Conductive Ppy-DS/Fe-MMT Layered Nanocomposites

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ABSTRACT

Conductive polypyrrole/montmorillonite (Ppy/MMT) nanocomposites were synthesized by the in-situ polymerization of Ppy in the gallery of MMT layers. The constrained environment of the interlayer gallery of clay host is expected to serve as a template within which a guest molecule is assembled, and to realize a high degree of polymer ordering. Fe³⁺ ions were intercalated into MMT gallery prior to the *in-situ* polymerization of Ppy. DS:Na was adopted as a dopant of the conductive Ppy polymer. X-ray diffraction patterns showed that all samples contain an organic polymer between all individual MMT sheets. Electrical dc conductivities are increasing with an increase of the basal-plane distance of nanocomposites, which indicates that the arrangement of Ppy polymer changes in the MMT gallery. Through the variable range hopping (VRH) analysis, two dimensional conduction is found to occur in Ppy-DS/Fe-MMT layered nanocomposites at lower temperature, although the pristine Ppy-DS polymer shows three dimensional conduction. This is caused by two dimensional alignment of Ppy in MMT sheets, which suggests that the interlayer gallery of MMT serves as a template of Ppy arrangement. VRH analysis reveals that the density of states at the Fermi level increases by increasing the interlayer distance of nanocomposites.

Keywords: conductive polymer, polypyrrole, montmorillonite, nanocomposite, variable range hopping

1 INTRODUCTION

Conductive polymers have attracted growing interest in basic research and technological fields concerned with materials science. The heightened interest in conductive polymers is mainly due to their possible applications as substitutes for metallic conductors and inorganic Conductive polymers offer reasonably semiconductors. high conductivity that can modulate over 15 orders of magnitudes by controlling the dopant type and the doping level. The electrical properties of the conductive polymers are primarily dependent on their synthesis conditions. Polymerization of monomers in the presence of an inorganic object leads a new organic/inorganic hybrid nanocomposite. Hybrid organic/inorganic materials based on conductive polymers and inorganic components have attracted a lot of attention due to a wide range of potential

applications of these materials as sensors, batteries, smart electronic devices, display devices, electromagnetic shielding, and conductive coatings.

In this study, conductive polypyrrole/montmorillonite (Ppy/MMT) nanocomposites are synthesized by the *in-situ* polymerization of Ppy in the gallery of MMT layers. Ppy is adopted as a novel conductive polymer due to its easy-synthesis and good thermal stability as well as its superior conductivity. As the conductivity of two-dimensional Ppy films is higher than that of three-dimensional Ppy bulks [1], it is expected that the conductivity of the Ppy polymer confined between the two-dimensional MMT gallery becomes higher than that of the PPY bulk polymer. The constrained environment of the interlayer gallery of the MMT host is expected to serve as a template within which a guest molecule is assembled, and to realize a high degree of polymer ordering.

2 EXPERIMENTAL

2.1 Reagents

MMT (SWy-2) was obtained from Source Clay Repository (Clay Minerals Society, Columbia, MO, USA) and purified by a standard procedure [2-5]. The inorganic starting materials used for all preparations described in this work were analytical reagent grade and used without further purification. Pyrrole (Aldrich) was used as received. Distilled and deionized water (DI water) was used in all preparations.

2.2 Synthesis of Ppy/MMT Nanocomposites

Ppy/MMT nanocomposites were synthesized by *in-situ* polymerization. Fe³⁺ ions, a chemical oxidant for the Ppy polymerization, were intercalated into MMT gallery prior to the *in-situ* polymerization of Ppy [6]. The Fe³⁺ ion-exchanged MMT (Fe-MMT) was prepared by stirring MMT in 1 mol/L FeCl₃ solution for one week. 0.3 g of freeze-dried Fe-MMT was dissolved in 200 mL of DI water. Sodium dodecyl sulfate (DS:Na) was adopted as a dopant of the conductive Ppy polymer. The mixture was cooled down to 4°C. 2 mL of pyrrole monomer was then added in the mixture, and was stirred for 24 h. The product was then collected by centrifugation, washed with copious DI water to remove unreacted monomer, and vacuum-dried for 12 h.

2.3 Characterization

X-ray powder diffraction (XRD) data were collected on a Rigaku RINT Ultima⁺ diffractometer, using Ni-filtered CuK α radiation, by 0.02° 2 θ step / 0.6 sec between 3 and 40°. Electrical dc resistivity was measured by the standard van der Pauw method. A powdered sample was pressed into a pellet 13 mm in diameter. Four electrodes were formed on the surface of the pellet by colloidal graphite paste (Electron Microscopy Sciences) with gold wire of 50 µm in diameter (Nilaco Co.). Temperature dependence of the electrical resistivity between 300 K and 10 K was measured on a Iwatani Gas MINI STAT CRT-105-RE closed-cycle helium refrigerator.

3 RESULTS AND DISCUSSION



Figure 1: XRD patterns of Ppy-DS/Fe-MMT nanocomposites at various DS concentrations and their ionexchanged Fe-MMT host.

Figure 1 shows the XRD patterns of Ppy-DS/Fe-MMT nanocomposites. α -quartz is shown to be contained in natural MMT powders as small impurity particles [4]. All samples have no XRD peaks of their host MMT at approximately 9.0° (d = 0.98 nm without H₂O) or 14.7° (d= 1.2 nm with the H_2O monolayer), indicating that Ppy are present between all the individual MMT sheets. All Ppy-DS/Fe-MMT nanocomposites show broad (001)diffractions around 5° in the XRD patterns. The basal plane expansions $\Delta c = 0.74 \sim 0.91$ nm are larger than the reported values of 0.54~0.62 nm for Ppy/MMT [4-5,7], 0.455 nm for Ppy/fluorohectorite [8] and 0.523 nm for Ppy/FeOCl [9]. This indicates that the conjugated planes of Ppy are arranged perpendicular to the MMT basal surfaces, because the width of the Ppy conjugated planes is estimated to be about 0.55~0.73 nm [3,10]. It was found that the electrical conductivities at room temperature are increasing with an increase of the basal-plane distance of Ppy-DS/Fe-MMT nanocomposites, as shown in Figure 2, which indicates that the arrangement of Ppy polymer changes in the MMT gallery.



Figure 2: The DC conductivity at room temperature dependence on the interlayer distance of Ppy-DS/Fe-MMT nanocomposites.

The dc conductivity of Ppy/Fe-MMT nanocomposite at room temperature is ~4 S/cm, which is lower than those of Ppy-DS polymer (12 S/cm). The dc conductivities of Ppy-DS/Fe-MMT nanocomposites showed semiconductor-like temperature dependence.

On the analogy of an amorphous semiconductor or a conductive polymer, the variable range hopping (VRH) conduction model could be available to represent electron transfer in nanocomposites. The electrical resistivity ρ is given by Mott's law [11-13],

$$\rho(T) = \rho_0 \exp\left[\left(T_0/T\right)^{\frac{1}{d+1}}\right] \tag{1}$$

where ρ_0 may be a virtually temperature independent material parameter, T_0 can be interpreted as an effective energy separation between localized states,

$$T_0 = \frac{\beta}{\alpha^d N(E_{\rm F})k_{\rm B}} \tag{2}$$

Here, β is constant: $\beta_{3D} = 1.66$ and $\beta_{2D} = 3$, which were calculated by Mott [11]. *d* is the dimensionality, α the localization radius, $N(E_F)$ the density of states at the Fermi level, and $k_{\rm p}$ the Boltzmann constant.

Typical results of the resistivity are presented as a function of $T^{-1/3}$ in Figure 3. Straight lines can be fitted in Figure 3 by using the least squares method, indicating that

the electron transfer system in Ppy-DS/Fe-MMT nanocomposite is two-dimensional, although the pristine Ppy polymer shows the three-dimensional conduction [7,14-18]. This is caused by the two dimensional ordering of Ppy in MMT sheets, which suggests that the interlayer gallery of MMT serves as a template of Ppy arrangement.



Figure 3: Temperature dependences of resistivity plotted as log ρ versus $T^{-1/3}$ for Ppy-DS/Fe-MMT nanocomposites.



Figure 4: The 2D density of states at the Fermi level dependence on Δc of Ppy-DS/Fe-MMT nanocomposites.

In order to determine the value of d unambiguously, Hill's method is adopted [15-16,19-20]. The reduced activation energy is defined as a logarithmic derivative of ρ ,

$$W(T) = -\frac{d\ln\rho(T)}{d\ln T}.$$
(3)

1/(d+1) can be determined directly from the slope of the plot of ln W(T) versus ln T which is normally found to be a straight line:

$$\ln W(T) = A - \frac{1}{d+1} \ln T.$$
 (4)

Mott's parameters obtained are listed in Table 1. Although α can be obtained numerically in 3D-VRH [25], it is very difficult to obtain α in 2D-VRH. In our study, it is assumed that $\alpha = \exp[-12.4-0.325 \times \ln T_0]$, which is obtained by using the least squares method from the published 2D-VRH parameters [26-28]. The hopping distance in 2D-VRH can be expressed as [29-30]

$$R_{\rm 2D} = \frac{\alpha}{3} \left(T_0 / T \right)^{\frac{1}{3}}.$$
 (5)

And the temperature dependence of the hopping activation energy in 2D-VRH is given by

$$E_{\rm 2D} = k_B T \left(2R_{\rm 2D} / \alpha \right). \tag{6}$$

The VRH analysis reveals that all samples exhibit the same hopping distance R_{2D} of 4.5 nm at lower temperature. This value of 4.5 nm is much larger than the pyrrole monomer unit of 0.3 nm. However, the density of states at the Fermi level, $N_{2D}(E_{\rm F})$, increases by increasing the interlayer distance of Ppy-DS/Fe-MMT lavered nanocomposites, as shown in Figure 4. As the conductivity increases with increasing $N(E_{\rm F})$, the result in Figure 4 is consistent with the relationship in Figure 2. This result suggests that the interlayer gallery of Fe-MMT serves as a template of PPY alignent. Moreover, this may imply that the higher conductivity can occur in Ppy/MMT layered nanocomposites by controlling the Ppy ordering between MMT layers.

DS / mM	$\Delta c / nm$	σ / Scm^{-1}	d	T_0 / K	$N_{\rm 2D}(E_{\rm F}) /{\rm cm}^{-2}{\rm eV}^{-1}$	<i>R</i> _{2D} / nm	$E_{\rm 2D}$ / meV
5	0.88	6.02×10^{-1}	1.91	4.44×10^4	4.43×10^{13}	4.44	86.1
10	0.82	2.16×10^{-1}	1.84	1.39×10^{5}	2.97×10^{13}	4.48	126
16	0.91	3.66×10^{0}	1.86	4.97×10^4	4.26×10^{13}	4.44	89.4
20	0.74	9.09×10^{-2}	1.95	1.87×10^{5}	2.68×10^{13}	4.49	139

Table 1: Dopant DS concentration, basal plane expansion Δc , and obtained parameters from 2D-VRH analysis.

4 CONCLUSIONS

Conductive Ppy/MMT nanocomposites were synthesized by the *in-situ* polymerization of Ppy in the gallery of MMT layers. XRD patterns showed that all samples contain an organic polymer between all individual MMT sheets. Electrical dc conductivities increase with an increase of the basal-plane distance of nanocomposites, which indicates that the arrangement of Ppy polymer changes in the MMT gallery. Through the VRH analysis, 2D conduction is found to occur in Ppy-DS/Fe-MMT layered nanocomposites at lower temperature, although the pristine Ppy-DS polymer shows 3D conduction. VRH analysis reveals that the density of states at the Fermi level increases by increasing the interlayer distance of nanocomposites. This result may imply that the higher conductivity in Ppy/MMT can occur lavered nanocomposites by controlling the Ppy ordering between MMT lavers.

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