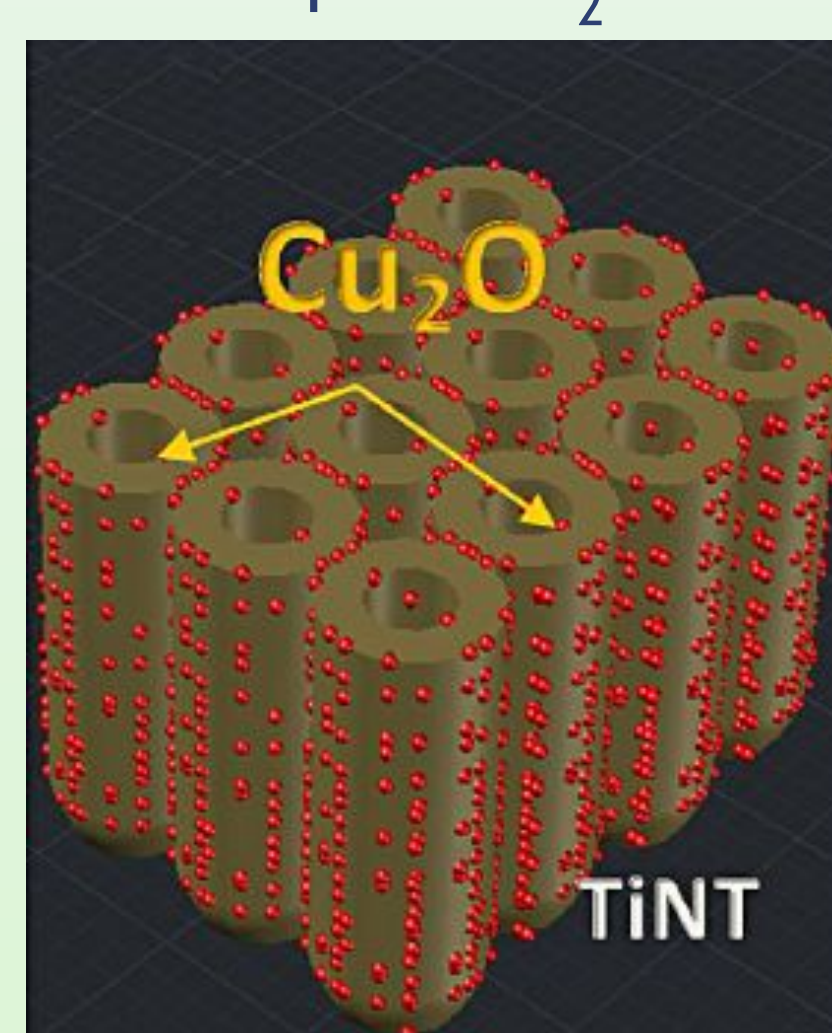


## INTRODUCTION

Low-dimensional nanostructural materials have attracted increasing scientific and technological attention due to their physical properties and their potential application. Dimensionality has a crucial role in determining the properties and performance of nanomaterials. Therefore, the control of size and shape of nanomaterials is of great importance [1, 2]. The intrinsic band gap of nanotube titania of about 3.1-3.3 eV allows the material to absorb light only in the ultraviolet range (up to 400 nm). Thus, in order to achieve more effective solar energy conversion applications with titania nanotube (TiNT) arrays, the light absorption range needs to be extended. Decoration of titania nanotubes (TiNTs) with lower band gap semiconducting nanoparticles, comparing to bare TiO<sub>2</sub>, results in heterojunction formation, thus enabling a visible-light photoresponse. However, the coupling of TiNTs by uniformly seeded nanoparticles of metal oxides with strong interfacial contact remains challenging. In this study, we report cost-efficient and simple process for decoration of TiNT walls with pure Cu<sub>2</sub>O nanoparticles of controllable size and content.



## EXPERIMENTAL

**Material:** 99.7 % Ti foil (Aldrich), 0.127 mm thickness

### Procedure:

**Pretreatment:** ultrasonic clearing in acetone, ethanol, and water, 6 min in each

**Anodizing:** in ethylene glycol (Etg) solution with 0.3 wt. % NH<sub>4</sub>F and 2 wt. % H<sub>2</sub>O at 20 °C, 50 V, 40 min, followed voltage decrease by 1.0 V min<sup>-1</sup> down to 30 V

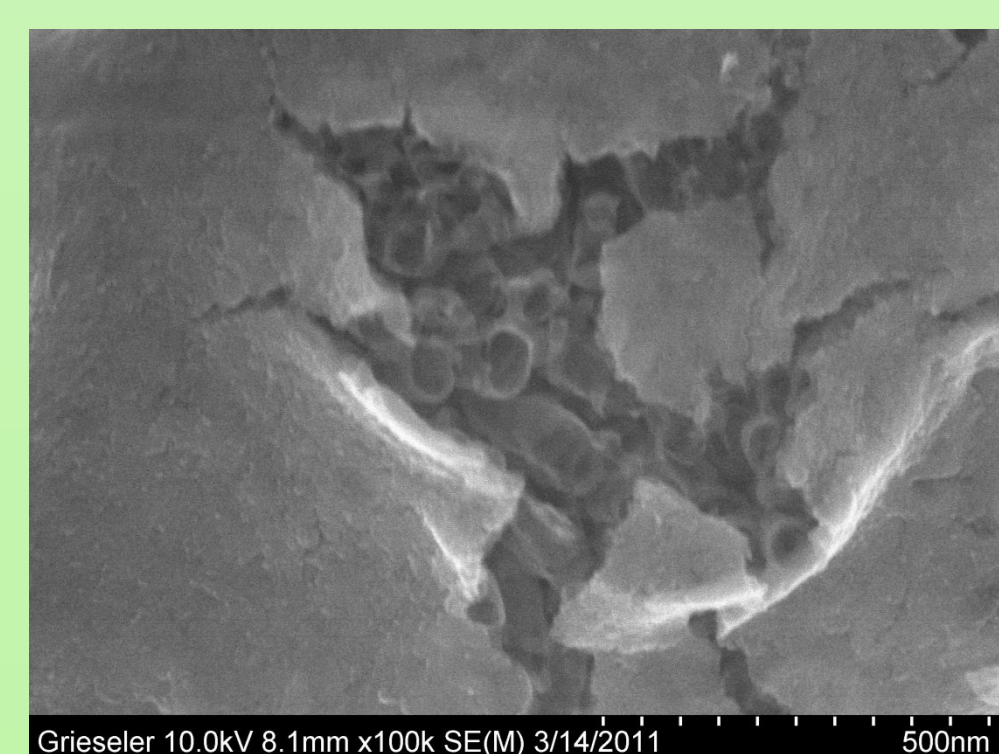
**Posttreatment:** ultrasonic agitation in ethanol for 5 s

**Heat treatment:** 500 °C, 10 ° min<sup>-1</sup>, 2 h

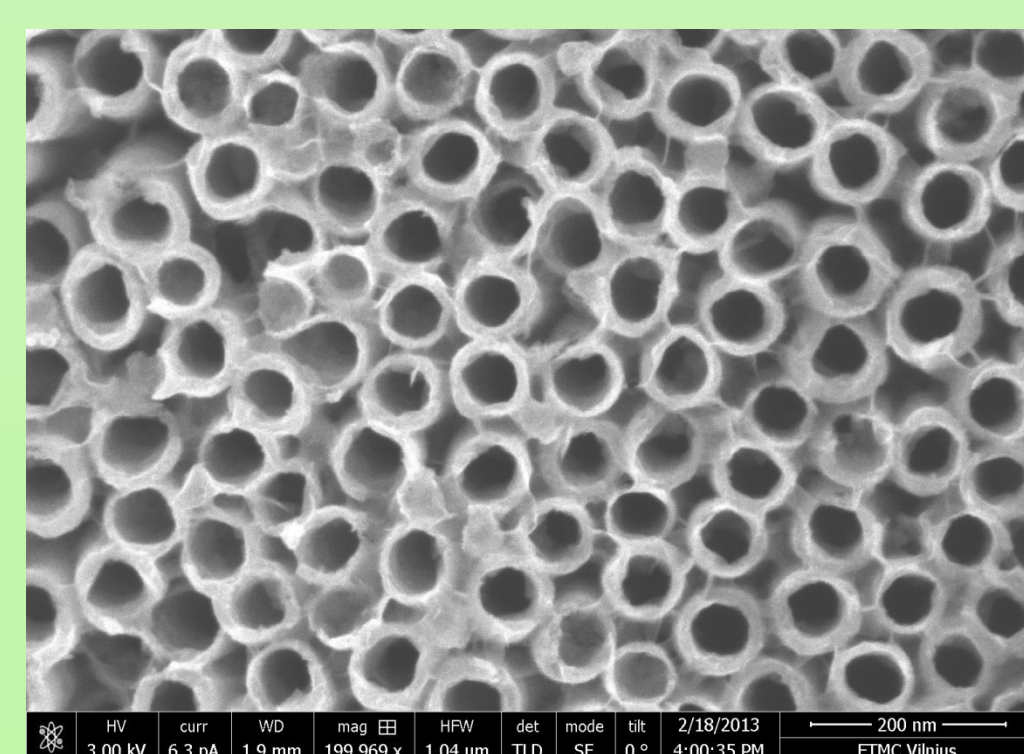
**AC treatment:** in the aqueous solution containing 0.1 Cu(CH<sub>3</sub>COO)<sub>2</sub> + 0.1 mol L<sup>-1</sup> Mg(CH<sub>3</sub>COO)<sub>2</sub> + CH<sub>3</sub>COOH up to pH 5.3 at a constant current density of 0.5 A dm<sup>-2</sup> for 10 min

**Characterization:** the current-time curves were recorded to control the anodizing process top-side and cross-sectional FESEM views of the TiNT film before and after AC treatment were analyzed by field emission scanning electron microscopy

The ultrasonic agitation in ethanol (posttreatment) of the samples is necessary in order to remove the debris from the surface of TiNT.

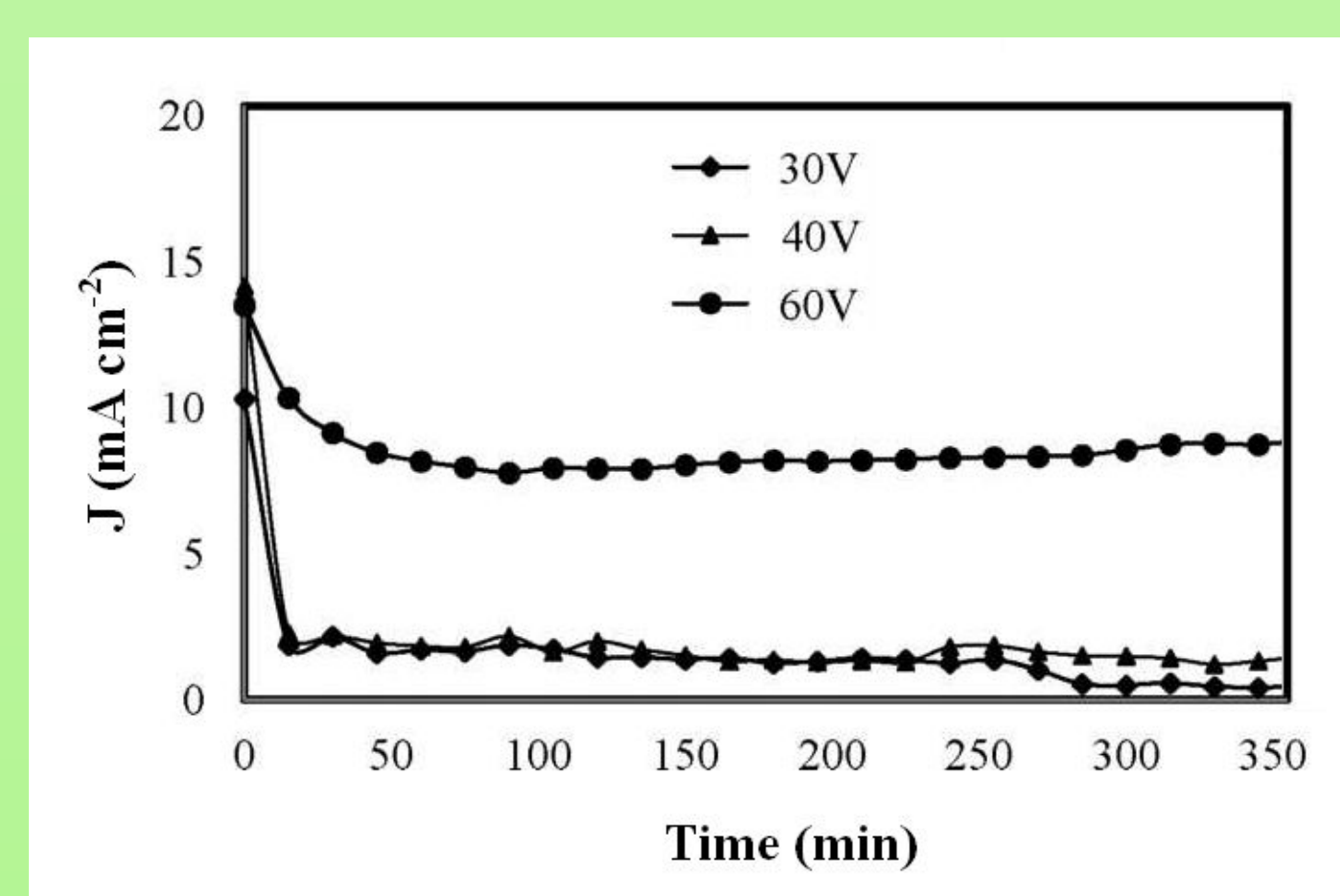


TiNT before treatment

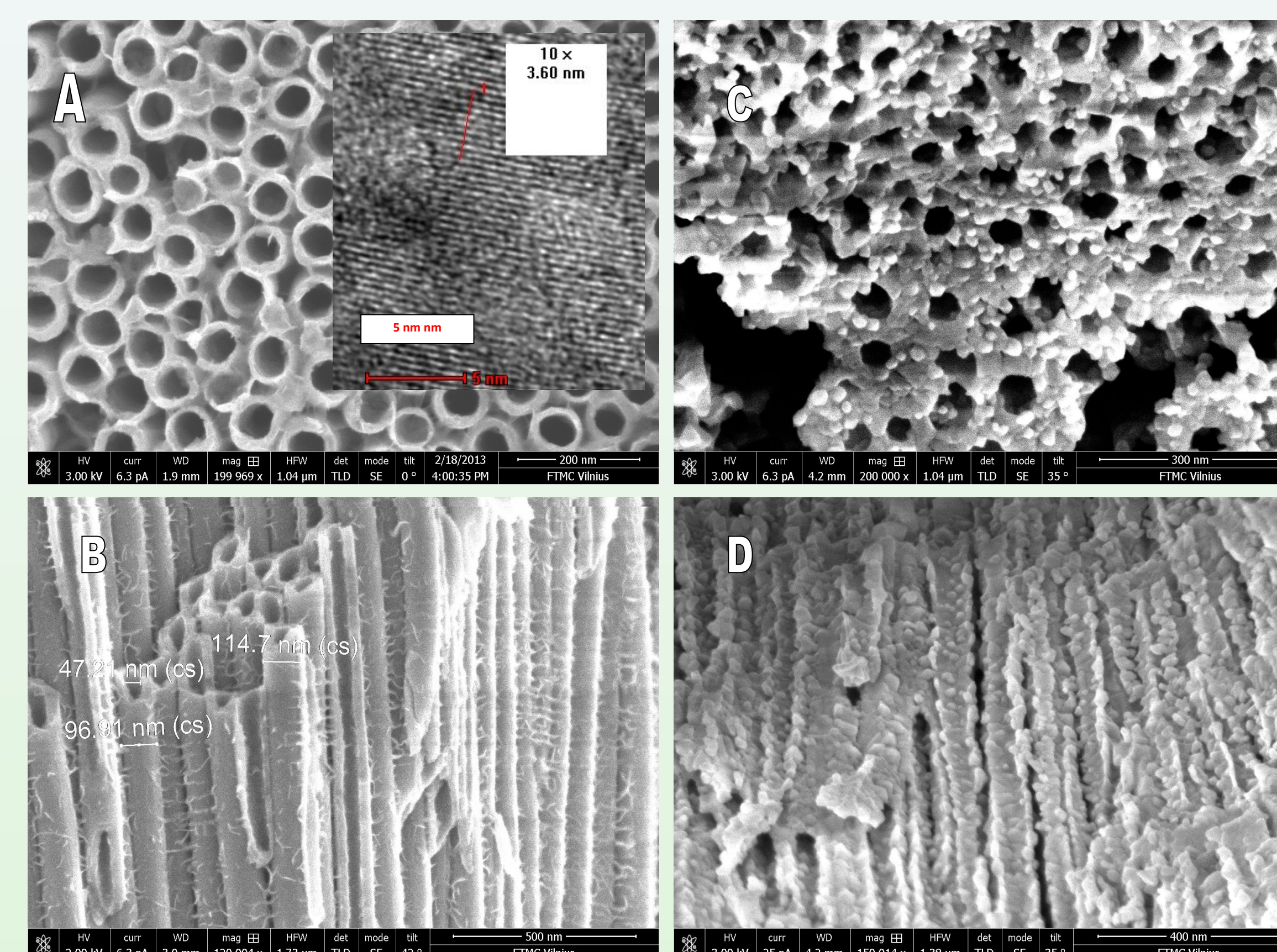


TiNT after treatment

The current-time curves for Ti anodizing in ethylene glycol solution containing NH<sub>4</sub>F and water at constant voltages of 30, 40 and 60 V



## RESULTS



Top-side (A,C) and cross-sectional (B,D) FESEM views of the TiNT film before (A,B) and after AC treatment in the solution containing 0.1 Cu(CH<sub>3</sub>COO)<sub>2</sub> + 0.1 mol L<sup>-1</sup> Mg(CH<sub>3</sub>COO)<sub>2</sub> + CH<sub>3</sub>COOH up to pH 5.3 at a constant current density of 0.5 A dm<sup>-2</sup> for 10 min. TiNT was formed by Ti surface anodizing in the Etg solution containing 0.3 NH<sub>4</sub>F and 2.0 wt% H<sub>2</sub>O at 50 V for 40 min followed voltage decrease by 1.0 V min<sup>-1</sup> down to 30 V and calcination at 500 °C for 2 h.

One can expect that owing to semiconducting properties of crystalline TiNT films alternating current can be an effective approach towards deposition of various materials inside the TiNTs providing that suitable solution composition and treatment regime is chosen. From the SEM images the covering of TiO<sub>2</sub>nanotubewalls and TiNT film surface with numerous particles can be clearly seen.

Note that just after ten minutes of AC treatment at alternating current density ( $j_{ac}$ ) of 0.35 A dm<sup>-2</sup> the inner diameter of TiO<sub>2</sub> tubes (45-50 nm in diameter at the open end) narrowed significantly but remained unclogging. Moreover, the AC treatment results in quite uniform deposition of nm-scaled species both inside and outside the tubes along the nanotube length of approximately 5.5 nm in the case of TiNT films formed during 30 min. Again, the content of deposited material and the size of particles can be easily controlled by duration of AC treatment and processing regime.

In our studies we employed quite wide range of AC current densities, starting from ~ 0.15 A dm<sup>-2</sup>. However, in the case of  $j_{ac} \geq 0.5$  Adm<sup>-2</sup> or longer deposition times even at  $j_{ac} \geq 0.35$  A dm<sup>-2</sup>, TiNT films were destroyed in the corners at some points of a specimen and peeled off from the Ti substrate.

## CONCLUSIONS

The influence of parameters such as applied voltages, anodizing time, electrolyte temperature and pH of electrolyte on the outer diameter of nanotubes and length of TiO<sub>2</sub> nanotubes were investigated. In the experiments the following parameters were used: applied voltage from 30 to 60; electrolyte temperature from 5 to 40 °C; 6, 7 and 8 for pH of electrolyte and 3, 6 and 10 h for anodizing time. It was shown that nanotube length increased with increasing voltage, temperature and anodizing time. Also outer diameter of nanotube increased with increasing voltage and temperature, whereas outer diameter of nanotubes decreased significantly with increasing pH and no considerable change was observed with increasing anodizing time.

It was shown that through alternating current treatments of TiNT film in the aqueous solution of Cu(II) and Mg(II) acetates a uniform loading of pure Cu<sub>2</sub>O nanocrystals in various amounts onto and inside the TiO<sub>2</sub> nanotubes can be obtained.

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