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TiO_2 NANOPARTICLE COATING FOR POTENTIAL ANTIMICROBIAL APPLICATION IN FOOD INDUSTRY

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ABSTRACT

This work aims to develop titanium dioxide (TiO_2) nanoparticle coating for potential antimicrobial application in food industry due to the unique and improved photocatalytic antimicrobial properties of the nanometer sized TiO_2. TiO_2 nanoparticles were produced by metal organic chemical vapour deposition (MOCVD) method and were dispersed and stabilized in aqueous suspension using polyacrylic acid (PAA). The suspension was then coated on quartz glass, whereby the light transmittance through the coated glass was determined using UV-vis spectrophotometer. The potential antimicrobial application of the nanoparticle coating was demonstrated via the agar diffusion test in which the coated glass was placed on the agar plate grown with the *Escherichia coli* (*E. Coli*) culture as the model microorganism. The concentration of *E. Coli* on the agar plate decreased upon illumination of UV light thus proved that the TiO_2 nanoparticle coating exhibit antimicrobial activity.

Keywords: *titanium dioxide, nanoparticle, coating, antimicrobial, food industry.*

INTRODUCTION

Nanoparticles have attracted considerable attention because they exhibit unique and improved properties compared to their bulk material counterparts [1]. They show quantum size effects in which the physical and chemical properties of materials are strongly dependent on particle size. At nano-scale level, the particle size decreases and surface area of the particles increases dramatically. This is one of the desired features for the nanoparticles to be used and exploited for photocatalytic applications. The most popular choice of photocatalyst is titanium dioxide (TiO_2) and the advent of nanotechnology has greatly improved the photocatalytic properties of TiO_2. The photocatalytic reaction of TiO_2 has been used to inactivate a wide spectrum of microorganisms [2, 3, 4].

TiO_2 is non-toxic and has been approved by the American Food and Drug Administration (FDA) for use in human food, drugs, cosmetics and food contact materials. Currently, there is considerable interest in the antimicrobial property of TiO_2 for meeting hygienic design requirements in food industry particularly in food processing and in food packaging surfaces. Bactericidal and fungicidal effects of TiO_2 on for example *Escherichia coli (E. Coli)*, *Salmonella chloeraesuis*, and *Vibrio parahaemolyticus* have been reported [4, 5]. The development of TiO_2-coated or incorporated food preparing equipment and food packaging has also received attention.

Numerous types of other substances have been utilized as antimicrobial agents in food industry including silver compound and polymers, predominantly chitosan. In food industry, the main purpose of antimicrobial agent is to act against microorganisms and enhance the functions of conventional food packaging, which are shelf life extension, maintenance of quality, and safety assurance [6]. The antimicrobial agents inhibit spoilage and reduce pathogenic microorganisms [7]. The antimicrobials helps extend the shelf life of foods by extending the lag period of microorganisms, thereby diminishing their growth and number.

Microorganisms can be killed with TiO_2 upon illumination of light due to its photocatalytic properties. Hydroxyl radicals and reactive oxygen species generated on the illuminated TiO_2 surface play a role in inactivating microorganism by oxidizing the polyunsaturated phospholipid component of the cell membrane of microbes [8, 9]. The use of nanometer sized TiO_2 has the potential to further enhances the antimicrobial activity of TiO_2. Effective antimicrobial agent that can extend the shelf life, maintain the quality, and assure the safety of the food can be developed by incorporating TiO_2 nanoparticles in food preparing equipment and food packaging materials. This creates a large commercial potential for TiO_2 nanoparticles application in food industry.

Note that to date, the migration issue of TiO_2 nanoparticles from food preparing equipment and from food packaging into food has become a safety concern in food industry. However, migration studies of TiO_2 nanoparticles are still ambiguous and insufficient. Thus, it cannot be ruled out that TiO_2 nanoparticles are actually migrate from food preparing equipment or food packaging into the food. More detailed studies need to be done in the future to verify this issue since TiO_2 itself has been approved by the FDA for use in food contact materials although the FDA might refer to the larger or bulk form of TiO_2.

MATERIALS AND METHODS

Preparation of TiO_2 Nanoparticle Coating.

TiO_2 nanoparticles were synthesized via a custom-built metal organic chemical vapour deposition (MOCVD) reactor at a fixed deposition temperature of 700°C. The precursor, titanium (IV) butoxide (TBOT) was introduced into the quartz tube using 400 mL/min nitrogen (N_2) as the carrier gas along with 100 mL/min oxygen (O_2) feed. The dimensions of the custom-built MOCVD system and the method used to produce TiO_2 nanoparticles have been described in detail elsewhere [10].

An amount of 0.05 g TiO_2 nanoparticles produced were then suspended in 100 mL of distilled water (pH adjusted to pH of 8.5). The nanoparticle aqueous suspension was dispersed and stabilized using 3 wt. % common dispersant which was polyacrylic acid (PAA) with average molecular weight (M_W) of 2000 g/mol. The suspension was ultrasonically irradiated using an ultrasonic homogenizer for 30 minutes. The detail method to prepare the TiO_2 nanoparticle suspension has been explained elsewhere [11].

Finally, the suspensions were coated on one side of 4 cm × 2.5 cm quartz glass using an air brush (AB931, Ingersoll Rand) and the coating were air dried. The light transmission spectra of the coating were determined using UV-vis spectrophotometer (Shimadzu UV-1650 PC) from 300 to 800 nm.

Agar Diffusion Test

To demonstrate that the TiO_2 nanoparticle coatings has the potential to be used in food industry, the antimicrobial activity of the coating was determined using a simple qualitative analysis via the agar diffusion test under UV light illumination.

Luria Bertani agar was first prepared as a medium for growing the *E. Coli*, one of the most common bacterial foodborne pathogens. An amount of 8.75 g of LB agar in powder form was mixed with 250 mL of distilled water in Duran bottle and the mixture was heated to allow all the solid particles to dissolve. The bottle together with the content was then autoclaved for 15 minutes at 121°C. After been cooled to 40°C, the mixture was poured into Petri dishes under laminar flow. The Petri dishes were inverted after the agar had been cooled and solidified.

E. Coli culture was then swabbed across the LB agar and the Petri dishes were put into the incubator at 37°C for 24 hours. After that, the nanoparticle coating (coated side) was placed on the agar covered with grown culture. The Petri dishes were then placed in a dark box. An 8W, 365 nm UV light was turned on. The images of the Petri dish before and after 12 hour of UV illumination were captured and compared.

RESULTS AND DISCUSSIONS

The characterization of the TiO_2 nanoaprticles and the nanoparticle aqueous suspension has been described in details elsewhere [10, 11]. According to our previous study [10, 11], the nominal size of the nanoparticles produced using this method was less than 50 nm and that the nanoparticles appeared to be relatively homogeneous and uniform in size. The mean particle diameter was found to be 12.7 nm while the

BET surface area of the sample was determined to be 86.9 m^2/g. The XRD pattern for the TiO_2 nanoparticles showed only peaks that correspond to the diffractions plane of anatase thus confirmed that the TiO_2 nanoparticles were in the pure anatase crystal structure. Moreover, the nanoparticle suspension prepared with addition of PAA dispersant remained stable for more 2 months. The addition of dispersant facilitated the TiO_2 nanoparticles to distribute evenly in the suspensions and hence produced better coatings.

A UV-vis spectrophotometer was used to determine the light transmittance through the coated glass produced in this study. This is important to ensure the visibility through the glass. The higher the light transmittance value, the better the visibility through the glass, hence the more aesthetic value of the glass that can be preserved. Fig. 1 shows that the percentage of light transmittance through the coated glass increases from around 80% to almost 99% as the wavelength was increased from 300 to 800 nm. The percentage of light transmittance value was low below 400 nm where the UV light range lies. At this range, more TiO_2 are available for absorption due to the excitation of electrons from valence band to the conduction band, thus decreases the transmittance.

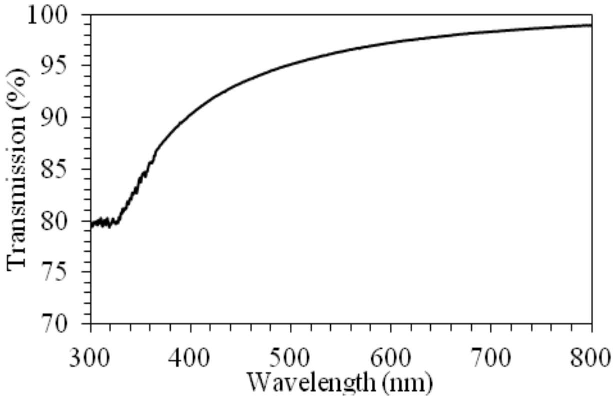

Fig. 1: Light transmission spectra of TiO_2 nanoparticle coating

Agar diffusion test was done to determine the potential ability of TiO_2 nanoparticle coating to be used as antimicrobial agent in food industry. Fig. 2 compared the concentration of the *E. Coli* culture on agar plate before and after the illumination of UV light. It can be seen from Fig. 2 that the coating exhibit antimicrobial ability because the coating was able to reduce the concentration of the *E. Coli* on agar plate after 12 hours period of time. It became more pronounced at the area where the coated glass was placed, whereby the zone is called the zone of inhibition. The zone of inhibition is the area where the growth of *E. Coli* is prevented by the antimicrobial agent. It is important to note that the size of the zone of inhibition (5.4 cm wide) is a measure of the antimicrobial agent's effectiveness. The larger the clear area around the coated glass, the more effective the antimicrobial agent. The concentration of the *E. Coli* increased as the distance from the coated glass increases.

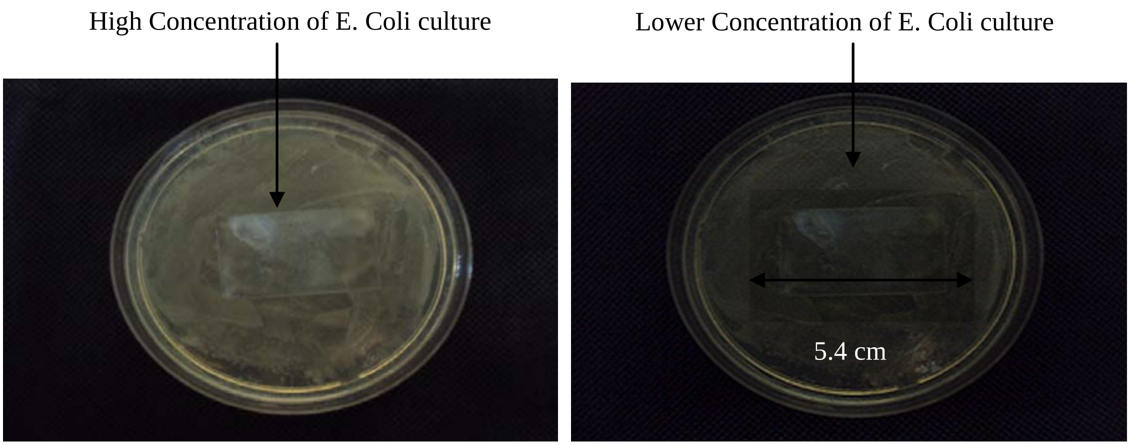

Fig. 2: The images of Petri dish with grown *E. Coli* culture (a) before and (b) after 12 hour of UV illumination.

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The mechanisms for the events occurred on the TiO_2 nanoparticle coating can be explained as follows. When TiO_2 nanoparticles are irradiated with light suitable to its bandgap energy of 3.2 eV or higher (wavelengths below 385nm), they have a tendency to experience all of the physical phenomena that include absorption, reflection, and scattering of light. Apart from that, TiO_2 nanoparticles will also involve in photophysical and photochemical processes. In a photophysical process, the absorbed photon of light will excite the electrons (e^-) from the valence band to the conduction band leaving holes (h^+) in the valence band thus generate electron and hole pairs (Eq. 1). These energized electron and hole pairs can either recombine and dissipate the energy as heat (Eq. 2) or dissociate because of charge trapping thus producing charge carriers available for the redox reactions (Eqs. 3, 4) in photochemical processes [12].

$TiO_2 + h\nu \rightarrow e^- + h^+$ (Photogeneration of electron and hole pairs) (1)
$e^- + h^+ \rightarrow$ light or phonon emission - heat (Electron and hole recombination) (2)
$D + h^+ \rightarrow D\bullet^+$ (Oxidation) (3)
$A + e^- \rightarrow A\bullet^-$ (Reduction) (4)

A portion of the photoexcited electron and hole pairs will diffuse to the surface of the TiO_2 nanoparticles and take part in the chemical reaction with the adsorbed electron donor (D) or adsorbed electron acceptor (A). The holes can oxidize adsorbed electron donor (Eq. 3) whereas the electrons can reduce appropriate adsorbed electron acceptor (Eq. 4) [13].

Water in air, acts as electron donor to react with hole to produce the highly reactive hydroxyl radical (OH•) (Eq. 5). Oxygen that is omnipresent on the particle surface acts as an electron acceptor by forming the superoxide ion (O_2^-) (Eq. 6). The holes, the hydroxyl radicals, and superoxide ion are very powerful oxidants that can be used to oxidize and naturally decompose common organic matters such as odor molecules, bacteria, and viruses to water and carbon dioxide (Eq. 7). Among them, hydroxyl radicals play the most important role in inactivating microorganism by oxidizing the polyunsaturated phospholipid component of the cell membrane of microbes.

$H_2O + h^+ \rightarrow OH\bullet + H^+$ (Formation of hydroxyl radicals) (5)
$O_2 + e^- \rightarrow O_2^-$ (Formation of superoxide ion) (6)
$OH\bullet$ + organic contaminants $\rightarrow\rightarrow xCO_2 + yH_2O$ (Radical oxidation of organic compound) (7)

CONCLUSIONS

This study demonstrated that the produced TiO_2 nanoparticle coating exhibit high potential for antimicrobial application in food industry. The aesthetic value of the coated glass was well-preserved based on the high percentage value of the light transmittance (around 80%). It is believed that the nanoparticle coating can not only be used to coat glass but also other food processing equipment as well as food packaging films. The use of nanometer sized TiO_2 has the prospective to further enhances the antimicrobial activity of TiO_2 especially for application in food industry whereby the antimicrobial agent is important in order to ensure the food safety.

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