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IMPROVING THE OPTOELECTRONIC PROPERTIES OF CONDUCTING POLYMER VIA POLYOXOMETALATE

ABSTRACT

A composite film formed by combining the polyoxometalate and the conducting polymer can contribute greatly to the improvement of the optoelectronic properties of the conducting polymers thanks to the strong electrostatic interaction between them. In the present work, CT, namely 2,4,6-tris((9H-carbazol-2-yl)oxy)-s-triazine has been synthesized from one step reaction of s-triazine and 2-hydroxycarbazole. The electropolymerization of POM/CT was carried out onto ITO-glass surface in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆)/acetonitrile (ACN) solution. The composite film displays enhanced electrochromic performance by incorporation of POM into the PCT film. The electrochromic and electrochemical property of the composite film is significantly improved, which results in an optical contrast of 59% at 670 nm and stability maintain 91% of its initial electroactivity at the end of the 300 cycles. These results indicate the important role of POMs in improving optoelectronic properties of PCT to expand application of electrochromic devices.

Keywords: Polyoxometalate, Conducting Polymer, Composite Film, Electropolymerization, Electrochromic

1. INTRODUCTION

Organic electrochromic conducting polymers have attracted notable attention owing to their advantageous properties such as processability, their ease of chemical and electrochemical synthesis, fast response times, high levels of coloration and long-term optical stability [1 and 5]. These advantageous features allow them to be prospective areas of widespread application like smart windows [2], display technologies [7 and 10] switchable mirrors [4]. Among these polymers, carbazole-based polymers are widely used in opto-electronic devices due to their poor processing capabilities, thermally stable, superior hole transporting capability. Carbazole-containing polymers as a class of electroactive polymers have been widely examined due to their interesting and practical opto-electrochemical properties. In general, the disadvantages existing in the direct polymerization of carbazole are that it requires a high potential for oxidation, and the polymerization proceeds quite slowly [12 and 14]. To solve this problem, a composite can be prepared with polyoxometalates (POMs), which are a redox active compound with electron-rich heterocycles at the terminal polymerization sites of carbazole. Polyoxometalates (POMs) are defined as one of the most important classes of metal-oxygen groups. Furthermore, these compounds are one of the promising special materials for forming nanocomposite materials [15 and 18]. These metal oxide clusters have technological application in many fields from sensing to catalysis to electrochemistry [19 and 21]. The

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functionality of the molecular structure and size of POMs gives them unique chemical and physical properties. Besides, these clusters have the ability not only to form electrochemically reduced and mixed valence clusters but also easily accept electrons [22 and 24]. These features make them very advantageous especially in the preparation of modified electrodes and also enables useful electrocatalytic properties with regard to challenging electrochemical processes. Because of these unique properties, the addition of POM clusters into conducting polymers could advance their optical and electrical properties. Up to now, Polypyrrole (PPy), polyaniline (PANI), and poly(4-vinylpyridine) (P4VP) modified electrodes have been used for electrocatalytic reduction of POMs containing anionic metal oxides of V, Mo, W, etc. Owing to their high stability in redox states and their participation in both fast and reversible electron transfer reactions, POMs could be used as an electron transfer mediator for an electrocatalytic application. Electroactive polymers such as polycarbazole (PCz) and polythiophene (PTh) have been used as hosts for heteropolyanions [15, 25 and 26]. Thanks to good solubility and film-forming ability of POMs, they provide composite formation together with the conducting polymers. At the same time, the strong electrostatic interaction between conductive polymers and POM further improves the properties of the composite material [27 and 28]. In this study, CT monomer in presence of monolacunary Keggin type POM ($K_7-xNa_xPW_{11}O_{39} \cdot 14H_2O$) have been synthesized by electrochemically polymerized to form an electroactive composite film. The electrochemical and optical properties of POM/PCT composite film formed by combining the POM and the PCT have been studied.

2. RESEARCH SIGNIFICANCE

In this study, inorganic-organic hybrid structures (POM/PCT) with superior optoelectronic properties have been designed by combining the organic polymerizable unit and the inorganic redox active compound POM compound effectively and easily. In addition, POM compound was synthesized in the Keggin structure and incorporated into the polymer structure and the improvement of the optical properties of the polymer was investigated by electrostatic interactions of the materials.

3. EXPERIMENTAL METHOD

3.1. Materials and Equipment Details

All chemicals and reagents were purchased from Aldrich. Electrochemical polymerization and characterization were performed with an Ivium Compactstat instrument. For all electrochemical experiments, Ag wire was used as the reference electrode, Pt wire as the counter electrode and indium tin oxide (ITO) coated glass slides were used as the working electrode. Spectroelectrochemistry of the material was performed using an Iviumstat potentiostat/galvanostat coupled with an Agilent 8453 UV-vis spectrophotometer. The surface morphology of the POM/PCT film was monitored using a Zeiss (EVOL510) model Scanning Electron Microscopy (SEM).

3.2. Synthesis of CT

The CT monomer was synthesized according to the synthetic methods described in our previous work [11]. 2,4,6-trichloro-s-triazine (2.5 mmol) was dissolved in acetone (5ml). Then, 2-hydroxycarbazole (7.5 mmol) and NaOH (7.5 mmol) in 2.5ml acetone/water (4:1v/v) were dissolved and the resulting solution was added dropwise to triazine solution. The reaction mixture was stirred firstly half an hour at 0°C, then 1 hour at 35°C and lastly 3 hours was refluxed.

Then, this mixture was cooled down to 0°C and the solution was filtered. The resulting white precipitate was cold acetone was washed. The monomer was acquired with 52% yields. CT compound was verified by NMR spectroscopy. ¹H-NMR (400MHz, DMSO-d₆) δH/ppm: 11.56 (s; 3H), 8.13 (m; 6H), 7.50 (t; 3H), 7.41 (m; 6H), 7.15 (m; 3H), 7.07 (dd; 3H).

3.3. Synthesis of POM

K_{7-x}Na_xPW₁₁O₃₉·14H₂O (POM) was obtained according to the literature [12]. 45.4 sodium tungstate dihydrate (Na₂WO₄·2H₂O) and 75mL of distilled H₂O were mixed to synthesize POM compound. Then 25 mL of 1 M phosphoric acid and 44 mL of glacial acetic acid was added to this mixture. The resultant solution reactants were allowed to react for 1 hour at 115°C to react. After 1 hour, 15 g of potassium chloride was added to this solution to give a white precipitate. The white precipitate was washed with cold water to remove unreacted metal groups and filtered to afford the POM compound and allowed to dry at room temperature.

3.4. Preparation of pCT/POM Film

POM doped pCT film was electrochemically synthesized using 5 mM CT and 0.25 mM POM and in 0.1 M TBAPF₆/ACN solution at 100 mV/s scan rate.

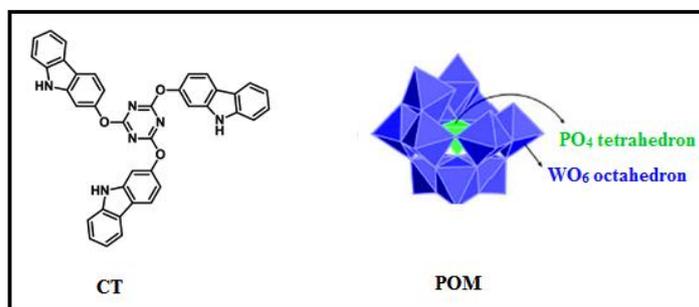


Image. Structures of CT monomer and POM

The pCT films were deposited onto the indium tin oxide (ITO) working electrode with a surface area of 1.2cm². In order to remove the unreacted monomers in films and inorganic salts on the surface were rinsed with ACN.

4. FINDINGS AND DISCUSSIONS

4.1. Electrochemical Polymerization of POM and POM/CT

The electrochemical studies have been conducted with cyclic voltammetry in a 0.1 M TBAPF₆/ACN solution. CV is a very utility technique which allows monitoring of the redox state during the polymerization of the monomer. POM has indicated one oxidation potential at 0.31V and a reduction at 0.96 V as shown in Figure 1a. The PCT/POM has been prepared in the potential range of 0-1.5V with 6 consecutive cycles (scan rate 100mV/s). From the first scan, the oxidation onset potential has been found 0.85V for POM/CT (Figure 1b). Also, the oxidation peak of POM/PCT was about 1.03V, while the reduction peak was observed at 0.58V.

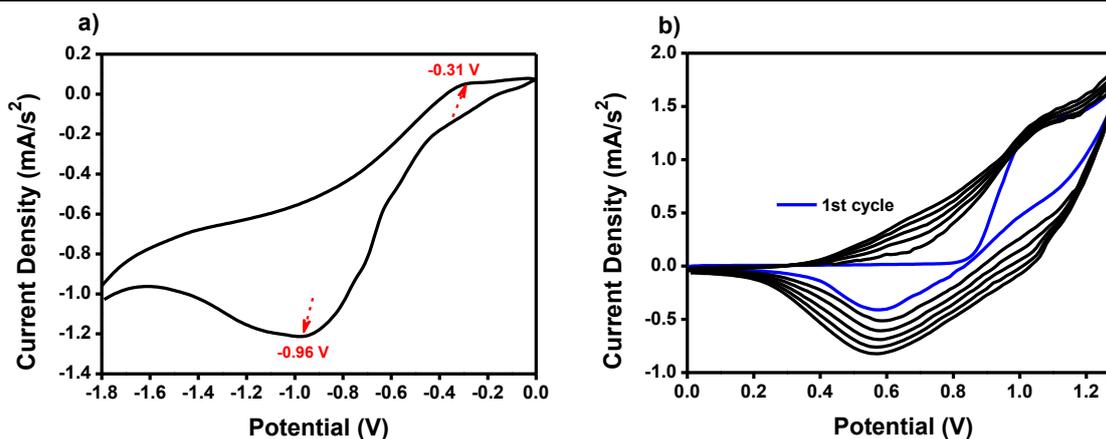


Figure 1. Electrochemical polymerization of a) POM b) POM/CT in 0.1 M TBAPF₆/ACN

4.2. Surface Morphology of POM/PCT Film

The surface morphology of electrochemically prepared polymer film has examined with SEM analysis. As shown in Figure 2, the POM/PCT composite film showed a rough and porous surface. The porous structure of the composite film leads to relatively large specific surface areas. This rough and porous structure not only increases the surface area but also could facilitate the electron transfer.

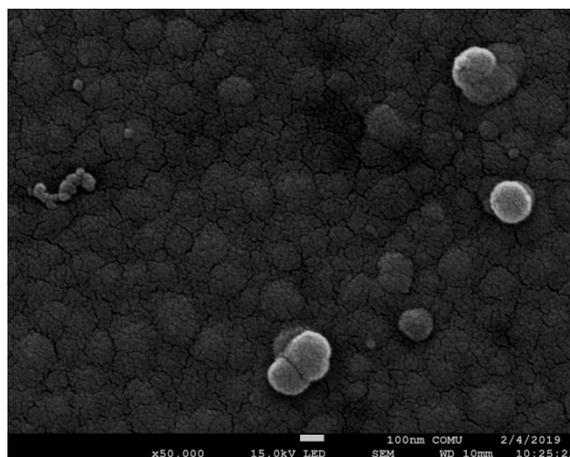


Figure 2. SEM image of POM/PCT at 50.000 kX magnification

4.3. Stability of POM/PCT Film

The stability of POM/PCT film is the most important parameter in the electrochemical application. The POM/PCT composite film was swept during 300 cycles using cyclic voltammetry in 0.1 M TBAPF₆/ACN at a scan rate of 100 mV/s. According to the CV presented in Figure 3, it was observed that the composite film maintained its stability between the initial and the 300th cycle to 91%. Under these conditions, the POM/PCT film has shown good stability. The long-term stability can be interpreted as a result of the strong electrostatic interaction between POM in anionic form and PCT polymer in cationic form.

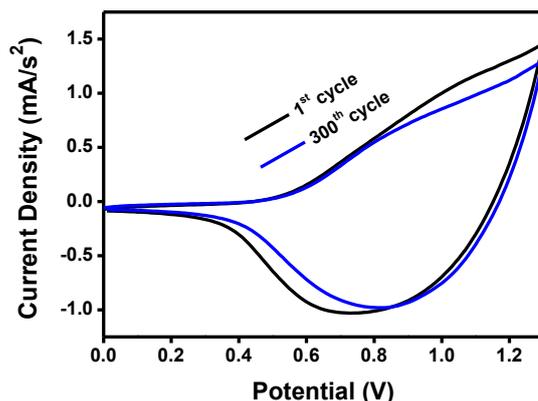


Figure 3. Stability of POM/PCT film in 0.1 M TBAPF₆/ACN

4.4. Spectroelectrochemical Property of POM/PCT Film

The spectroelectrochemical studies have been performed in 0.1 M TBAPF₆/ACN solution to investigate the electrochromic behaviors of as-prepared film. The POM/PCT composite film has shown absorption at 295 nm because of π - π^* transitions (Figure 4). When the values of 430 and 670 nm were examined, it was observed that polaron and bipolaron peaks increased with increasing potential. The optical contrast (ΔT) of POM/PCT film has been measured as 59% at 670 nm. In the presence of POM, the optical contrast showed a significant increase, which is due to the strong electrostatic interaction between PCT and POM [29, 31 and 32]. Table 1 summarized the electrochemical and optical properties of POM/PCT composite film.

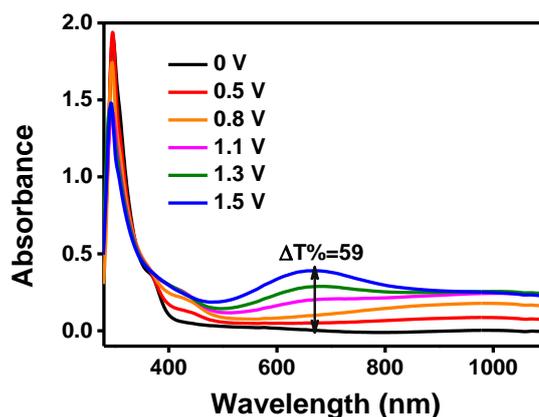


Figure 4. Spectroelectrochemical graphs of POM/PCT at a various applied potential

Table 1. Electrochemical and optical properties of POM/PCT

Polymer	HOMO (eV)	LUMO ^a (eV)	λ_{\max} (nm)	E _g (eV)
POM/PCT	-5.44	-2.06	295	3.38

4.5. Kinetic Study of POM/PCT Film

Optical contrast and response time has been measured to investigate the electrochromic properties of the obtained PCT film. The optical contrast of the POM/PCT composite film is 59% with the response time of 3.7 s, as shown in Figure 5.

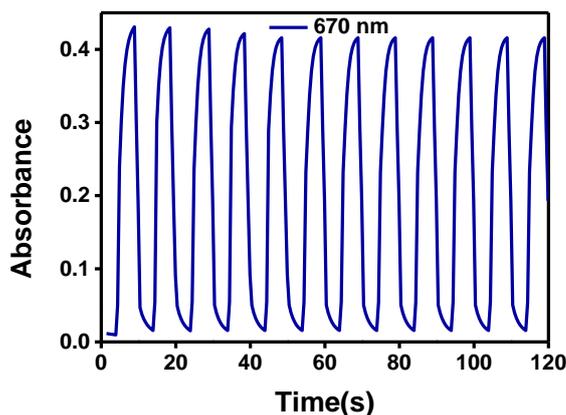


Figure 5. Absorbance-time graph of the POM/PCT at 670 nm in 0.1 M TBAPF₆/ACN

5. CONCLUSION AND RECOMMENDATIONS

In summary, the composite film was prepared by electrochemical polymerization of CT and the Keggin type POM. Optoelectronics properties of the composite film were examined in 0.1 M TBAPF₆/ACN. The POM/PCT composite film has shown high optical contrast. Moreover, POM/PCT composite film has long-term stability and reasonable optical contrast which makes it a good candidate for smart windows and ECDs applications.

NOTICE

This study was presented as an oral presentation at the 2nd International Eurasian Conference on Biological and Chemical Sciences (EurasianBioChem 2019) on 28-29 June 2019.

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