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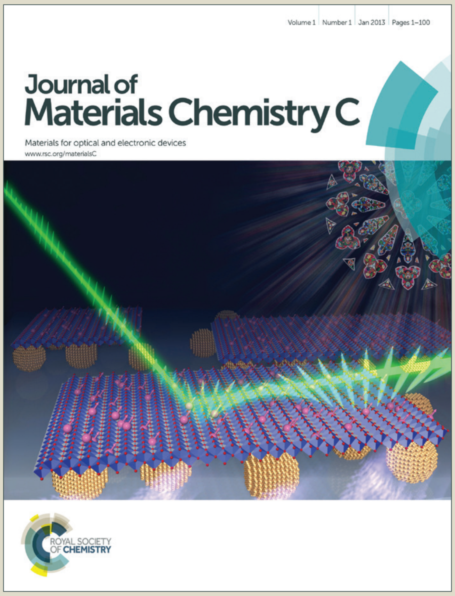

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Large in-plane/out-of-plane anisotropic conduction in PEDOT-based hybrid films: Lamellar assemblies structured by mono-layered nano-sheets

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Poly(3,4-ethylenedioxythiophene) (PEDOT) is a promising conductive polymer for electrical applications, and increases in its conductivity, transparency, stability, stiffness and strength have been explored. Here, we demonstrate a facile fabrication method for PEDOT film that exhibits large anisotropic conduction along in-plane directions. An aqueous solution of PEDOT salted with polystyrene sulfonate (PSS) is mixed with an insulating oxide nano-sheet based on montmorillonite (MMT) dispersed in aqueous media. Structural studies demonstrated it to be a hybrid film with lamellar-like assembly that was structured by mono-layered sheets. In addition, an inhomogeneous mixture of pristine MMT (insulating) and PEDOT-rich (conductive) lamellar grains is proposed. The ratio between these two grains is controlled by tuning contents of the PEDOT:PSS solution in the initial mixing process. Increases in the content of PEDOT increase the electrical conductivity. This dependence is explained by a percolation model with random arrangements of PEDOT-rich conductive and insulating grains. The conductivity showed large anisotropy between in-plane and out-of-plane measurements. The ratio reached almost 10^5 and remained over a wide range of temperatures. The lamellar structure of the PEDOT and nano-sheets is ascribed to the large anisotropy.

Introduction

Organic-inorganic hybrids compose a large class of functional materials that include catalysts, materials for photonic/electric applications and bio-medical materials.[1-6] An inorganic host binds an organic guest through covalent bonds or non-covalent interactions. According to the traditional classification based on covalent and non-covalent interactions, hybrids are classified into two categories: class I and class II, respectively.[6] Covalent substitution for class II hybrid in some case may require considerable efforts for synthesis. However, class I hybrids are especially easy to fabricate, so host and guest are mixed within proper solvents, which leads to the formation of supramolecular bindings. There is a variety of inorganic host compounds, but oxides are often used because their surfaces are usually covered by oxygen, hydroxide or water ligands, leading to the fabrication of class I hybrids. Characteristics such as high stability against chemical and physical stress and wide diversity of composition, morphology and particle size provide unique supramolecular spaces for guest compounds. Examples include oxide clusters as zero-dimensional lattices, two-dimensional nano-sheets (cf. clay materials), and three-dimensional structures (cf. zeolite).[7-10] They give well-defined oxide platforms and provide a supramolecular lattice for hybrid materials.

The conductive polymer PEDOT has been given considerable attention for applications such as electrodes, sensors and active materials for electrochromic systems.[11] Enhancement in conductivity has been explored by tuning the film-fabrication procedure. These explorations are mainly directed to enhance the structural order of the PEDOT chain. In addition to conductivity, the transparency, stability, stiffness and strength are also important characteristics for electrical materials. Among these additional properties, a large anisotropic conductivity is one of the most important issues.[12] Since a pristine PEDOT:PSS (polystyrenesulfonate) spin-coat film is constructed by pancake-like particles of PEDOT separated by lamellae of PSS, the in-plane and out-of-plane anisotropic conductivity differ by only 3 orders of magnitude.[13-14] Thus, current leakage and crosstalk are unavoidable in the conventional PEDOT-based electrical materials. Here, we report the large in-plane and out-of-plane anisotropic conduction of PEDOT (a difference of 5 orders of magnitude), where the supramolecular lamellar lattice is structured by monolayer nano-sheets.

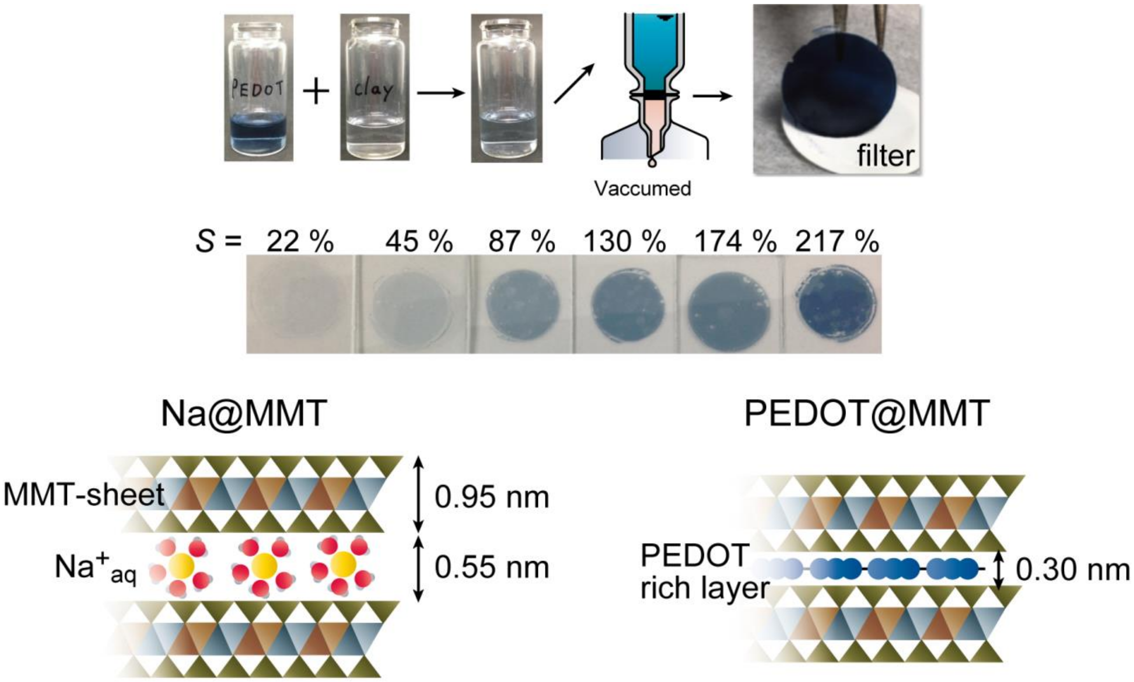

Figure 1. Film fabrication procedure and pictures of the hybrid film for surface coverages of PEDOT on the nano-sheet (*S*; see equation 1) of 22, 45, 87, 130, 174 and 217%, as well as schematic pictures of structures for pristine MMT (Na@MMT) and a hybrid film (PEDOT@MMT) with their possible thicknesses.

Hybrids between PEDOT and nano-sheets have been investigated to achieve enhanced stability and electrical performance. In general, two types of PEDOT/nano-sheet hybrids are known: an intercalative structure and an exfoliated structure. The latter has been known to have better properties (stiffness, strength and higher conductivity) than the former.[15] However, an exfoliated structure constructed of higher degree of exfoliation was prepared by *in situ* electro-polymerization in solvent media.[16] In contrast to the time-consuming fabrication of exfoliated structures, intercalative structures, which are usually superior to exfoliated structures in terms of performance, are prepared through supramolecular assembly of nano-sheets and PEDOT.

In addition to the development of PEDOT-based nano-sheet hybrids, well-defined lamellar structures with organic guest molecules or dyes have been reported.[17] Highly diluted dispersions of clay mineral provide monolayers of oxide nano-sheets, and they electrostatically bind guest molecules in a two-dimensional space.[17] This technique enables the fabrication of optically transparent/flat films at a bulk size due to the regular array of guest compounds supported by the oxide lamellar lattice, by which the anisotropic structure is constructed.[18] In this paper, we applied this technique for the first time to PEDOT systems. A mono-layered nano-sheets were highly dispersed in aqueous media and mixed with PEDOT:PSS in aqueous media. After filtration of the suspension through a membrane filter, self-standing films were successfully obtained. Structural studies by X-ray diffraction analysis and spectroscopy revealed the layer-by-layer structure of nano-sheets and PEDOT. In addition, electrical conductivity measurements showed a large anisotropic conduction with a ratio of ~10^5 between the in-plane and out-of-plane conductivities, where the in-plane conductivity was comparable to that of reported for exfoliated structures. The lamellar structure demonstrated large anisotropic conduction.

Results and discussion

Film fabrications

MMT has particle size of ~1 μm, which is intrinsically larger than the typical length of PEDOT polymer. Negatively charged layers in MMT usually have a composition of $[(Al, Mg)_2Si_4O_{10}(OH)_2]^{0.33-}$ and are compensated by exchangeable inorganic cations, which are located in the interlayer space as hydrates, giving a layered structure with alternating anionic sheets and cationic ions through electrostatic interactions. It is known that the anionic layers are homogeneously delaminated into single layers through sonication in aqueous media for 1 h (for MMT concentrations below 0.1 g/L).[17] Dispersions that include delaminated layers were prepared at 0.02 g/L (10 mL) of MMT and then mixed with PEDOT:PSS aqueous solution diluted to 0.013 wt % under stirring and kept for 12 hours (figure 1). To investigate the dependence of the structure and electrical properties of the hybrid film on the PEDOT content, dispersions were prepared with different volumes of PEDOT:PSS solution, where the amount of MMT sheets was constant.

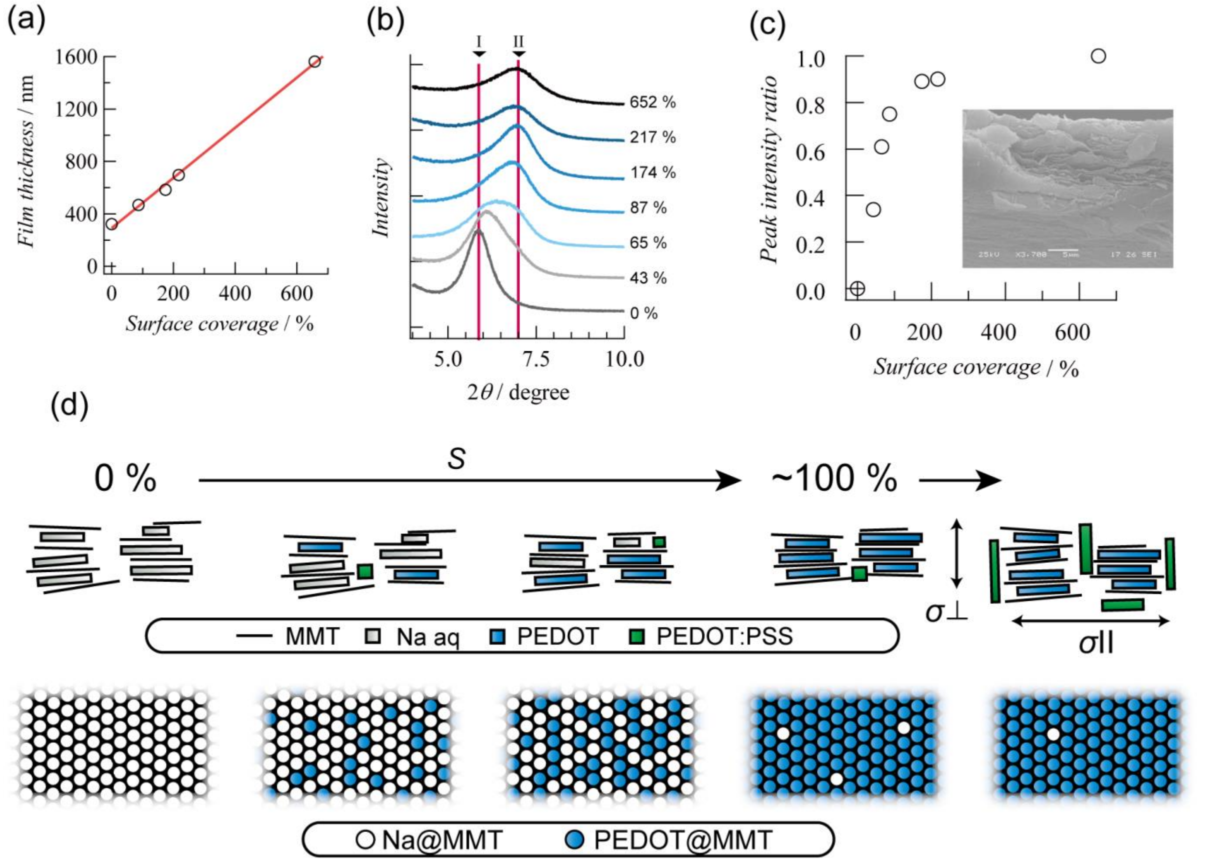

Figure 2. (a) Plots of film thickness with *S*. (b) XRD spectra of hybrid films prepared for surface coverage at 0, 43, 65, 87, 174, 217 and 652% (peaks I and II correspond to those originating from the intrinsic Na-rich MMT and PEDOT-rich MMT hybrid films, respectively). (c) Plots of the peak intensity ratio between peaks I and II with surface coverage values where the value at 652% was defined as the unit value. The inset shows a cross sectional SEM image of the hybrid film prepared with 65% coverage. (d) Structural model for hybrid films from a side view (top; solid lines represent MMT nano-sheets that intercalate Na hydrate or PEDOT) and the top view (bottom; each circle represents a grain in which either hydrated Na of PEDOT is the main component, colored white or blue, respectively) for high PEDOT samples, where hydrated Na-rich grains were replaced by PEDOT-rich grains.

Filtration of the suspensions using membrane filters (0.1-μm mesh) resulted in the formation of thin films on the filter, where the filtrates were almost colorless, indicating the successful transfer of PEDOT to the film.Then, a film was deposited onto a glass substrate, followed by drying for 24 hours in vacuum. Given the molecular surface area of the EDOT monomers with vdW radii of C, H, S, and O, the surface coverage of PEDOT on the sheet (*S* %) was estimated by

$$S = \frac{A_{\mathrm{PEDOT}} \times V_{\mathrm{PEDOT}} \times C_{\mathrm{PEDOT}}}{A_{\mathrm{MMT}} \times V_{\mathrm{MMT}} \times C_{\mathrm{MMT}} \times CEC} \times 100, \qquad (1)$$

where parameters *A*, *V*, and *C* are the area of structures obtained through the van der Walls model and the volume and weight concentrations for each component, respectively. We defined A_{PEDOT} and A_{MMT} per unit charge (A_{PEDOT} was estimated for three EDOT unit). The CEC value is the cation exchange capacity (1.15 mEq/g), and similar discussions of surface coverage have been utilized to describe the guest contents in nano-sheet hybrids.[19] Here, hybrid films were prepared for $10 \leq S \leq 652\%$. Films gradually changed color to deep-blue at high PEDOT concentrations due to the graduated contents of PEDOT in the hybrids (figure 1).

The thicknesses of films (*h*) were characterized. The pristine MMT film prepared with the procedure above (but not including any PEDOT:PSS) had a film thickness of 321 nm. With increasing PEDOT:PSS content, *h* increased linearly with *S* (Figure 2a). From the slope, we estimated the differential density caused by increases in guest content to 1.06 g cm^{-3} (given that the diameter of the hybrid film is the same as that of the membrane filter). The value was assumed to correspond to the density; for example, 1.33 and 1.11 g cm^{-3} for EDOT and polystyrene sulfonic acid, respectively.

UV-vis-NIR and FTIR spectra

As shown in the photograph of the hybrid films (figure 1), optically transparent/flat films were obtained. UV-vis-NIR spectra were characterized for samples of *S* = 65% (figure S1), showing absorption bands similar to that of the pristine spin-coated film of PEDOT:PSS. The hybrid films do not scatter light, as is expected with conventional clay materials. In addition, the film fabrication processes were inert to the redox (charge doping) states of PEDOT. FTIR spectra were also characterized using the same films (figure S2). In the hybrid films, peaks belonging to the EDOT units are observed as well as those for the PSS anions and MMT. It is suggested that hybrid films still contain PSS anions. Electronic absorption spectra from the UV to IR region clearly showed successful hybridization of PEDOT polymer in the MMT-supported films.

XRD measurements

Figure 2b shows XRD patterns of hybrid films with different *S*. At *S* = 0%, a peak was observed at 6.86° (peak I; inter-layer distance of 1.50 nm). This value corresponds to that observed for pristine MMT. Taking into account a thickness of the oxide layer of 0.95 nm, the interlayer distance *d* was deduced to be 0.55 nm. The value corresponds to the space that hydrated sodium ions occupy. With increases in *S*, additional peaks at 7.01° of 2θ grew (peak II). The estimated *d* value of 0.31 nm showed almost the expected thickness of a π-molecule that is stacked in a face-to-face manner between nano-sheets. A similar *d* value has been reported for a system using pyridinium intercalated between oxide layers, where the *d* value was estimated to be 0.30 nm in the hybrid.[20] SEM imaging of the hybrid film prepared for 65% coverage showed a lamellar structure (figure 2c, inset).

It is also important to discuss the *S* dependent growth of peaks. The peak at 7.01° showed increases in its relative intensity compared to the peak at 6.86°. Figure 2c plots the relative peak intensity of the two peaks with *S*. The peak at 7.01°increased with *S*, and then it reached a constant value. This is ascribed to the saturation of intercalation at higher *S*. In the case where ion exchange occurred homogeneously (where all nano-sheets participate equally in the ion-exchange reaction, resulting in similar interlayer spacing for all grains), the inter-layer spacing should be coincident with all grains in the film (the value be larger for either intercalated hydrated sodium or PEDOT; here, it is hydrated sodium). It should be possible to describe hybrids as a mixture of two different grains consisting of pristine MMT (with hydrated sodium) or PEDOT/MMT hybrid. They are randomly arrayed with different contents according to the initial mixing ratios.

With the studies above, we deduced the structure of the hybrid films (figure 2d); (a) film was constructed of a layered structure supported by oxide nano-sheets, (b) PEDOT was intercalated between sheets with face-to-face packing (c) bulk hybrid films were constructed as a mixture of two different grains of pristine MMT and PEDO-rich hybrid, (d) PSS anions are still included in the hybrid films.

Electrical properties

CONTENT DEPENDENCE. The in-plane conductivity of the hybrid films was characterized at room temperature (under vacuum) with varying *S* (figure 4). The linear current-voltage (*I*-*V*) characteristics were observed between -1.0 and 1.0 V. The conductivity at *S* = 0 was below the measurement range, demonstrating insulating characteristics that originated from the nano-sheets. With increases in PEDOT content, the conductivity increased and then changed to low-dependence regime at 10^{-1}-10^{0} Scm^{-1}. Given the inhomogeneous mixture of insulating (sodium-rich) grains and conductive (PEDOT-rich) grains, a bulk conductivity was ensured by percolation theory, which is often used to explain mixture between conductors and insulators. An observed conductivity (σ_{obs}) was calculated by

$$\sigma_{\text{obs}} = \sigma_h\,(1-f/f_c)^t, \qquad (2)$$

where σ_h, f, f_c and t are the conductivity of the conductor phase, the volume fraction of the insulator, the critical (percolation) volume fraction for the insulator and the exponent, respectively.[21] We assumed the conductivity of the insulator to be zero and f = (100-*S*)/100. The relation implies that σ_{obs} commonly shows a jump at f_c. As shown in figure 3, the model illustrates the content dependent conductivity observed well. The values of σ_h, f_c and t were decided by fitting to 0.1 Scm^{-1}, 66% for the insulator (corresponding to *R* = 33) and 1.2, respectively. The magnitude of σ_h is within the range that has been reported for PEDOT-based films. The two-component mixed structure of insulating and conductive grains was suggested, and it agrees well with that obtained from the XRD analysis above.

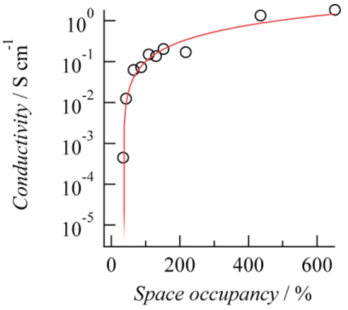

Figure 3. Plots of conductivities versus surface coverage. The red line represent a curve based on percolation theory, fitted by $\sigma_{\text{obs}} = \sigma_h\,[1-(100-S)/(100\cdot f_c)]^t$.

ANISOTROPIC AND TEMPERATURE-DEPENDENT CONDUCTION. The *I*-*V* characteristics are symmetric between -1 and +1 V for both out-of-plane and in-plane measurements. However, the non-ohmic regime was entered for out-of-plane directions. At room temperature, the conductivities are increased by almost a factor of two at +1 V compared to the value that was estimated when the electric field approached zero. A similar electric field dependence on conductivity has been reported for high-electric-field measurements.[14] Higher electric fields for out-of-plane measurements are assumed to induce non-Ohmic behavior, and details are under exploration.

Table 1 summarizes the conductivities at 300 K for both in-plane and out-of-plane directions prepared with coverages of 65% and 217%. The out-of-plane conductivity is described by average values measured at +1 V and −1 V. Both samples showed large anisotropic conductions that differ by almost a factor of 10^{5}. Pristine PEDOT:PSS film (spin-coat film) is known to show anisotropic conduction with a difference of ~10^{3}.[14-15]

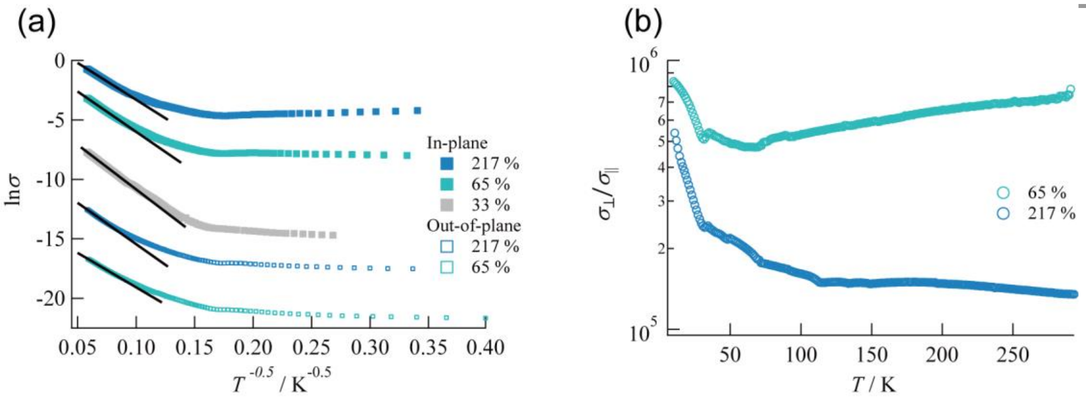

Figure 4. (a) Temperature dependence of the low bias conductivity (average value measured at -1 V and +1 V) of PEDOT/MMT hybrids prepared with coverages of 33%, 65% and 217%. Conductivities measured along the in-plane ($\sigma\perp$) and out-of-plane ($\sigma\|$) directions are shown by linear fitting by equation 3 (shown by the straight lines). (b) Temperature dependence of the ratio between $\sigma\perp$ and $\sigma\|$.

This was ascribed to the phase-segregated structure by conductive PEDOT-rich grains (anisotropic particles 20-25 nm in diameter and 5-6 nm height). Enhanced anisotropy in our hybrid films was considered to originate from the regular array of lamellar structures in which charge transportation is reduced along the lamellar direction due to insulating MMT. Temperature dependences were characterized using samples prepared for S = 33%, 65% and 217%. Conductivities (average values at +1 V and −1 V) in-plane and out-of-plane and their ratios are plotted in figure 5 versus temperature. The out-of-plane conductivity for S=33% was below the measurement range. The in-plane and out-of-plane ratios are within a range of 10^5-10^6. Large anisotropies remain even at low temperature. The temperature dependence of the conductivity has been discussed to understand the charge transport mechanism. In the case of highly conductive PEDOT, a fluctuation-induced tunnelling model can be applied. However, hopping of charge carriers dominates in less conductive films. A rapid decrease in conductivity toward low temperature was usually observed for the hopping transport. PEDOT:PSS films or structures have been known to be governed by following equation:

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/2}], \quad (3)$$

where σ_0 and T_0 are constants, and the latter was summarized in table 1. The temperature-dependent conductivity was well-described by equation 3 above 50 K. Similar temperature dependence and comparable values of T_0 were observed for PEDOT:PSS thin films, showing electronic conduction rather than ionic conduction in our hybrids.[23] The temperature-dependent conductivity is usually described by the energy barrier for carrier transportation. In addition, it has been reported that the parameter T_0 decreases with increasing conductivity, which is in accordance with the conduction model claiming that the charge localization length will increase as the conductivity decreases.[11] The less anisotropic characteristics of the T_0 values, in spite of the large anisotropic conductivity, suggest that the largest barrier energies that govern conductions are similar for each direction. Given that excess PEDOT:PSS is still contaminated in the hybrid, the observed T_0 is corresponded to the energy barrier at the grain boundaries with excess PEDOT:PSS.

Apart from intrinsic anisotropic effect seen in pristine PEDOT:PSS films, an enhancement in lamellar ordering was achieved by hybridization with nano-sheets, and it further enhances the anisotropic conduction. More studies on the charge transport properties in the low temperature regime and non-ohmic I-V characteristics are currently being investigated by high-field measurements.

Table 1. Summary of electrical propitiates

S / %	33(∥[a])	65(∥)	65(⊥[b])	217(∥)	217(⊥)
σ(300 K)/ S cm^{-1}	4.49×10^{-4}	6.28×10^{-2}	1.00×10^{-7}	1.71×10^{-1}	3.50×10^{-6}
T_0 / K	5625	4225	3249	3783	3969

[a] ∥; in-plane measurement. [b] ⊥: out-of-plane measurement. T_0 is a constant obtained according to equation 3.

Experimental

Materials. PEDOT/PSS was purchased from Aldrich and used as received. MMT used here has a full composition of $(Na_{0.84}Ca_{0.07})^{+0.98}[(Si_{7.77}Al_{0.23})(Al_{3.06}Mg_{0.71}Fe_{0.21})O_{20}(OH)_4]^{-0.98}$ and was purchased from Clay Science Society of Japan.

Film fabrication

Hybrid films were fabricated by an ion-exchange reaction by mixing an aqueous dispersion of MMT and a solution of the PEDOT:PSS. After sonication of the aqueous suspension of MMT for 1 h (0.02 g/L), the PEDOT:PSS solution (0.013 wt%) was mixed and stirred for 12 h. Hybrid films with different surface coverages were prepared by changing the volume of the PEDOT:PSS solution. Composite films were obtained by filtering the aqueous mixtures through a mixed cellulose ester membrane filter (Advantec, A010A025A; pore size: 100 nm; diameter: 25 mm). The residue was colored, whereas the filtrates were colorless. Hybrid films on the filter were transferred onto glass. After drying on the glass substrate, structural analyses were performed. FTIR spectra were characterized using diluted samples by KBr after removing hybrid films from the glass.

Measurements

Film thicknesses were characterized using a Dektak 3 Surface Profilometer. X-ray diffraction (XRD) data were collected using a Rigaku Ultima-IV diffractometer with monochromatized Cu Kα radiation (λ = 0.154 nm). UV-vis-NIR spectra and SEM image were characterized using a V-670-UV-VIS-NIR (Jasco) and a JSM-6360LA (JEOL), respectively. Electrical conductivity measurements were performed by DC two-probe measurements. For in-plane measurements, a clean glass substrate was deposited with gold electrodes with 1-mm inter-electrode distances. Hybrid films were transferred onto the glass substrate. Gold paste was utilized for electrical contact with gold wires. Out-of-plane measurements were performed using samples where the gold electrode was directly deposited to both sides of the film. The temperature dependence and current-voltage (I–V) characteristics were measured under vacuum using a commercially available cryostat with a temperature control system over the range indicated in the main text. The current was monitored with a Keithley 6517 electrometer.

Conclusions

Here, we propose a method to fabricate PEDOT-based films that exhibit large anisotropic conduction. This was achieved with a hybrid between PEDOT and insulating nano-sheets of MMT. Structural studies using FTIR and UV-vis-NIR suggested incorporation of MMT and PEDOT. The XRD analysis clearly showed the lamellar structure of hybrid films with inhomogeneous mixtures of pristine MMT (Na-rich, insulating) and PEDOT-rich (conductive) grains. The content of PEDOT in the initial hybridization process directly influenced the ratio between these two grains and the charge transport properties. Concentration-dependent electrical conductivities are explained well by percolation theory, in which conductive and insulating grains are randomly mixed. The conductivity showed large anisotropy between measurements for in-plane and out-of-plane directions. The ratio reached almost 10^5. Enhanced charge transportation along the in-plane direction is considered as a consequence of PEDOT-rich grains that show high conductivity at c.a. 0.1 S/cm^{-1} as estimated by the percolation model. However, the temperature coefficient of T_0 that represents the energy barrier for charge transportation is almost independent of the content of PEDOT and the direction of the conductivity measurement. This suggests the existence of excess PEDOT by which each grain was electrically wired. Our results demonstrate an easy fabrication method for PEDOT films with large anisotropic conduction. Both enhanced conductivity and large anisotropy are expected to increase in further explorations and will be reported with details on electronic transportation phenomena.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: UV-vis spectra FTIR spectra, and electric properties. See DOI: 10.1039/b000000x/

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Large in-plane/out-of-plane
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Hybrid film between conductive polymer of PEDOT and nano-sheet exhibited large anisotropic conduction at 10^5 for in-plane and out-of-plane directions.