

Preparation and Characterization of Exfoliated Organic Montmorillonite/Poly(3,4-Ethyldioxythiophene) Nanocomposites

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ABSTRACT: Montmorillonite, organically modified by octadecylamine salt, has been adopted to successfully fabricate the exfoliated organic montmorillonite/poly(3,4-ethyldioxythiophene) (OMMT/PEDOT) nanocomposites by *in situ* polymerization in aqueous media. Hydrochloric acid, 1,5-naphthalenedisulfonic acid, and sodium benzenesulphonate have been employed to activate the polymerization of 3,4-ethyldioxythiophene by offering active sites on the layers of montmorillonite. The resulting exfoliated nanocomposites have been characterized by Fourier trans-

form infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, thermogravimetric analysis, and electrical conductivity measurement and showed controllable conductivity in the range of 10^{-7} to 10^{-2} S/cm and improved thermal stability compared with pure PEDOT. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2400–2407, 2009

Key words: organoclay; conducting polymers; nanocomposites; TEM; thermalgravimetric analysis

INTRODUCTION

Clays are one type of interesting inorganic layered materials because of their ready availability, small particle size, and well-known propensity for intercalation. The most commonly used clay is the smectite group mineral such as montmorillonite (MMT), which belongs to the general family of 2 : 1 layered silicates.¹ MMT has unique layered structure, high mechanical strength, and excellent chemical resistance, and thus is a good candidate for preparation of inorganic/organic nanocomposites.^{2–4} Conducting polymers encapsulated in MMT layers have been the subject of considerable research interest in recent years. The encapsulated conducting polymers in the interlayer spaces of MMT may provide remarkable hybrid properties, such as electrical conductivity and good physical properties. These systems represent a new class of molecular composites with diverse electrical, optical, mechanical, and thermal properties. Recent studies on MMT/conducting

polymer composites have mainly focused on the MMT/polyaniline (PANI) composites (MPIs),^{5–24} MMT/polypyrrole (PPy) composites (MPYs),^{25–32} and MMT/polythiophene composites (MPTs).³³

Among conducting polymers, poly(3,4-ethyldioxythiophene) (PEDOT), one of the derivatives of polythiophene, has attracted much attention because of its high electrical conductivity, transparency, structural stability, suitable morphology, and fast doping/undoping mechanism.^{34,35} People have yearned to develop the new hybrid nanocomposites showing novel properties via the combination of various inorganic materials and PEDOT, such as MMT/PEDOT system, for some number of years. Recently, it has been reported that clay-PEDOT nanocomposites (CPNs) can be prepared with different synthetic routes using a standard Wyoming MMT and processed as thin films. Unfortunately, the conductivity of the nanocomposites is as low as 10^{-4} S/cm.³⁶

According to the earlier reports, MPIs^{5–22} and MPYs^{25–32} usually have the intercalative structure. The exfoliated nanocomposites, however, should be more desirable than intercalated ones, because strong synergistic effects between conductive polymer and silicate layers could be obtained, and the properties of the composite materials could be optimized in exfoliated systems.²³ Complete exfoliation of MMT layers in MPIs and MPYs is a challenging task, and sometimes, it requires special

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modifications of MMT with cocamidopropylhydroxysultaine as an intercalating agent²⁴ or presynthesis of a water soluble PANI or PPy graft copolymer.^{23,37} Moreover, these two methods to obtain exfoliated nanocomposites are complicated or less economical. Therefore, to explore a facile and economical strategy to obtain exfoliated MMT/conductive polymers, especially MMT/PEDOT nanocomposites, is strongly demanded.

Appropriate chemical modification of MMT is very important, because it enlarges the MMT gallery to accommodate the monomer or organic polymer, renders MMT surface organophilic, lowers the surface energy of clay surface, and improves the compatibility between MMT and the organic polymer or monomer.^{38,39} Considering the difficulties of synthesizing PEDOT into MMT in an aqueous system, efforts have been made to organically modify MMT by inserting long chain surfactants in the galleries of MMT. In this study, OMMT, a commercial, organically modified MMT with octadecylammonium (ODA) salt, has been used. For the first time, we report the preparation of an exfoliated OMMT/PEDOT nanocomposites (OPNs) by *in situ* polymerization. Hydrochloric acid (HCl), 1,5-naphthalenedisulfonic acid (1,5-NDA), and sodium benzenesulphonate (DBSNa) have been used to enhance the polymerization activity of EDOT in an OMMT aqueous suspension. The results show that PEDOT with nanofiber or nanoribbon-like structure can be successfully synthesized with the help of OMMT and chemically modified OMMT. The fabricated exfoliated nanocomposites exhibit satisfactorily controllable electrical conductivity and improved thermal stability. Furthermore, another reportable advantage of this study is the mild synthesis conditions with water as reaction medium at room temperature, which is desirable in the development of environmentally benign and economical processes.

EXPERIMENTAL

Materials

The clay used in this study as a host material is organically modified sodium MMT, OMMT, which is supplied by Chinese Academy of Sciences. The OMMT was prepared by ion-exchanging reaction between sodium montmorillonite and octadecylammonium (ODA) salt.⁴⁰ The presence of ODA cations in the galleries provides hydrophobicity for the sodium MMT. EDOT (Aldrich) was purified by distillation under reduced pressure and stored in a refrigerator prior to use. The oxidant ammonium persulfate (APS) was of analytical grade and purchased from Shanghai Lingfeng Chemical Reagent Company (Shanghai, China). HCl, 1,5-NDA, and

DBSNa were used as received from Nanjing Chemical Reagent Company (Nanjing, China).

Preparation of the nanocomposites

Preparation of OPNs

OMMT (0.1 g) was added to 20 mL deionized water and sonicated for 30 min. One hundred ten microliters of EDOT monomer (1 mmol) was then added dropwise to the colloidal suspension of OMMT and stirred for 10 min. Two millimoles of APS dissolved in 5 mL deionized water was then added to the above mixture. After stirring for 24 h at room temperature, the resulting composites were isolated by centrifugation, thoroughly rinsed with deionized water. The final product was dried under vacuum at 70°C overnight.

Preparation of chemically modified OPNs

OMMT (0.1 g) was added to 20 mL of HCl (1M), 1,5-NDA, and DBSNa aqueous solution (1 mmol 1,5-NDA or DBSNa was added into 20 mL of deionized water), respectively, and stirred for 18 h to complete the chemical modification of OMMT. One hundred ten microliters of EDOT monomer (1 mmol) was then added dropwise to the above colloidal suspension and stirred for 10 min. The followed procedure was repeated as described earlier.

Characterization

The scanning electron microscopy (SEM) images were obtained by a JSM-5610 scanning electron microscope. The specimens were platinum-coated prior to examination. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded from KBr pellets on a Bruker VECTOR22 FT-IR spectrometer. Transmission electron microscopy (TEM) was operated with a JSM-6300 microscope. The samples for TEM were prepared by evaporation of a drop of diluted aqueous solution of the nanocomposite onto a copper grid. XRD patterns were obtained with a Rigaku D/MAX-RC X-ray diffractometer with Cu K α radiation. Thermogravimetric analysis (TGA) was carried out using Pyris 1 TGA instrument under nitrogen atmosphere at a heating rate of 20°C/min. The electrical conductivity measurements were conducted on pressed pellets by the conventional four-probe technique at room temperature.

RESULTS AND DISCUSSION

Chemical polymerization of EDOT itself in an aqueous system is a major challenge. However, in the water system existing OMMT or chemically modified OMMT, EDOT seems to be activated for its

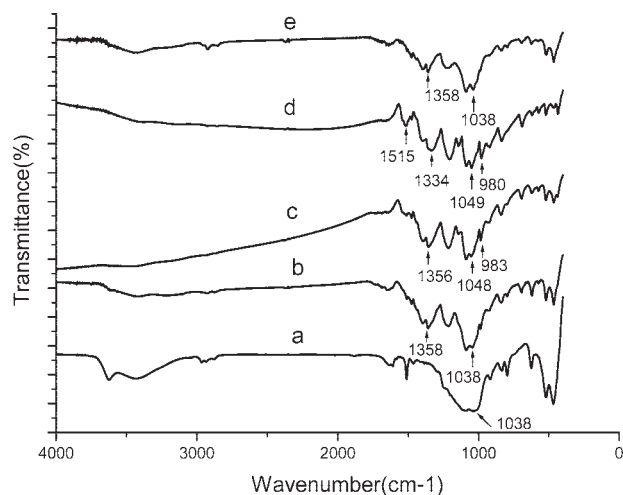


Figure 1 FTIR spectra of (a) OMMT; (b) OPNs; (c) 1,5-NDA-modified OPNs; (d) HCl-modified OPNs; and (e) DBSNa-modified OPNs.

polymerization, which could be observed clearly from the color change of reaction system from milky to navy blue in 30 min. As is known, PEDOT exhibits an electronic band gap, defined as the onset of the π - π^* absorption, of 1.6–1.7 eV and a λ_{max} of ~ 610 nm, making it deep blue in color.⁴¹ The successful polymerization of EDOT in/on OMMT could be confirmed from FTIR spectral analysis of OMMT, OPNs, and chemically modified OPNs (Fig. 1). In the spectrum of OMMT [Fig. 1(a)], the bands in the region of 2800–3000 cm^{-1} and centered at about 1470 cm^{-1} are attributed to CH_2 vibrations of ODA salt.⁴² The broad doublet bands near 1038 and 1089 cm^{-1} are assigned as the characteristic absorption of OMMT for Si–O stretching vibrations in the tetrahedral sheet. The bands centered at 519 and 467 cm^{-1} are attributed to Si–O bending vibrations due to Si–O–Al and Si–O–Si, respectively.⁴³ Moreover, the band centered at 3628 cm^{-1} is ascribed to O–H stretching of lattice water in OMMT.⁴⁴ Comparing with the spectrum of OMMT, FTIR spectra of OPNs, and chemically modified OPNs exhibit characteristic bands of PEDOT in the range of 1052–837 cm^{-1} . It is noticed that the band centered at 892 cm^{-1} , attributed to the bending mode of C–H in EDOT monomer (Fig. 2), does not appear, implying the formation of PEDOT with α - α' -coupling.^{45,46} Also, the stretching absorption band of ethylenedioxy group of PEDOT at 1052 cm^{-1} (Fig. 2) is overlapped by Si–O–Si stretching of MMT, resulting in the narrower doublet bands in the range of 1038–1089 cm^{-1} . Especially for the case of 1,5-NDA-modified OPNs and HCl-modified OPNs, the doublet band has shifted respectively, to 1048 and 1049 cm^{-1} [Fig. 1(c,d)], indicating that more PEDOT could be obtained in these two composites due to the more powerful efficacy of 1,5-NDA and HCl to activate

OMMT. Furthermore, for HCl-modified OPNs, other two spectral changes can be readily observed. Firstly, the vibration band attributed to C–C stretching in the thiophene ring has a red shift from 1358 to 1334 cm^{-1} . This fact should be related to the electrostatic interaction between EDOT cations and negatively charged sites in the chemically modified OMMT. Secondly, the C=C stretching in the thiophene ring (1515 cm^{-1}) (Fig. 2) displays a higher intensity relative to those of DBSNa or 1,5-NDA-modified OPNs. It could be explained that the inorganic acid could modify effectively OMMT with inorganic framework due to the “like dissolves like” and increase the number of sites responsible for adsorption of EDOT molecules. The acid treatment of OMMT and the hydrophobicity of ODA favor the polymerization of EDOT in/on OMMT layers, making more PEDOT form in HCl-modified OPNs compared with DBSNa- or 1,5-NDA-modified OPNs. Moreover, the color change for HCl-modified OPNs is the fastest (in 10 min) among the chemically modified OPNs, which is probably another evidence for the easy polymerization of EDOT for HCl-modified OPNs.

SEM micrographs of OMMT, OPNs, and chemically modified OPNs are shown in Figure 3. It can be seen from Figure 3(a) that a considerable amount of OMMT layers overlap tightly together with an irregular form. After the polymerization, the nanocomposites obtained show significant changes in morphology. Figure 3(b–e) reveal similar cauliflower-like loose surface morphologies for OPNs and chemically modified OPNs, which are caused probably by the presence of PEDOT and the exfoliation of OMMT layers.

To further confirm the morphology of the nanocomposites, we adopted TEM to visualize the structure of the nanocomposites. The TEM micrographs,

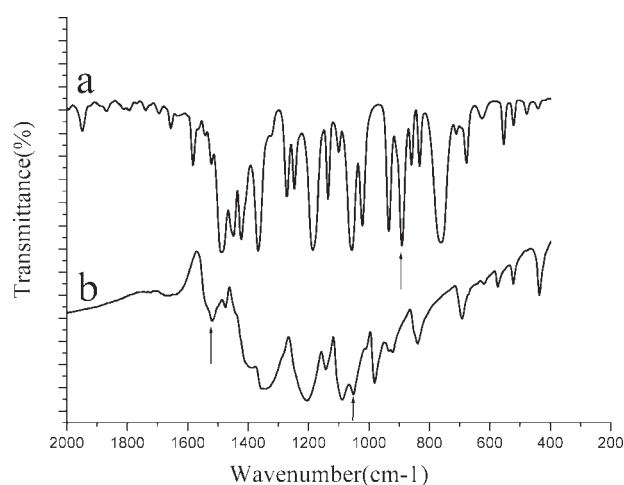


Figure 2 FTIR spectra of (a) EDOT and (b) PEDOT in the 2000–200 cm^{-1} region.

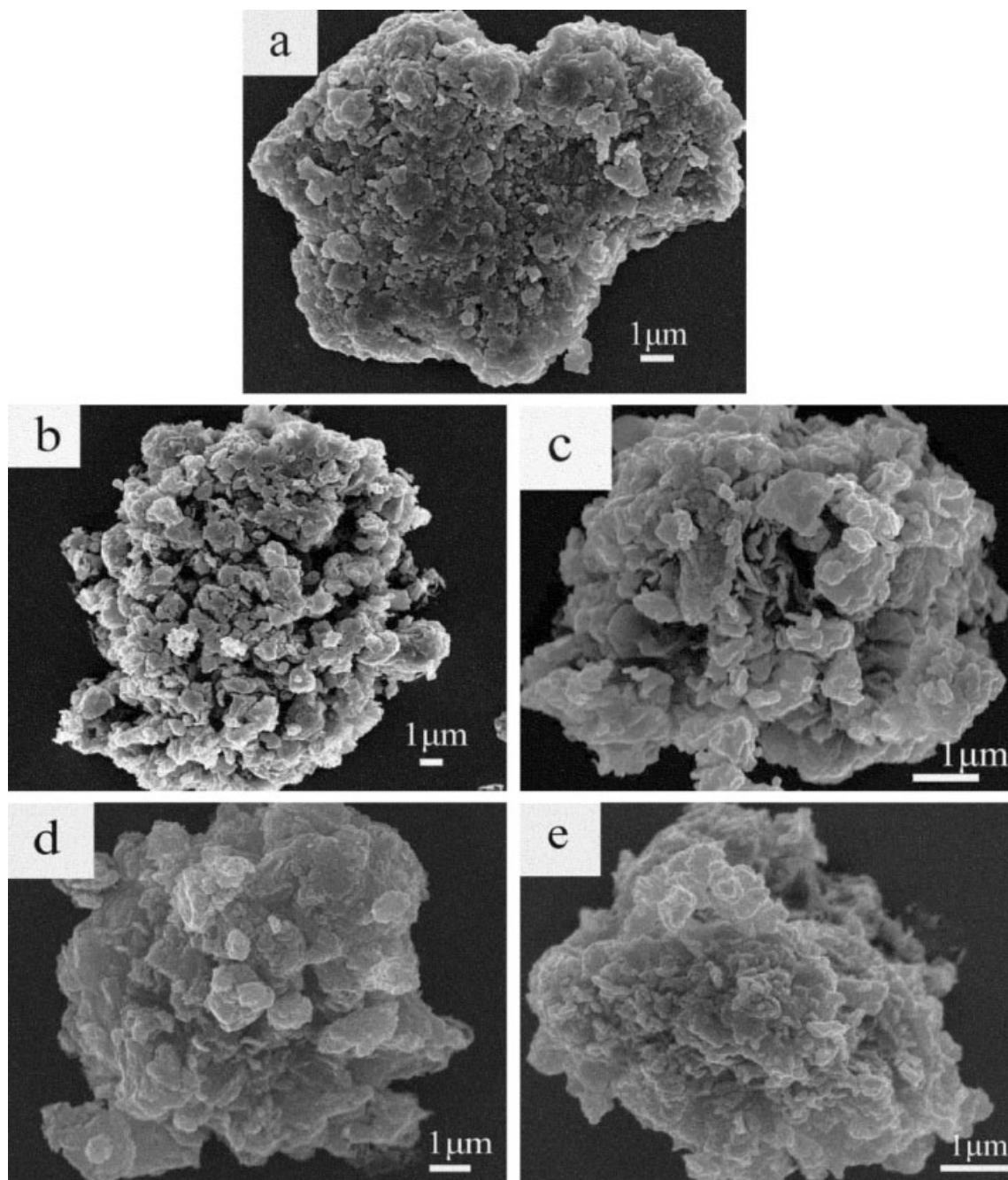


Figure 3 SEM images of (a) OMMT; (b) OPNs; (c) 1,5-NDA-modified OPNs; (d) HCl-modified OPNs; and (e) DBSNa-modified OPNs.

as shown in Figure 4, reveal some interesting morphological differences between OMMT and the different OPNs. TEM image of OMMT shows the MMT layers stacking together as expected. However, for different OPNs, most of the MMT layers have exfoliated into individual platelets or small tactoids, as shown in Figure 4(b–e), on which the polymerization of EDOT could be induced even in aqueous media. PEDOT formed in/on OPNs exhibits different morphologies such as random coil [Fig. 4(b)], accumulative short fibers [Fig. 4(c)], floccules entangled [Fig.

4(d)], and ribbons intertwined each other [Fig. 4(e)]. It is known that powders and films of PEDOT obtained so far have granular or particulate morphology. The special morphologies of PEDOT resulted in this study suggest that the exfoliation of OMMT layers and the chemical modification of OMMT may have an important contribution for the polymerization of EDOT, not only promoting EDOT to be polymerized in an aqueous system, but also inducing PEDOT to grow with special/ordered morphology.

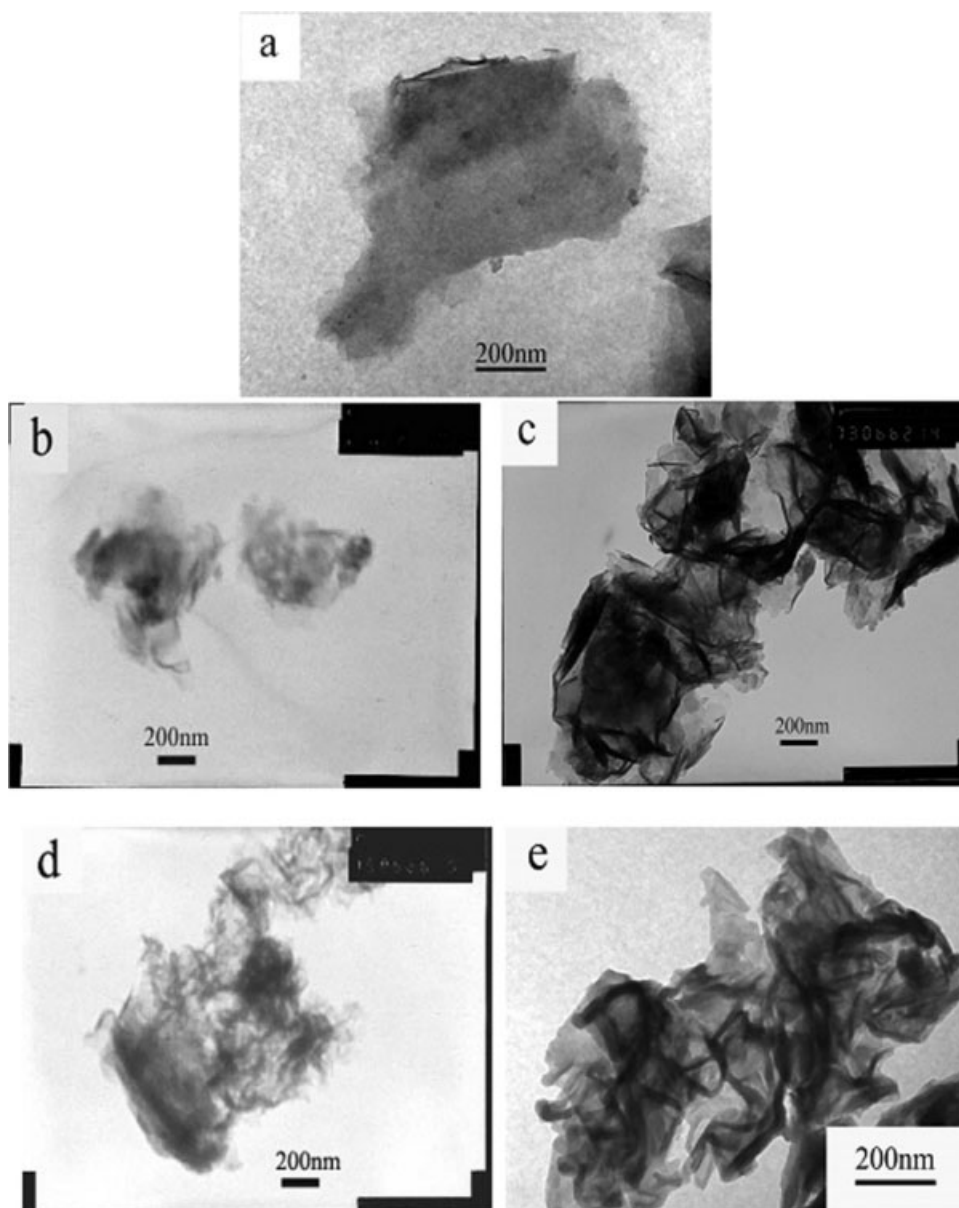


Figure 4 TEM images of (a) OMMT; (b) OPNs; (c) 1,5-NDA-modified OPNs; (d) HCl-modified OPNs; and (e) DBSNa-modified OPNs.

XRD patterns provide beneficial information about the d -spacing of OMMT and the nanocomposites by following Bragg's Law: $d = n\lambda / (2\sin \theta)$ at peak positions. It can be seen from Figure 5 that the XRD pattern of OMMT is different from that of OPNs and chemically modified OPNs at lower angles. A strong diffraction peak around $2\theta = 5.88^\circ$ is displayed for OMMT, equaling a d -spacing of 1.50 nm for the layered silicates in OMMT. The basal reflection of OMMT is extinguished in the X-ray diffractograms of the nanocomposites, further confirming the exfoliation of MMT layers in the nanocomposites.³⁵ In such exfoliated nanocomposites, the role of OMMT is to act as a "supporter" to assist the polymerization

of PEDOT and also provide better physical properties such as stiffness, strength, and barrier property for the OPNs and chemically modified OPNs.

According to the experimental results mentioned above, it is reasonable to give the following conjecture. For the case of OPNs, with the addition of the monomer EDOT, the layered silicates of OMMT are apt to be exfoliated due to the adsorption of EDOT on the OMMT layers and its aggregation around the ODA cations. After the oxidant APS is added, PEDOT is polymerized mainly around the long chains of ODA (Fig. 6). In the case of 1,5-NDA and DBSNa-modified OMMT, H-bond may be formed between the sulfonic group in 1,5-NDA or DBSNa

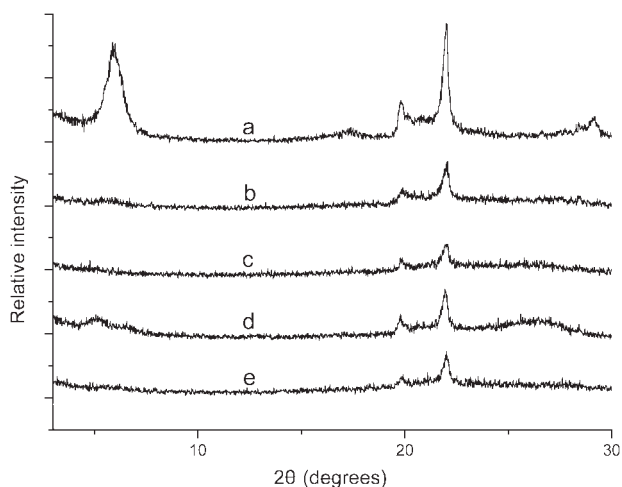


Figure 5 XRD patterns of (a) OMMT; (b) OPNs; (c) 1,5-NDA-modified OPNs; (d) HCl-modified OPNs; and (e) DBSNa-modified OPNs.

and the —OH on the surface of OMMT (Fig. 7). These preadsorbed 1,5-NDA or DBSNa could be referred as the anchoring sites of EDOT, which might facilitate the ordered growth of PEDOT in/on chemically activated OMMT in aqueous system to form the nanocomposites. The PEDOT formed in 1,5-NDA-modified OPNs should be more than that in DBSNa-modified OPNs because of the more sulfonic groups provided by 1,5-NDA than DBSNa. During the treatment of OMMT with HCl, initial interlayer cations are partially replaced with H^+ ions, the octahedral Al^{3+} ions are preferentially released from the OMMT structure, leading to formation of additional Al—OH and Si—OH bonds without much affecting the original OMMT structure.⁴⁷ In addition, acid treatment of OMMT removes metal ions and partial ODA cations from the OMMT lattice, partially delaminating the OMMT.⁴⁸ The surfaces of HCl-modified OMMT, which have been opened up by the delamination process provide with exposed —OH and O atoms. When EDOT is added, the long chains of ODA cations favor the solubility of EDOT

in the aqueous suspensions. As the oxidant is added, the electronegative —OH and O atoms on the partially delaminated HCl-modified OMMT surfaces might act as the “active sites” for the polymerization of EDOT. More PEDOT might be obtained due to the abundant “active sites” induced by HCl modification of OMMT.

The conductivity of the samples has been summarized in Table I. The OPNs show only one order increase of conductivity compared with the pristine OMMT. The chemically modified OPNs by DBSNa and 1,5-NDA provide higher conductivity of 3×10^{-6} and 5×10^{-4} S/cm, respectively. Such difference in conductivity can be attributed to the more sulfonic groups 1,5-NDA provided. Usually, for chemical polymerization of PEDOT, the most common dopant used is polystyrenesulfonic acid (PSS), which results in an aqueous dispersion of PEDOT-PSS.⁴⁹ However, in our case, the resulted PSS-modified OPNs display a low conductivity, which may be due to the steric effect of PSS. The highest conductivity in Table I is observed for the sample HCl-modified OPNs. Interweaved flocculent morphology of PEDOT in the sample observed in Figure 4(d) and more PEDOT formed in HCl-modified OPNs might be responsible for the higher conductivity. Compared with the reported MPTs,³³ MPIs,^{5–24} and MPYs^{25–32} mentioned earlier, the conductivity of HCl-modified OPNs is higher than that of the reported CPNs and MPTs, close to that of MPIs, and lower than that of MPYs. The reason might relate to microstructures of composites prepared by different conductive polymers and MMT. The lately reported CPNs³⁶ with intercalative structure showed a relatively low conductivity of 10^{-4} S/cm. In this study, OMMT layers have been exfoliated in the OPNs and the conductivity of resulting HCl-modified OPNs is much higher than that of reported CPNs. We consider that the utilization and chemical modification of OMMT as well as the exfoliated structure of the resulted OPNs might attribute to the enhanced conductivity.

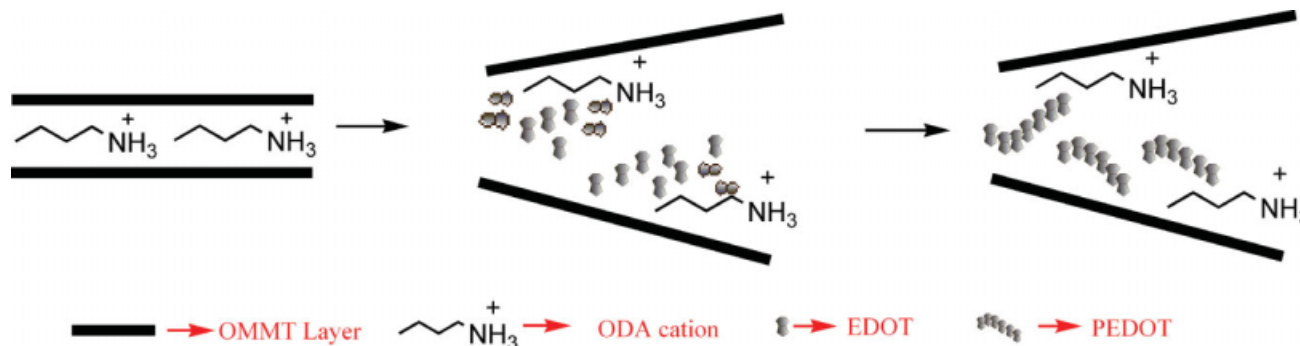


Figure 6 The exfoliation process of OMMT in OPNs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

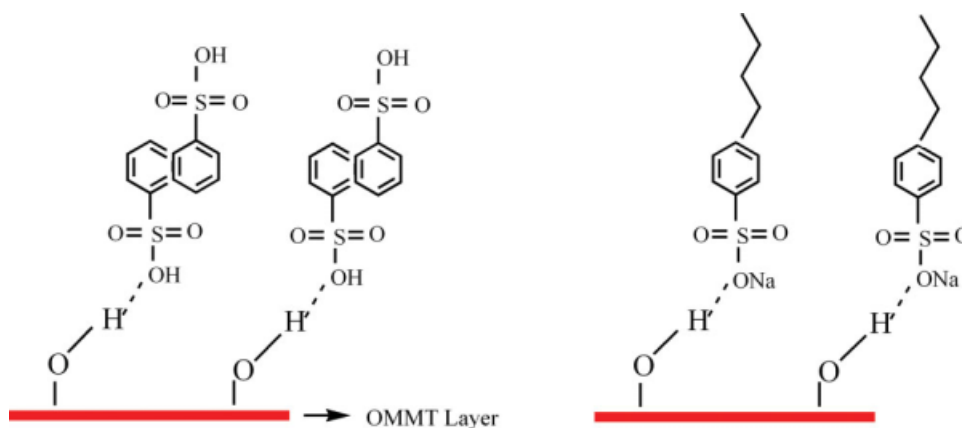


Figure 7 H-bond formation between OMMT layer and 1,5-NDA or DBSNa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TGA curves of pure PEDOT and the nanocomposites are shown in Figure 8. Evidently, the thermal decomposition of those composites all shift toward the higher temperature range than that of pure PEDOT. According to the published reports on polymer-clay nanocomposite materials, it is MMT with layered silicate structure that boosts the thermal stability of polymers.⁵⁰ Here, the exfoliated MMT layers act as barriers to heat flow due to their high aspect ratio and thereby hinder the degradation process.

CONCLUSIONS

OPNs and chemically modified OPNs have been successfully fabricated by *in situ* polymerization in an aqueous system. The successful polymerization of EDOT in/on OMMT and chemically activated OMMT to form the exfoliated nanocomposites can be summarized in three aspects. First, because of the preferential absorption of EDOT around the ODA cations, the layered silicates of OMMT are apt to be exfoliated. Second, the formation of H-bond between the sulfonic group in 1,5-NDA or DBSNa and the —OH on the surface of OMMT make 1,5-NDA or DBSNa adsorbed on the OMMT layers surface. These preadsorbed 1,5-NDA or DBSNa as well as the long chains of ODA onto the OMMT layers favor

the ordered growth of PEDOT. Third, the acid activation of inorganic strong acid HCl for OMMT may increase the number of “active sites” for polymerization of EDOT and thus facilitates the synthesis of PEDOT in an aqueous system. Among the nanocomposites, HCl-modified OPNs provide the highest electrical conductivity. The resulting exfoliated nanocomposites show a combined virtue of the electrical conductivity of PEDOT and high thermal stability of OMMT. The process of fabricating exfoliated nanocomposites, in this study, is a new effective approach to increase the water solubility of EDOT in an aqueous system by chemically modifying the surface of materials to achieve the preparation of novel nanocomposites with improved integrated performances, which could be expected to be used widely

TABLE I
Electrical Conductivity of OMMT, OPNs, and Chemically Modified OPNs

Materials	Electrical conductivity (S/cm)
OMMT	5×10^{-8}
OPNs	5×10^{-7}
DBSNa-modified OPNs	3×10^{-6}
1,5-NDA-modified OPNs	5×10^{-4}
HCl-modified OPNs	8×10^{-2}

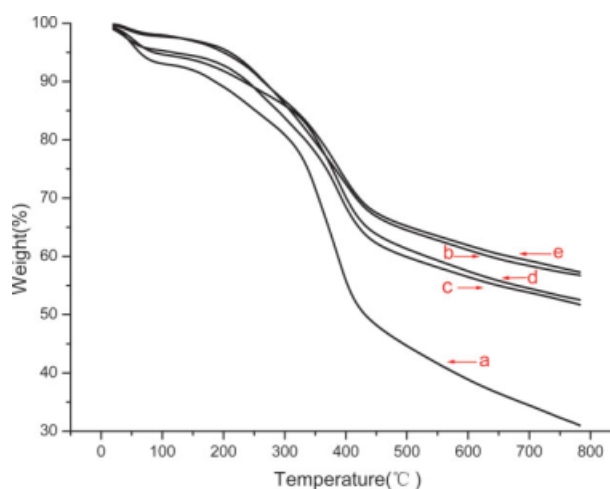


Figure 8 TGA curves of (a) PEDOT; (b) OPNs; (c) 1,5-NDA-modified OPNs; (d) HCl-modified OPNs; and (e) DBSNa-modified OPNs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for developing various new nanocomposites based on inorganic layered materials and polymers. Further studies are underway to explore the physical properties and potential application of these nanocomposites.

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