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The relationship between modulated morphology of attapulgite/polypyrrole composites and electrical property



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ABSTRACT

Attapulgite/polypyrrole composites (ATP/PPys) with morphology difference were synthesized in water–ethanol mixture via modulating the surface property of ATP to expound the relationship of morphology and electrical property. The surface property of ATP shows important impacts on the modulated morphology of ATP/PPys, and their morphologies are closely related with the inherent property. The results indicate that the pristine ATP is beneficial to generate the rod–film composites, and the rod–film ATP/PPys have preferable electrical conductivity and specific capacitance compared with the rod–sphere ones.

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1. Introduction

Polypyrrole (PPy), a very typical conductive polymer, has been extensively exploited for electrical energy storage devices (EESD) including battery and capacitor because it has desirable charger density and favorable degree of flexibility in electrochemical processing as compared with the others [1]. However, it is difficult for the single PPy to satisfy the development and requirement of constantly improving EESD. Thus, its composites, especially the composites with clay as the carrier, receive urgent concern. Attapulgite (ATP), natural Mg–Al silicate clay mineral with one-dimension crystal morphology [2], is attracting increasing interests in potential conductive composites such as ATP/polyaniline [3], ATP/PPy [4], and ATP/polythiophene [5]. Among them, ATP/PPy composites (ATP/PPys) have been acknowledged as a most promising conductive material due to its low-cost production and particular advantages.

As we all know, the electrical property of conductive material is strongly related to its intrinsic structure as well as extrinsic morphology. It was reported from relevant literatures that corn cob-like ATP/PPys were emphatically investigated [4,6]. In this

study, we surprisingly found that the morphology of ATP/PPys varied with the evolution of ATP surface property, which would provide theoretical significance for the industrial application of ATP/PPys. Herein, ATP/PPys of different morphologies were fabricated by simply modulating the ATP surface property and were evaluated by using transmission electron microscope (TEM), field emission scanning electron microscope (FE-SEM), contact angle, Zeta potential, and electrochemical experiments to clarify the relationship of the morphology of ATP/PPys and their electrical property.

2. Material and methods

ATP (2.0 g, 100 mesh) was first put into 100 mL of 3.0 mol/L HCl solution. After stirring for 5 h at 85 °C, the suspension was filtered and washed several times. The acidic ATP was dispersed again in 100 mL of water–ethanol mixed solvent (1:1, volume ratio), subsequently, pyrrole (1.5 g, CP) monomer and dodecyl sulfonic acid sodium salt as a dopant (1.8 g, CP) were added to the above mixture simultaneously, and thus FeCl₃ · 6H₂O (13.9 g in 30 mL of water, AR) was added dropwise with vigorous stirring within 20 min, the system was maintained at 0 °C for 2 h. Afterward, the black dispersion was filtered and washed with deionized water, the ATP/PPys were dried at 60 °C for 10 h (marked S1). The original ATP (2.0 g) was also applied to prepare ATP/PPys under the similar technological conditions (marked S2).

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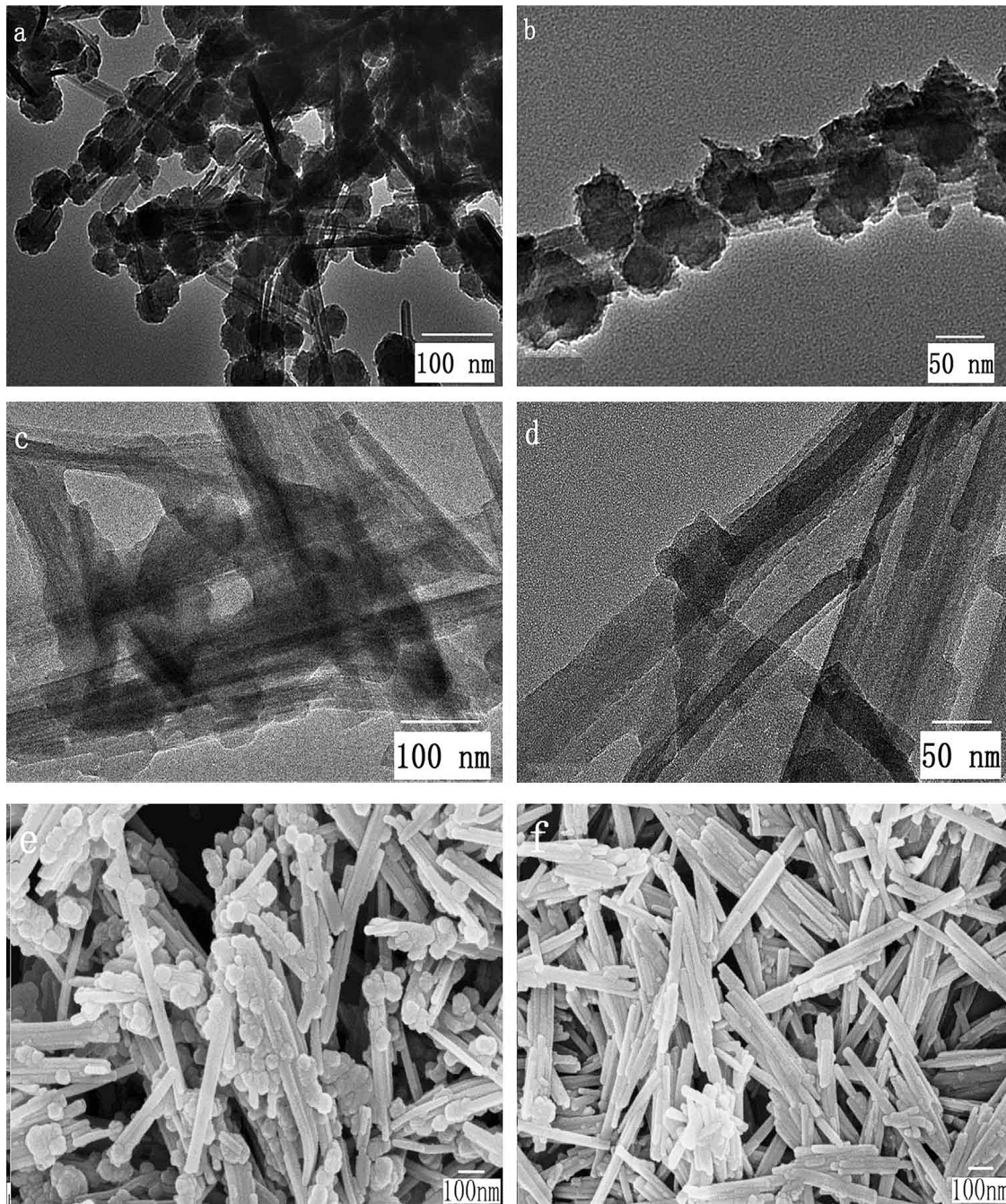


Fig. 1. TEM and FE-SEM images of ATP/PPys: S1 (a, b and e) and S2 (c, d and f).

The morphologies of the composites were examined by JEOL Corporation (Japan) JEM-2100 TEM and Carl Zeiss Corporation (Germany) SUPRA-55 FE-SEM, respectively. Zeta potential was obtained using a Malvern Corporation (British) ZEN 3600 potential analyzer. Contact angle experiments were carried out on a JC2000D1 contact angle goniometer (Zhongchen Digital Technic Apparatus, Shanghai). Electrochemical measurements were performed on a CHI 660D electrochemistry workstation (CH instruments, Shanghai) as we reported previously [7].

3. Results and discussion

Fig. 1 conducts the TEM and FE-SEM images with different morphologies of ATP/PPys. As can be seen, S1 presents a rod-

sphere shape, just like tomatoes on sticks, which can be attributed to intense interactions of the Lewis acid–base type between –OH and the N–H bond and/or the positively charged PPy backbone, similar to the mechanism that is proposed by Liu et al. [6]. The homogeneous membrane on the pristine ATP surface is observed distinctly from S2, revealing that the above interface interactions almost disappear in the preparation as a result of few –OH on the ATP surface. We think that each of Py monomers is adsorbed physically on the ATP surface in the same probability to produce rod–film shape with well covered core–shell morphology. This difference indicates that the ATP surface property has a vital effect on the morphology of ATP/PPys.

To further distinguish the relationship between morphology of ATP/PPys and their electrical property, contact angle (θ) and Zeta potential experiments were first shown in Fig. 2. It can be

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