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EFFECT OF COPPER CONCENTRATION ON THE MORPHOLOGY AND STRUCTURAL PROPERTIES OF COPPER LOADED TITANIA NANOTUBES PREPARED BY ELECTRODEPOSITION

Aslam Muhammad Mahmud[1], Lim Ying Chin[1,2],
Zuraida Khusaimi[2] and Zulkarnain Zainal[3]

[1]*Faculty of Applied Sciences, Universiti Teknologi MARA,*
40450 Shah Alam, Selangor, Malaysia

[2]*NANO-SciTech Centre (NST), Institute of Science (IOS),*
Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

[3]*Advanced Materials and Nanotechnology Laboratory*
Institute of Advanced Technology (ITMA),
Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia

Corresponding author: drlam88@yahoo.com

ABSTRACT

TiO_2 nanotubes (TiNT) is a promising semiconductor photoelectrode used in photoelectrochemical cell (PEC) but its commercialization is shielded by its low utilization of solar energy due to its wide bandgap. In this study, TiNT was fabricated via electrochemical anodization of Ti whereas various $CuSO_4$ concentrations (1, 10, 100 and 400 mM) were electrodeposited onto the anodized TiNT and later were characterized by using FESEM, EDX and XRD. Uniform TiNT was succesfully obtained after anodization at 20 V. Cu particles were deposited on TiNT, except for those deposited in 1 mM $CuSO_4$ as supported by EDX analysis. Additionally, the nanotubes hole seem partially filled up by copper particles in 10, 100 and 400 mM $CuSO_4$ with large Cu particles were obviously formed on TiNT in 400 mM solution. The structural investigation by XRD indicated that unmodified TiNT contained mixture of anatase and rutile phase and no phase changes upon electrodeposition of Cu.

Keywords: electrodeposition; titania; nanotube; copper

INTRODUCTION

An extensive achievement has been accolades by titanium dioxide nanotubes (TiNT) since it can be applied in numerous technology application. TiNT prominently employed in many advance technology fields such as photocatalytic degradation of pollutants [1], photovoltaic cell [2], lithium batteries [3], gas chemical sensor [4], energy and solar fuel [5], dye-sensitized solar cell [6] and others. Photoelectrochemical (PEC)

application has been rejuvenated with emergence of TiNT [7]. Interestingly, the morphology, crystal structure and film thickness of TiNT can be manipulated with adjustment on the anodization conditions. Moreover, TiNT is favorably employed as it possesses versatile attributes such as vertically oriented nanostructured, high surface area, and excellent charge transport properties coupled with economical cost effective. Nevertheless, TiNT as a n-type semiconductor has a wide band gap of 3.2eV (anatase form). Thus, it absorbs merely about 3-5% of ultraviolet ray from sunlight spectrum. Additionally, TiNT experienced a low quantum efficiency as rapid recombination of photogenerated electron-hole pairs severely hampered overall performance of energy conversion efficiency [8]. 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 Cu_2O-TiNT).

Copper oxide (Cu_2O or CuO) typically procured as p-type semiconductor. Cu is abundantly available, non-toxic, minimal production cost complement with good electrical and optical properties [9]. Cu is favourable as dopant since it has a narrow band gap (Eg=1.9-2.2eV). Cu doped TiNT might prolong the absorption of TiNT into the visible range of solar spectrum instead of ultra violet (UV) region [10, 11].

In this study, electrochemical deposition technique was executed to deposit Cu onto TiNT. We aimed to investigate the influence of different concentration of $CuSO_4$ that might exert on the morphological and structural of Cu-TiNT. It is believed that an optimum concentration of $CuSO_4$ should sufficiently facilitate copper oxide penetration onto pores of TiNT material instead on the surface of TiNT.

EXPERIMENTAL

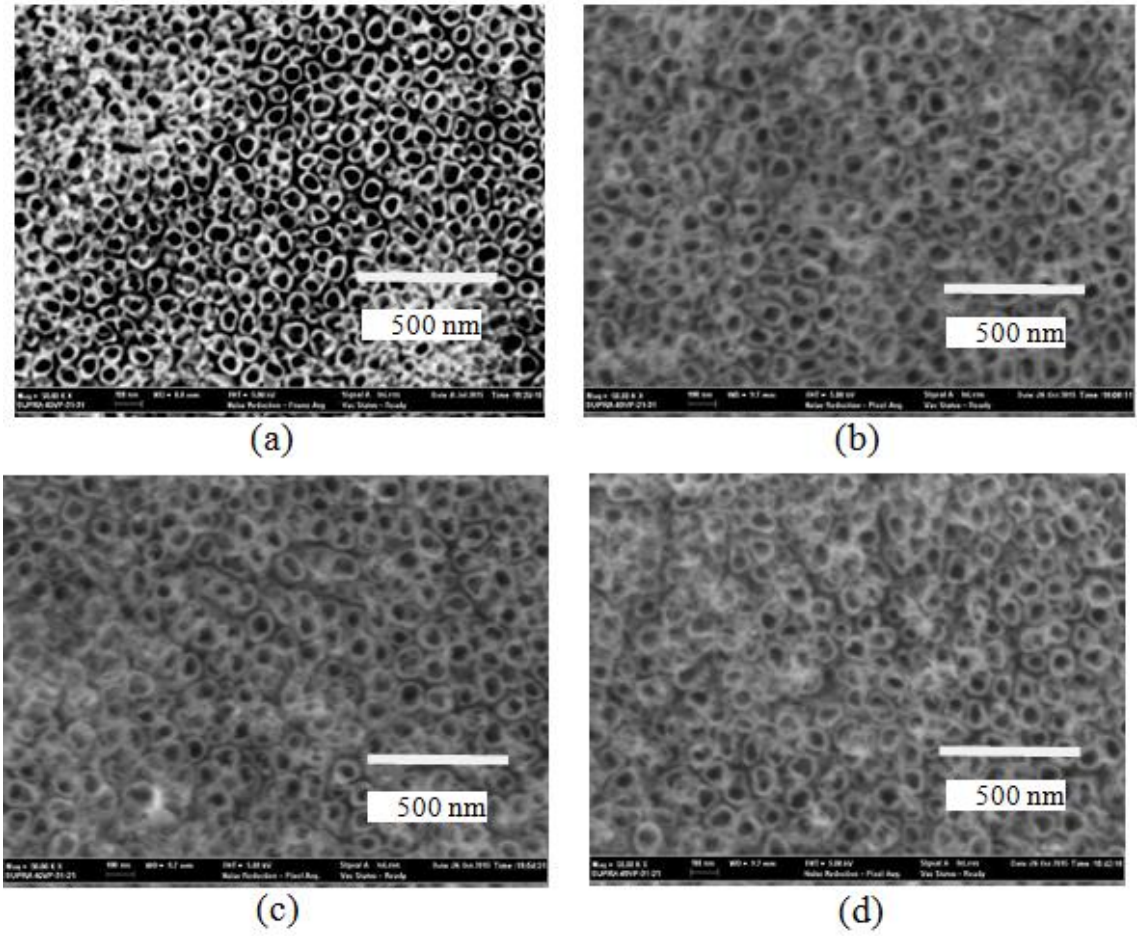
The TiNT samples were synthesized via anodization of Ti foils (0.127 cm; 99.7% purity) in an electrolyte solution comprising of 0.5 wt.% NH_4F in equal volume of ethylene glycol and glycerol. The two-electrode configuration of electrochemical cell constitutes of Ti as anode and graphite as the cathode operating at 20 V for 30 min. Next, annealing of TiNT was performed 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. The TiNT act as the working electrode, a Pt gauze act as the counter electrode and a Ag/AgCl as the reference electrode. Various $CuSO_4$ concentration (1, 10, 100 and 400 mM) were electrodeposited at -0.2V for 600 seconds. Next, the samples were characterized using FESEM (Carl Zeiss supra 40VP) equipped with EDX and XRD to study their morphological and structural properties.

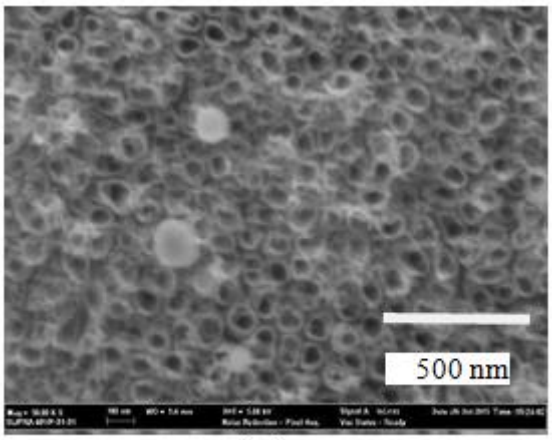
RESULTS AND DISCUSSION

The FESEM image of unmodified TiNT prepared at 20V for 30 minutes was depicted in Figure 1(a). A regularly arranged pore structures were succesfully obtained upon

applying 20 V for 30 min. Indeed, the anodized Ti noticeably open at the top. An average internal diameter of TiNT approximately at 51 nm and an average wall thickness of about 17 nm. Subsequently, these crystalline TiNT with well-aligned nanotubes array were utilized as substrate for Cu nanoparticles deposition.

Figure 1 (b-e) shows the FESEM micrograph of Cu nanoparticles deposited on TiNT in different concentration of $CuSO_4$ solution. At -0.2 V, copper was successfully deposited on the surface and inside the TiNT pores, with exemption for those deposited in 1 mM of $CuSO_4$probably ascribed to very low concentration of $CuSO_4$ used (from EDX analysis). Round shape of Cu particles with a diameter of 93 nm were formed on the surface of TiNT electrodeposited in 400 mM $CuSO_4$ solution (Figure 1e). The size of deposited Cu particles drastically shrinked once the concentration were reduced between 10 mM to 100 mM. The particles tend to reside inside the TiNT pores instead of the surface of the TiNT substrate. The Cu particles were not detected on TiNT substrate for concentration lower than 10 mM $CuSO_4$.





(e)

Figure 1: FESEM images of (a) unmodified TiNT (b) Cu-TiNT(1mM) (c) Cu-TiNT (10mM) (d) Cu- TiNT (100mM) and (e) Cu-TiNT (400mM)

Table 1 exhibits the EDX analysis of the Cu-doped TiNT with various concentrations at 1, 10, 100 and 400mM. The Cu-doped TiNT prepared in 400 mM exhibited the highest amount of Cu presence at 2.02 at.%. The amount of Cu presence in TiNT experienced a downward trend with reducing Cu concentration. The EDX analysis for Cu-TiNT with 1 mM CuSO4 is in agreement with the observation obtained in Figure 1(e) as Cu particles were undetectable neither on the surface nor inside TiNT substrate. Additionally, carbon, C was found in all samples due to the carbon trace-based chemical (e.g.; glycerol and ethylene glycol) employed during anodization of Ti.

Table 1: EDX analysis of Cu-TiNT prepared in various concentration of $CuSO_4$

Element	Atomic Percentage (%)			
	Cu-TiNT (1mM)	Cu-TiNT (10mM)	Cu-TiNT (100mM)	Cu-TiNT (400mM)
Cu	Not detected	0.17	0.43	2.02
Ti	43.98	45.00	44.81	42.68
O	54.97	53.87	53.61	53.71
C	1.05	0.97	1.14	1.58

The XRD analysis was executed to measure the changes of phase structure of TiNT prepared with various concentrations of Cu using electrodeposition technique as shown in Figure 2. The XRD diffraction peaks at 2q=25.38°, 48.10° and 54.5° were assigned to

anatase (101) and (200) planes [JCPDS 00-021-1272] and rutile (211) [JCPDS 00-021-1276] phase of TiNT, respectively . The peak of crystalline of Cu_2O was less noticeable in all Cu-deposited TiNT although Cu was successfully detected via EDX analysis probably due to high dispersion of Cu on the surface of TiNT. Additionally, similar observation was obtained by Lai et al. (2012) and suggested that either Cu has been incorporated into the TiO_2 lattice thus established Cu-Ti-O bonds or situated at interstitial sites as the ionic radius of Cu^{2+} (0.702Å) is quite close to the Ti^{4+} (0.745Å) [12].

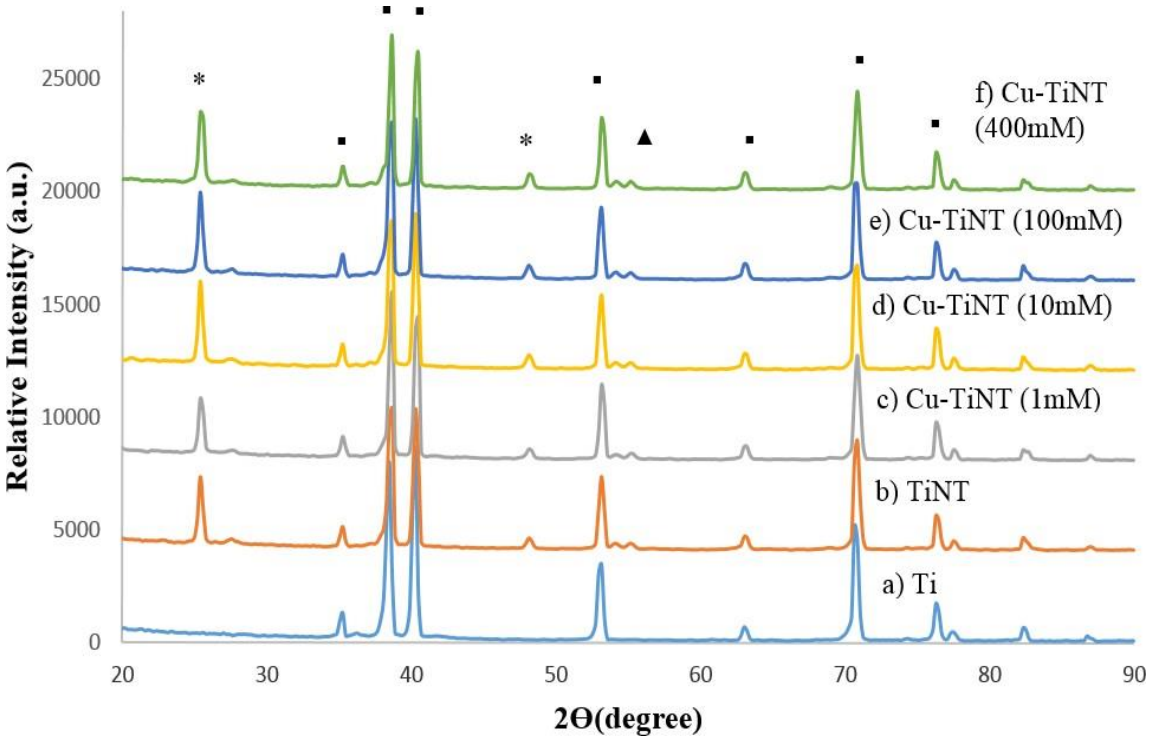


Figure 2: XRD patterns of (a) Ti, (b) TiNT, (c) Cu-TiNT (1mM), (d) Cu-TiNT (10mM), (e) Cu-TiNT (100mM), (f) Cu-TiNT (400mM). Legend: : ▪ (Titanium); * (Anatase); ▲ (Rutile)

CONCLUSION

Copper particles were succesfully deposited on titania nanotubes by electrodeposition at -0.2 V (E vs. Ag/AgCl) in 10-400 mM $CuSO_4$ solution. Cu-TiNT prepared in 400 mM $CuSO_4$ evidently demonstrate better deposition morphology on TiNT compared to the others concentration.

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