Conducting Properties of Polypyrrole Coated Imogolite

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Imogolite which has chemical composition, $(HO)_3Al_2O_3SiOH$, was synthesized with orthosilicate acid and aluminium chloride at low pH solution. It has extremely large aspect ratio with an external diameter of 2nm and the length of a few micrometers. The high aspect ratio of the imogolite could make the material as the filler for the high strength fiber and as the wire for the electronic applications. Here, Imogolite that derives considerable microporosity from a nanometer-sized tubular structure has been modified with a conducting polymer, polypyrrole. Its bonding and wiring structure were confirmed by IR and TEM. The measured conductivity after modification with polypyrrole increased with polypyrrole thickness at various voltage conditions.

Key Words : Imogolite, Polypyrrole, Conducting polymer, Nano tube

Introduction

Imogolite, consisting of hollow tubes with an external diameter of 2 nm and the length of a few micrometers, is a naturally occurring hydrous aluminosilicate polymer found in soils of volcanic origin with a net composition $(HO)_3Al_2O_3SiOH$.[1-4] The tubes have curved gibbsite sheets with SiOH groups on the inner surface and AlOH groups on the outer surface. Since synthetic method of imogolite was proposed by Farmer *et al.*, several research papers which have studied the structure and the modification of Imogolite have been published.[5] To make imogolite soluble in an organic solvent, it is necessary to modify the surface of imogolite or to introduce functional groups on the imogolite that have an attractive interaction with imogolites.[6] The modification of phosphonic acid with an alkyl chain and the adsorption of neutral molecules on imogolite have been reported.[7] Because the surface of imogolite has Al-OH groups, amphiphilic molecules with different hydrophilic functional groups were introduced in order to consider the interaction between Al-OH and amphiphilic molecules. Here, we are interested in the modification of to generate conducting materials. Conducting polymers like polypyrrole (ppy) have been paid many attentions because these materials have potential to use in the electronic displays, batteries, sensors, molecular electronic circuit, and so on.[8] Polypyrrole is a conducting polymer and has high conductivity, and good stability in ambient conditions. We investigate the electrically conductive ppy-imogolite prepared by vapor-phase polymerization method[9] and compared the conductivity between pure imogolite and ppy-imogolite. Figure 1 shows the chemical structure of (a) imogolite and (b) ppy modified imogolite.

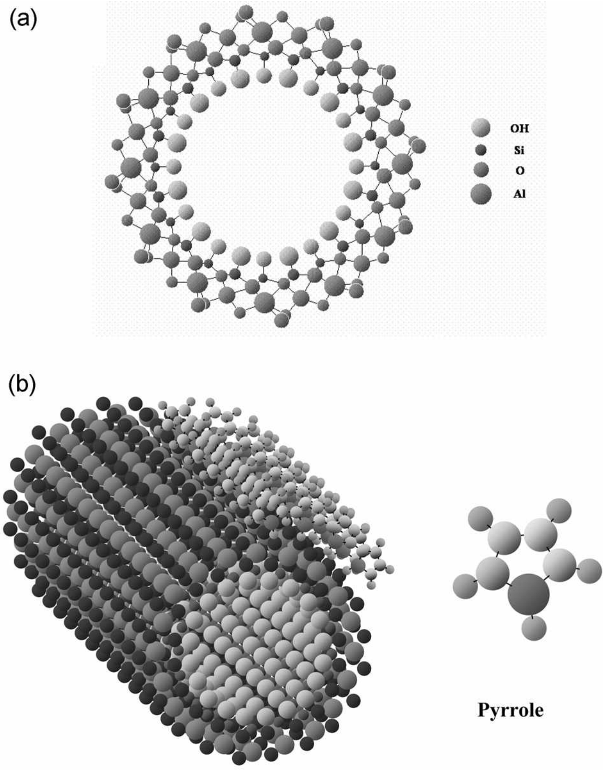

Figure 1. Chemical structure of (a) imogolite and (b) ppy-imogolite.

Experimental

Materials. Tetraethyl orthosilicate (Aldrich, 99.999%), aluminum chloride (Aldrich, 99.99%), pyrrole monomer (Aldrich, 98%), methyl alcohol (Aldrich, 98%), $FeCl_3 \cdot 6H_2O$ (Aldrich, 98%) were used. We used double-distilled water as preparative solutions.

Preparation of Imogolite.[11] Imogolite was synthesized using the method of Wada et al. According to the method, an aqueous solution of aluminum chloride was slowly added to an aqueous solution of tetraethylorthosilicate so that the final concentrations were 2 mM with aluminium, and 1 mM with

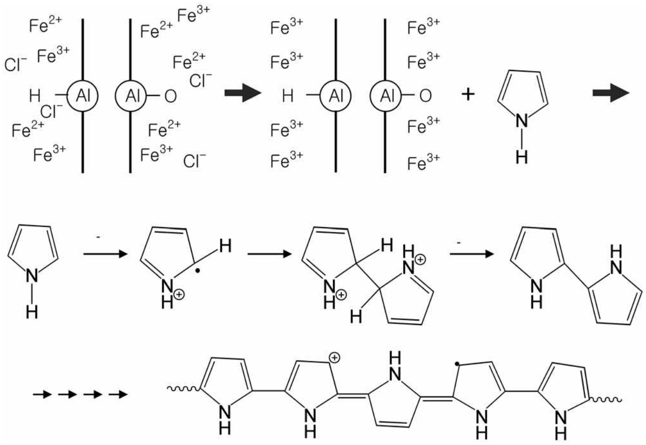

Figure 2. Scheme to prepare ppy-Imogolite in a doping state with an acceptor dopant ($FeCl_3$) and its polymerization mechanism.

silicon. NaOH solution was added at the rate of 0.5 mL/min until the Al : Si : OH ratio reach at 2 : 1 : 4. Then the solution was stirred for 3 hours and heated at 97-98 °C for 3 days. Saturated NaCl solution was added to get a white gel and the pure white gel was obtained by using low speed centrifuge. A pure imogolite was collected by freeze drying, and was characterized by Infrared spectroscopy and transmission electron microscopy.

Preparation of ppy-Imogolite. A 3 wt.% solution of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in methyl alcohol (MeOH) was prepared, and then a pure imogolite was dipped in the solution to be pretreated with $FeCl_3 \cdot 6H_2O$ as an oxidant. $FeCl_3 \cdot 6H_2O$ absorbed imogolite was dried for a few minutes at 80 °C and exposed to a pyrrole vapor for 3 minutes in a glass-ware under ambient conditions. After polymerization, the polypyrrole imogolite was washed with methyl alcohol to get rid of byproducts and unreacted oxidant. Finally, the polypyrrole imogolite was dried for a few minutes at 80 °C. The thickness of polypyrrole was changed by a concentration of ferric chloride hexahydrate, time of dipping and exposing, and temperature of drying. Figure 2 shows the scheme of the process to synthesize the Imogolite and ppy-Imogolite.

Measurement of Conductivity. Ppy-imogolite was placed between two electrodes and each electrode was connected by silver paste which was prepared by sputtering method. Conductivity of ppy-imogolite was measured by source meter, Keithley 2400.

Results and Discussion

Structure and General Properties of Imogolite. TEM (transmission electron microscopy) image of imogolite is given in Figure 3. The length scale of individual imogolite was confirmed by AFM, diameter is around 2.0 nm and its length is about 100 nm or more as shown in insert Figure 3. At pH 3.0, the nanofiber structure of imogolite was confirmed by TEM image, however imogolite could not be characterized at pH above 7.0 because the imogolite formed a solid aggregate. The imogolite consists mainly of fibers, which are aligned in bundles with diameters ranging from 5 to 25 nm and typical lengths of at least 0.5 μm. The average diameter of these fibers is ~2.7 nm. The bundling effect was observed also in electron micrographs of natural imogolite.[10] The bundling of Imogolite was reported by the processes of sample drying and vacuum evaporation.[11] After coating with polypyrrole the external diameter of ppy-imogolite increases about two times (10-50 nm) and ppy-imogolite is more dispersed than pure-imogolite in solution. These facts are observed in TEM images. Ppy-imogolite bundle makes good dispersion at pH 3. A lot of initiator might react with each imogolite in bundle and antistatic properties of polypyrrole separate each others after polymerization.

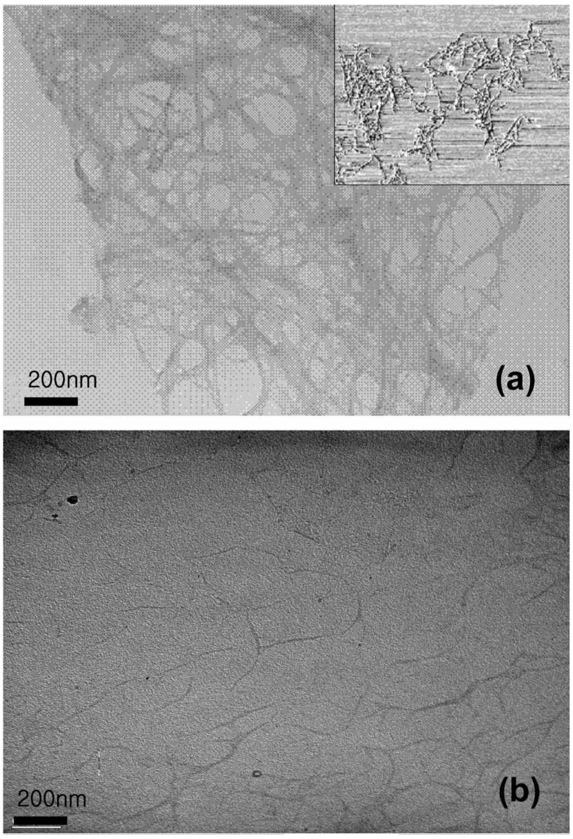

Figure 3. TEM (transmission electron microscopy) images of (a) imogolite and (b) ppy-imogolite.

Figure 4(a) shows the infrared spectra of bare imogolite. Generally, non-crystalline aluminosilicates show absorption bands in the infrared region 950-1025 cm^{-1} and 400-700 cm^{-1}.[12] However, the band resolves into two sharp peaks at 940 and 995 cm^{-1} in the same region. These two sharpens in imogolite are attributed to Si-O-Si stretching vibration and Si-O-Al stretching vibration. A second feature of Imogolite is the peaks at 500, 600 and 695 cm^{-1}. These bands are assigned to Al-OH bonding. Imogolite obtained by synthesis must be a fiber-like material that is a clear distinction from the imogolite of amorphous as shown in reference.[13] Ppy-imogolite was also characterized with infrared spectroscopy. Several peaks are the same with pure-imogolite except a peak at 1550 cm^{-1} which is C-N-C stretching band in as

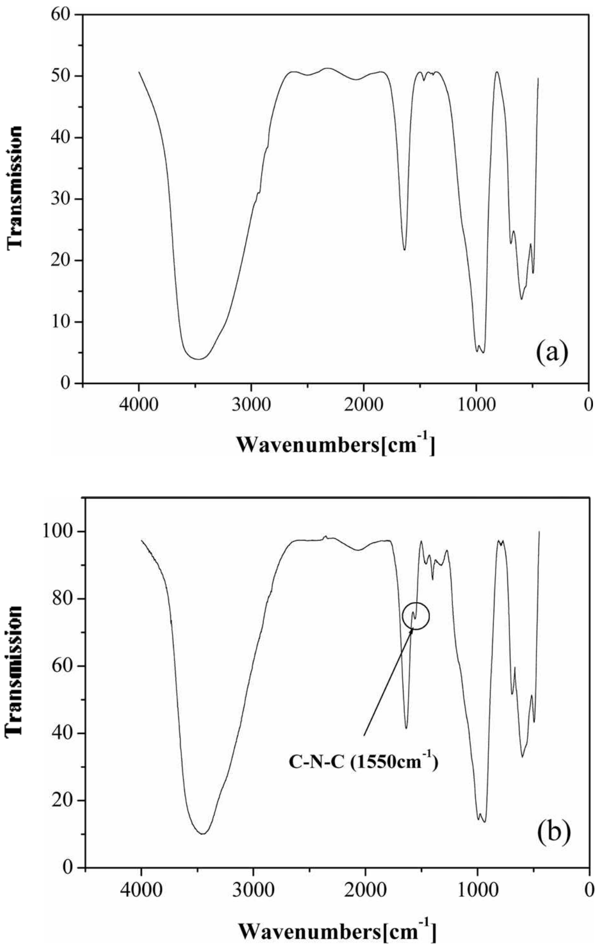

Figure 4. Infrared spectra of (a) bare imogolite and (b) ppy-imogolite.

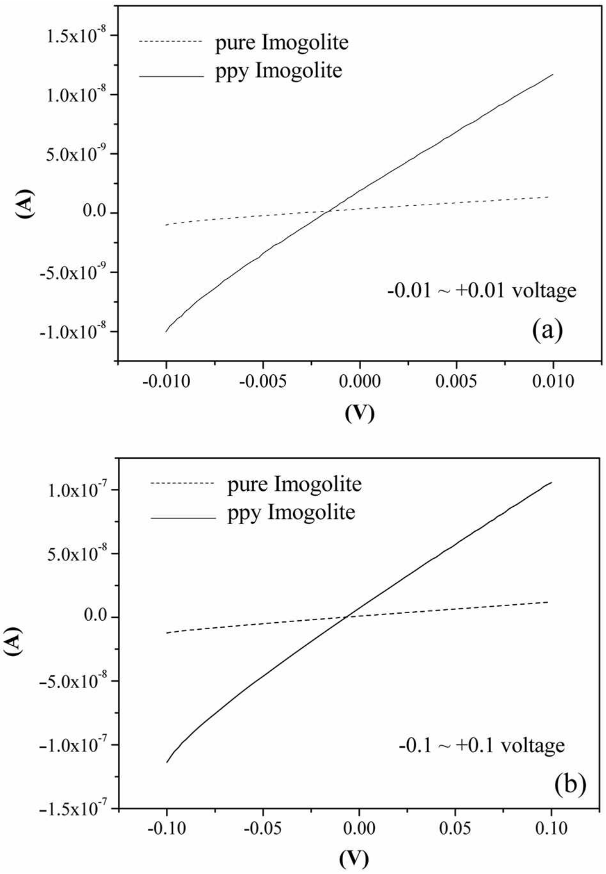

Figure 5. Pure and ppy Imogolites' conductivities in various voltages: (a) −0.01 ~ +0.01 V, and (b) −0.1 ~ +0.1 V.

shown Figure 5(b). This band is associated with the ring stretching of polypyrrole, which is a supportive evidence of the synthesis of polypyrrole on Imogolite.[14]

In case of non-crystalline aluminosilicates, there are only two broad signals centered at 13° and 25°. But it is shown that there are five signals at 3°, 4.5°, 9.4°, 13° and 26° in crystalline aluminosilicates. XRD patterns have been assigned to the scattering of individual tubes, $2\theta = 7°$, 1.51 nm, $2\theta = 12°$, 0.874 nm, $2\theta = 17°$, 0.66 nm.[15] The exact diffraction can vary from imogolite to proto-imogolite, the imogolite of amorphous, depending on alignment.[16] These distinction between imogolite and proto-imogolite account for the 9.4° and 13° diffractions. Hence, the XRD data of imogolite confirm that crystalline aluminosilicates present in imogolite.

Conducting Properties of ppy-Imogolites. Iron(III) salts is conveniently used not only as dopant ions for π-conjugated organic polymers having the hetero-aromatic structures such as ppy, but also as an oxidant for polymerization. Because pyrrole monomer has relatively high vapor pressure, the polymerization of pyrrole under in situ vapor-phase can be readily initiated by exposing an oxidant to pyrrole vapor. While 2.25 equivalents of an oxidant are theoretically required per mole of pyrrole for its oxidative polymerization, the amount of the consumed oxidant is more than the theoretical value by 100-200%.[17] By the above-mentioned method, the conductive ppy-imogolite was prepared under various reaction temperatures and times (especially 80, 3 minutes).

The pure-imogolite which is similar to the shape of carbon nanotube has conductivity ~0.1 μA at various voltages in a room condition. Putting thin ppy-imogolite on each end of a glass, each part was connected by silver paste, and the conductivity of both imogolite and ppy-imogolite was measured by a source meter. Conductivity of two different samples of imogolites was illustrated in Figure 5 and summarized in Table 1. We prepared several different samples and measured conductivities by applying voltages from 0.001 V to 0.5 V. Conductivity of ppy-imogolite was varied from 1.12 to 2.12 μA. Conductivity of pure imogolite, ~0.01 μA, might be due to the electrical charge and electrical conductivity on imogolites which are affected by the adsorption of hydrogen ions in pure imogolite. Tube and wire structure of imogolite also increase the surface area and enhance the surface conductivity. The conductivity of ppy-imogolite is not a dramatically large value, but it is depending on the thickness of the coating layer on the imogolite. Polypyrrole was coated by vapor deposition method in this experiment, which generated ~10 nm thickness layer on the imogolite. Comparing with both pure imogolite and ppy-

Table 1. The average conductivity of pure and ppy imogolites in 0.001-0.5 voltages. Two different trial with different batch of samples. (A unit of conductivity is S (Siemens/cm))

	0.001 V	0.005 V	0.01 V	0.05 V	0.1 V	0.5 V	Average
Ppy Imogolite 1	2.08×10^{-6}	2.05×10^{-6}	2.11×10^{-6}	2.04×10^{-6}	2.12×10^{-6}	2.06×10^{-6}	2.08×10^{-6}
Ppy Imogolite 2	1.12×10^{-6}	1.04×10^{-6}	9.89×10^{-7}	1.09×10^{-6}	9.84×10^{-7}	1.12×10^{-6}	1.06×10^{-6}

imogolite, conductivity of ppy-imogolite increases by ten times than that of pure-imogolite in wide range of voltages.

In summary, conducting polypyrrole was successfully coated on the aluminum silicate nanowire, Imogolite, which could be used as a CNT (carbon nanotube). The conducting nanofiber can be utilized in the electronic applications.[18]

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