



# Electrochromic Characteristics of Nitrogen-Doped Graphene/TiO<sub>2</sub> Nanocomposite Electrodes



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## ABSTRACT

Nitrogen-doped graphene (NDG)/titanium dioxide (TiO<sub>2</sub>) nanoparticles were coated on indium-tin oxide (ITO) glass substrates to fabricate NDG-TiO<sub>2</sub> nanocomposite electrodes. 3-methylthiophene (3MT) was electrochemically deposited on the NDG-TiO<sub>2</sub> films to form poly(3-methylthiophene) (P3MT/NDG/TiO<sub>2</sub>) composite electrochromic electrodes. The introduction of NDG and TiO<sub>2</sub> mesoporous films significantly increased the initial maximum optical contrast ( $\Delta T\%$ ) to 70% as compared 41% of pure ITO electrodes, whereas the P3MT/NDG/TiO<sub>2</sub> composite electrodes enhanced the adhesion of P3MT polymers to the NDG/TiO<sub>2</sub>/ITO substrate, thereby increasing the long-term stability of the corresponding electrochromic devices. Experimental results reveal that P3MT/NDG/TiO<sub>2</sub> composite electrodes retained up to 90% of  $\Delta T\%$ , relative to 70% remaining  $\Delta T\%$  of pure ITO electrodes. This illustrates the enhanced long-term stability achieved through the introduction of a NDG-TiO<sub>2</sub> nanocomposite films in electrochromic devices. These devices demonstrated excellent response time characteristics and  $\Delta T\%$  value of 6 s and ca. of 70%, respectively. This work has shown that conductive polymer/NDG/TiO<sub>2</sub> composite electrodes are well suited to electrochromic devices for the promotion of performance and stability.

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## 1. Introduction

Electrochromic devices (ECDs) have been greatly expanded to the application in optical modulation. Various organic and inorganic electrochromic materials demonstrate different absorption characteristics in the range of visible light, resulting in different colors. Electrochromic materials are the key roles which were assembled in the ECDs, such as conductive polymers (CP) [1,2]. Conductive polymers are the result of a material doping state produced through the addition of dopants conjugated along the molecular chains. These materials generate electron or hole pairs, resulting in conductivity and variations in optical absorption. An electrochromic device having two electrochromic layers respectively formed on opposite two electrodes and containing a gel-type electrolyte such as an alkali metal salt in a polymer solution which fills up the gap between the two electrodes. The optical properties of electrochromic components need to be recognizable, to actuate a strong visual effect and provide display characteristics. In addition, the reversible process of color change needs to be rapid and stabilized through applied driving potential. Polythiophene derivatives [3] have shown excellent electrical conductivity

and doping/de-doping reversible behavior through electrochemical polymerization [4]. Meanwhile, polythiophene film appears bright red in a neutral state however, with a change in the potential of oxidation, is converted to light blue (or gray green). In polythiophene derivatives, poly(3-methylthiophene) (P3MT) has good physical performance and chemical nature, producing a clear electrochromic change in color. Indium tin oxide (ITO) was coated with P3MT and fabricated as an electrochromic device [5], demonstrating a maximum optical contrast of 35% at a wavelength of 530 nm with applied potentials between -0.3 and 2.5 V. Ionic electrolytes have been used in all electrochromic devices. Poly-(3,4-ethylenedioxythiophene) was coupled with P3MT in a dual-layer device [6], in which the ionic electrolyte of tetra-butyl ammonium fluoroborate was used as an electrolyte. This kind of ECD shows the optical contrast ( $\Delta T$ ) to 46% at  $\lambda = 655$  nm; however, the stability remains an un-solved problem over long periods of time. Therefore, increasing stability over the long term is the most important issue in the application of ECD. In our previous work [7], TiO<sub>2</sub> film has been successfully implemented as a buffer matrix to form P3MT electrochromic film using cyclic voltammetry because TiO<sub>2</sub> film is capable of providing a meso-porous layer and moderate electric conductivity. These layers were then sandwiched with salt (lithium perchlorate) within ECD devices. The performance of electrochromic has been improved by inserting a TiO<sub>2</sub> buffer layer in the P3MT-based electrochromic devices.

Graphene is widely considered to be an ideal material for the use in solar cells [8], electrochemistry [9], and optoelectronics

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[10,11] because of its unique two-dimensional structure, remarkable electrical conductivity, and optical transparency to visible and near-infrared light (380–1300 nm). Many studies on graphene-based photovoltaic applications have been achieved, in which graphene was used as active layer materials [12,13], electron transport bridges [14,15], and transparent electrodes [8,16]. However, the low efficiency of the dye-sensitized solar cells (DSCs) based on graphene counter electrode is primarily to the poor catalytic activity of graphene film. The limited number of active sites in graphene is the main reason for the poor electrocatalytic activity. Hence, modification of graphene is required to enhance electrocatalytic activity for further application. Theoretical calculations and experimental studies have proven that nitrogen doping of graphene can efficiently control its physical/chemical properties, provide more active sites, and improve its reactivity and electrocatalytic activity [17]. Therefore, nitrogen-doped graphene (NDG) is considered as a candidate material for the modified electrode of ECDs.

In this work, NDG nanosheets are prepared by a hydrothermal reduction of graphite oxide (GO) using ammonia as the nitrogen source and employed to incorporate in meso-porous TiO<sub>2</sub> layer of P3MT-based ECDs. The ECD characteristics of the P3MT-NDG-TiO<sub>2</sub> electrodes with and without NDG loading are investigated. Spectroelectrochemical experiments demonstrate that the incorporation of NDG presents a higher optical contrast and long-term stability as compared both of a bare ITO and a TiO<sub>2</sub>-ITO electrode.

## 2. Experimental

Graphite (300 mesh, 99%, Alfa Aesar), potassium permanganate (KMnO<sub>4</sub>, J. T. Baker), sodium nitrate (NaNO<sub>3</sub>, Aldrich), titanium(IV) oxide (TiO<sub>2</sub>, P25, Degussa), 3-methylthiophene (Alfa), acetonitrile (J. T. Baker), lithium perchlorate (Alfa), propylene carbonate (PC, Fluka), and poly(ethylene oxide) (PEO, MW=400000, Aldrich) were used as received.

### 2.1. Preparation of TiO<sub>2</sub> mesoporous layer

We synthesized hydrothermally processed TiO<sub>2</sub> colloid [7,18]. In brief, 3 g TiO<sub>2</sub> nanoparticles (P25) were dispersed in 100 mL 10 N NaOH and heated to 130 °C in an autoclave for 1 day. The precipitate was then re-dispersed in 100 mL 1 N HNO<sub>3</sub>. This suspension was subjected to autoclaving at 240 °C for 12 h to obtain the TiO<sub>2</sub> colloid. The TiO<sub>2</sub> specimens were baked at 450 °C in air for 30 min. The TiO<sub>2</sub> colloid solution was mixed with polyethylene glycol (PEG-20000) (Fluka) to form a viscous TiO<sub>2</sub> dispersion at a 0.15 of PEG/TiO<sub>2</sub> ratio, which was spin-coated onto an indium-tin oxide (ITO)-coated glass (8 Ω/□, Merck) to form a TiO<sub>2</sub> film with an area of 1.0 cm<sup>2</sup>. The TiO<sub>2</sub> film was controlled at a desire thickness. The film was dried in air at 120 °C for 30 min and calcined at 450 °C for 30 min.

### 2.2. Preparation of nitrogen-doped graphene (NDG)

Graphite oxide (GO) was prepared by the oxidation of graphite using the Hummer's method [19]. A 2 g portion of natural graphite powder, 2 g of NaNO<sub>3</sub>, and 96 mL of concentrated H<sub>2</sub>SO<sub>4</sub> were mixed at 0 °C. The above mixture was continuously stirred using a magnetic stirrer. 12 g of KMnO<sub>4</sub> was gradually added to the above mixture while keeping the temperature at 0 °C. The mixture obtained was first stirred at 0 °C for 90 min and then at 35 °C for 2 h. Distilled water (80 mL) was slowly dropped into the resulting solution, over a period of around 30 min, to dilute the mixture. Then 200 mL of distilled water was added followed by 10 mL of H<sub>2</sub>O<sub>2</sub>

(30%), and the stirring continued for 10 min to obtain a GO suspension. The graphite oxide was collected from the GO suspension by the suction filtration, and repeatedly washed with distilled water until the pH = 7. NDG was prepared through a hydrothermal reduction of graphite oxide in the presence of ammonia [17]. 100 mg of GO was ultrasonically dispersed into 150 mL distilled water. This solution was adjusted the pH value to 11 using 28% ammonia, and then transferred into a Teflon-lined autoclave and heated at 150 °C for 24 h. A black precipitate was obtained and collected with centrifugation, followed by washing with a large amount of distilled water. Finally, the collected NDG powders (3 mg) were ultrasonically dispersed into 10 mL distilled water to form the resulting NDG dispersion.

### 2.3. Fabrication of NDG-TiO<sub>2</sub>-ITO working electrode

The NDG electrodes were fabricated by drop casting above dispersion on the mesoporous TiO<sub>2</sub> nanocrystalline-ITO substrates with an area of 1.0 cm<sup>2</sup> and drying at room temperature. The estimated NDG loading was 2 μgcm<sup>-2</sup>.

### 2.4. Materials analysis

The microstructure of the sample was investigated by scanning electron microscopy (SEM, Hitachi, S-4800). Raman spectrum was recorded with a Raman Station 400F dispersive Raman spectrometer (PTT/BWII Ramaker). X-ray diffraction (XRD) analysis was performed on a Bruker D8 instrument using Cu Kα radiation.

### 2.5. Electropolymerization of P3MT films

Electrochemical polymerization and characterization were performed on a PGSTAT320 electrochemical analyzer (AUTOLAB Electrochemical Instrument, The Netherlands). A three-electrode cell assembly was utilized using an Ag/AgNO<sub>3</sub> electrode as a reference and a platinum wire was used as a counter electrode. Several substrates of ITO, TiO<sub>2</sub>-ITO, NDG-TiO<sub>2</sub>-ITO with an area of 1.0 cm<sup>2</sup> were used as working electrodes. A luggin capillary, with the tip set at a distance of approximately 1 mm from the surface of the working electrode, was used to minimize errors due to an iR drop in electrolytes. All electropolymerization and measurements were performed under nitrogen atmosphere. The potentials are reported here in terms of the Ag/Ag<sup>+</sup> reference electrode.

For electrochemical polymerization, 0.1 M 3MT monomer and 0.1 M LiClO<sub>4</sub> supporting electrolyte were dissolved in acetonitrile under N<sub>2</sub> atmosphere. Electro-polymerization was achieved by cycling the potential in the range of -200 to 1300 mV with a sweep rate of 50 mVs<sup>-1</sup> and cyclic voltammograms (CVs) were recorded simultaneously with electropolymerization.

### 2.6. Assembly of electrochromic devices

Gel-type electrolyte was first prepared as follows: 0.1 M LiClO<sub>4</sub> and 1 wt % PEO were dissolved in propylene carbonate (PC) to form a gel-type electrolyte. A P3MT-deposited electrode, a bare ITO glass, and the gel-type electrolyte were sandwiched to assemble an electrochromic device structure: ITO|P3MT||LiClO<sub>4</sub>-PEO-PC||ITO, ITO|TiO<sub>2</sub>|P3MT||LiClO<sub>4</sub>-PEO-PC||ITO, and ITO|TiO<sub>2</sub>|NDG|P3MT||LiClO<sub>4</sub>-PEO-PC||ITO, respectively.

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