



Inexpensive sol-gel synthesis of multiwalled carbon nanotube-TiO₂ hybrids for high performance antibacterial materials

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ABSTRACT

This study reports an inexpensive sol-gel method to synthesize TiO₂-CNT hybrid materials. Synthesized TiO₂-CNT materials show strong antibacterial activity in the absence of light. Cheap TiO₂ source TiOCl₂ is used during synthesis in the absence of high temperatures, high pressures and organic solvents. TiO₂-CNT materials with 0, 2, 5, 10, 15 and 20 wt% of CNT were synthesized and compared for antibacterial activity, surface area, porosity, crystalline structure, chemical state, and HaCaT cell proliferation. The antibacterial strength of hybrid materials increased significantly with the increase in CNT loading amount, and the TiO₂-CNT samples with a CNT loading of 10 wt% or more nearly removed all of the E.coli bacteria. HaCaT cell proliferation studies of synthesized hybrid materials illustrated that prepared TiO₂-CNT systems exhibit minimum cytotoxicity. The characteristics of prepared materials were analyzed by means of XRD, FTIR, Raman spectroscopy, XPS, TEM, and nitrogen gas physisorption studies, compared and discussed.

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1. Introduction

Titanium dioxide (TiO₂ or titania) is an important material for applications in self-cleaning surfaces, air purification, and water purification. TiO₂ possesses antibacterial properties due to its superhydrophilicity and strong oxidation activity in the presence of light [1]. Biomedical applications of TiO₂-based materials are widespread primarily because of its nontoxicity, ability to produce reactive oxygen species (ROS) under light and potential binding specificity for DNA and proteins [1,2]. These characteristics have motivated numerous biological studies on TiO₂, notably in the fields of drug delivery, imaging guided therapy, binding of proteins, binding of antibodies, biodegradable materials, anti-fungal materials, and antibacterial materials [1–3].

The use of titania as a disinfectant offers many advantages because of its stability, non-toxicity, and low-cost [4]. Yet commercial use of TiO₂ as antibacterial material for advanced biomedical applications is obstructed due to certain complications. Fundamentally TiO₂ possesses antibacterial and antifungal properties in the presence of light, presumably due to the generation of reactive oxygen species such as hydroxyl radicals ($\cdot\text{OH}$), hydrogen peroxide (H₂O₂) and superoxide ions (O₂^{•−}) [5]. However, UV irradiation, which is required for the generation of reactive oxygen species from TiO₂, is expensive, hazardous, and kills bacteria even in the absence of disinfectant materials. Furthermore, only 5%

of sunlight radiation is in the UV region, so it is practically not possible to use sunlight either. The cytotoxicity of TiO₂ nanoparticles in the presence of light (phototoxicity) is an additional limitation to various biomedical applications [1,6].

Blending TiO₂ with other materials is a successful strategy for enhancing the physicochemical properties of TiO₂ [7]. For instance, incorporation of 5–7% Fe₂O₃ into TiO₂ can improve the surface area, porosity, crystal structure, and optical properties of TiO₂ [8–10]. Likewise, the intriguing goal of synthesizing TiO₂ materials with antibacterial properties in the absence of light irradiation can be accomplished by incorporating strong antibacterial materials into TiO₂ matrix. Ideally, surface properties of the antibacterial dopant should allow efficient contact with TiO₂ and bacteria. CNTs are a good candidate for this purpose due to their robust antibacterial properties and exceptional morphological characteristics [11]. Various studies have demonstrated that carbon nanotubes exhibit strong antimicrobial characteristics of carbon nanotubes due to synergistic physical and chemical effects [11,12]. The physical destruction of bacteria by CNTs is attributed to the lysing of walls and membranes of microbes [13]. The loss of the membrane potential of bacteria occurs through the release of DNA and RNA [13]. Chemical bacteria destruction process occurs, as CNTs can increase the cellular oxidative stress to interrupt a specific bacterial process [12,14].

TiO₂ is typically synthesized from titanium chloride (TiCl₄) or titanium alkoxides (Ti(OR)₄) [15]. Adopting Titanium oxychloride (TiOCl₂) as TiO₂ precursor is inexpensive and it avoids the use of high temperatures, high pressures and organic solvents [16]. Furthermore, TiOCl₂ yields the

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Table 1

Intended weight percentages and weight percentages obtained from EDS for TF, TFC2, TFC5, TFC10 and TFC20.

Samples	Intended weight %			Weight % obtained from EDS		
	CNT (carbon)	TiO ₂	Fe ₂ O ₃	CNT (carbon)	TiO ₂	Fe ₂ O ₃
TF	0	95	5	0	93.8	6.2
TFC2	2	93.1	4.9	2.2	93.7	5.1
TFC5	5	90.2	4.8	5.2	89.9	4.9
TFC10	10	85.5	4.5	10.1	85.3	4.6
TFC20	20	76	4	19.9	76.1	4

TiO₂ with high purity and even distribution [15–17]. Likewise, synthesis of TiO₂-CNT hybrid materials is possible through several techniques including sol-gel method, arc discharge method, electrospraying, and hydrothermal fabrication. Covalent and non-covalent approaches for the synthesis of these hybrids have been investigated [18]. The synthesis strategies for creating TiO₂-CNT structures typically involve multifaceted processes, the use of oxidizing agents, acidic environments or linker molecules. Recently, Ashkarran et al. [19] reported the synthesis of TiO₂-CNT hybrid nanostructures by a combination of the arc discharge and a sol-gel method. Zhang et al. [20] used MCPBA (m-chloroperbenzoic acid) in benzene as an oxidizing agent for CNT to synthesize TiO₂-CNT nanocomposites and heat treated the TiO₂-CNT precursor solution at 700 °C followed by a press at 250 kg/cm². In one of the pioneering works on using TiO₂/CNT heterojunctions for antibacterial purposes, Akhavan et al. used Si substrate to grow TiO₂/CNT arrays [21]. In another work, Akhavan et al. [22] prepared CNT-doped TiO₂ thin films with various CNT contents and demonstrated the photoinactivation of *Escherichia coli* (E.coli) bacteria. In their work, the sol-gel method was used to prepare CNT-doped TiO₂ in the presence of nitric acid, and products were dip coated to obtain films. To this end, direct, inexpensive synthesis of TiO₂-CNT hybrids while avoiding the addition of oxidizing agents, extra linker molecules, extended reaction times, expensive equipment and preserving the intrinsic properties of both the CNTs and the TiO₂ is a reasonably attractive goal [18].

In the present work, an inexpensive in-situ sol-gel technique was used to obtain TiO₂-CNT hybrid materials with desired compositions. The synthesized materials possess strong antibacterial properties in the absence of light. A slight addition of 5 wt% CNT was enough to decrease the bacteria survival rate to as low as 22%. Bacterial survival rate for the samples treated with TiO₂-CNT hybrids with 10 wt% and 20 wt% were less than 10%. The effects of increasing CNT content on the porosity, surface area, chemical state and further physicochemical properties of TiO₂ were investigated and discussed in detail.

2. Experimental methods

2.1. Materials

TiOCl₂ (25 wt% (weight %)) was obtained from Kukdong Chemicals Company Limited, South Korea. Multiwalled carbon nanotubes (CM-100) were supplied by Hanwha Nanotech, South Korea. FeCl₂·4H₂O (Reagent plus-99%) and FeCl₃·6H₂O were purchased from Sigma-Aldrich. *N,N*-dimethylformamide (DMF, 99.5%) and ammonium hydroxide (extra pure) were procured from Daejung Chemical and Metals Company Ltd., South Korea. All chemicals were used as obtained without further treatment.

2.2. Synthesis of TiO₂-CNT hybrids

TiO₂-CNT samples were synthesized by an in-situ sol-gel technique, with the loading amount of CNT varied from 0 to 20 wt%. Several reports indicate that the addition of 5–8% Fe₂O₃ in TiO₂ increases the surface characteristics such as porosity and surface area [8,9]. For this, 5 wt% Fe₂O₃ was added to TiO₂. As a standard, 65 g TiOCl₂, 1.19 g FeCl₃·6H₂O

and 0.34 g of FeCl₂·4H₂O were added to 150 mL of distilled water and stirred. 0 g, 0.14 g, 0.35 g, 0.7 g and 1.4 g of Multi-walled carbon nanotubes (MWCNTs) were added to this solution for the synthesis of 0%, 2%, 5%, 10% and 20% CNT in TiO₂, respectively. CNTs were dispersed in the DMF solution by sonication for 30 min before addition. After stirring well, ammonia was added dropwise until the pH of the reaction solution reached 9, and then the solution was left for aging at 80 °C for 2 h. After aging, particles were separated by centrifugation (10,000 rpm for 10 min). The obtained solids were washed with sufficient ethanol and distilled water and centrifuged again. Multiple cycles of washing and centrifugation were performed to ensure the removal of unwanted chemicals. The obtained materials were dried in a convection oven for 12 h at 80 °C. After drying, the products were calcined at 400 °C for 2 h. During synthesis, only the MWCNT feeding amount was changed, i.e., the amounts of the Ti and Fe precursors were not changed. However, for synthesizing pure TiO₂, no Fe precursors or MWCNT were added. The rest of the procedure was the same.

Nomenclature of the synthesized materials was introduced for simplicity: TiO₂ was named T, TiO₂ and Fe₂O₃ with no CNTs was named TF, and TiO₂, Fe₂O₃, and CNT materials were named TFC. Digits were added after TFC to signify the weight percentage of CNT in the material. For example, 10 wt% CNT material was named TFC10. Furthermore, TFC10 is the material calcined at 400 °C. The as-synthesized, un-calcined form of TFC10 is TFC10-AS.

2.3. Antibacterial activity tests

The gram negative bacteria strains of *Escherichia coli* (E.coli) were used to test the antibacterial properties of prepared samples. No light source was used during antibacterial tests. All glassware and samples were sterilized by autoclaving (Biofree autoclave) at 120 °C for 30 min at 15 psi prior to the microbiological evaluation. In our experiments, the E.coli TOP10 test strain was grown in Luria–Bertani (LB) medium (Difco Laboratories, Detroit, Michigan, USA) at 37 °C. The media was solidified with 1.8% (w/v) agar (Duchefa Biochemie BV, Haarlem, The Netherlands) as necessary. The concentration of E.coli TOP10 was adjusted to 1 × 10⁵ CFU/mL (colony-forming units per milliliter). Approximately 0.1 mL of bacterial strains (E.coli TOP10) at different concentrations of the prepared samples was mixed in a petri dish (90 mm). The prepared mixture was spread on a nutrient agar plate (Duchefa Biochemie BV, Haarlem, The Netherlands) and incubated at 37 °C for 24 h. The visible cells of each plate were then counted by quantifying the colony forming units (CFUs). The percentage of each group was calculated by comparing to a control. Each test was performed thrice and average values were reported. In addition to this test, concentration-contact testing/quantitative suspension test method was also carried out to verify the antibacterial characteristics of TiO₂-CNT hybrids. Detailed procedure of concentration-contact test is reported in our previous report [23]. Same procedure is followed in this study.

2.4. Cell viability assay

The human immortalized keratinocyte cell line, HaCaT, was grown in Dulbecco's modified eagle's medium, which included high glucose (DMEM) (Gibco BRL, Carlsbad, CA, USA) supplemented with 10% FBS (Wisent, St-Bruno, QC, Canada) and 1% penicillin-streptomycin (p/s) (Gibco BRL, Carlsbad, CA, USA) under standard culture conditions, i.e. 37 °C and 5% CO₂. Upon 80–90% confluence, the cells were enzymatically lifted and counted using a hemocytometer. Approximately 1 × 10⁴ cells/well were seeded in a 96 well plate. The following day, cells were treated with different concentrations (i.e., 0.5, 2.5, 6, and 12 µg/mL) of each TF/TFC composition for 72 h. Cells were observed under a light microscope (Olympus, Tokyo, Japan) and representative images were captured. Thereafter, the proliferation of cells was evaluated using a 4-[3-(4-iodophenyl)-2-(4-nitrophenyl)-2H-5-tetrazolol]-1,3-benzene disulfonate (WST-1) EZ-cytox cell viability assay kit (ITSBIO, Seoul,

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