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Review

Organic/inorganic electrochromic nanocomposites with various interfacial interactions: A review

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ABSTRACT

Electrochromic properties of organic or inorganic materials can be improved through preparing organic/inorganic electrochromic nanocomposites. In electrochromic nanocomposites, the interfacial interactions between the organic and inorganic phases play three important roles in preparation and application of the nanocomposites. Firstly, the interfacial interactions result in stable molecular structures. Secondly, they also improve the electron conduction and ion transport process in the nanocomposites. Thirdly, they enhance the electrochemical and electrochromic properties of the nanocomposites. In this paper, we review the common interfacial interactions including covalent bond, coordination bond, electrostatic interaction, hydrogen bond and π-π stacking interaction between the organic and inorganic phases in the electrochromic nanocomposites. The preparation method, the relationship between the structure and properties, and the mechanism of modulation of electrochromic effect in the nanocomposites with various interfacial interactions are surveyed. The strong interfacial interaction, e.g., covalent bond, is helpful for obtaining electrochromic nanocomposites with high electron conduction and high structural strength. However it is very complicated to construct covalent bond between the organic and inorganic phases. Another strong interfacial interaction, the coordination bond is mainly confined to preparation of electrochromic complex of metal ion and pyridine derivative. While, the weak interfacial interactions, e.g., electrostatic interaction, hydrogen bond and π-π stacking interaction, exist widely between the organic and inorganic phases in the electrochromic nanocomposites. Relative to single strong interaction, the multiple weak interactions may be a development direction for achieving high performance electrochromic effect in the organic/inorganic nanocomposites, owing to their integrated effect and various adjusting mechanisms of electrochromic properties.

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1. Introduction

Electrochromic devices have vast application prospects in the fields of energy-saving building, automotive industry, display, military camouflage, satellite thermal control, etc., owing to their reversible optical change in wide electromagnetic spectra regions from the visible to infrared light and microwave [1]. Electrochromic materials dominate the major electrochromic performances of electrochromic devices. Generally, electrochromic materials can be divided into organic electrochromic materials, inorganic electrochromic materials and organic/inorganic electrochromic nanocomposites. The advantages of organic electrochromic materials are characterized as rich color, ease of modification, good processability and low cost [2]. Meanwhile, the advantages of inorganic electrochromic materials are characterized as wide working temperature range and good chemical and electrochemical stabilities [3]. Organic/inorganic electrochromic nanocomposites can combine the advantages of organic and inorganic electrochromic materials and provide further enhanced electrochromic performances.

In organic/inorganic nanocomposites, the interfacial interactions between the organic and inorganic phases (or between the matrix and dispersed phase) have large impact on the properties of the nanocomposites. As we know, the dispersion states of nanophases in the matrix and their interfacial interactions determine the mechanical properties of structural nanocomposites. Similarly, for organic/inorganic electrochromic nanocomposites, better dispersion and stronger interfacial interactions between the organic and inorganic phases may also lead to enhanced electrochromic performances [4]. Consideration of the volume change, electron conduction and ion transport during the electrochromic process, a good interface contact and enough interfacial interaction between the organic and inorganic phases are necessary. The electrochromic nanocomposites suffer periodic volume change causing by the ion extraction and insertion during the electrochromic switching process, strong interfacial interactions are helpful for maintaining the structural stability of the nanocomposites and avoiding structural damage caused by the volume change. Moreover, the interfacial interactions are conducive for providing unobstructed ion channels and improving the electron conduction between the organic and inorganic phases, owing to facile conduction pathway and short conduction distance. So the interfacial interactions play the important roles in improving the structure strength, mass transport, electron conduction and electrochromic performances of nanocomposites.

With electrochromic research becoming the hot topic in recent years, many research and review papers are published. Among of these reviews, the general topics include organic electrochromic materials [5,6], inorganic electrochromic materials [7,8], conjugated polymer based electrochromic materials [9], electrochromic devices [10,11], etc. Electrochromic nanocomposites combine the advantages of various electrochromic materials. They have been studied widely owing to their improved electrochromic properties. However, only few reviews are focus on the electrochromic nanocomposites [12]. Interfacial interactions between the organic and inorganic phases in the electrochromic nanocomposites play important roles in the electrochromic film fabrication and property-enhancement. The purpose of this review is to survey the structures, preparations and properties of electrochromic nanocomposites with several kinds of interfacial interactions, and to propose possible property-modulating approaches for further understanding the electrochromic process and property-enhancement mechanism of electrochromic nanocomposites.

2. Types of organic/inorganic electrochromic nanocomposites

According to the electrochromic activities of the organic and inorganic phases, the organic/inorganic electrochromic nanocomposites can be divided into three types, namely, two types of single electrochromic activity materials (either the organic or inorganic phase possessing electrochromic feature), and one type of dual electrochromic activity material (both the organic and inorganic phases possessing electrochromic feature). For the nanocomposites with the organic phase having electrochromic activity, the inorganic phase can improve the stability and electrical conductivity of the nanocomposites. For the nanocomposites with the inorganic phase having electrochromic activity, the organic phase can provide processability and flexibility for the nanocomposites. For both the organic and inorganic phases having electrochromic activities, the color, contrast and switching speed of the nanocomposites can be enhanced directly. But for the dual electrochromic activities organic/inorganic nanocomposites, the working potentials and optical absorbance region of the organic and inorganic phases need to be matched. Otherwise, overload or under voltage can happen to either the organic or inorganic phase [4]. Also, if the colors of organic phase under positive and negative potentials are similar to the colors of inorganic phase under negative and positive potentials, respectively, the contrast of the whole device may be reduced due to the low color difference caused by color overlapping of the organic and inorganic phases under different potentials.

The interfacial interaction types can be used as another classification standard of the organic/inorganic electrochromic nanocomposites. Except simple physical contact, the typical interactions between the organic and inorganic phases in the electrochromic nanocomposites include covalent bond, coordination bond, electrostatic interaction, hydrogen bond and π-π stacking interaction. The covalent bond and coordination bond are two kinds of strong interactions, while the electrostatic interaction, hydrogen bond and π-π stacking interaction can be assigned to weak interactions. This review is written according to the types of interfacial interactions in the electrochromic nanocomposites.

3. Interfacial interactions between the organic and inorganic phases in electrochromic nanocomposites

3.1. Covalent bond interaction

Covalent bond is a primary valence bond, which has the highest bond energy (~100 kJ mol^{-1} to 500 kJ mol^{-1}) among all of the interfacial interactions. So the covalent bond can supply solid strength for the organic/inorganic electrochromic nanocomposites. And the electron conduction between the organic and inorganic phases can be converted from indirect inter-chain jumping to