Chapter 14
Modification of Titanium Dioxide Nanotubes with Copper via Electrodeposition Technique and Its Applications

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Abstract
Advancement in nanotechnology field has been celebrated with many significant breakthroughs rapidly flourishing in this 21\textsuperscript{st} century. It has tremendously accelerated the advancement of functional materials to a new height. Among them, one-dimensional titanium dioxide, TiO\textsubscript{2} nanotubes (TiNT) is one of the versatile functional material being widely studied. TiNT serves as multifunctional materials with a promising capability to overcome an extensive range of great technological challenges. Recent potential applications of TiNT have been reported in degradation of organic pollutants, water splitting, CO\textsubscript{2} conversion, environmental analytical chemistry sensor, rechargeable lithium-ions batteries, optoelectronics, biocompatible and biomedical materials, photovoltaic cell, catalysis, drug delivering, dye-sensitized solar cells, photoelectrochemical (PEC) cell, among others. TiNT is well-known for its high surface area, high carrier mobility, non-toxicity, chemical stability against photocorrosion (photostability), superior electron transport properties, excellent controllability, economical cost effective with simple and easy fabrication by anodization technique. Nevertheless, TiNT as a \textit{n-type} semiconductor has a wide band gap of 3.2 eV (anatase-formed). Thus, it absorbs merely about 3-5\% of ultraviolet ray from sunlight spectrum. Additionally, TiNT experiences a low quantum efficiency as rapid recombination of photogenerated electron-hole pairs severely hamper overall performance of energy conversion efficiency. It is believed that the conversion efficiency in visible range and the charge separation issue can be solved via establishment of heterostructure TiNT coupled with any narrow band gap semiconductor material (such as copper). Copper oxide (Cu\textsubscript{2}O or CuO) typically procures as a \textit{p-type} semiconductor which is abundantly available, environmentally benign, non-toxic, low production cost with good electrical and optical properties. Cu is favorable to couple with TiNT since it has a narrow band gap (E\textsubscript{g} = 1.9 - 2.2 eV). Cu doped TiNT (Cu/TiNT) might prolong the absorption of TiNT into the visible range of solar spectrum instead of ultra violet (UV) region. In this study, electrodeposition technique has been proposed to deposit Cu onto TiNT substrate. This study provides an overview for the modification of TiNT with Cu deposition and its potential technological potential in photoelectrochemical cells.

Introduction/Background
Advance technology compliment with tireless effort of scientific community has produced many great finding breakthroughs including nanotechnology such as advanced functional material of titania nanotubes (TiNT). An incredible potential can be explored using TiNT including in photocatalysis, solar energy conversion devices, gas sensing, biomedical, electrochromic devices, and self-cleaning material (Centi, Passalacqua, & Perathoner (2016); Comini, Galstyan, Faglia, Bontempi, & Sberveglieri (2015); Pessoa, Fraga, Santos, Massi & Maciel (2015); Sugathan, John, & Sudhakar (2015); Suman, Khann & Pathak (2015); Wong, Tan & Mohamed (2011); and Zhang, J. J. (2013)), to list a few names.

TiNT simply admired due to its versatility properties. Among them, TiNT is highly ordered with large surface area, chemically stable, and low cost. Nevertheless, two main issues of TiNT remain to be solved. The first hurdle related to low efficiency of TiNT. It is known that TiNT has a wide band gap (about 3.2 eV, anatase-formed). Upon UV light illumination, the photogenerated electrons gain sufficient energy and being excited to conduction band (CB) – leaving the hole, h\textsuperscript{+} at valence band (VB). The electrons could recombine with the holes in valence band (VB). Therefore, it is vital to prolong the separation between the electron-hole (e\textsuperscript{-}/h\textsuperscript{+}) pairs or alternatively let them...
being took part in other process. Otherwise, a low current efficiency is observed. Another limitation of TiNT is it is only activated by UV light and only small portion of UV-light (≤5%) exist in sunlight region. However, both limitation of TiNT can be overcome via modification of TiNT with Cu deposition (Ren, Gan, Young, Moutassem & Zhang (2013); Tsui & Zangari (2014); Wang, Qiao, Xu, & Gao (2014)).

Copper, Cu is abundant and readily available, non-toxic, antimicrobial, low cost and has narrow band gap. Fabrication of Cu/TiNT is possible to prolong the separation of electron-hole (e⁻/h⁺) pairs. Additionally, Cu/TiNT can be extended the light absorption towards visible light region (Lai & Sreekantan (2012); and Tsui, Wu, Swami & Zangari (2012)).

**Problem Statement**

TiNT is an excellent functional materials which is beneficial to various advanced applications. However, TiNT has two main drawbacks. Firstly, TiNT has a wide bandgap leading to a low energy conversion efficiency. Secondly, the light absorption of TiNT mainly restricts to ultraviolet (UV) region which constitutes less than 5% in sunlight (visible light). Deposition of Cu onto TiNT using electrodeposition technique is capable to overcome the problems by lowering the band gap and extend the light absorption towards visible light.

**Objectives**

1) To fabricate titania nanotubes via anodization of Ti foils.
2) To deposit Cu onto TiNT via electrodeposition technique.
3) To characterize the Cu/TiNT using FESEM-EDX analysis.
4) To perform photoelectrochemical test on the as-prepared Cu-TiNT photoanode.

**Novelty**

1) Simple fabrication.
2) Capable to produce a high yield of energy conversion efficiency under sunlight.
3) Capable to extend the light absorption towards visible light compared to an undoped TiNT

**Benefit To User and Society**

1) Improve an energy conversion efficiency.
2) The narrowed band gap of TiNT can be used for various advance applications.
3) Simple fabrication which utilize nonhazardous chemical
4) Economically efficient cost

**Results and Discussion**

The TiNT samples were synthesized via anodization of Ti foils (0.127 cm; 99.7% purity) in an electrolyte solution comprising of 0.5 wt. % NH₄F in equal volume of ethylene glycol and glycerol. The two-electrode configuration of electrochemical cell constitutes of Ti as anode and graphite as the cathode operating at 20 V for 30 min. Later, TiNT was annealed at 500 °C for 2h in air to obtain crystallize form of TiNT. Electrochemical deposition of Cu onto TiNT was conducted using a three-electrode configuration of potentiostat as depicted in Figure 1(a). The TiNT acts as the working electrode, a Pt gauze act as the counter electrode and a Ag/AgCl reference electrode.

Fig. 1(b) shows the FE-SEM micrograph of unmodified TiNT prepared at 20V for 30 minutes. A regularly arranged pore structures were successfully obtained upon applying 20 V for 30 min. The anodized Ti noticeably open at the top. An average internal diameter of TiNT approximately at 51.09 nm and an average wall thickness of about 17.03 nm. These crystalline TiNT with well-aligned nanotubes array were utilized as substrate for Cu nanoparticles deposition. Next, Fig. 1(c) shows that copper was successfully deposited on the surface and inside TiNT pores with the execution of -0.2 V applied potential.

The photoelectrochemical (PEC) test on Ti foil failed to detect any generated photocurrent as depicted in Fig. 2(a). Fig. 2(c) shows a significant increment of energy conversion energy with Cu deposition onto TiNT compared to unmodified TiNT in Fig 2(c).
Fig. 1 The schematic diagram of electrochemical technique of Cu/TiNT
(a) FE-SEM of unmodified TiNT (b) FE-SEM of Cu/TiNT

Fig. 2 The photoelectrochemical (PEC) test of (a) Ti foil (b) unmodified TiNT (c) Cu/TiNT.

**Conclusion**

Modification of TiNT with Cu deposition via electrodeposition technique and its applications has been overviewed. Cu/TiNT photoanode is managed to generate higher yield of energy conversion efficiency and extend the light absorption towards visible light compared to the undoped TiNT.

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