

ELECTROPHORETIC DEPOSITION OF TiO₂-MULTI-WALLED CARBON NANOTUBE COMPOSITE COATINGS: MORPHOLOGICAL STUDY

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Abstract: A homogenous TiO₂ / multi-walled carbon nanotubes(MWCNTs) composite film were prepared by electrophoretic co-deposition from organic suspension on a stainless steel substrate. In this study, MWCNTs was incorporated to the coating because of their long structure and their capability to be functionalized by different inorganic groups on the surface. FTIR spectroscopy showed the existence of carboxylic groups on the modified carbon nanotubes surface. The effect of applied electrical fields, deposition time and concentration of nanoparticulates on coatings morphology were investigated by scanning electron microscopy. It was found that combination of MWCNTs within TiO₂ matrix eliminating micro cracks presented on TiO₂ coating. Also, by increasing the deposition voltages, micro cracks were increased. SEM observation of the coatings revealed that TiO₂ /multi-walled carbon nanotubes coatings produced from optimized electric field was uniform and had good adhesive to the substrate.

Keywords: Carbon nanotubes, TiO₂ nanoparticles, Electrophoretic deposition, Nanocomposites, Coatings.

1. INTRODUCTION

Electrophoretic deposition (EPD) is a famous method to produce carbon nanotube – ceramic nanocomposite coatings and films from powder suspensions [1]. EPD is achieved via movement of charged particles in aqueous or organic suspensions and deposited onto an oppositely charged electrode under the action of an applied electric field. EPD can produce thin and nanostructure films on different and irregular shaped substrates with short deposition time, no required binder, easy control of coating thickness, low cost and production of a film with high purity [1-2].

TiO₂ due to its high biocompatibility, chemical stability and thermal durability as well as high hardness and corrosion resistance, making it a very attractive material for biomedical applications, high efficient solar cells and wear protection coatings [3-8]. Photocatalysis is another field where TiO₂ is used, the crystalline phase anatase being a very effective photocatalyst with wide band gap [9-11].

MWCNT are composed of concentric tubes that are held together by van der Waals bonding between the layers. The properties of nanotubes depend on the helicity (the orientation between

the graphitic hexagons and the nanotube axis), the diameter and length of the tubes, and the crystalline quality [12]. The high potential of CNTs for applications in functional and biomedical devices is based on their nanomorphology and outstanding mechanical and electrical properties [13-15].

Composing of CNTs and TiO₂ nanoparticles can lead to exciting novel composite materials and devices for development of functional applications, biomedical implant coatings and tissue engineering scaffolds [16-17]. CNTs are outstanding carrier substrates for TiO₂ nanoparticles [18], because CNTs have a wide range of length scale, its ability of forming a carboxylic group on the surface [12,19-21] and high surface area. Moreover a dispersion of TiO₂ on the MWCNTs surface could create many active sites for the photocatalytic degradation [22] improvement of TiO₂ mechanical properties [21]. In addition, Jarernboon et al. found that carbon nanotubes could be a suitable material in diminishing TiO₂ film crack and improving the solar cell efficiency [21]. Adding a material which is long and contains carboxylic group into the TiO₂ solution, should result in bonding to the hydroxyl groups on the surface of TiO₂ particles.

In this study, the effect of the carbon nanotube concentration and deposition voltages on microcracks formation was investigated.

2. Experimental procedure

2. 1. Modification of MWCNTs

Multiwall carbon nanotubes (MWCNTs) were modified by nitric acid in ultrasonic bath for 10 min and refluxed in boiling points of acid then the oxidized tubes were washed to pH [7], giving a yield of about 50 wt%.

2. 2. Preparation of TiO₂ and TiO₂/MWCNTs Films

The stainless steel 316L was used as cathode and anode for coating the TiO₂ film and TiO₂/MWCNTs composite films were prepared by electrophoretic co-deposition. The used TiO₂ nanoparticles was the commercially available type P25 (Degussa, Germany) with particle size 21nm. The TiO₂ suspension consists of 0.5g nanocrystalline TiO₂ powder and 0.04g I₂ in 50 ml acetylacetone. The TiO₂ films were prepared at different voltages (10V, 15V and 20V) for 4 min deposition time. The TiO₂/MWCNTs suspensions were contained at various weight ratios of CNT to TiO₂ (1:4 and 1:100).

2. 3. Characterization of Deposits

The surface morphology of coatings was analyzed by scanning electron microscopy

(SEM). The film crystallization and carbon nanotubes chemistry was characterized by X-ray diffraction and Fourier transform infrared (FTIR), respectively. FTIR was used to recognize the presence of COOH groups on the modified carbon nanotube.

3. RESULTS AND DISCUSSION

3. 1. Characterization of TiO₂ Deposits

Fig. 1 shows the XRD pattern of the TiO₂ nanopowders that was used for the present work. Its crystallographically is composed of anatase (70%) and rutile (30%). The TiO₂ coating was

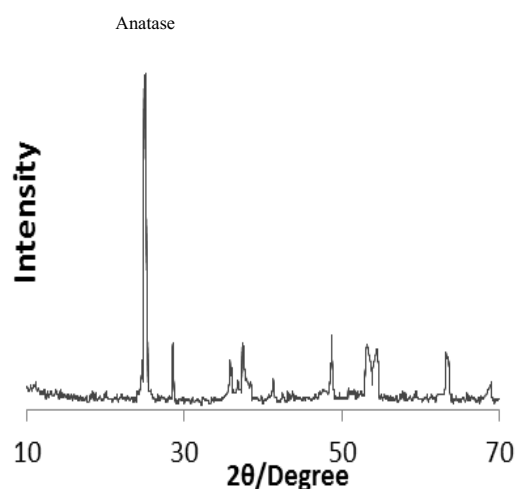


Fig. 1. XRD pattern of the titania raw materials

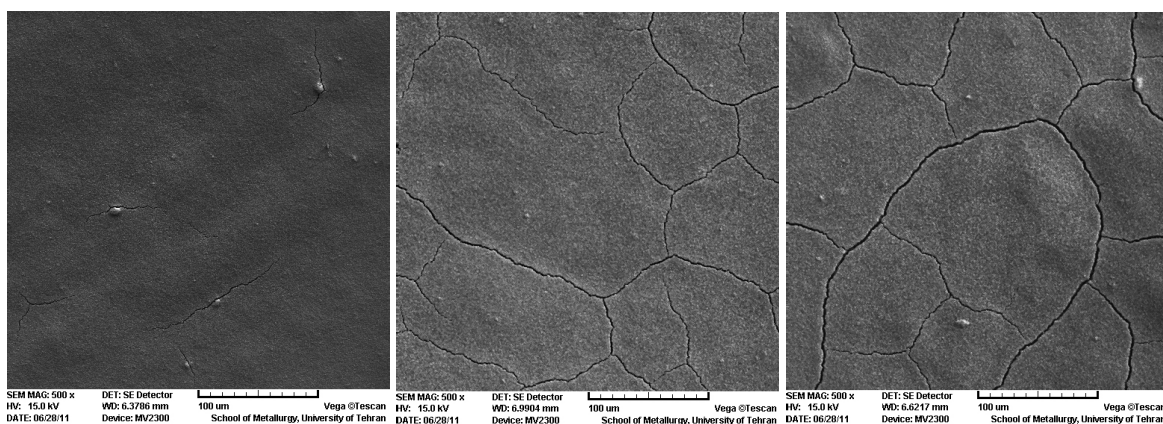


Fig. 2. Low magnification SEM images at TiO₂ films deposited at (a) 10 V (b) 15 V (c) 20 V in constant times 4min.

successfully produced on stainless steel 316 by EPD. Due to electrostatic attraction force between TiO_2 and a cathode surface, nanoparticles were deposited on the conductive substrate. TiO_2 nanopowders make the electrostatic force with the cathode surface, because TiO_2 nanoparticles were accumulated with positive charges which were generated from an interaction between I_2 and acetylacetone [22]. The surface of the pure TiO_2 coatings in various voltages were analyzed with SEM as shown in Fig. 2. These data demonstrate that cracks increases with an increase of the deposition voltage on the surface of TiO_2 films.

3. 2. Synthesis, Characterization of MWCNTs and MWCNTs Coating

In this study, MWCNTs were used because of their long structure and their ability in producing carboxylic groups on the surface. The presence of COOH on the modified CNTs surface was

analyzed by FTIR spectroscopy and is shown the existence of $\text{C}=\text{O}$, $\text{C}-\text{O}$ stretching of carboxylic groups (see Fig. 3). The functionalized carbon nanotubes film can be prepared on different substrate by the EPD method [17]. Because of its negative charged on the surface, MWCNTs can be deposited on the positive electrodes. SEM image of the MWCNTs coating by electrophoretic deposition is shown in Fig. 4.

SEM observation of the TiO_2 / MWCNTs deposited reveals that the quality of the coatings is varied, intensively. As shown in Fig. 5, combination of MWCNTs within TiO_2 matrix prevents microcracks that are presented on the pure TiO_2 coating and with increasing the deposition voltages, the microcracks are increased. The coating for the weight ratio 1:4 exhibit a homogenous coating without crack at a 10V deposition voltage (a) and by increasing the voltages (c and e), the microcracks were appeared in the coatings compared with pure TiO_2 in the same voltages; the cracks length were

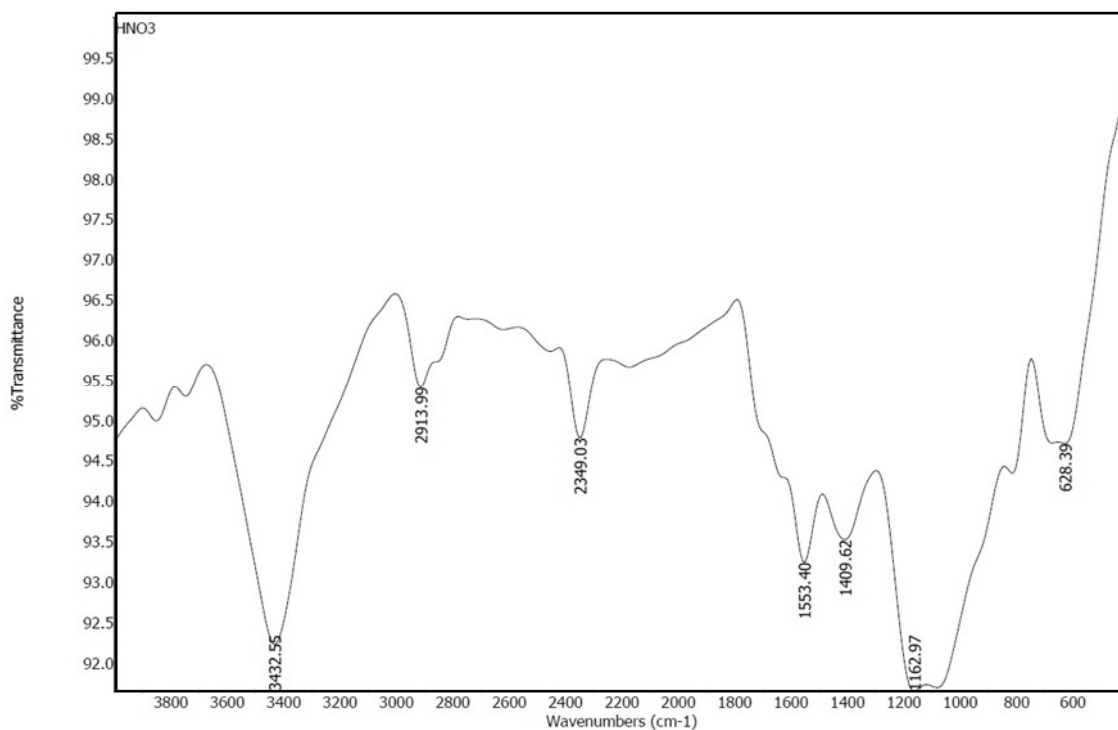


Fig. 3. FTIR spectra of the acid treated multiwall carbon nanotubes

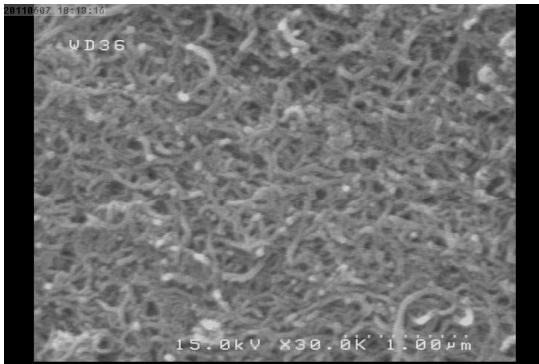


Fig. 4. SEM image of MWCNT film obtained by EPD on stainless steel substrate.

very short and small. The coatings in concentration ratio of (CNT:TiO₂) 1:100 did not exhibit uniform surfaces in all applied voltages because of very low amount of MWCNTs.

MWCNTs eliminate microcracks by creation the bonding to TiO₂ nanoparticles via interaction of carboxylic groups with hydroxyl groups of TiO₂ as shown in Fig. 6. By bonding H⁺ on the surface of TiO₂ with negative ions on the surface of MWCNTs, it probably blocks the way to interaction hydroxyl groups of TiO₂ with the

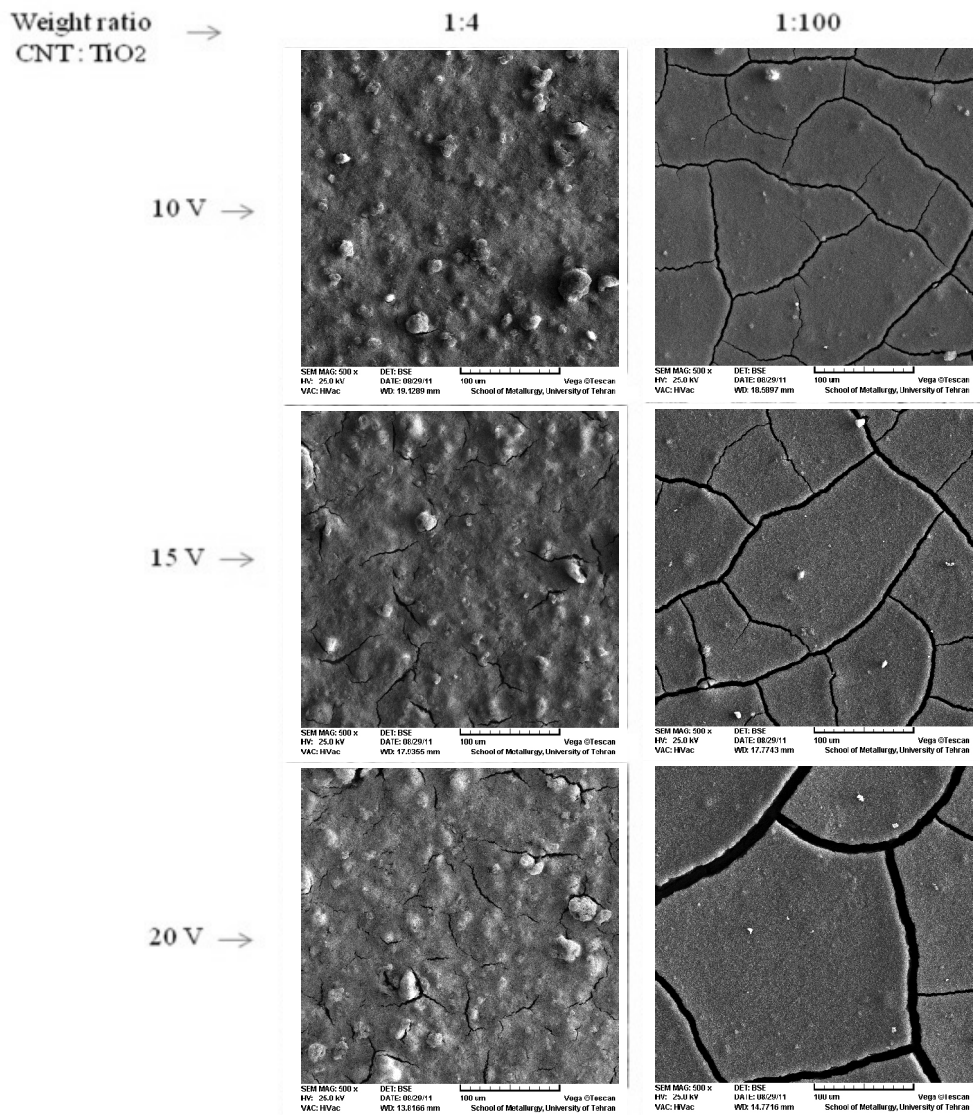


Fig. 5. Low magnification SEM images of the weight ratio 1:4 and 1:100 CNT:TiO₂ composite films for all three deposition voltages (5 V, 10 V, 15V).

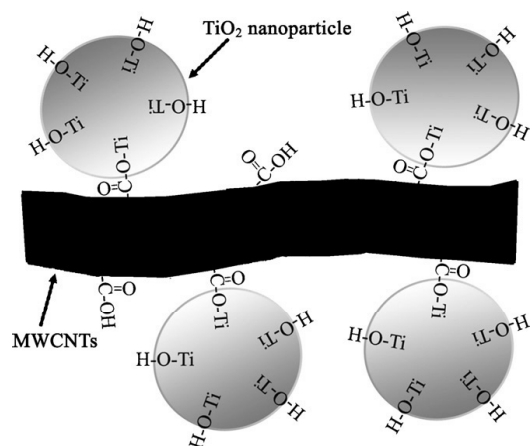


Fig. 6. Schematic illustrating the possible chemical interaction between the modified MWCNTs and TiO_2 nanoparticles.

remained carboxylic groups. Therefore, positive ions are dominant in the suspension and are moved to cathode electrode [21].

Fig. 6. Schematic illustrating the possible chemical interaction between the modified MWCNTs and TiO_2 nanoparticles [22].

4. CONCLUSION

TiO_2 , MWCNTs and $\text{TiO}_2/\text{MWCNTs}$ composite films could be deposited successfully on the stainless steel substrate by electrophoretic deposition. The homogeneity of $\text{TiO}_2/\text{MWCNTs}$ composite films was dependent upon the weight ratio of MWCNTs and the deposition voltages. It was observed that by adding MWCNTs into the TiO_2 solution the microcracks of the films were considerably reduced compared to the TiO_2 coatings. The crack problem is reduced by bonding hydroxyl and carboxylic group on the surface of TiO_2 and MWCNTs, respectively. SEM images revealed that the quality of the coatings was obtained in weight ratio of 1:4 (MWCNTs: TiO_2).

REFERENCES

1. Boccaccini, A. R. and Zhitomirsky, I.,

- “Application Of Electrophoretic And Electrolytic Deposition Techniques In Ceramics Processing”. *J. Solid State Mater Sci.*, 2002, 6, 251-260.
2. Boccaccini, A. R., Cho, J., Subhani, T., Kaya, C. and Kaya, F., “Electrophoretic deposition of carbon nanotube–ceramic nanocomposites”. *J. European Ceramic Society.*, 2010, 30, 1115-1129.
3. Cui, C., Liu, H., Sun, J., Wang, R., Liu, S., Greer, L., “Fabrication And Biocompatibility Of Nano- TiO_2 / Titanium Alloys Biomaterials”. *J. Mater. Lett.*, 2005, 59, 3144-3148.
4. Sadeghzadeh Attar, A., Sasani Ghamsari, M., Hajiesmaeilbaigi, F. and Mirdamadi, Sh., “Modifier ligands effects on the synthesized TiO_2 nanocrystals”. *J. Mater. Sci.* 2008, 43, 1723-1729.
5. Janitabar Darzi, S., Mahjoub, A. R., Nilchi, A. R., Rasouli Garmarodi, S., “Heat treatment effects on non-thermal sol-gel driven mesoporous $\text{TiO}_2/\text{SiO}_2$ ”. *Iran. J. Mater. Sci. Eng.*, 2011, 8, 20-26.
6. Kokubo, T., Kim, H.M. and Kawashita, M., “Novel bioactive Materials With Different mechanical Properties”. *J. Biomater.*, 2003, 24, 2161-2175.
7. Janitabar Darzi, S., Mahjoub, A. R. and Sarfi, S., “Visible-Light-Active Nitrogen Doped TiO_2 Nanoparticles Prepared By Sol-Gel Acid Catalyzed Reaction”. *Iran. J. Mater. Sci. Eng.*, 2012, 9, 17-23.
8. Hashimoto, K., Irie, H. and Fujishima, A., “ TiO_2 Photocatalysis: A Historical Overview And Future Prospects”. *J. Appl. Phys.*, 2005, 44, 8269-8285.
9. Safaei-Naeini, Y., Aminzare, M., Golestani-Fard, F., Khorasanizadeh, F. and Salahi, E., “Suspension Stability Of Titania Nanoparticles Studied By UV-VIS Spectroscopy Method”. *Iran. J. Mater. Sci. Eng.*, 2012, 9, 62-68.
10. Iijima, S., “Carbon nanotubes: Past, present, and future”. *J. Physica. B.*, 2002, 323, 1-5.
11. Cho, J., Schaab, S., Roether, J. A. and Boccaccini, A. R., “Nanostructured Carbon NanoTube/ TiO_2 Composite Coatings Using Electrophoretic Deposition (EPD)”. *J. Nanopart. Res.*, 2008, 10, 99-105.

12. Jitianu, A., Cacciaguerra, T., Benoit, S., Delpeux, S., Be'guin, F. and Bonnamy, S., "Synthesis and characterization of carbon nanotubes-TiO₂ nanocomposites". *J. Carbon.*, 42, 2004, 1147-1151.
13. Jac Faripour Maybody, J., Nemati, A. and Salahi, E., "Synthesis And Properties Of MWCNT-HAP Composites Via Sol-Gel Technique". *Iran. J. Mater. Sci. Eng.*, 2013, 10, 57-63.
14. Zanello, L. P., Zhao, B., Hu, H. and Haddon, R. C., "Bone Cell Proliferation On Carbon Nanotubes". *J. Nano Lett.*, 2006, 6, 562-567.
15. Yu, Y., Yu, J. Y., Yu, J. G., Kwok, Y. C., Che, Y. K. and Zhao, J. C., "Enhancement Of Photocatalytic Activity Of Mesoporous TiO₂ By Using Carbon Nanotubes". *J. Appl. Catal.*, 2005, 289, 186-196.
16. Boccaccini, A. R., Cho, J., Roether, J. A., Thomas, B. J. C., Minay, E. J. and Shaffer, M. S. P., "Electrophoretic deposition of carbon nanotubes". *J. Carbon* 44., 2006, 3149-3160.
17. Gao, B., Yue, G. Z., Qiu, Q., Cheng, Y., Shimoda, H., Fleming, L. and Zhou, O., "Fabrication And Electron Field Emission Properties Of Carbon Nanotube Films By Electrophoretic Deposition". *J. Adv. Mater.*, 2001, 13, 1770-1773.
18. Oh, S. J., Zhang, J., Cheng, Y., Shimoda, H. and Zhou, O., "Liquid-phase fabrication of patterned carbon nanotube field emission cathodes". *J. Appl. Phys. Lett.*, 2004, 84, 3738-3740
19. Thomas, B. J. C., Boccaccini, A. R. and Shaffer, M. S. P., "Multi-Walled Carbon Nanotube Coatings Using Electrophoretic Deposition (EPD)". *J. Am. Ceram. Soc.*, 2005, 88, 980-982.
20. Lee, S. and Sigmund, W. M., J. "Formation Of Anatase TiO₂ Nanoparticles On Carbon Nanotubes. *Chem*". *Commun.*, 2003, 225, 780-781.
21. Jarernboon, W., Pimanpang, S., Maensiri, S., Swatsitang, E. and Amornkitbamrung, V., "Effects Of Multiwall Carbon Nanotubes In Reducing Microcrack Formation On Electrophoretically Deposited TiO₂ Film". *J. Alloys and Compounds.*, 2009, 476, 840-846.
22. Grätzel, M., "Conversion Of Sunlight To Electric Power By Nanocrystalline Dye-Sensitized Solar Cells". *J. Photochem. Photobiol. A.*, 2004, 164, 3-14.