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# Electrochromic and electrochemical capacitive properties of tungsten oxide and its polyaniline nanocomposite films obtained by chemical bath deposition method

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ABSTRACT

Polyanine and its nanocomposite $WO_3$/PANI films were deposited on fluorine doped tin oxide (FTO) glass slides by simple chemical bath deposition method. The morphology structure of the composite film was studied using atomic force microscopy (AFM) and scanning electron microscopy (SEM), while the electrochemical capacitive properties were determined using cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). The $WO_3$/PANI nano-composite exhibited multiple colors (electrochromism) during the CV scans, from brownish green to transparent to light green then back to brownish green. Surprisingly, the integration of the PANI with the $WO_3$ led to synergistic performance of nanohybrid wherein a true electrochemical double layer capacitor was obtained. Also, interestingly and unlike literature reports, the CBD method led to excellent capacitance retention (>98%) of the PANI even at 1000 continuous cycles. This work demonstrates that simple CBD can be used to get $WO_3$/PANI films that give good electrochromism and pseudo-capacitance comparable to the ones obtained by other methods. Hence the obtained nanocomposite film of $WO_3$/PANI can be a promising material for electrochromic and energy storage applications.

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## 1. Introduction

Tungsten oxide ($WO_3$) is an attractive transition metal oxide that has been widely studied due to its multifunctional properties that leads to a wide range of applications. It has shown good electrochromic, optochromic and gasochromic properties [1–3]. Tungsten oxide's band gap is within the solar spectrum range making it one of the solar energy materials for photo catalytic, photoconductivity and photovoltaic applications [4,5]. The electrochromic (EC) effect, i.e., a reversible color change induced by an electric field of $WO_3$ was first reported by Deb in 1969 [3] and is considered the best material for EC applications due to its high coloration efficiency [6,7].

Various models have been proposed to explain the EC mechanism in $WO_3$. One of such is that by Schirmer et al. [8], in which they proposed that the optical absorption of the films is caused by the small polaron (SP), or transitions between two non-equivalent sites of tungsten ($W^{5+}$ and $W^{6+}$):

$$h\nu + W^{5+}(A) + W^{6+}(B) \rightarrow W^{5+}(B) + W^{6+}(A) \quad (1)$$

According to this model, inserted electrons are localized in $W^{5+}$ sites and polarize their surrounding lattice to form small polarons. It is widely believed that $WO_3$ thin films undergo a chemically reversible electron and cation intercalation reaction to form tungsten bronzes ($M_xWO_3$) during coloration and an electron and cation deintercalation reaction during bleaching [7,9] according to the following equation:

$$WO_3 + xM^+ + xe^- \leftrightarrow M_xWO_3 \quad (2)$$

where $M^+ = H^+$, $Li^+$, etc.

Conducting polymeric materials like polypyrrole (PPy), polyaniline (PANI) and polythiopheres etc. have been considered as

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EC materials but among these, PANI has emerged as the most promising active materials for electrochromic devices due to its high capacitive characteristics, relative ease in preparation, good environmental stability and tuneable conductivity [10]. PANI has been shown to give four distinct colors corresponding to four redox states which are: yellow (leucoemeraldine base), green (emeraldine salt), blue (emeraldine base) and purple (pernigraniline base) [11]. One drawback of polyaniline film is that it shows low conductivity where it can affect its electrochromic behavior [12]. To improve the performance of PANI, some conductive fillers are introduced in the PANI structure forming nanocomposites. The aim is to obtain materials with synergetic or complementary properties to PANI. Some of those improvements were shown by Wei et al. [13], using nanocomposite of PANI and graphite oxide. Others include the works done by Gupta and Miura [10], Shahazmi et al., [12] using PANI/carbon nanotube composite, PANI/ZnO nanocomposite [14,15], PANI/$WO_3$ nanocomposte [16–22], etc.

$WO_3$ along with some other transition metal oxides and some conducting polymers have also been considered as good materials for psuedocapacitors. Among these, the most intensively investigated is ruthenium oxide ($RuO_2$) which has been shown to give appreciable specific capacitance of up to 1500 F $g^{-1}$ over a wide potential range of 1.4 V [23–25] but its commercial application is limited due to high cost and high toxicity. To reduce the cost of $RuO_2$ some low cost metal oxides such as NiO, CoOx and $MnO_x$ etc. have been investigated as electrode materials for electrochemical capacitors [26,27]. Nano-composites of these metal oxides with high surface area carbon materials have been shown to enhance the capacitance as reported by Zheng et al. [28]. Although tungsten oxides especially in its crystalline state shows little capacitance, the pseudocapacitive properties of amorphous tungsten oxide synthesized by microwave irradiation investigated over the potential range of 0–0.5 V vs SCE displayed a volumetric capacitance of 231 F $cm^{-3}$ [29]. The high specific capacitance was ascribed to the participation of proton provided by the tungsten oxide.

Conducting polymers like PANI, PPy and polythiopheres are also good materials for electrochemical capacitors due to their excellent capacity for energy storage, slow charge discharge, easy synthesis, high energy and power density and good chemical stability. The shortcoming of these polymers is the degradation that occurs due to its swelling and shrinking during cycling. This occurs because the insertion and removal of ions causes a volume change in the polymer. This problem is overcome by the use of composite structures as indicated earlier. Hybrid organic/inorganic materials in general represent the natural interface between two worlds of material science. The main challenge is managing to synthesize inorganic–organic hybrid combinations that keep or enhance the best properties of each of the components while eliminating or reducing their particular limitations. Tungsten oxide shows electroactivities over comparatively negative potential range and is a cathodic EC material which changes color from transparent or yellow to deep blue with large optical modulation when it is reduced by $H^+$ or $Li^+$ while PANI is an anodic coloration material [9,30]. Nano-composite film of $WO_3$/PANI tends to enhance the properties of the two materials singly while reducing their shortcomings.

Quantitative parameters of the electrochromic and psuedocapacitive properties of tungsten oxide and PANI strongly depend on its structural, morphological and compositional characteristics and, therefore on the deposition techniques and deposition parameters. $WO_3$ thin film is deposited by various techniques including physical vapor deposition (thermal evaporation and sputtering) [31,32], electrochemical methods [33] and chemical methods (sol–gel and hydrothermal approach) [5,34,35]. PANI thin films is mainly prepared by the oxidation of aniline oligomer with ammonium peroxydisulfate in acidic aqueous medium [36,37] and by electrochemical deposition method [16–18,38]. One major disadvantage of $WO_3$ is that it has a slow response time compared to other electrochromic materials like NiO etc. [6] while PANI gives a relatively low electrochemical stability [16]. This imposes a challenge to their applications.

In this paper we investigate the electrochromic and electrochemical capacitive properties of nancomposite film of $WO_3$/PANI obtained by a simple chemical bath deposition (CBD) method. The enhancement of electroactivity within the applied potential window without losing any electroactivity due to the presence of the component is advantageous for the utilization of such composites for electrochromic and super capacitive applications. To the extent of our knowledge, the electrochromic and electrochemical capacitive properties of this nanocomposite deposited by this method have not been investigated. Most of the work that investigated these properties for the nanocomposite deposited PANI on $WO_3$ electrochemically. However, the electrochromically deposited polyaniline exhibit substantial resistivity, which is attributed to the lack of conducting pathways at the nanoscale associated with random deposition morphology [12]. Also, CBD method offers greater advantage for easy scale-up for commercialization than electrochemical deposition. In this work, we clearly show that the CBD method provides much higher energy storage properties compared to the values reported for electrochemical deposition. The morphology and structure of the composite films were studied using atomic force microscopy (AFM) and scanning electron microscopy (SEM). The optical properties were investigated using UV–vis spectroscopy while the capacitive behaviors of the films for electrochromic and energy storage device applications were investigated using cyclic voltammetry, galvanostatic charge–discharge cycling and electrochemical impedance spectroscopy.

## 2. Experimental details

### 2.1. Deposition of tungsten oxide ($WO_3$)

$WO_3$ was deposited on fluorine doped tin oxide (FTO) coated glass substrates (resistance 17–30 Ω) using simple chemical bath deposition method. The deposition conditions (temperature, concentrations, time of deposit and pH) were optimized and we arrived at hydrolyzing 0.07 M sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) in distilled water. The deposition is pH dependent hence 0.6 M HCl was added to the solution to get a pH of 5. The volume ratio of $Na_2WO_4{\cdot}2H_2O$:HCl was 1:1. The FTO substrates which have been cleaned with detergent and water, rinsed with distilled water and sonicated in distilled water for 5mins were immersed into the solution and the bath temperature kept at 40 °C. The deposition time was varied but the sample we used for this analysis was deposited after 7 h. The films were then removed and rinsed with distilled water. It was found that at higher concentration of the $Na_2WO_4{\cdot}2H_2O$, the solution precipitates and gives no deposit while at room temperature the reaction is incomplete resulting also to lack of deposit. At higher temperature the solution precipitates quickly. The films were annealed at 400 °C during which the color changed from white to milky color.

### 2.2. Tungsten oxide/polyaniline nanocomposite ($WO_3$/PANI)

PANI films were deposited by oxidation of aniline in an acidic aqueous medium using ammonium peroxydisulfate as the oxidant. 0.25 M ammonia persulfate was dissolved in 60 ml of 1 M HCl to which 2 mL of aniline is added. The deposition was at room temperature and time of deposit was 1 h after which the film was rinsed with distilled water and air dried. To get thicker films the above process was repeated for up to five times (1–5 deposit times). It was noticed that the polymerization reaction is completed by 1 h after which the solution precipitates and no more deposit occur on the

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