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ANTIBACTERIAL TITANIA NANOCOMPOSITES

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by

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ABSTRACT

Titania nanoparticles with antibacterial shells were synthesized by two methods: silane method and atom transfer radical polymerization (ATRP) method. Fourier-transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) results prove the successful graft of DMAEMA salt polymer chains from the surface of titania nanoparticles. TGA shows that the amount of DMAEMA salt polymer grown from titania by ATRP method is higher than that by silane method. Transmission electron microscope (TEM) measurements and scanning electron microscope (SEM) measurements displays the obtained titania-DMAEMA nanohybrids have a core-shell structure. In addition, the functional nanocomposites demonstrate antibacterial property. We compared the antibacterial effects of titania nanocomposites with different alkyl chain lenghths, and the results show that titania modified by DMAEMA salt polymer with eight carbon alkyl chain have the best antibacterial effects. The synthesized titania nanocomposites have potential application in coatings.

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Introduction

Titania nanoparticles

Titania is one of the most important white pigments currently used in the world, with a total annual production capacity approaching five million tons.[1] Titania pigment is used widely in the paint, papermaking, plastic, cosmetic, and pharmaceutical industries due to its outstanding physicochemical properties. The paint industry is the largest titania pigment consumer, using nearly 60% of the global pigment consumption.[2]

The use of photocatalysts to destroy organic compounds in contaminated air or water has been extensively studied for the last 25 years. The P25 formulation of titanium dioxide (TiO_2) from Degussa Chemical Company (Teterboro, N.J.) is the most widely used photocatalyst. TiO_2 in the anatase crystal form is a semiconductor with a band gap of 3.2 eV or more. Upon excitation by light whose wavelength is less than 385 nm, the photon energy generates an electron hole pair on the TiO_2 surface. The hole in the valence band can react with H_2O or hydroxide ions adsorbed on the surface to produce hydroxyl radicals (OH·), and the electron in the conduction band can reduce O_2 to produce superoxide ions(O_2^-). Both holes and OH· are extremely reactive with contacting organic compounds. Detection of other reactive oxygen species (ROS), such as hydrogen peroxide (H_2O_2) and singlet oxygen, has also been reported. Complete oxidation of organic compounds and Escherichia coli cells to carbon dioxide can be achieved.[3,4] In the absence of O_2 or a suitable electron acceptor, no photocatalytic reaction occurs due to the extremely deleterious electron hole recombination processes.[5] The detailed mechanism of

the TiO_2 photochemical reaction and the various ROS produced have been well-documented.

In 1985, Matsunaga and coworkers reported that microbial cells in water could be killed by contact with a TiO_2-Pt catalyst upon illumination with near-UV light for 60 to 120 min.[6] Later, the same group of workers successfully constructed a practical photochemical device in which TiO_2 powder was immobilized on an acetylcellulose membrane. An E. coli suspension flowing through this device was completely killed.[7] The findings of Matsunaga et al. created a new avenue for sterilization and resulted in attempts to use this novel photocatalytic technology for disinfecting drinking water and removing bioaerosols from indoor air environments.[8] Killing of cancer cells with the TiO_2 photocatalyst for medical applications has also been reported.[9] Because of the widespread use of antibiotics and the emergence of more resistant and virulent strains of microorganisms, there is an immediate need to develop alternative sterilization technologies. The TiO_2 photocatalytic process is a conceptually simple and promising technology.

Although a wealth of information has demonstrated the efficacy of biocidal actions of the TiO_2 photocatalytst, the fundamental mechanism underlying the photocatalytic killing process has not been well-established yet. An in-depth understanding of the mechanism is essential in order to devise a strategy and apply the technology in a practical system to efficiently kill a wide array of microorganisms. The first mechanism proposed was the mechanism proposed by Matsunaga and coworkers, who believed that direct photochemical oxidation of intracellular coenzyme A to its dimeric form was the root cause of decrease in respiratory activities that led to cell death.[6,7] They reported that the

extent of killing was inversely proportional to the thickness and complexity of the cell wall. Saito and workers[10] proposed that the TiO_2 photochemical reaction caused disruption of the cell membrane and the cell wall of Streptococcus sobrinus AHT, as shown by leakage of intracellular K^+ ions that paralleled cell death. Leakage of intracellular Ca^{2+} ions has also been observed with cancer cells.[11,12] Perhaps more direct evidence that outer membrane damage occurs was described recently by Sunada et al.,[13] who studied E. coli and found that the endotoxin, an integral component of the outer membrane, was destroyed under photocatalytic conditions when TiO_2 was used. Pin-Ching and coworkers[14] proposed for the first time that the TiO_2 photocatalytic reaction indeed causes the lipid peroxidation reaction to take place and that, as a result, normal functions associated with an intact membrane, such as respiratory activity, are lost. Therefore, the loss of membrane structure and membrane functions is the root cause of cell death when photocatalytic TiO_2 particles are outside the cell.

Polysurfactants

Antibiotic-resistant bacterial infections currently pose a major threat to public health. To meet this urgent need, substantial efforts have been devoted to the development of synthetic antibiotics to combat bacterial resistance. Synthetic polymers containing quaternary ammonium salts attached to long hydrophobic alkyl side chains, or polysurfactants, have been extensively studied in the development of antimicrobials. It has been asserted that polysurfactants bind to bacterial cell membranes and disrupt the barrier function of the membrane, leading to loss of the transmembrane potential, leakage of cytoplasmic contents, and concomitant cell death.[15] The purpose of incorporating cationic charges in these polymers is to enhance their affinity to anionic components of

the bacterial cell membranes by electrostatic attraction. Synthesis of such compounds is not labor intensive or costly, rendering their production feasible on the industrial scale. For examples, poly(vinyl alcohol)s, polyacrylates, polyamines, polystyrenes, polysiloxanes, and polyurethanes have been functionalized with quaternary ammonium salts groups and successfully used as bactericides.[16] The application of antibacterial polymers has attracted much attention because they minimize the environmental problems accompanying low-molecular weight conventional disinfectants or antimicrobial agents, such as toxicity of residues of these agents after leaching into the environment. Polymers containing quaternary ammonium salts and hydrophobic groups have shown great promise for application as permanently disinfecting surfaces. On the other hand, if such polymers are to be potentially useful in a broad range of applications, their toxicity to human cells must be considered. Quaternized 2-(Dimethylamino)ethyl methacrylate (DMAEMA) polymer have been extensively applied in the development of antimicrobials because of its easy synthesis and relatively good antibacterial property. Tuning the hydrophobic/hydrophilic balance of the PDMAEMA can dramatically change the antibacterial and hemolytic activities. As different materials (such as in different substrates), DMAEMA have different hydrophobic/hydrophilic balances which can induce best antibacterial effects.

Antibacterial Surfaces

Infections caused by microorganisms remain a major concern, especially in the healthcare sector where bacterial infections arising from implants and medical devices can result in increased suffering, prolonged hospital visits, rejections of transplants, recurrent operations, and sometimes even death.[17,18] Antimicrobial surfaces are widely

used to prevent microbial infection in a wide range of industrial, medical, community and private settings. Different strategies have been developed to address the growing need for antibacterial surfaces. A useful approach is to permanently attach the active antimicrobial agents on the surface through covalent interactions. The antibacterial action results from the contact of the microorganisms with the biocidal surface without releasing the biocide into the environment. Such approach also reduces the likelihood of generating drug resistance to the active agent throughout the microbial realm.[19] Antimicrobial surfaces have been successfully prepared via covalent immobilization of antimicrobial polymers onto various substrates. The biocidal polymer generally contained cationic groups, such as alkyl pyridinium or quaternary ammonium moieties. Cationic antimicrobials therefore play a key role in the development of permanent and non-leaching antibacterial surfaces.

Silanization

The utility of organosilane-modified surfaces has been demonstrated in a variety of fields ranging from their use as stationary phases for chromatography,[20] antimicrobials,[21] catalysts,[22] immobilized enzymes,[23] and fiber reinforced composites.[24] To better tailor surfaces with specific properties, it is necessary to understand how reaction conditions affect reaction mechanisms and surface structure. The quality and durability of the silanized materials depend primarily on the nature of the attachment to the surface. The silane coupling agents are widely used now for surface modification. Silane-based self-assembly methods can be applied on such surfaces as silica, glass, and metal oxides, where surface hydroxyls can react with proper chemically active groups, typically methoxy- or chlorosilanes. Such silane-based linkers have taken on special significance in recent years in the field of surface modification.[25] Well-ordered assemblies and

monolayers of silanes are desired and can be used in many applications. Many efforts were made to identify and optimize the factors affecting silanization and monolayer formation. The reaction conditions such as temperature, water content, nature of a silane, type of catalyst, and type of substrate have influence on the rate of reaction and the assembly structure. Different types of the surface assembly structure can be obtained upon slight change in reaction conditions. The presence of water can cause the vertical polymerization of silane.[26] In dry solvent, amine can be applied as catalyst of silanization reaction which can form monolayer coverage. The amine attaches to the surface silanols and renders the Si-O group of the silanol more nucleophilic, which then attaches to the silicon atom of the incoming silane.[27] Amines with exchangeable hydrogen ions exhibit greater catalytic effect than amines without exchangeable hydrogen ions. And post-reaction curing is unnecessary in the presence of an amine catalyst. [28]

ATRP

The development of strategies for the synthesis of novel ceramic/polymer composites is of great current interest because of the unique properties that are likely to emerge from such materials. One of the most important challenges in the area is the synthesis of composites where the polymer chains are covalently bonded to the ceramic particles. The optimum solution to this problem is a living polymerization system that initiates from the surface of the ceramic particles, such as by atom transfer radical polymerization (ATRP).[29] To date, ATRP has been employed to anchor homopolymers on to silica, cadmium sulfide/silica, gold particle and titania surfaces.[30-33] Some vinyl monomers containing tertiary amino groups, such as 2-dimethylaminoethyl methacrylate (DMAEMA) can be polymerized or copolymerized via ATRP, followed by

quaternizaiton, to induce the antimicrobial activity. Control over both the polymer length and the effective number of quaternary ammonium groups could result in a highly effective biocidal polymer. Accordingly, surface-initiated ATRP has been used to impart antibacterial surfaces on filter paper,[19] titanium,[34] gold,[35] glass,[36] silicon,[37] polyolefin,[38] fibers,[39] polymer microspheres[40] and poly(vinylidene fluoride).[41] The original idea of preparing permanent, non-leaching antibacterial surfaces via ATRP was proposed by Matyjaszewski's group as shown in Scheme 1.[19]

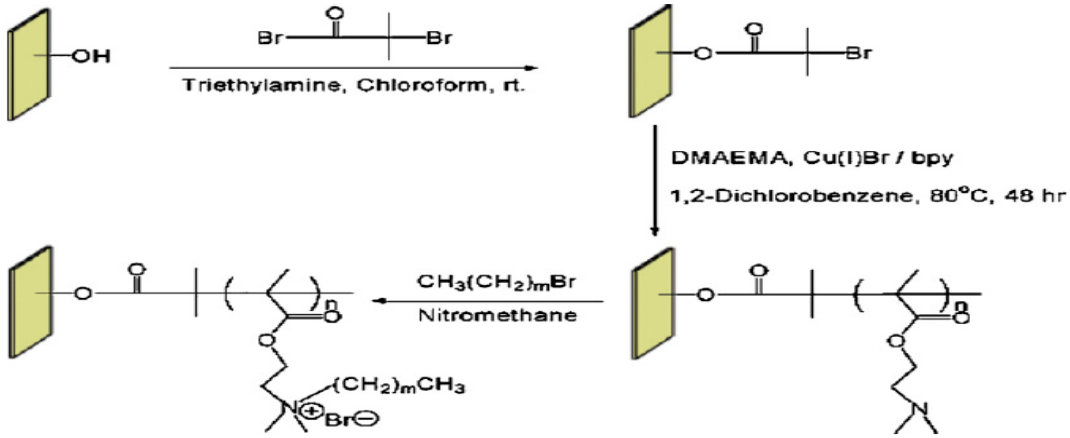


Fig. 1. Surface-initiated ATRP of DMAEMA, and subsequent quaternization , from cellulose surfaces.

Experimental

Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA) , bromobutane, bromohexane, bromooctane, bromodecane, titania, ammonium persulfate, triethylamine, N,N,N',N'-Tetramethylethylenediamine, N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA), copper(I) bromide (CuBr), 2-bromopropionic acid were purchased from Sigma-Aldrich.

Toluene, acetonitrile, chloroform and acetone were high purity solvent and purchased from EMD biosciences. Toluene was purified by the solvent purification system which is free from water and oxygen. Acetone was dried by 3A molecular sieves before use.

(3-bromopropyl)trimethoxysilane was purchased from Gelest.

Escherichia coli (E. coli) was obtained from the American Type Culture Collection. Bacterial growth media and agar were purchase from Difco.

Deionized water was used for all experiments and preparations of solutions. All measurements were made at room temperature (25°C) unless mentioned otherwise.

Instruments

FTIR

FTIR measurement were carried out on a Bruker IFS 66/s spectrometer with an MCT detector. The acquisition mode is Spectra-Tech Collector Diffuse Reflection with the acquisition parameters as follows: average 400 scans acquired at 6 cm^{-1} resolution. KBr

was used as the reference material which was purchased from International Crystal Laboratories.

XPS

XPS measurements were carried out on a Kratos Axis Ultra spectrometer (Kratos Analytical Ltd., Manchester, England) with a monochromatic Al K-alpha X-ray source. The X-ray source was run at a pass energy of 80 eV with hybrid lens mode and charge neutralizer on. The samples were mounted on 3M double-sided tape with the analysis area of approx 1 x 1.5 mm.

TGA

TGA measurements were carried out on a TA instrument SDT 2960. Thermogravimeteric Analysis (TGA) measures the amount and rate change in the weight of a material as a function of temperature or time in a controlled atmosphere.Measurements are used primarily to determine the composition of materials and to predict the thermal stability at temperature up to 15000C.The technique can characterize materials that exhibit weight loss or gain due to decomposition, or dehydration. Small size of the sample is placed in the sample pan (Alumina) and the test procedure is established on the computer. The Analysis was done under carrier gas (HPArgon), with heating profile 100C/min up to 6000C.

TEM

Images were collected via a low electron dose conditions (70um condenser aperture, low beam convergence and binning of 2 for image acquisition,). The shells were not observed under higher electron doses in a 120kV TEM with W filament.

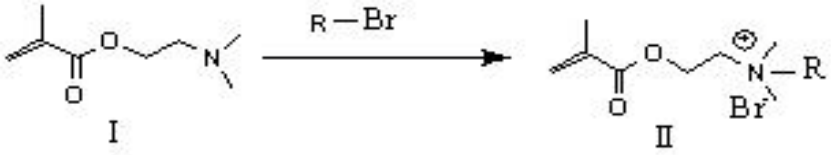
SEM

SEM images were taken with a Zeiss Leo-1530 model Field-Emission Scanning Electron Microscope (FESEM) using 1 kV imaging voltage.

Methods

Schemes:

Monomer: DMAEMA salt



Scheme 1:

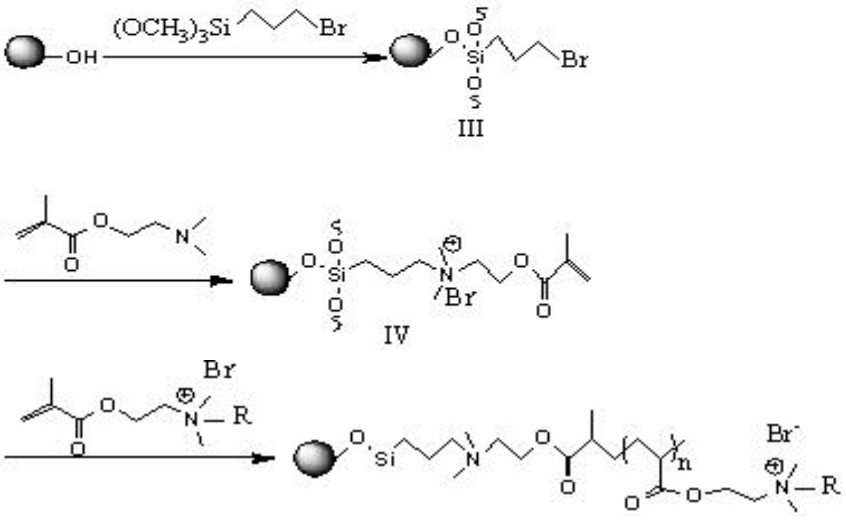


Fig. 2. Scheme of silane method

Scheme 2:

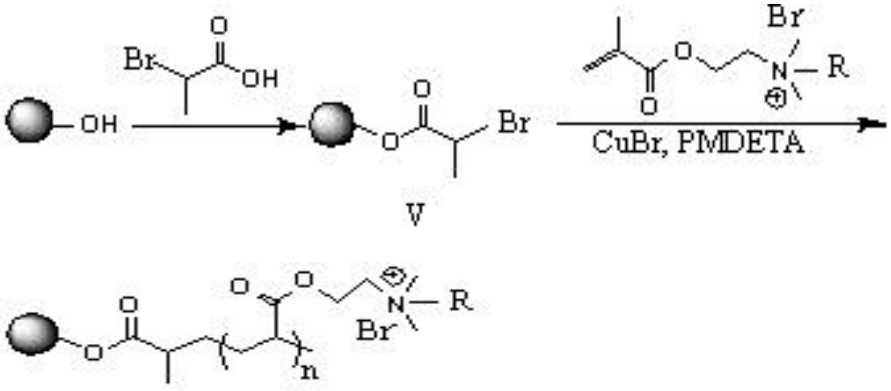


Fig. 3. Scheme of ATRP method

Pretreatment of titania

Titania nanoparticles were soaked in 4M NaOH for 30min to regenerate fresh hydroxyl group, washed by distilled water until pH=7, dried under vacuum overnight.

Silane method

Scheme 1:

Preparation of III: In dry box, 30ml toluene was added in a 50ml conical flask, 2g pretreatment titania were added, 2g silane was added, 0.5 ml Et_3N was added as catalyst, stir @ room temperature for 24h. Take it out of dry box, the reaction suspension was transferred to a 50ml centrifuge tube, centrifuged , and rinsed with dry toluene three times, in the end, the particles were dried in vacuum oven @ 60 °C overnight.

Preparation of IV: 25ml $CH_3CN/CHCl_3$ (2:1) mixture solvent was added in 50ml round bottom flask, 1g III was added, 1g I was added, stirred in 40°C oil bath overnight. After

the reaction, the suspension was transferred to a 50ml centrifuge tube, centrifuged, and rinsed with acetone three times, dried under vacuum.

Polymerization: 2.7g II (9.18mmol) was dissolved in 10ml distilled water in a 20ml glass vial, 0.2g IV was added, 1.8ml 0.1M ammonium persulfate (0.18mmol) was added, 1.8ml 0.1M N,N,N',N'-Tetramethylethylenediamine (0.18mmol) was added, stirred in 40°C oil bath overnight. The suspension was transferred to a 15ml centrifuge tube, centrifuged, rinsed with distilled water five times to remove the homopolymers, in the end transfer the turbid liquid into a petri dish which was put in lyophilizer to remove water.

ATRP method

Scheme 2:

Preparation of V: 30ml dry THF was added in 50ml round bottom flask, 3g 2-bromopropionic acid was added, 1.6g pretreatment titania was added, reflux @ 85°C oil bath for 18h. Cool down, the suspension was transferred to a 50ml centrifuge tube, rinsed with dry acetone three times, dried under vacuum.

Polymerization: 2g (6.8mmol) II was dissolved in 20ml methanol in a 50ml conical flask, 19.5 mg (0.136mmol) CuBr was added, 23.6mg (0.136mmol) PMDETA was added, stirred @50°C in dry box for 24h. Take it out of dry box, the suspension was transferred to a 50ml centrifuge tube, centrifuged, rinsed with distilled water 3 times, the suspensions were transferred to a petri dish which was put into lyophilizer to remove the water.

Antibacterial Test

Biosafety: Bacteria are potentially hazardous and care should be taken while working with them. Standard biosafety lab techniques were followed while handling bacteria and various media. Gloves were used during all experimentation, and any accidental spills were immediately sterilized using 70% ethanol/water after completion of work. Unused media and bacterial suspensions were first deactivated with commercial bleach for 1 h before being disposed in biosafety bags. All material that had come in contact with bacteria (e.g., pipet tips, tubes, agar paltes, etc.) was also thrown in biosafety bags in tightly closed bins. Biosafty bags were autoclaved for 2 h before final disposal.

Bacterial Culture: *E. coli* DH5-α (Clontech) was grown at 37°C and maintained on LB plates (Luria-Bertani broth, Lennox modification, with 1.5% agar). The relationship between absorbance at 590nm (OD_{590}) and colony-forming unites per milliliter was determined using the plate count method as described by Herigstad et al. This allowed the standardization of assay inoculums by measurements of OD_{590}. Bacteria were cultured in a shaking incubator for 16-18 h in LB broth, and cell counts were quantified by OD_{590} measurement which is c.a. 10^9 colony-forming units per milliliter. The cultures were then diluted to the appropriate density in LB broth.

Evaluation of antibacterial acitivity: For the kinetic tests against Gram-negative *E. coli*, 100 mg of the powder state sample was prepared in sterilized test tubes (12 ml) and then inoculated with 5 ml of bacterial suspension (10^5/ml). After a specific contact time (18 h), the suspension was centrifuged and the upper solution was diluted by 10^4 and 10^5 times. 200µl of the diluted solution were withdrawn from each test tube and cultured in

LB agar plates. The LB agar plates were kept at 37 °C for 24h and the number of survival bacterial colonies was counted. The survival percentage was used to evaluate the antibacterial effect.

Results and Discussion

Silane method

There is a large amount of Ti-OH groups existing on the surface of titania nanoparticles and they provide the potentiality to modify the titania with organosilanes. Thus, the inorganic hydroxyl groups with low reactivity on surface of titania are transformed into more reactive organic functional groups for further functionalization. Our strategy to modify titania nanoparticles is described in Scheme 1. Firstly, alkyl bromides were introduced onto the surface of titania by the reaction of organosilane with hydroxyl-contained titania nanoparticles. Secondly, the amine contained monomer was introduced onto the titania surface by reacting with alkyl bromide so that the carbon double bond was introduced onto the titania surface. In the end, the radical polymerization was initiated from the carbon double bond so that polymer grew from the surface of titania nanoparticles.

FT-IR (Fig.4) , XPS (Fig.5) spectra and TGA (Fig.6) were used to characterize the organically modified titania nanoparticles. In the FT-IR spectrum of original titania (Fig.4a), 3700 cm^{-1} (the stretching vibration of O-H groups) is clearly detected. The band between 1630 cm^{-1} and 1640 cm^{-1} is the –OH deformation band of water. In the FT-IR spectrum of the silane modified titania (Fig. 4b), 2900 cm^{-1} (the stretching vibration of C-H groups) could be clearly detected. It indicates the successful anchoring of organosilane onto the surface of titania. Compared with silane modified titania, the FT-IR spectrum (Fig. 4c) of second step modification titania demonstrates the characteristic absorption bands occurred at 1700 cm^{-1} (the C=O groups), which indicate the successful linkage of

monomer to titania surface. XPS (Fig.5) spectra provide more detailed evidences to prove that bromide groups have been grafted onto the surface of titania nanoparticles successfully.

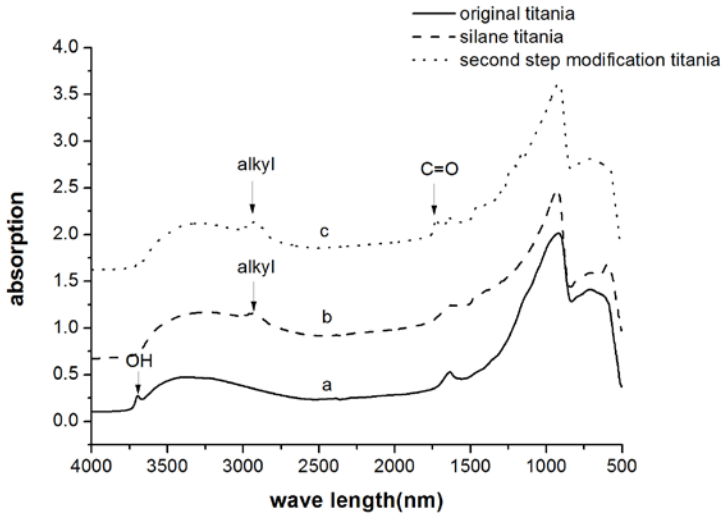


Fig. 4. FT-IR spectra of silane method.

In the XPS spectra of silane modified titania, the characteristic peaks of Br 3d were found around 71.55 eV, Br 3p were found around 184 eV and 190 eV, Si 2s were found around 152.61 eV. Thus, it can be concluded that by modifying as received titania nanoparticles with (3-bromopropyl)trimethoxysilane, the inert inorganic titania have been changed into functional hybrid nanoparticles.

The TGA curves show a major decomposition in the temperature range at 200-450 ^{o}C, which should be attributed to the thermal degradation of DMAEMA salt polymers coated on the titania particles when compared to the TGA curve of DMAEMA salt polymers. Thus, the DMAEMA content in silane method modified titania is ca. 7.2%.

Furthermore, the result of TGA measurements is well consistent with TEM characterization. TEM reveals a thin shell on titania nanoparticles. In addition, the shell was only observed on a small fraction (<5%) of the particles (100) imaged. An amorphous phase is also observed between the particles as shown in Fig.7.

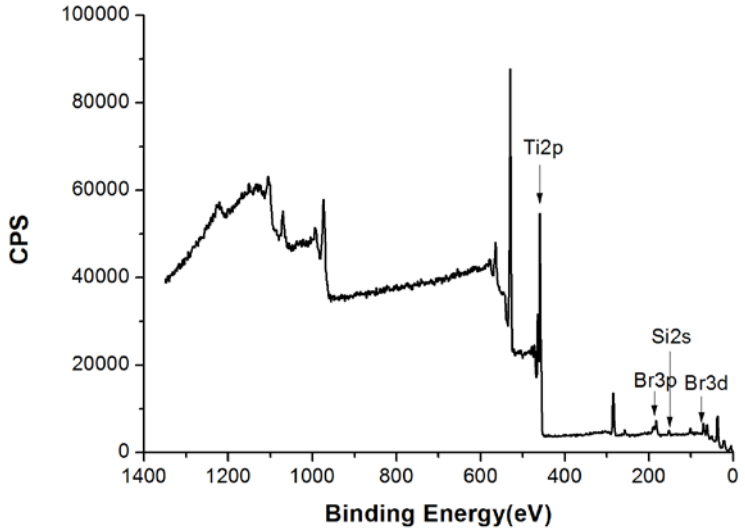


Fig. 5. XPS spectrum of first step modification titania of silane method.

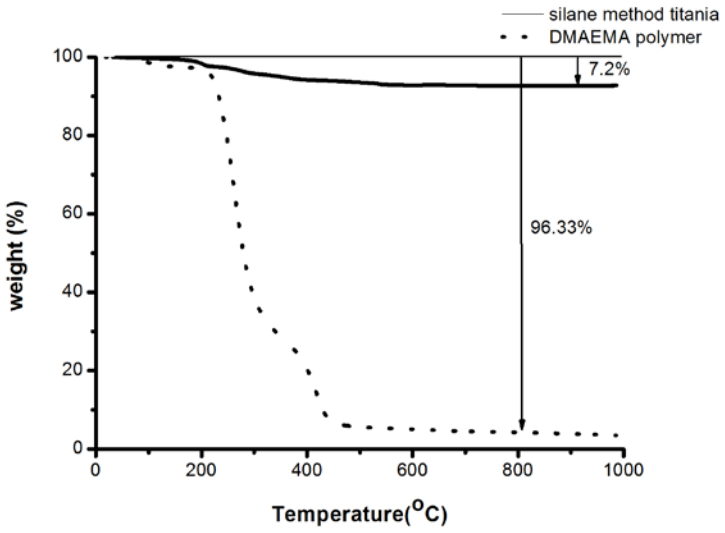


Fig. 6.TGA curve of titania synthesized by silane method and DMAEMA polymer.

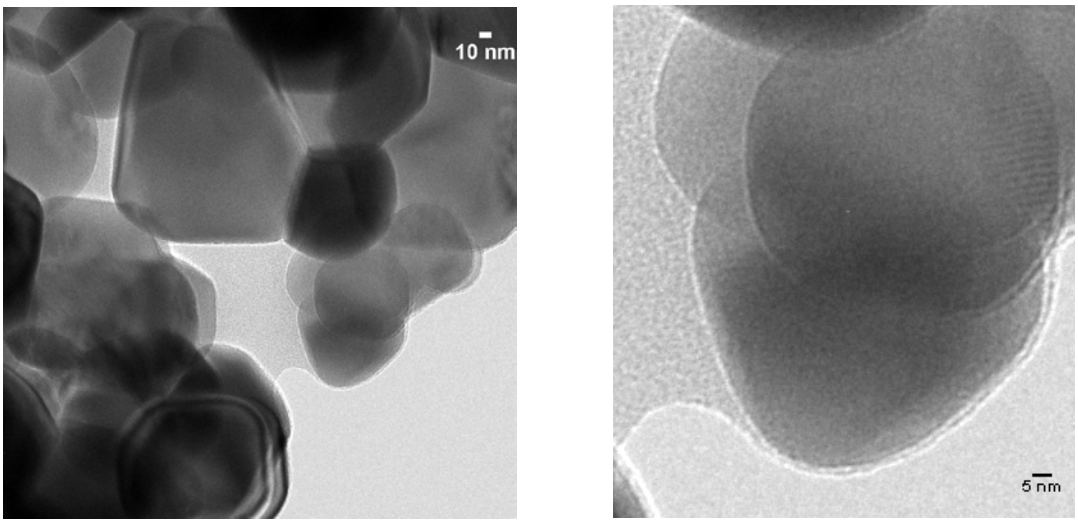


Fig. 7. TEM images of silane method titania. (The right figure is the zoom in of the left figure and it shows detail of the core-shell structure.)

ATRP method

The strategy to modify titania nanoparticles through ATRP method is shown in fig. 2. Firstly, the initiator was introduced to the surface of titania through the reaction of carboxyl acid and hydroxyl groups on the surface of titania. Then grafting polymerization of DMAEMA salt from TiO_2-Br was carried out by means of in situ ATRP, resulting in TiO_2-DMAEMA salt nanocomposites.

The characterization of surface modified titania particles include FT-IR (Fig. 8) , XPS (Fig. 9 and Fig. 11), TGA (Fig. 10) , TEM (Fig. 13). SEM (Fig. 12) was also applied to characterize the nanocomposites. Compared with as received titania, the FT-IR spectrum (Fig. 8b) of TiO_2-Br demonstrates the characteristic absorption bands occurred at 1680 cm^{-1} (carbonyl groups) and 3000 cm^{-1} (alkyl groups). XPS (Fig. 9) spectra provide more detailed evidences to prove that bromide groups have been grafted onto the surface of titania nanoparticles successfully. In the XPS spectra of TiO_2-Br, the characteristic peaks

of Br 3d were found around 69.5 eV, Br 3p were found around 182.5 eV and 190.5 eV. Therefore, by modifying as received titania nanoparticles with 2-bromopropionic acid, the inert inorganic titania nanoparticles have been changed into functional hybrid nanoparticles with many ATRP initiators. The TiO_2- DMAEMA salt were prepared via in situ ATRP of DMAEMA salt monomers from the surface of TiO_2-Br. The XPS spectrum shows characteristic peaks of nitrogen and bromine. Br 3d peak was found around 68 eV, Br 3p peaks were found around 187 eV and 179 eV and N 1s peak was found around 402.4 eV. According to the structure of DMAEMA salt polymer which contains nitrogen and bromine, the XPS spectrum provided evidence that the polymer has successfully grown on the surface of titania nanaparticles. Further evidence was provided by TGA measurement. As shown in Fig. 10, the weight loss of ATRP titania is ca. 21.17%, which means that the weight percentage of DMAEMA salt polymer grown on the surface of titania is ca. 21%. The content of DMAEMA salt polymer of ATRP method (21.17%) is higher than that of silane method (7.2%). Therefore, the ATRP method is more effective in modifying titania with DMAEMA salt polymer than silane method. The above results are consistent with morphology characterization of SEM and TEM. SEM images show the polymer network between particles compared to the as received titania nanoparticles. TEM images reveals an amorphous shell on some of the particles. Amorphous “bridges” were also observed between particles.

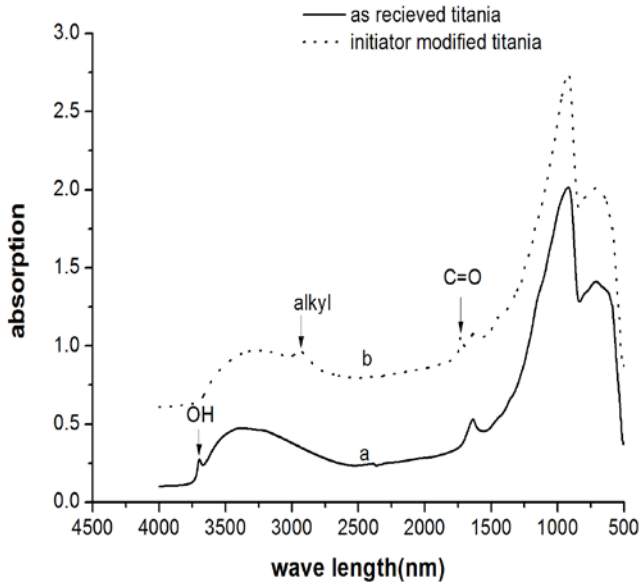


Fig. 8. FT-IR spectra of titania and first step modified titania by ATRP method.

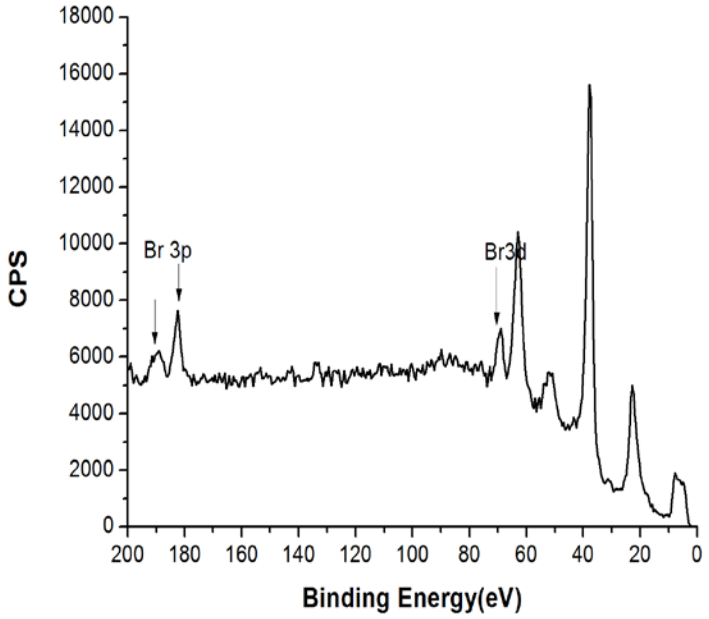


Fig. 9. Bromine peaks of XPS for first step modification titania by ATRP method.

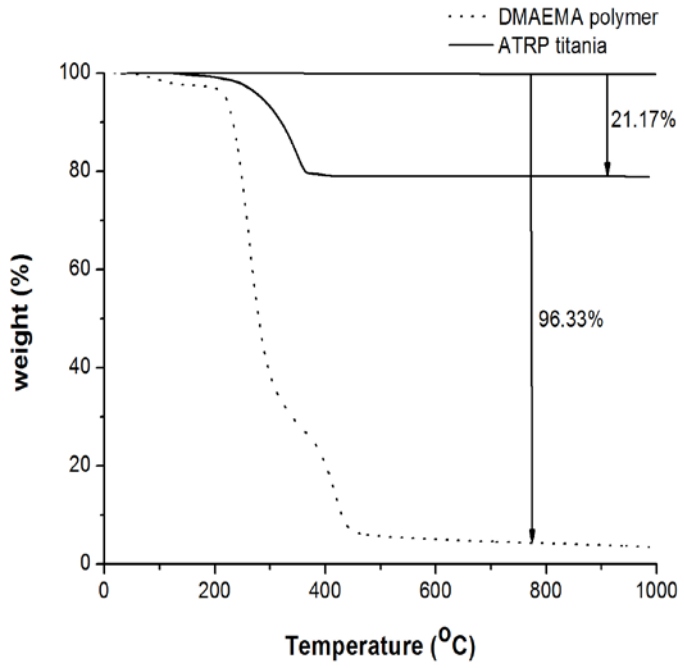


Fig. 10. TGA curve of titania by ATRP method.

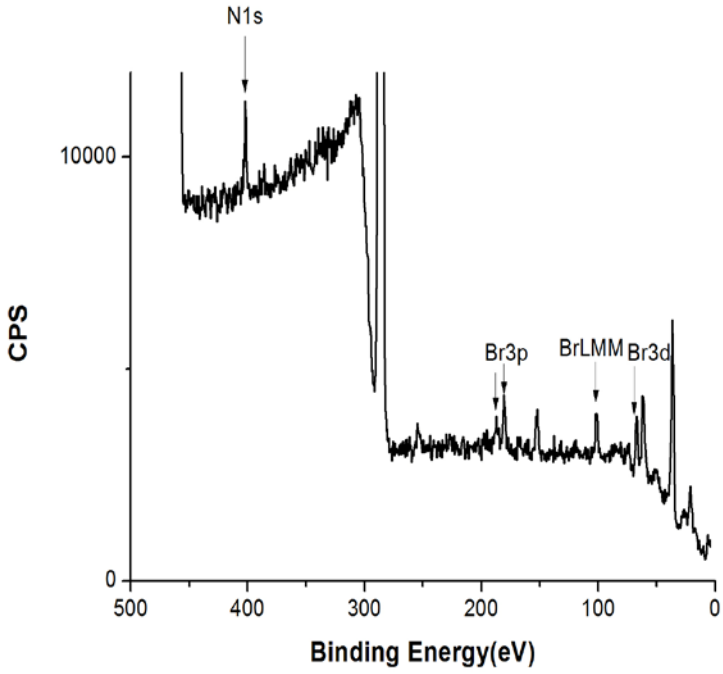
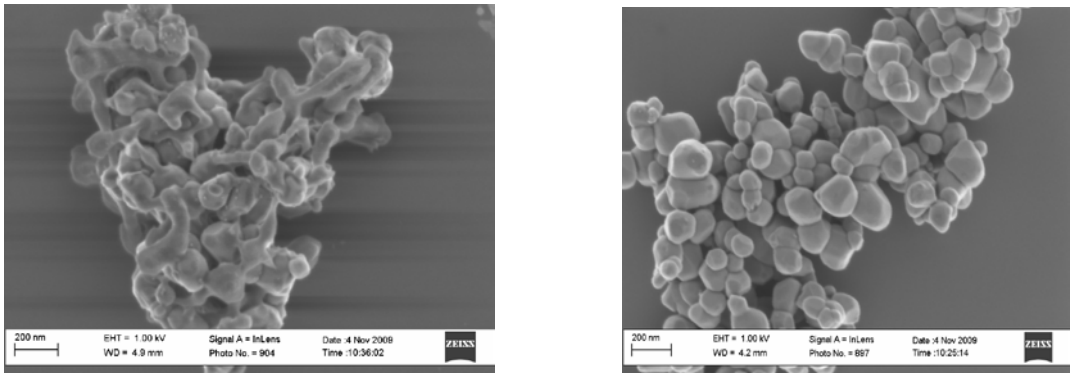


Fig. 11. XPS spectrum titania by ATRP method



Functionalized titania As recieved titania

Fig. 12. SEM images of titania and functionalized titania

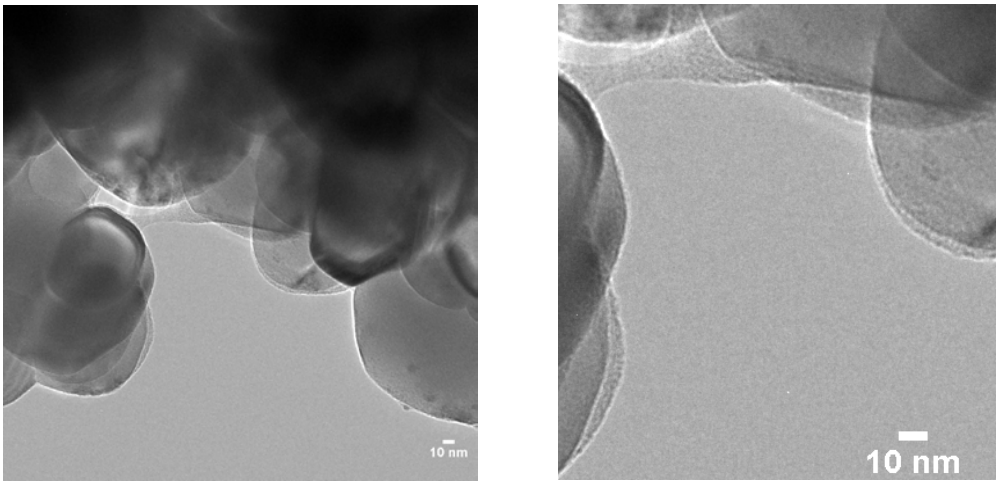
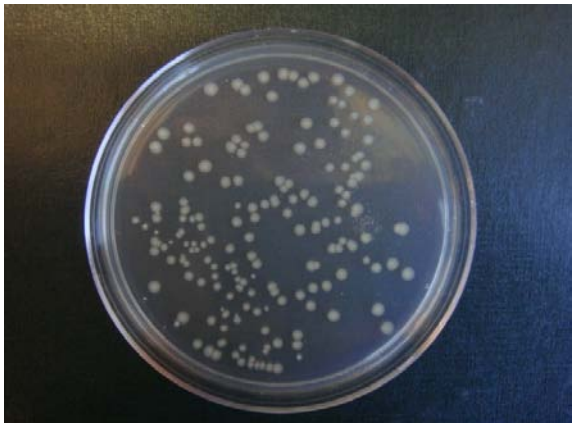


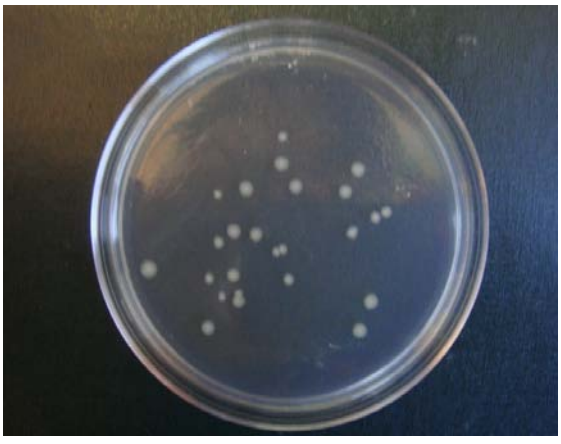
Figure 13: TEM images of titania nanocomposites prepared by ATRP method.

Antibacterial Test

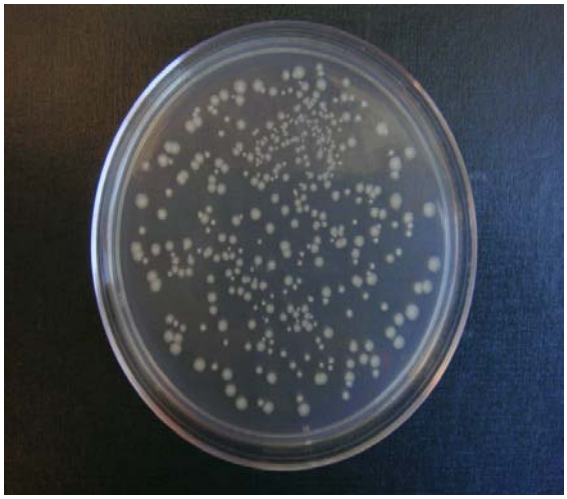


As received titania control, 10^5 times diluted bacterial solution

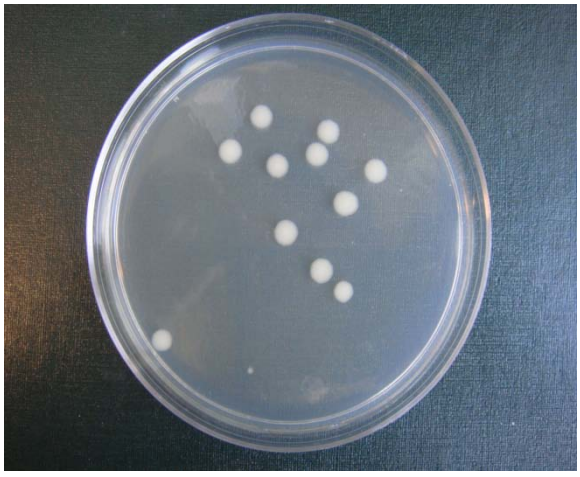
As received titania control, 10^4 times diluted bacterial solution



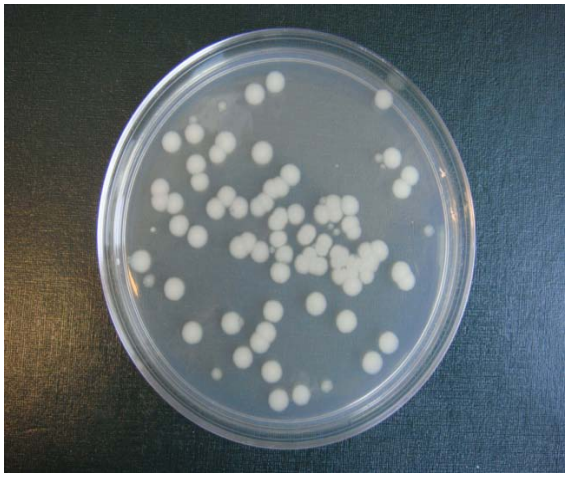
C4 modified titania, 10^5 times diluted bacterial solution



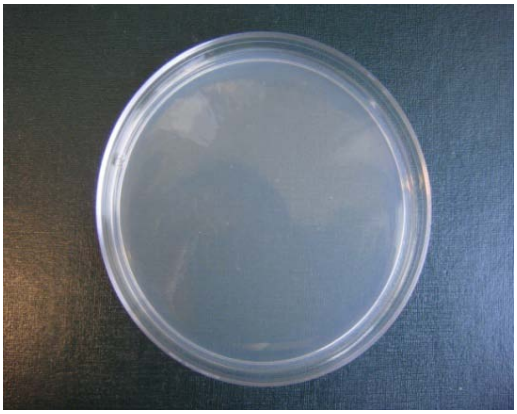
C4 modified titania, 10^4 times diluted bacterial solution



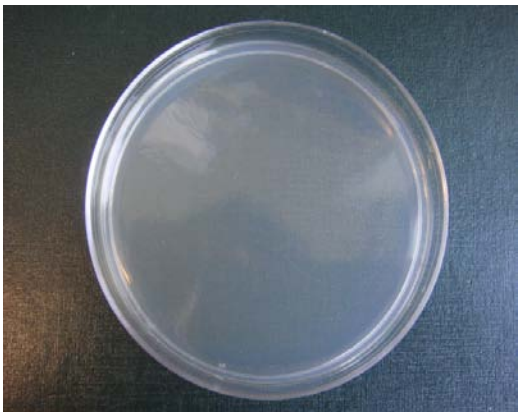
C6 modifed titania, 10^5 times diluted bacterial solution



C6 modified titania, 10^4 times diluted bacterial solution

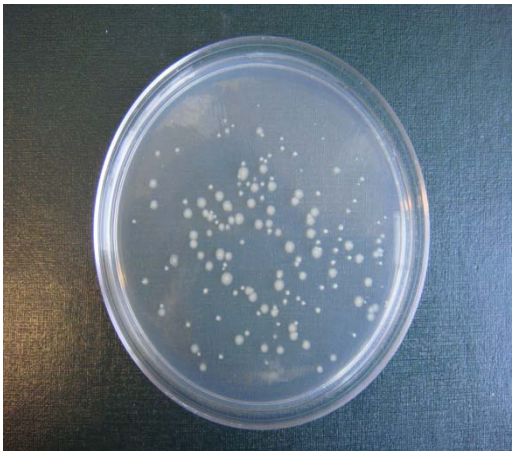


C8 modified titania, 10^5 times diluted bacterial solution



C8 modified titania, 10^4 times diluted bacterial solution

C10 modified titania, 10^5 times diluted bacterial solution



C10 modified titania,10^4 times diluted bacterial solution

Fig. 14. LB agar plates of antibacterial testing

To evaluate the antibacterial activity of TiO_2-DMAEMA salt polymer, titania nanoparticles were used as comparative materials. Titania nanoparticles modified with DMAEMA salt polymers of different lengths hydrophobic chains by ATRP method are tested. A total mass of 100 mg of the samples was inoculated with 5 ml (10^5 CFU · ml^{-1}) volume of the Gram-negative bacteria *E. coli* solutions for a period of time. The bacteria solution was diluted and cultured on LB agar plate. And the number of survival bacterial colonies was counted. I cultured the bacteria in the same condition, but some colonies are larger than others. The growth mechanism of bacteria needs more investigation. As shown in Fig. 14, for the 10^5 times diluted sample, the control agar plate has c.a. 200 bacteria colonies, the C4 agar plate has c.a. 20 bacteria colonies, the C6 agar plate has 11 bacteria colonies, the C8 agar plate has 0 bacteria colony, the C10 agar plate has only 1 bacteria colony. The results showed that C8 DMAEMA titania has the best antibacterial effect. This result is consistant with 10^4 times diluted samples. Therefore, by tuning the hydrophobic and hydrophilic balance of the titania nanocomposites, we found that titania

modified with DMAEMA salts polymer of eight carbon alkyl chain have the best antibacterial activity.

Future directions

In this project, we synthesized the antibacterial polymer modified titania nanocomposites by two methods: silane method and ATRP method. The ATRP method is more effective in modifying polymers outside titania nanoparticles. However, the conversion rate of ATRP method is still very low. In the future, we need to adjust the reaction conditons, such as solvent, catalyst, reaction temperature etc. to improve the conversion rate of the monomer. Another future direction is investigation of dispersion property of modified titania. Titania is one of the most widely used pigment in the world. To achieve the optimum visual and economical benefits of a pigment, the dispersion process is critical. The dgree to which the pigment particles are dispersed is indeed a major factor in the quality and stability of the finished paint. After the surface modification by the antibacterial polymer, the surface property of titania has been changed. Therefore, further investigations are needed to find the proper dispersants for the modified titania nanocomposites. Lastly, titania is a typical photocatalyst and the stability of polymer modified titania under the illumination of UV light needs more research.

Possible application

As mentioned above, titania is one of the most important white pigments currently used in the world. After the modification of antibacterial polymer, the modified titania nanocomposits are still white. Therefore, the modified titania nanocomposits can still be applied in paint. Furthmore, they have antibacterial polymer as shells, so the paint will be antibacterial without UV light. Therefore, even at night the paint still can kill bacteria and the paint will be antibacterial day and night. The antibacterial polymer modified titania nanocomposites have potential application as permanent antibacterial coatings.

Conclusions

In this work we have synthesized antibacterial polymer modified titania nanocomposites. For our study we used two types of synthesis method: silane method and ATRP method. For the ATRP method, we succesfully polymerized cationic monomers from the surface of nanoparticles for the first time rather than polymerize DMAEMA followed by quaternization of the polymer chain. We characterized the nanocomposites by FTIR, XPS, TGA, TEM and SEM. And the weight loss of the nanocompostes by ATRP method is 21%, which is higher than those by silane method 7.285%. Therefore, the ATRP method is more effective than silane method in modifying polymers outside titania nanoparticles. We also grew polymers with different alkyl chains outside titania, tested the antibacterial activity of the titania nanocomposites and we found that titania modified by polymers with eight carbon alkyl chain have the best antibacterial activity.

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