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A controlled release strategy of antifouling agent in coating based on intercalated layered double hydroxides

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ABSTRACT

A controlled release method of antifouling agent was demonstrated *via* the model coating which was fabricated by sodium paeonolsilate (PAS) intercalated into Zn_2Al Layered Double hydroxides (LDH) and then dispersed in the mixture of acrylic resin and colophony with weight ratio of 2:1. The powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) confirm the intercalation of PAS into the galleries of Zn_2Al-LDH. Some larger particles of Zn_2Al-PAS-LDH composite in the coating were observed owing to its aggregation, which was revealed by Laser scanning confocal microscope (LSCM). The release tests of the Zn_2Al-PAS-LDH coating in 3.5% NaCl solution showed that no burst release phenomenon occurred at the beginning stage and a slower release rate of PAS (0.54 ppm/d) was obtained compared with the pristine PAS coating (1.06 ppm/d), exhibiting its preferable controlled release behavior. The adhesion experiment using *Ulva* zoospores indicated that Zn_2Al-PAS-LDH composite obviously increases the utilization rate of PAS owing to its controlling release property. Therefore, the present work provided a useful strategy to decrease the waste of antifouling agent and prolong the lifetime of antifouling coatings.

1. Introduction

The settlement of marine organisms (bacteria, algae, mollusks), known as fouling or biofouling, is a particular problem for any structure immersed in the sea, including ships' hulls, pipelines, fishing nets, and bridge pillars. This unwanted colonization has serious impacts with deterioration of the surfaces, increased roughness, increased fuel consumption, and loss of maneuverability of the vessels [1]. Currently, one of the most effective strategies is to paint chemically active antifouling coatings (AF) on the surface of structures, which is made of tin-free active compounds (called biocides) embedded in a polymer matrix [2]. The biocide in the antifouling coatings is released to kill or repel fouling organisms when structures coated with antifouling coatings are immersed into seawater. However, the chemically active paints do not maintain an AF protection for more than 3–5 years, as the erosion and the release rates are too high during the early immersion period and rapidly decrease thereafter [3]. Therefore, it is highly necessary to design a biocide delivery and controlled release system to prolong the lifetime of AF coatings.

Recently, preparation of surface coatings or thin films from inorganic matrix materials with controlled release performances plays an important role in drug release system[4]. Among inorganic matrices, layered double hydroxides (LDH), whose structure can be generally expressed as $[M^{II}_{1-x}M^{III}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ (M^{II} and M^{III} are divalent and trivalent metals respectively, and A^{n-} an n-valent anion), are one type of important layered materials which have been extensively studied in drug delivery [5] because of the advantages of facile manipulation, low-cost, biocompatibility and environment-friendliness. It has been reported that a series of pharmaceutically active compounds, such as ibuprofen, diclofenac, gemfibrozil, naproxen, 2-propylpentanoic acid, 4-biphenylacetic acid and tolfenamic acid, etc., have been intercalated into LDHs [6,7]. Thus, this inspires us to employ LDH as antifouling agent carrier to build a controlled release system, for the purpose of prolonging the lifetime of antifouling coatings.

In this work, therefore, sodium paeonolsilate (PAS) employed as antifouling agent was incorporated into Zn_2Al-LDH matrix to prepare a controlled release composite, and the composite (Zn_2Al-PAS-LDH) are characterized by means of XRD, FT-IR and elemental analysis. The model coating was prepared *via* dispersing Zn_2Al-PAS-LDH composite in a mixture of acrylic resin and rosin with weight ratio of 2:1. To illuminate the controlled release and antifouling effect of Zn_2Al-PAS-LDH composite, the release test and

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settlement assay with *Ulva* spores were carried out.

2. Experimental section

2.1. Materials

PAS was purchased from J&K Chemical Ltd. Analytical grade chemicals including $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and NaOH were purchased from the Beijing Chemical Co. Ltd., and used without further purification. Acrylic resin and colophony were provided by Xiamen Sunrui Ship Coating Co. Ltd. The deionized and decarbonate water was used in all the experimental processes.

2.2. Synthesis of PAS-LDH composites

The Zn_2Al–NO_3-LDH precursor was synthesized by the hydrothermal method reported previously [8]. Subsequently, the PAS intercalated LDH was prepared by the ion-exchange method as following: PAS (4 g, 14.9 mmol) was dissolved in a aqueous solution with pH adjusted to 7.5 by adding NaOH solution (0.1 m), and then 1.82 g prepared Zn_2Al–NO_3-LDH (15.2 mmol) was added. The mixture was stirred at 70 °C under N_2 atmosphere for 48 h. The resulting precipitate Zn_2Al-PAS-LDH was centrifuged, washed with deionized water, and dried at 60 °C for 12 h.

2.3. Fabrication of a model coating

Zn_2Al-PAS-LDH coating was obtained as following: Zn_2Al-PAS-LDH (1.08 g in which contains 0.48 g PAS) was placed in a glass beaker (50 ml) with a mixture of acrylic resin (10 g), rosin (5 g) and xylene (10 ml), and the mixture was dispersed uniformly by ultrasonic grinder and coated on iron plates ($100 \times 50 \times 0.5$ mm each). The net weight of prepared coating on each iron plates is 0.60 ± 0.05 g after getting dried at ambient temperature for 48 h. According to the result of element analysis, Pristine PAS and Zn_2Al-LDH coatings with the same amount of PAS and LDH used for comparison were fabricated following the same procedure, respectively.

2.4. The release test and determination of Ulva spores adhesive

PAS release test was carried out at constant temperature (20 °C) by immersing the coatings in a beaker with 1000 ml of NaCl solution (3.5%) stirred with a speed of 200 r/min. The released PAS was measured at predetermined time by UV–vis absorbance at 270.0 nm. The green macroalga *Ulva* were collected from Qingdao beach, China. Zoospores were released according to the report by Callow et al. [9]. Zoospore suspensions containing 1.5×10^6 spores ml^{-1} were allowed to settle onto coatings for 24 h in the dark. Unsettled zoospores were removed by flow apparatus with the wall shear stress of 54 Pa for 5 min in a fully turbulent water channel. Spore density on the coatings after exposure to flow was recorded using the Hirox digital microscope KH-8700. Spores were counted in 15 fields of view (0.059 mm^2 each) in each of three parallel coatings to provide cell settlement data.

2.5. Techniques of characterization

The powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation ($\lambda = 0.15418$ nm) at 40 kV with a 2θ angle ranging from 3° to 70°. FT-IR spectra were recorded on a Nicolet 8700 Fourier transfer infrared spectrophotometer using the KBr disk method with a resolution of 2 cm^{-1}. Metallic elemental analysis was performed by atomic emission spectroscopy with a Shimadzu ICPS-7500 instrument. C, H, N content was determined using an Elementar vario elemental analysis instrument. The images of Laser scanning confocal microscope (LSCM) were obtained using an OLS 4000. The UV–vis adsorption spectra were collected in the range from 200 to 600 nm on a Hitachi U-2800 with the slit width of 1.0 nm.

3. Results and discussion

The powder XRD pattern of Zn_2Al-LDH and Zn_2Al-PAS-LDH are shown in Fig. 1A. For the Zn_2Al-LDH precursor (Fig. 1A-a), the 003 reflection gives the interlayer distance of 8.92 Å, in accordance with the reported value for NO_3-LDH [10]. After the anion-exchange reaction, the basal reflection (003) of PAS-LDH composite (Fig. 1A-b) shifted to lower 2θ angles, and the basal spacing expanded to 20.1 Å for the Zn_2Al-PAS-LDH sample. The result indicates that PAS anion has been intercalated into the Zn_2Al-LDH lamellar.

The FT-IR spectra of NO_3-LDH, pristine PAS and Zn_2Al-PAS-LDH are shown in Fig. 1B, respectively. The spectrum of NO_3-LDH (Fig. 1B-a) shows a strong absorption band at 1380 cm^{-1} and a weak one at 830 cm^{-1} that can be attributed to the ν_3 and ν_2 stretching vibration of NO_3^- group respectively. The characteristic absorption band of carbonate at 1360 cm^{-1} was not observed, confirming the absence of carbonate in precursors. In the spectrum of pristine PAS (Fig. 1B-b), the strong absorption bands at 1196 and 1068 cm^{-1} are due to the $O{=}S{=}O$ stretching vibration of the sulfonate group[11]. For the Zn_2Al-PAS-LDH composite (Fig. 1B-c), the

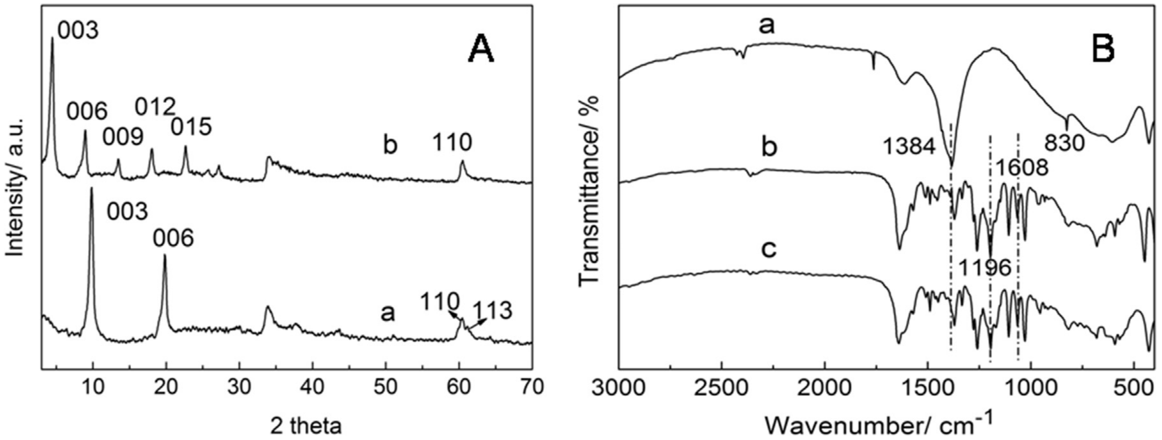

Fig.1. (A) XRD patterns for (a) Zn_2Al-LDH and (b) Zn_2Al-PAS-LDH powder samples. (B) FT-IR spectra of (a) Zn_2Al-LDH, (b) pristine PAS and Zn_2Al-PAS-LDH powder samples.