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Facile synthesis of phytic acid@attapulgite nanospheres for enhanced anti-corrosion performances of coatings

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ABSTRACT

This paper presents the first phytic acid @ attapulgite (PA@ATP) nanospheres using natural rod-like ATP as the raw material through a convenient hydrothermal method. The morphologies of the nanocomposites were investigated by SEM and TEM, and the compositions and structures of synthesized products were characterized by FTIR, XPS, ICP-AES, EDX and XRD. When the nanospheres were blended with water-based epoxy resin, the as-obtained nanocomposite coatings exhibited excellent anti-corrosion properties.

1. Introduction

Layer structured aluminosilicate clays such as kaolinite, attapulgite (ATP), and montmorillonite have drawn much attention over the decades due to their excellent physical and chemical properties [1–5]. These clays are always consisted of nanometer-sized aluminosilicate nanoplatelets with large surface areas and abundant active groups, and may find applications in heavy metal absorption [6,7], catalysis [8], electrode [9,10], and so on. To provide these natural layered minerals with ideal mechanical and processing properties, modifications are usually inevitable to graft flexible organic molecules/polymers onto clay surfaces [3,11–19]. A common strategy to prepare polymer-clay composites contains two steps as follows: (1) surface modification of clays by free radical initiators to introduce active sites; [20] (2) *In situ* polymerization of monomers onto these clays [21,22]. During modification, Na^+ ions between the clay layers exchange with alkylammonium cations (incurred by surfactants) to increase both layer gap and layer hydrophobicity [23,24]. The subsequent polymerization may happen either on the outer clay surfaces or within the layer gap to obtain homogeneous composite structures [25–28].

ATP, one of the most commonly used clays, has unique structure of discontinuous octahedral layers which elongate in the c-direction and alternate with continuous tetrahedral ones [26]. Previous researches were mainly focused on the properties and applications of ATP as absorbents [6] and catalysts [27], little was involved in its anti-corrosion property based on the best of our knowledge. In this study, we successfully synthesize for the first time Phytic acid (PA) @ ATP composite nanospheres through a convenient hydrothermal method. During hydrothermal treatment, ATP was decomposed into fragments which were then self-assembled with phytic acid molecules into novel nanospheres. The as-obtained nanocomposites exhibited better compatibility with water than natural ATP and more durable anti-corrosion performance after forming continuous films on steel substrates.

2. Experimental section

2.1. Materials

The ATP clay was supplied by Jiu Chuan Nano Material Technology Co. Ltd. (Jiangsu Province, China) and milled into around 500 meshes. Phytic acid (PA), ethanol (99.7 wt%), acetone (99.5 wt%), and aqueous ammonia (25–28 wt%) were purchased from Shanghai Chemical Reagent Co. Ltd. Waterborne epoxy resin (50 wt% of solid content) was provided by Dow Chemical Co. Ltd.

2.2. Synthesis of ATP clay hydrogel

5 g of ATP clay powder was dispersed in 495 mL of deionized water under mechanically stirring at 1000 r/min and room temperature for 40 min to form a homogeneous dispersion. This dispersion was then separated by centrifugation and washed by ethanol, acetone, and deionized water respectively, followed by redispersion in deionized water to obtain 5 wt% ATP clay hydrogel.

2.3. Modification of ATP

Typically, 5 g of ATP clay hydrogel was blended with 25 mL of PA under vigorous magnetic stirring at room temperature for 10 min. The

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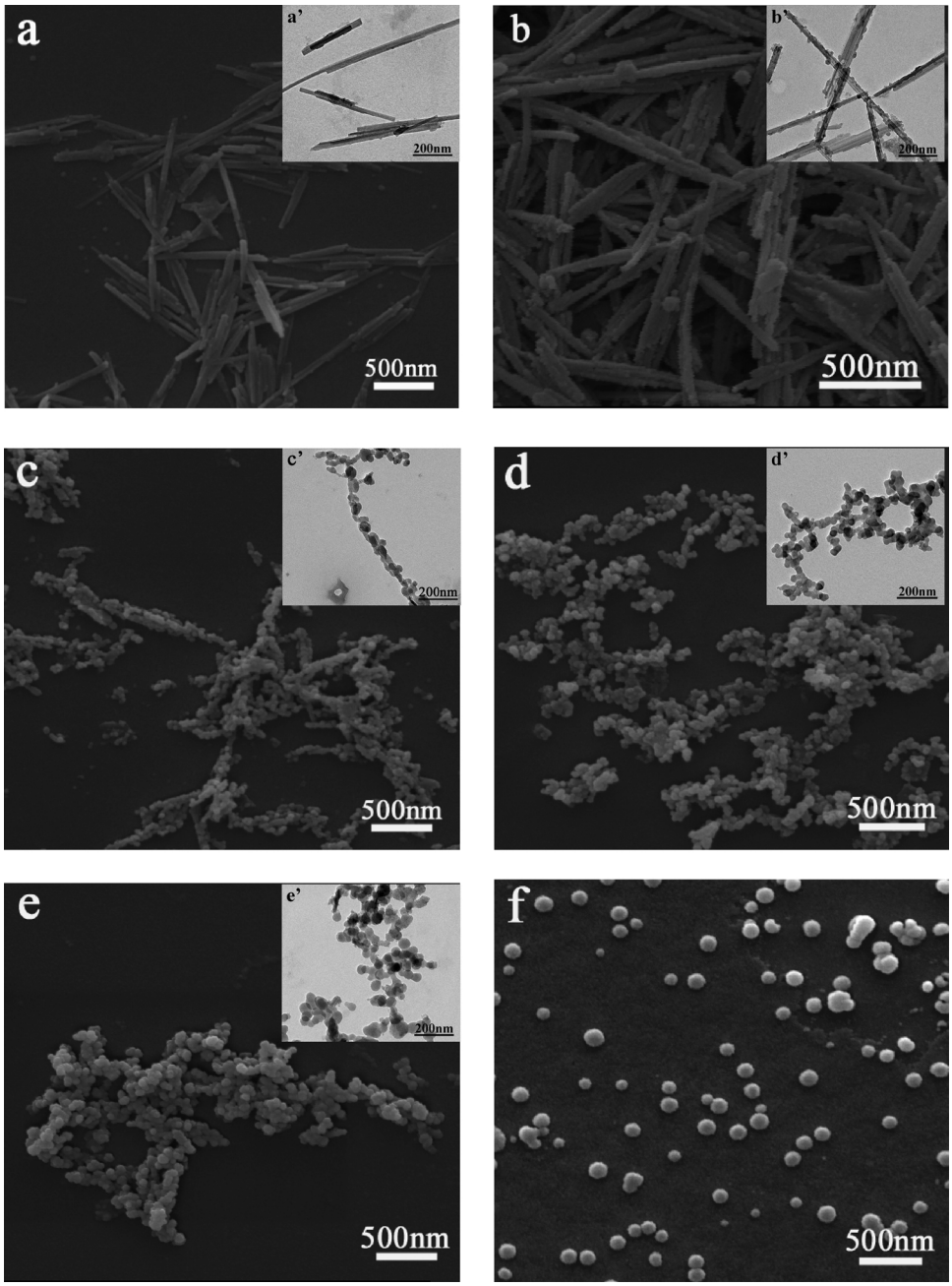

Fig. 1. SEM images of natural ATP clay hydrogel (a), PA/ATP nanocomposites with various mass ratios: (b) 1:9, (c) 1:1, (d) 2:1, (e) 5:1, (f) the nanospheres were redispersed into water. The insets are corresponding TEM images.

system was then increased to 80 °C and maintained at that temperature under 250 r/min magnetic stirring for 1 h. Then the modified ATP nanocomposites were collected and washed several times with deionized water and dried at 80 °C for 24 h.

2.4. Synthesis of PA @ ATP nanospheres

Typically, 5 g of ATP clay hydrogel was blended with 25 mL of PA under vigorous magnetic stirring at room temperature for 1 h. This system was adjusted to a desired pH values by ammonia, and then poured into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 24 h. Finally after being cooled to room temperature, the as-prepared PA@ATP nanospheres were collected and washed several times with deionized water and dried at 80 °C for 24 h.

2.5. Preparation of waterborne epoxy/ATP and waterborne epoxy/PA @ ATP nanocomposite films for EIS test

In a typical operation, 3 g PA@ATP nanospheres and natural ATP was added to mixture of 40 g waterborne epoxy resin under vigorous stirring, respectively. The 304 stainless steel substrate was polished by grade 600 and 1000 emery papers, washed by water and acetone, and finally dried in the air. Epoxy/ATP and epoxy/PA @ ATP nanocomposite films were obtained by dip-coating and air-drying cycles (60 ± 2 °C for 1 h). The dried film thickness was controlled at 30 ± 0.3 μm by surfcorder ET 3000 (Kosaka Laboratory Ltd.).

2.6. Preparation of waterborne epoxy/ATP and waterborne epoxy/PA @ ATP nanocomposite films for salt-fog and natural environment exposure test

The substrate was changed to mild steel. The treatment method and coating technology were same as method describe in 2.5.