Australian Journal of Basic and Applied Sciences, 8(4) Special 2014, Pages: 601-603

AENSI Journals
Australian Journal of Basic and Applied Sciences
ISSN:1991-8178
Journal home page: www.ajbasweb.com

Preparation of Intrinsically Conducting Poly (Cyclopentadithiophene) and Its Hybridization With Silica

[1]N. Kumazawa, [1]T. Uno, [1]T. Itoh and [2]M. Kubo

[1]*Graduate School of Engineering, Mie University,Tsu 514-8507, Mie, JAPAN.*
[2]*Graduate School of Regional Innovation Studies, Mie University,Tsu 514-8507, JAPAN.*

ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form 24 January 2014
Accepted 29 January 2014
Available online 5 April 2014

Keywords:
Intrinsically Conducting
Poly(Cyclopentadithiophene)
Hybridization With Silica

ABSTRACT

A novel water-soluble intrinsically conducting polymer, poly[4,4-bis(4-sulfobutoxyethyl)- cyclopenta[2,1-b:3,4-b']dithiophene] (PCPDT-SO_3H), based on a cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) was prepared. Hybridization of the self-doped PCPDT-SO_3H was successfully achieved utilizing the polycondensation reaction of tetreethoxysilane (TEOS) and triethoxymethylsilane (TEMS) in the presence of PCPDT-SO_3H. The electrical conductivity of the resulting hybrid can be tuned by changing the polymer content in the hybrid and by adding polystyrenesulfonic acid (PSS) as an external dopant.

To Cite This Article: N. Kumazawa, T. Uno, T. Itoh, and M. Kubo., Preparation of Intrinsically Conducting Poly(Cyclopentadithiophene) And Its Hybridization With Silica. ***Aust. J. Basic & Appl. Sci.,*** *8(4): 601-603, 2014*

INTRODUCTION

Transparent conductive oxides (TCO) are doped metal oxides used in optoelectronic devices such as flat panel displays and photovoltaics (including inorganic devices, organic devices, and dye-sensitized solar cell). To date, the industry standard in TCO is ITO, or tin-doped indium-oxide. However, ITO has the drawback of being expensive. Indium is rare metal (6000 metric tons worldwide in 2006), and its price fluctuates due to market demand. For this reason, development of alternatives to ITO has drawn much attention in the past several years. These alternatives include transparent conducting oxides (TCOs) other than ITO, various silver/nanosilver coatings and inks, nanocarbon; mostly nanotube preparations and conductive polymers such as poly(3,4-ethylene-dioxythiophene) (PEDOT). In this work we report a novel preparation of self-doped intrincically conducting polymer based on a polycyclopenta[2,1-b:3,4-b']dithiophene (PCPDT) and its incorporation into silica to obtain a organic/inorganic hybrid with electrical conductivity as a new candidate for ITO alternative

RESULTS AND DISCUSSION

We are interested in PCPDT as a basic backbone structure of self-doped intrinsically conductive π-conjugated polymer because poly(4,4-dioctylcyclo- penta[2,1-b:3,4-b']dithiophene) (Oc_2-PCPDT) are reported to be doped with iodine (I_2) or 2,3-dichloro-5,6-dicyano- 1,4-benzoquinone (DDQ) to form a transparent conductor with high conductivity. Further, the doped polymer has low absorption of the visible spectrum with an absorption band centered around 1050 nm. When doped with iodine, a conductivity of 0.35 S/cm can be achieved. However, the iodine has a tendency to diffuse out in air, making the iodine-doped Oc_2-PCPDT unstable. DDQ itself has a conductivity of 1.1 S/cm. However, DDQ-doped Oc_2-PCPDT also tends to reduce its conductivity in air. DDQ-doped polymer has better stability than the iodine-doped polymer, but the stability is still below that of PEDOT. Here, we designed a self-doped intrinsically conducting PCPDT-SO_3H as shown in Figure 1. The repeating unit of PCPDT-SO_3H contains two SO_3H groups as an internal dopant. Further, the existence of SO_3H groups can increase compatibility between PCPDT-SO_3H and silica through polar or electrostatic interaction. Hybridization of intrinsically conductive PCPDT-SO_3H with silica will provide a novel conductive material with good mechanical and environmental stabilities.

Corresponding Author: N. Kumazawa, Graduate School of Engineering, Mie University,Tsu 514-8507, Mie, JAPAN.

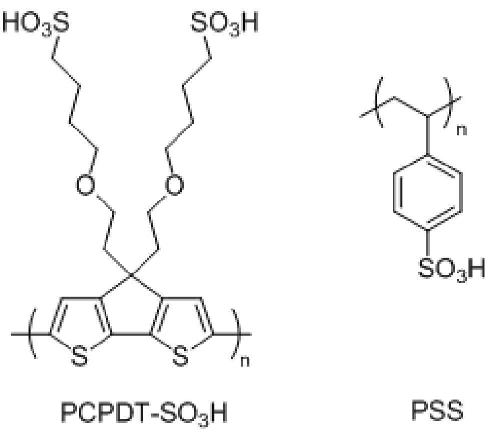

Fig. 1: Chemical structures of PCPDT-SO_3H and PSS.

Figure 2 shows the synthetic pathway of PCPDT-SO_3H using a CPDT[2,3] as a starting material. The first step is introduction of OH-protected bromoethhanol onto CPDT in the presence of potassium hydroxide in dimethylsulfoxide (DMSO). After deprotection of THP group under acidic conditions, reaction with butanesultone was carried out using sodium hydride as a base to obtain water-soluble CPDT monomer. The sodium salt monomer was polymerized in water by chemical oxidative polymerization using $FeCl_3$ as a catalyst. The polymer was purified by dialysis and further washed by Soxhlet extractor using acetonitrile as a solvent. Finally, the sodium salt polymer was dissolved in water and treated with an ion-exchange resin (Dow HCR-W2) to convert to the sulfonic acid form. The acid form of the polymer was then freeze-dried to remove the water. The obtained PCPDT-SO_3H was not soluble in tetrahydrofuran (THF), acetone, chloroform but soluble in polar solvents such as dimethylsulfoxide (DMSO) and methanol. Especially, PCPDT-SO_3H exhibited good solubility in water.

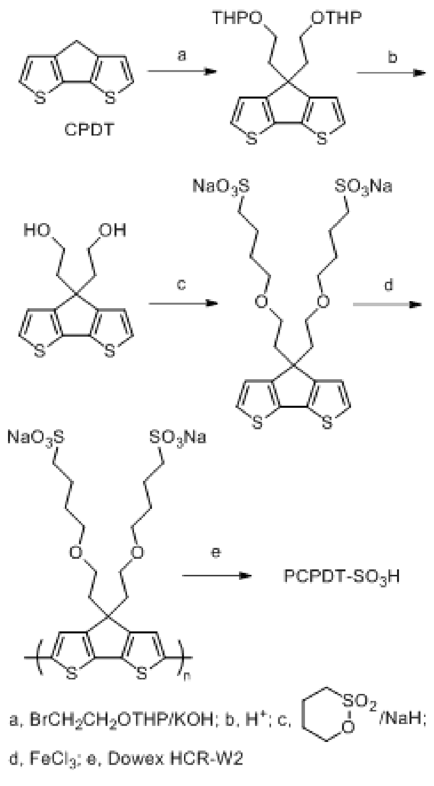

Fig. 2: Synthetic pathway of CPDT-SO_3H.

The hybridization of PCPDT-SO_3H with silica was achieved utilizing conventional hydrolysis and polycondensation reaction of tetraethoxysilane (TEOS) and triethoxymethylsilane (TEMS), so called sol-gel reaction, in the presence of PCPDT-SO_3H. Since PCPDT-SO_3H carries acidic SO_3H groups on the side chains, the sol-gel reaction occurred without adding external acid. that PCPDT-SO3H was immobilized into silica matrix retaining its doped (conducting) structure.

Three PCPDT-SO_3H/SiO_2 hybrids were prepared by changing the amount of PCPDT-SO_3H in the pre-gel solution. The electrical conductivities of these hybrids are summarized in Table 1. The hybrids with polymer content below 20% showed very low electrical conductivity because silica is insulator. It was found that 30wt% incorporation is enough to show electrical conductivity.

Table 1: Electrical conductivity of PCPDT-SO_3H/SiO_2

run	polymer content, wt%	conductivity, S/cm
1	20	$< 10^{-5}$
2	30	0.0004
3	40	0.003

Condition: [TEOS]:[TEMS] = 1:9.

Table 2 summarizes the influence of added PSS as an external dopant on the electrical conductivity of PCPDT-SO_3H/PSS/SiO_2. The electrical conductivity of PCPDT-SO_3H/PSS/SiO_2 hybrid was increased with increase of PSS content. These experimental results suggest that the electrical conductivity of the resulting hybrid can be tuned by changing the polymer content in the hybrid and by adding PSS.

Table 2: Electrical conductivity of PCPDT-SO_3H/PSS/SiO_2

run	[PSS]:[PCPDT-SO_3H]	conductivity, S/cm
1	3:1	$< 10^{-5}$
2	15:1	0.08
3	30:1	0.20

Condition: PCPDT content = 30 wt%.

Summary:

We prepared a novel self-doped intrinsically conductive polymer, PCPDT-SO_3H, based on CPDT. Although PEDOT ia not soluble in water, PCPDT-SO_3H exhibited high solubility in water. The high solubility of PCPDT-SO_3H makes it possible to form homogeneous pre-gel solution for hybridization with silica. Thus, we have demonstrated that PCPDT-SO_3H was successfully immobilized in silica retaining its electro conductivity to give a novel organic/inorganic hybrid conducting material by using sol-gel technology. The hybrid exhibited electrical conductivity above 30wt% polymer incorporation. Since incorporation of electrical conducting polymer into silica is considered to be a effective methodology to improve environmental stability and mechanical properties of the conducting film, such hybrid conducting materials will find a wide variety of use in touch panel, sensor, antistatic coating, and electrode.

REFERENCES

Coppo, P., R. Schroeder, M. Grell, and M.L. Turner, 2004. “Investigation of solution processed poly(4,4-dioctyl-cyclopentadithiophene) thin films as transparent counductors”,*Synthetic Metals*, 143: 203-206.

Pal, B., W.C. Yen, J.S. Yang, C.Y. Chao, Y.C. Hung, S.T. Lin, C.H. Chuang, C.W. Chen and W.F. Su, 2008. “Substituent Effect on the Optoelectronic Properties of Alternating Fluorene-Cyclopenta-dithiophene Copolymers”, *Macromolecules*, 41: 6664-6671.

Chen, C.H., C.H. Hsieh, M. Dubose, Y.J. Cheng, C.S. Hsu, 2010. “Synthesis and Characterization of Bridged Bithiophene-Based Conjugated Polymers for Photovoltaic Applications: Acceptor Strength and Ternary Blends”,*Macromolecules*, 43: 697-708.