Transport of Ions, Electrons and Molecules in Nanostructured Liquid Crystals for Their New Applications

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Abstract

Here we present our recent approaches to use a variety of nanostructured liquid crystal materials forming smectic, columnar, and bicontinuous cubic structures for transport of ion, electron, and water molecules. They are applied to thin-film materials for electrolytes of lithium ion batteries and solar cells, and water treatment membranes.

1 Introduction

Liquid crystals have been widely used for informational flat-panel display in our daily life due to their anisotropic structures and stimuli-responsive properties.[1] Recently new generation of supramolecular assemblies and nanotructured liquid crystals with unconventional design of molecular and assembled structures have attracted much attention.[1-3] Nanostructured liquid-crystalline (LC) materials exhibit bicontinuous cubic, smectic, columnar, micellar cubic strucrues.(Figure 1) These materials have been shown to have great potentials in the field of energy, resources, environment, and healthcare. Functionalization of liqud crystals for tansport of ions and elctrons are useful to widen the applicability of the materials in these fields [2,4-16]. For exmple, they are applied to transport thin-films for electrolytes for lithium ion batteries [4,5], and elctrolyets for dye-sentisized solar cells (DSSCs) [6-8], and water treatment membranes [13-16]. Non-conventional molecular design of LC materials and control of molecular assembled structures were necessary to achieve these functionalization. Here we review our approaches to nanostructured LC polymeric materials for new generation of functional materials for enegy devices and water treatment membranes.

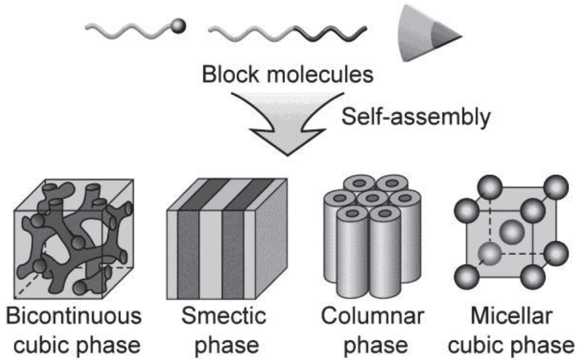

Figure 1. Self-assembly of block molecules forming nano-ordered LC structures.

2 New Functional Nanostructured Liquid Crystals

We have prepared a variety of nanostructured LC polymeric assemblies forming bicontinuous cubic, smectic, columnar, and micellar cubic structures, which are used to induce 3D (three dimensional), 2D, 1D, and 0D channels (Figure 2). These materials are formed by self-assembly of molecules through intermolecular interactions such as ionic interactions, hydrogen bonding, and pi-pi interactions. They exhibit ionic, electronic, photonic, and separation functions.

For example, 2D LC materials are used for energy devices such as lithium ion batteries and DSSCs (Figure 2) [4-8]. Smectic liquid crystals of ionic complexes consisting of mesogenic molecule **1** bearing a polar carbonate moiety and lithium bis(bistrifluoromethanesulfonyl)imide (LiTFSI) have been successfully applied as electrolytes in lithium-ion batteries [4,5]. For example, compound **1** and 10 mol% of LiTFSI form a smectic A phase from 0 to 114 °C. This material form 2D ion transport channels. Reversible charge-discharge of half cells consisting of lithium metal, the electrolytes and Li-insertion electrodes have been achieved. Ionic-smectic liquid crystals have also been applied for DSSCs. For conventional DSSCs, a normal organic solvent such as acetonitrile has been used, which make the DSSCs thermally unstable.[4-8] However, use of LC electrolyte for 2D transport improved thermal stability of the DSSCs. One of DSSCs containing LC electrolytes show power conversion performance at temperature above 90 °C. In addition, LC DSSCs devices show excellent long-term stability over 1000 h of storage. We have also developed photo-responsive ion conductors.[9] The directions of ion transport are controlled by combination of photo-irradiation and thermal treatment for ionic liquid crystals containing a photochromic moiety.

1D and 3D LC materials are used for ion transporter [10-13] and water treatment membranes [14-16] (Figure 2). For ion transporting materials, lithium ion conducting membranes have been obtained by in-situ photo-polymerization of self-assembled polymerizable ionic liquid crystals. For example, fan-shape molecule **2** forms a columnar LC phase.[10] After achieving vertical alignment of the columnar materials, the oriented structure has been preserved by in-situ photo-

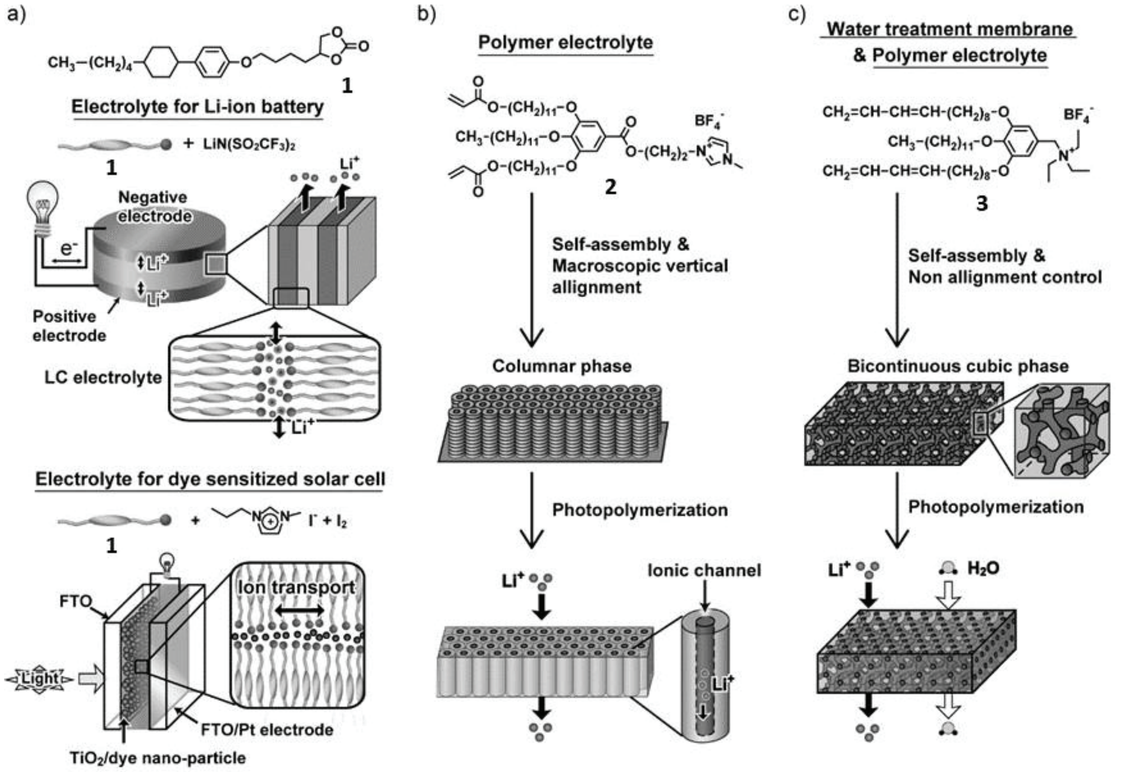

Figure 2. Preparation of nano-structured ion-transporting and water treatment polymer films.

polymerization. This leads to the formation of nanostructured free-standing self-organized thin-films bearing 1D nano-ionic channels. These channels have been shown to transport lithium ion and water molecules. 3D ion transport polymer thin-film materials have been obtained by in-situ polymerization of compound **3**.[12,13] The free-standing polymer film obtained by the mixture of **3** and lithium salts gives ion-conductive polymers that show 10^{-4} S cm^{-1}. Proton conductors have also been developed based on ionic nanostructured liquid crystals.[2]

Nano- and subnano-channels with controlled sizes achieved by using nanostructured liquid crystals are applied for water treatment membranes [14-16], while the channels of normal water treatment membranes are relatively random. Salt rejection have been observed for these 1D and 3D LC polymer membranes obtained from cationic polymerizable compounds. For example, sub-nanoporous membrane consisting of **3** has the fixed bicontinuous LC structure.[14,16] It is of interest that sodium chloride has been rejected for 70 %, while larger sodium sulfate having larger anion was less rejected to be 27 %. These results show that selective transport of sulfate ion has been achieved. The molecular interactions between cationic part of the channels and anionic divalent sulfate ions contribute selective transport of sulfate anions. We also found that the LC membranes act as excellent virus rejection membranes.[15]

3 Conclusion

This short review paper summarizes our approaches to new applications of nanostructured liquid crystals, new energy devices and water treatment membranes. This functionalization of materials has been achieved by using new molecular assemblies based on more complex molecular structures. The application of the nanostructured liquid crystals opens up new direction of LC materials as a next generation of materials.

4 Acknowledgements

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