respectively. The electrophoretic mobility result showed that the PEGS have intercalated into LDHs, and only little polymer adsorbed on the surface of the composites. It cannot result in the protein denaturation, which make it become LDHs modifier to be a precursor to prepare bio-molecule/LDHs.

We have successfully prepared PEGS/LDHs nanocomposites by simple ion-exchanged method. As an organic modified agent, PEGS could easily assembled in the surface of LDHs by the reaction of the polar group $-OSO_3^-$ and the surface of LDHs. The assembly of polymer PEGS did not change the electrophoretic mobility of LDHs particles. The result of IR and TG indicated that there was few PEGS adsorbed on the surface of LDHs, and this made it was useful modifier which could not result in the proteins denaturation. Thus, this modified nanopartical, which consisted of the structure of LDHs and water-soluble polymer PEGS, will be a new kind of functional material with novel properties and a candidate to act as a suitable precursor to prepare bio-molecule/LDHs.

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Received 9 September
and accepted 15 November 2004