



# New nanocomposite hydrogels containing layered double hydroxide

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## ABSTRACT

Novel nanocomposite hydrogels were prepared with agarose, which is an uncharged biopolymer, and delaminated lactate-containing layered double hydroxide (lactate-LDH). An aqueous colloidal dispersion of delaminated lactate-LDH was added to a hot aqueous solution of agarose at various agarose/LDH ratios. The mixtures were gelled by cooling to room temperature. The gels were frozen in liquid nitrogen, freeze dried, and observed with a field emission scanning electron microscope. Nanoscale dispersion of the lactate-LDH nanoplates in the polymer network was confirmed.

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## 1. Introduction

Because of the high charge density, layered double hydroxides (LDHs) were thought to be difficult to delaminate into thin lamellae (Ma et al., 2006). However, some researchers delaminated LDHs by using appropriate combinations between interlayer anions and media (Adachi-Pagano et al., 2000; Hibino and Jones, 2001; Hibino and Kobayashi, 2005; Li et al., 2005; Wu et al., 2005; Iyi et al., 2008). Delamination made it possible to obtain stable colloidal dispersions of LDHs in liquid media. Meanwhile, Xu et al. (2006a,b) reported disaggregation of LDH nanocrystallites in water as a different way of obtaining colloidal dispersions of LDHs. Although the LDH nanocrystallites seemed to be thicker than the delaminated LDH layers, both the LDH nanocrystallites and the delaminated LDH layers can be seen as nanoplates.

The surfaces of hydroxide layers of the LDH nanoplates, as aforementioned, should be far more accessible for anions or anionic substances than the interlayer surfaces in crystalline LDHs. Nevertheless, when the dispersion medium of such samples is removed by evaporation, such high accessibility will be destroyed by restacking or reaggregation of the colloidal LDH nanoplates. If the LDH nanoplates could be entrapped in a porous matrix, better accessibility of the LDH surface would be gained, thus creating a promising material for application as an adsorbent for hazardous anions or for the controlled or sustained release of anionic substances.

For these reasons, the author investigated the immobilization of delaminated LDH nanoplates in an agarose hydrogel matrix. The polymer gel consists of a cross-linked network and a liquid medium filling the interstitial spaces of the network. Solute transport primarily occurs within the liquid medium in the spaces within the polymer

network (Amsden, 1998; Suzuki et al., 2009). Agarose is an essentially uncharged polysaccharide. This condition is advantageous when the nanocomposite gels are used for adsorbing anions or for sustained release of anionic substances, because the quantity of positive charge on the LDHs is not wasted within the agarose polymer matrix.

Various nanocomposite hydrogels (Schexnailder and Schmidt, 2009), such as polymer–smectite nanocomposites (Haraguchi, 2007), were studied. Investigations of nanocomposite gels were extended to those using LDHs as inorganic nanoparticles (Lee and Chen, 2004a,b, 2005, 2006; Lee and Lee, 2006; Zhang et al., 2008, 2009a,b,c). Most of these nanocomposite hydrogels were obtained by in situ polymerization of appropriate monomers in the presence of organo-modified LDHs. Such polymer–LDH nanocomposite hydrogels were investigated in terms of swelling, water absorbance, mechanical properties, and suitability for applications in enzyme immobilization or drug release.

The aforementioned previous studies did not examine how the LDH particles were dispersed in the polymer networks in detail. To observe the state of LDH dispersion in polymer network, the network must be kept intact as much as possible. To this end, freeze drying of samples or the use of cryogenic scanning electron microscopy is a useful method. In this paper, nanocomposite gels that contained varying amounts of LDH, up to 1:1 mass/mass LDH/polymer, were prepared, freeze dried, and analyzed through field emission scanning electron microscopy to reveal the states of the LDH dispersion in the polymer network.

## 2. Materials and Methods

### 2.1. Preparation of LDHs and their aqueous mixtures

Two types of LDHs were synthesized at room temperature by coprecipitation at constant pH (pH = 10): 1) lactate-containing LDH (lactate-LDH) and 2) carbonate-containing LDH (CO<sub>3</sub>-LDH). Lactate-

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**Table 1**  
Agarose/LDH Mass Ratios of the Hybrid Hydrogels.\*

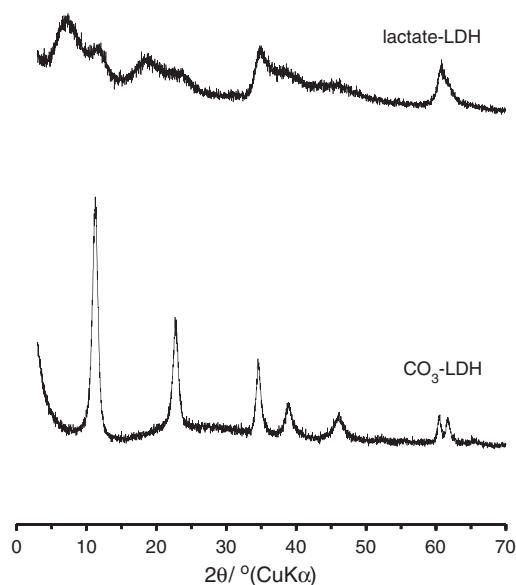
Sample	Agarose	Lactate-LDH	CO <sub>3</sub> -LDH
AG	100	0	0
AG/Lac-5	100	5	0
AG/Lac-10	100	10	0
AG/Lac-20	100	20	0
AG/Lac-50	100	50	0
AG/Lac-100	100	100	0
AG/CO <sub>3</sub> -20	100	0	20
AG/CO <sub>3</sub> -100	100	0	100

\*Ratios are expressed as parts per 100 parts of agarose by mass.

LDH was prepared in air in a similar manner as described in our previous report (Hibino and Kobayashi, 2005). A mixed aqueous solution of [CH<sub>3</sub>CH(OH)COO]<sub>2</sub>Mg · 3H<sub>2</sub>O and [CH<sub>3</sub>CH(OH)COO]<sub>3</sub>Al ([Mg] + [Al] = 0.1 M, Mg:Al = 3:1, 250 mL; Solution A) and 2 M NaOH aqueous solution (Solution B) were simultaneously added dropwise to 350 mL of an aqueous solution of DL-lactic acid that was initially adjusted to pH = 10 with Solution B. The lactic acid solution contained the same quantity of lactate anions as in Solution A. Solution A was added at a constant rate of 250 mL · h<sup>-1</sup>, and the pH of the mixture was maintained at pH = 10 by the addition of Solution B. The product was washed with water by several repetitions of alternating dispersion in fresh water and centrifugation. Washing of lactate-LDH with water was possible, because the delamination of lactate-LDH in water was a slow reaction. After washing, the wet sample was divided into two portions. One portion was dried at 80 °C. Another portion was dispersed in water. The aqueous lactate-LDH mixture became a translucent colloidal dispersion within a couple of days at room temperature. CO<sub>3</sub>-LDH (Mg:Al = 3:1) was prepared in a similar manner as described by Yun and Pinnavaia (1995). Washing, drying, and preparation of its aqueous mixture were carried out in the same way as those for lactate-LDH. CO<sub>3</sub>-LDH readily settled down from its suspension and did not form a stable dispersion. The aqueous mixture was intensely shaken before use to redisperse the particles.

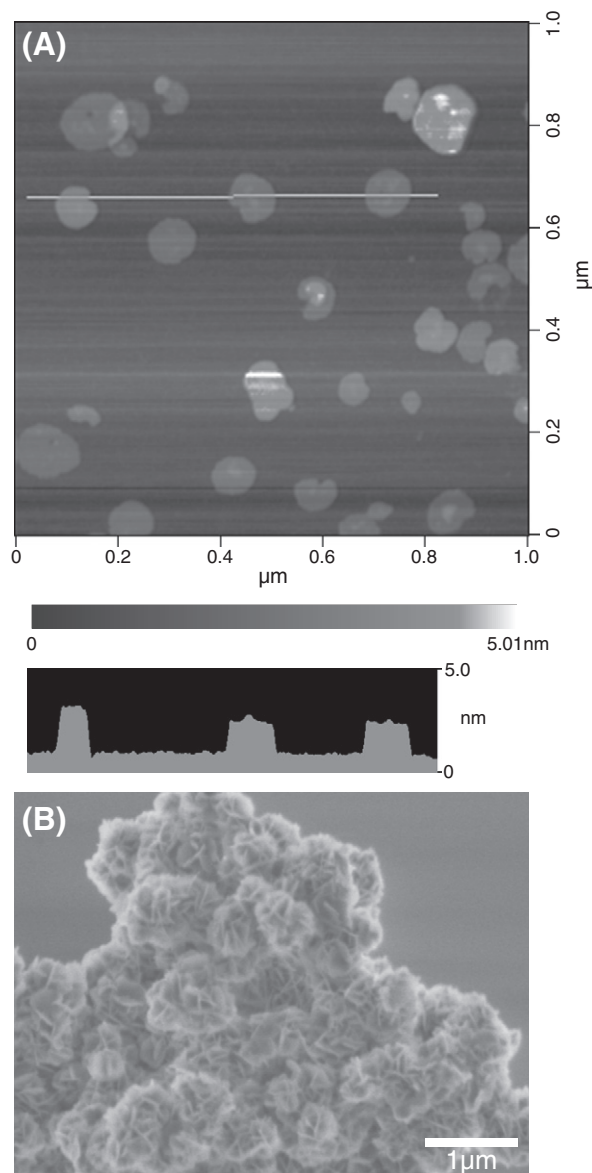
## 2.2. Preparation of the hybrid hydrogels

First, the content of LDH in the colloidal dispersion of lactate-LDH or the suspension of CO<sub>3</sub>-LDH was measured by air drying (11.2 g · L<sup>-1</sup> for lactate-LDH colloidal dispersion and 14.8 g · L<sup>-1</sup> for CO<sub>3</sub>-LDH



**Fig. 1.** XRD patterns of LDH samples that were obtained by drying LDH pastes at 80 °C immediately after washing with water.

suspension). Agarose (Agarose-H, content of SO<sub>4</sub> ≤ 0.2%, Nippon Gene Co., Ltd.) with water was heated to slightly above 90 °C with a water bath. After dissolution of the agarose, the calculated quantity of the colloidal dispersion of lactate-LDH or the suspension of CO<sub>3</sub>-LDH was added. The mixture of agarose, LDH, and water was kept at about 90 °C with intermittent stirring for about 10 min before being removed from the water bath. The approximate quantity of water that was lost by evaporation during mixing was quickly added to adjust the agarose content to 1 mass% of the total mass of the aqueous mixture. The mixture was stirred well again while it was hot and then was cooled to room temperature to form a gel. The ratios of LDH to agarose used in this paper are listed in Table 1. For samples AG/Lac-100 and AG/CO<sub>3</sub>-100, the colloidal dispersion of lactate-LDH or the suspension of CO<sub>3</sub>-LDH was added before heating. This modification to the experimental procedure was necessary to ensure the complete dissolution of agarose in the case of preparation of samples with high LDH content. The resulting gels were divided into multiple portions.



**Fig. 2.** Observation of air-dried aqueous mixtures. (A) Dynamic-force-mode (tapping-mode) AFM image of delaminated lactate-LDH nanoplates on mica. Height profile along the line marked in the topographic image is shown beneath the topographic image. The sample was prepared from a colloidal dispersion diluted to approximately  $5 \times 10^{-4}$  mass %. (B) FE-SEM image of CO<sub>3</sub>-LDH aggregates on mica substrate. The sample was prepared from a diluted suspension of CO<sub>3</sub>-LDH particles.

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