



Enhancement in the photo-electrocatalytic activity of SnO₂-Sb₂O₄ mixed metal oxide anode by nano-WO₃ modification: Application to trypan blue dye degradation



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ABSTRACT

The SnO₂-Sb₂O₄ (MMO) and SnO₂-Sb₂O₄-WO₃ (MMO-WO₃) electrodes were prepared by electrodeposition followed by dip coating and characterized by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray diffraction (XRD) analysis. The electrochemical (EC) and photoelectrochemical (PEC) degradation studies were carried out on trypan blue (TB) dye. These studies revealed that the characteristics and performance of MMO electrode improved significantly on nano-WO₃ modification. The oxygen evolution potential (OEP) increased from 2.07 V (vs Ag/AgCl) to 2.21 V and the accelerated service life increased by 1.7 times. 88 and 93% color removal was achieved on electrolysis for 240 min using MMO electrode; whereas, 100% color removal was achieved within 120 min by both EC and PEC using MMO-WO₃. The percentage chemical oxygen demand (COD) removal achieved using MMO electrode by EC and PEC were only 60 and 63% respectively; whereas, it increased to 78 and 84% with MMO-WO₃ electrode. A probable pathway for TB degradation was proposed on the basis of liquid chromatography–mass spectrometry (LC–MS) analysis and quantum chemical calculations were performed on TB molecule to corroborate the proposed degradation pathway.

1. Introduction

The contamination and exhaustion of fresh water resources has left us with no option but to treat the wastewater for reuse. Different methods are employed in wastewater treatment depending upon the nature of wastewater matrix [1–3]. Physico-chemical (filtration [4], adsorption [5], coagulation-flocculation [6,7]) and biological or enzymatic wastewater treatment are the most commonly used methods [2,8,9]. In recent years, the Fenton's process [10–12], photo-Fenton's process [13–15], electro-Fenton's process [16], photocatalysis [17–19] and other the advanced oxidation processes also have received much importance [20,21]. However, a single technique suitable for the treatment of wastewater containing varying nature of organic pollutants can hardly be found. The biological method is slow and ineffective on the refractory organic pollutants; whereas, the physico-chemical methods and advanced oxidation processes necessitate the addition of chemical reagents [22,23]. In this context, electrochemical technologies satisfactorily complement the need of a compact, economic and

swift wastewater treatment method. In particular, “electrochemical oxidation process” (EOP) is an advanced oxidation process characterized by the *in-situ* generation of reactive oxidants without the addition of any chemical reagent ($\cdot\text{OH}$; $E^\circ = 2.8 \text{ V vs SHE}$) [24–26]. The $\cdot\text{OH}$ (hydroxyl radical; $E^\circ = 2.8 \text{ V vs SHE}$) is capable of oxidizing almost all organic compounds into CO₂ and H₂O. The immobilized anode acts as an active center for the oxidation of organics and plays critical role in the oxidative degradation of organics [22]. The physically adsorbed $\cdot\text{OH}$ on the non-active anode surface are readily available for the oxidation of organics and aid “combustion” (complete oxidation) of organics into CO₂ and H₂O; whereas, the chemically adsorbed $\cdot\text{OH}$ on the surface of active anodes leads to selective oxidation and “conversion” of organics into simpler molecules [27].

Several metals, alloys, carbonaceous materials and mixed metal oxide coated electrodes have been tested for their applicability in the electrochemical wastewater treatment [22,28]. However, the metal oxide coated anodes have gained huge importance owing to their excellent dimensional stability and electrocatalytic activity. It is found

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that the most extensively studied anode materials for electrochemical wastewater treatment are derived from the four metal oxides; SnO₂, PbO₂, IrO₂ and RuO₂ [22]. Amongst these anodes, antimony doped tin oxide (Sb-SnO₂) is the most extensively studied non-active anode owing to its excellent electrocatalytic activity for ·OH generation, ease of fabrication, wide operating potential window offered between oxygen and hydrogen evolution reactions and low cost [29,30]. If the stability is sufficiently enhanced, Ti/Sb-SnO₂ could be a potential replacement for the expensive boron doped diamond (BDD) electrode; which is recognized as the most efficient anode for electrochemical wastewater treatment. Extensive research has been carried out by many research teams selecting different fabrication procedures to enhance the electrocatalytic activity and stability of Ti/Sb-SnO₂. The performance of Sb-SnO₂ electrode was significantly improved by;

- Doping SnO₂ with metal/non-metals [31,32].
- Using several combinations of different fabrication techniques (thermal decomposition, electrochemical, spray pyrolysis, hydrothermal) [22,28].
- Incorporation of an interface layer of mixed metal oxide [28,33,34].

These studies recognize Sb as the most suitable dopant with indispensable role in improving the conductivity and electrocatalytic activity of SnO₂. The Sb centers present in the metal oxide deposit act as the site for ·OH generation. The Sb dopant content in SnO₂ matrix plays critical role in altering the electrocatalytic activity of the electrode. The highest electrocatalytic activity of SnO₂ was reported for 6–9% Sb concentration and the OEP increased with increase in Sb content [35,36]. Sb content beyond this limit results in the formation of SnO₂-Sb₂O₄ mixed metal oxide. Consequently, the stability and catalytic activity of the electrode decreases with higher Sb concentration due to the difference in thermal expansion coefficient between Sb and Sn [33]. This leads to inhomogeneous distribution of Sb in the metal oxide coating. However, the Sb₂O₄ has excellent catalytic activity and it is widely used in the oxidation and ammoxidation of hydrocarbons in combination with other metal oxides [37,38]. Also, both SnO₂ and Sb₂O₄ are n-type semiconductor materials with wide band gap of 3.5–3.8 eV and 3.5–3.6 eV, respectively [39,40]. Nevertheless, the performance of SnO₂ in combination with Sb₂O₄ as mixed metal oxide anode has been rarely studied in EOP and the photocatalytic activity of SnO₂-Sb₂O₄ mixed metal oxides has been rarely utilized in assisting EOP [41,42].

The electrocatalytic activity and stability of metal oxide anodes depend on the nature of the substrate. It has been reported that the stability and photoelectrocatalytic activity of SnO₂ anode improved on using highly ordered vertically aligned Ti/TiO₂-nanotubes (NTs) as substrate for metal oxide loading [43,44]. The insertion of metal oxide into the highly ordered TiO₂-NTs produced a compact stacked microstructure and improved the stability of the electrode. Similarly, Shao et al. [45] and Li et al. [46] showed that TiH_x and TiO_xH_y interlayers increased the stability and conductivity of SnO₂. Xu et al. fabricated Ti/Cu nanorods/Sb-SnO₂ electrode [47]. The Sb-SnO₂ deposited on Cu-nanorods showed excellent electrocatalytic activity, high stability and service life. As recently reported by Duan et al., the electrocatalytic activity and stability of the metal oxide anodes can also be significantly improved by compositing the host Sb-SnO₂ with nano-CeO₂ and nano-TiN [48,49]. Similar results were obtained by Hu et al. on modifying Sb-SnO₂ with Cr₃C₂-CNTs (carbon nanotubes) [50].

In the present work, our objective is to fabricate a stable SnO₂-Sb₂O₄ electrode (MMO) by electrodeposition-dip coating method on Ti/TiO₂-NTs array substrate and to study the influence of nano-WO₃ modification on the service life, electrocatalytic and photoelectrocatalytic activities of MMO. The rationale behind choosing nano-WO₃ photocatalyst for MMO modification is to refine the crystal structure of SnO₂-Sb₂O₄ and to enhance the photoactivity of the electrode. Trypan blue (TB) was used in the evaluation of photo-electrocatalytic activities of

the electrodes. TB is an o-tolidine based dye used in dyeing textiles, leather and paper. TB is known to exhibit carcinogenic and teratogenic effects in animals and hence it is necessary to eliminate TB from wastewater before disposal. A probable pathway of TB degradation has been proposed based on the LC-MS analysis and quantum chemical studies.

2. Experimental

2.1. Preparation of TiO₂-NTs array, MMO and MMO-WO₃ anodes

Vertically aligned TiO₂ nanotube arrays were generated on Ti foil (20 mm × 15 mm) (0.25 mm thick, 99.5% purity, Alfa Aesar, Bengaluru) by single step anodization as described elsewhere [51]. The anodized Ti foil was subjected to ultrasonication for 1 min in ultrapure water (Elix 3 Milli-pore system, Resistivity, > 18 MΩ cm at 25 °C) to remove the debris accumulated during anodization and annealed at 500 °C for 60 min.

The TiO₂-NTs were reduced in 0.5 M Na₂SO₄ for 3 min at –1.5 V (vs SCE) to improve its conductivity before electrodeposition [51]. An inner layer of SnO₂-Sb₂O₄ was electrodeposited from a solution containing SnCl₂·2H₂O (9.0 g, AR grade, Sigma Aldrich, Bengaluru), SbCl₃ (0.5 g, AR grade, Sigma Aldrich, Bengaluru), HCl (4 mL, S.D.fine chemicals limited, Bengaluru) and ethanol (50 mL, S.D.fine chemicals limited, Bengaluru). Vertically immersed TiO₂-NTs substrate was subjected to ultrasonication for 5 min in this electrolyte. Then, continuous electrodeposition was carried out at a current density of –20 mA cm^{–2} for 20 min with Pt foil as anode and TiO₂-NTs as cathode. The obtained deposit was annealed at 520 °C for 60 min with heating/cooling rate of 5 °C min^{–1}. The primary SnO₂-Sb₂O₄ layer was then dip coated in a precursor solution of same composition as that of electrolyte bath. The substrate was vertically dipped in the precursor solution for 5 min, slowly pulled out, dried at 100 °C and annealed at 520 °C for 10 min in a muffle furnace. This process was repeated for 5 times and finally annealed 520 °C for 60 min. 0.03 g of nano-WO₃ (150–200 nm, Sigma Aldrich) was added to the electrolyte and the precursor solution in the preparation of MMO-WO₃ electrode following the same procedure. The MMO-WO₃ electrode fabrication steps are shown in Fig. 1.

2.2. Characterization of electrodes

The surface morphology and composition of the as-prepared electrodes were characterized by scanning electron microscopy (SEM, Tecan Vega-3 LMU, made in Czech Republic) equipped with energy-disperse spectrometer (EDS) analyzer (Ametek, USA). The X-ray diffraction pattern of the electrode material was recorded by grazing angle (1°) X-ray diffraction analysis using Cu Kα-radiation (λ = 1.5406 Å) in the 2θ range from 10 to 80° (scan rate 4° min^{–1}, Rigaku, Smartlab XRD, 40 kV, 30 mA). Diffuse Reflectance UV–vis spectra (UV-DRS) were recorded with reference to BaSO₄ as standard using UV–vis spectrophotometer (HR 4000, UV–vis-NIR light source, DT-MINI-2-GS, Jaz detector).

2.3. Electrochemical experiments and transient photocurrent measurements

The electrochemical characteristics of as-prepared electrodes were evaluated using CH instrument 660C-electrochemical work station (USA) in a conventional three electrode system at room temperature with Ag/AgCl (3 M KCl) as reference electrode and a platinum wire as auxiliary electrode. The working electrode dimension was 10 mm × 10 mm. Electrochemical impedance spectroscopy (EIS) was recorded in the AC frequency range 100000–0.1 Hz with an amplitude of 5 mV under the applied potential of 2 V. The electrochemical equivalent circuit (EEC) was selected for the best fit with less than 3% measurement error in the impedance data using ZSimpWin software. The cyclic voltammetry (CV) experiments were performed in 0.25 M

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