IOP Conference Series: Earth and Environmental Science

PAPER • OPEN ACCESS

Anatase Tio2 Nanoparticles Sensitized With Organic Dyes as Efficient Antibacterial Agents

To cite this article: Yanxia Xing *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **252** 022057

Anatase Tio2 Nanoparticles Sensitized With Organic Dyes as Efficient Antibacterial Agents

Yanxia Xing[1], He Zhu[1, 2], Guifang Chang[1], Mei Yu[1], Min Zhao[1], Fengli Yue[1, *]

[1]Key Laboratory of Shandong Education Department, Shandong University of Agricultural Engineering, Jinan 250100, China
[2]National Engineering Laboratory of Rice and By-Products Deep Processing, Central South University of Forestry and Technology, Changsha 410000, China

*Corresponding author e-mail:sdau_zhuhe@126.com

Abstract. Highly effective antimicrobial agents are critical to human health. In this study, we treated nano titanium sensitized with different dose of Fuchsin Acid, Alizarin red and Tartrazine. We investigated the antimicrobial activity of Anatase-sensitized with different organic dyes from same ratio as 0.2, 1, 2 Wt. %. Different dyes sensitizing nano titanium dioxide all exhibited different strong antimicrobial capacity than pure-titanium dioxide. Modification methods of Titanate were adopted to broaden the photo absorption region and improve photo-quantum efficiency, which is a useful way to enhance the antimicrobial capacity.

1. Introduction

Bacteria have always been the cause of many diseases. To kill bacteria, antibiotic drugs are widely used, although certain results have been achieved, but lots of antibiotics will be used after the emergence of drug resistance. The development of high activity and broad-spectrum antimicrobial agents is critical to prevent the threat of antibiotics to pathogens. To achieve this, many metal materials have been choosed as antibacterial agents, such as, CuO, Ag, ZnO [1-3],

Compared to Ag, Titania is a premium photocatalyst because of its high absorption capability, slow rate of charge carrier recombination and lower toxicity [2-5]. Meanwhile, antimicrobial properties of Titania must be involved in oxygen, which limits the ability of the TiO_2 photocatalyst to inhibit some anaerobic bacteria. Thus, a battery of technologies that based on Titania had been developed to improve the antibacterial efficiency of Titania.

Such as , doped with metal ion, including Ag+, Fe+, Zn+, Mn2+ [6,7], dye-sensitized [8,9], and doped with metal oxide ,WO3,SNO2 [10]. Though they possessed better performance than dyes-sensitized Titanium, they are high toxicity [11, 12, 13, and 14].

The photocatalytic antimicrobial with titania has significant effect [15, 16], but this cannot be changed as a catalyst in the presence of a short absorption wavelength, visible light absorption rate is low (4%).

Related research shows that Anatase has a wider absorption range from invisible light to visible light under the dye modified.

Meanwhile, these paper also shows, the antimicrobial of the nano titanium dioxide increased significantly due to the wider absorption range [13, 14]. Therefore, dyes sensitized Nano Titanium is expected to become a clinically effective and highly effective antibacterial drug.

Research on manipulate the surface of Titanium with eifficient safe and cheaper dyes, is a critical focus in inorganic antibacterial research filed recently.

Dyes including pure organic dyes and metal organic dyes, pure organic dyes including oxygen and poly methyl and a number of natural dyes such as Eosin, phthalo cyanine, porphyrines, rose red. Hidaka[19] et al. has studied the photocatalytic of Anatase in solution system under the irradiation of UV light and sunlight, and metal dyes-nano titania shows a better light absorption and antibacterial capacity than pure organic dyes-nano titania, however, metal organic dyes are several hundred times more expensive than organic dyes, shorter life of excitation state, and more

Applications in the energy field. Alizarin red, Fuchsin Acid, Alizarin belong to organic dyes, which is cheaper than metal dyes. They have been confirmed better antioxidant activity than other orangic dyes according to Z. Ling *et al* [20], however, few articles have examined their different antimicrobial properties.

Meanwhile, M. Muruganadham *et al* [15] found that Fuchsin, Alizarin red monohydrate, Tartrazine have better performance than other oraganic dyes in antimicrobial properties, however, they didn't continue to search on the dose-response relationship.

We mainly research on 3dyes-sensitizing Anatase Titanium nanoparticles to promote the study including Alizarin red, Fuchsin Acid, and Alizarin in the article.

The Anatase Titanium nanoparticles and the dyes modified particles all prepared with efficient sol-gel phase (The dyes was added directly to the sol stage, and then stired), annealed at different temperatures [11, 12].

Then, the dye modified Anatase were analyzed with XRD, UV–Vis. Escherichia coli(*E. coli*) was described as a model, the organic dyes sensitized nano titania have been proven to own particular antibacterial activity.

2. Materials and Methods

2.1. Chemicals

Tetrabutyl titanate (TTIP, C16H36O4Ti), absolute ethanol (C2H6O), methanol (CH3OH), acetic Acid (HAc), polyvinyl alcohol (PVA), ammonia (NH3) and other chemicals were purchased from Spectrochem Pvt. Ltd (Tianjin,China). Fuchsin Acid, Alizarin, Tartrazine was obtained from Alfa Aesar's parent company (Aksaray,Turkey). E. coli (ATCC 10536) was obtained from Manassas, VA, USA. Tryptone and yeast extract were obtained from QingDao Hopebio-Technology Co., Ltd. (Qingdao, China).

2.1.1. Synthesis of titania nanoparticles. The Nano Titania were synthesized by sol-gel method using TTIP as titania source [21], anhydrous ethanol as solvent and hydrochloric acid as inhibitor.

Process:

①17ml of TTIP was added dropwise to 60 ml of ethanol, the mixture was stirred at 55℃ magnetically, then formed solution A.

②40ml absolute ethanol mixed with 2.5ml distilled water, adjusted with hydrochloric acid to pH=0.5-1, then formed solution B.

③B was added dropwise to A, and stirred about 2h magnetically, then formed solution C.

④Aging in air, formed Titania gel after 24h.

⑤Dry out the water and organic solvents in the gel according to 80℃ thermostatic, then formed the yellow xerogel.

⑥Xerogel was treated with the agate mortar, grinded for 15mins, then formed the Nano Titania particles.

⑦The powders were calcined 3h at 450℃.

2.1.2. Synthesis titania nanoparticles with Acid Fuchsin, Alizarin red, Tartrazine. During the phase③, different dyes was added to the mixture of A and B, and stirred with the mixture, and all the conditions were kept same. In order to facilitate record, the different weight of organic dyes mixed into Nano Titania simplified with Wt**.** %(0.2, 1, 2), the weight of the pure Nano Titania was 5g.

2.2. Materials Characterization

The information about crystallinity and purity of the samples were procured by X-ray diffraction (XRD, AXS Company, D8ADVANCE). Based on the strongest diffraction peaks and the SCHERRER formula, to calculate the average particle size of the corresponding crystal.

The UV–Vis absorption spectra of the particles were recorded with a UV–Vis spectrometer (HACH Company, DR6000).

2.3. Antibacterial Capacity Tests

After the synthesis , the weight of all particles is approximately 15mg, we choosen 1mg of every nanoparticlesdissolved into 10mL for analysis.The antibacterial properties were evaluated by standard disk diffusion test [22], all kinds of nano titanias (0.1mg/mL)were impregnated into discs, and distilled water loaded the filter papers (6 mm in diameter) with 10ul. 0.3*108cfu/ml E. coli were cultured on aseptic agar plates (9cm in diameter). All discs were carefully placed on the top of agar. The plates are kept after 24 hours of incubation at 30℃ under the sunlight.

The prepared inoculum has been used in 15min. Dipped the sterilized cotton swab into the liquid and rotate it several times on the tube wall to remove too much bacterial fluid. Then coated with the test medium throughout the surface of the medium, repeated several times, each time the plate rotated 60 degrees, and finally along the plate around the two laps, to ensure uniform coating. Sticked the drug sensitive test paper until the moisture on the plate was absorbed by the agar and began to stick the paper. In order to promise termediate plate reached the temperature of the incubator, the plate has placed separately in the reaction box, and reaction box have been sterilized. Meanwhile, the concentration of sterile saline (10 L) as control was 0.1mg/mL.

2.4. Statistical analysis

Data were processed with SAS software, analyzed by one-way ANOVA analysis to evaluate the difference among dye grades. A P-value of 0.05 was used to determine statistical significance, to determine the relationship among dye content correlation analysis was performed.

3. Results

3.1. Crystallographic phase transition and phase identification

The phase and phase purity of Anatase particles prepared at annealing temperatures of 450 ℃, was detected with X-ray diffraction patterns. The peaks are situated at 2θ = 25.36, 37.77, 47.99, 54.21. The peak centred at 25.36 with FWHM, after calculated with Debye-Scherrer equation, the size of the prepared materials was 22 nm.

Interestingly, the crystallite size was found to be decreased when anatase was sensitized with dyes also hints the existence of core_shell nanostructures. The size of Anatase-Acid Fuchsin and Anatase-Alizarin red was calculated as 20.8 and 21.1 nm, respectively, while the size of Anatase-Tartrazine was calculated as 21.3nm(under 0.2wt% dyes modified, respectively).

However, there was no correlation between the dye concentration and the size of obtained crystallite according to repeated experiments, Furthermore, the size of bare Anatase and dyes modified Anatase were also not correlated.

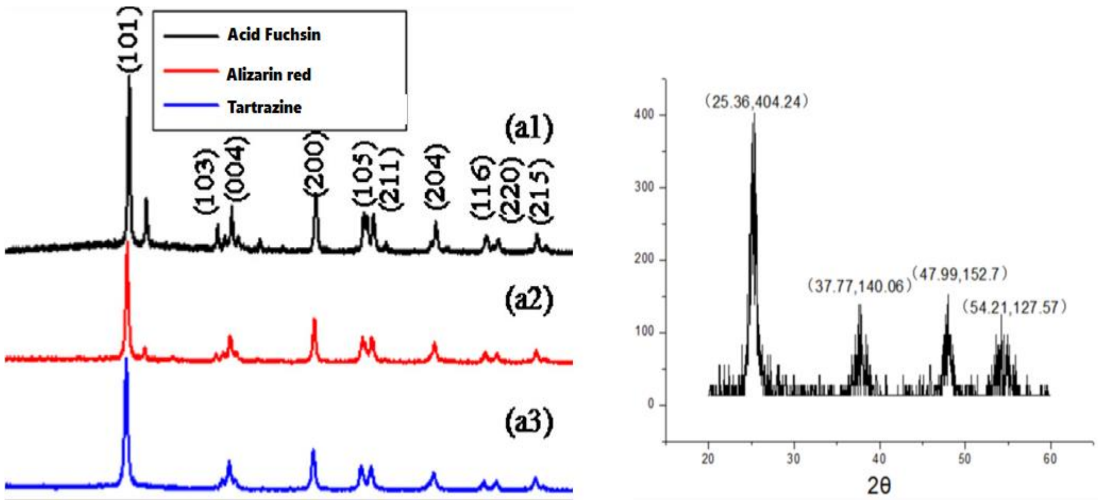
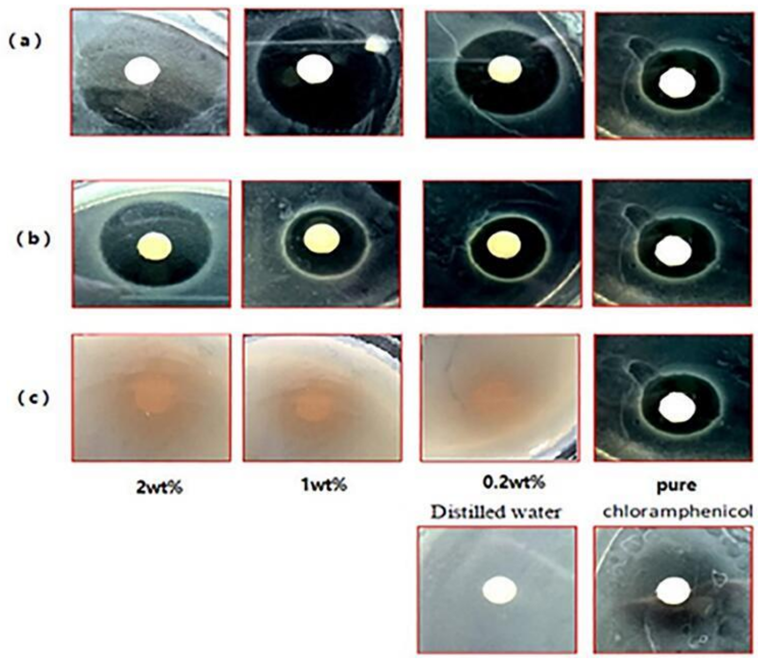


Figure 1. XRD pattern of (a1) Anatase-Acid Fuchsin, (a2) Anatase-Alizarin, (a3) Anatase- Anatase-Tartrazine, (b) Pure-Anatase

3.2. Antimicrobial activity under sunlight

3.2.1. ZI of antimicrobial activity. Figure 2 (d1) shows the ZI (Zone of Inhibition) of pure Anatase samples under sunlight. After 24h, the higher the Anatase content in the plate, the bigger ZI is. ZI is linearly related to the amount of Anatase incorporation. With the increase of the content of Anatase, the value of ZI increased. A positive correlation was observed between the ZI and pure Anatase content ($R= 0.81$, $P < 0.05$).



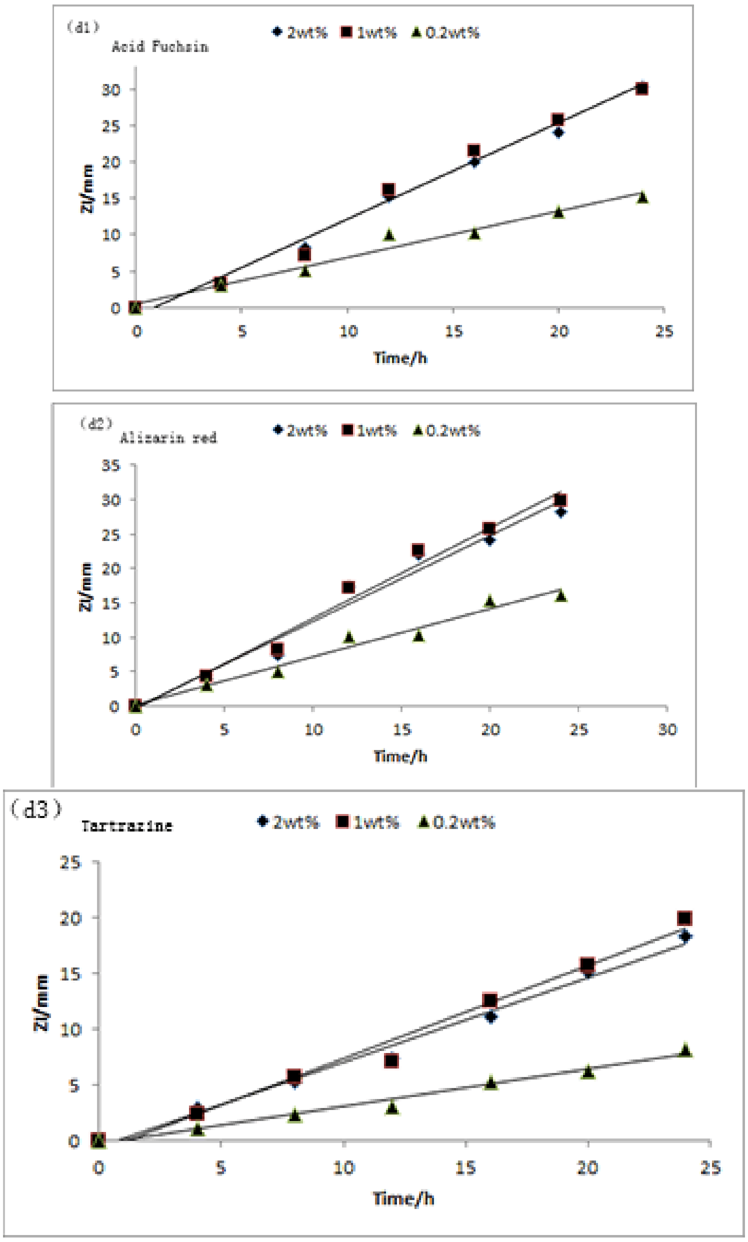


Figure 2. (A) ZI Acid Fuchsin; (b) ZI of Tarazin ;(c) ZI of e Alizarin red. (d) Relationship between concentration and ZI

Meanwhile, Figure 2 (a)(b)(c), (d1) (d2) (d3)shows that, with the increase of the content of dyes-Anatase, the value of ZI increased, same as the dyes increased. In the present study, the ZI increased when the dyes content increased. A positive correlation was observed between the ZI and Tartrazine content ($R= 0.54, P < 0.05$).

However, there is no significant difference between dyes-Anatase (1Wt. %) and dyes-Anatase (2Wt. %) level both in Acid Fuchsin and Alizarin red group. After 24h, there is no significant difference between Acid Fuchsin and Alizarin red group (at 1Wt. % and 2Wt. %) too.

After 24h, all dyes- Anatase possessed a higher significant different ZI value than pure-Anatase. At 2Wt.% level, the best was Acid Fuchsin group, it increased 2.97 times than pure-Anatase, Alizarin red group increased 2.91times than pure- Anatase, Tartrazine group increased 1.63 times than pure-Anatase.

3.2.2. UV-Vis Analysis

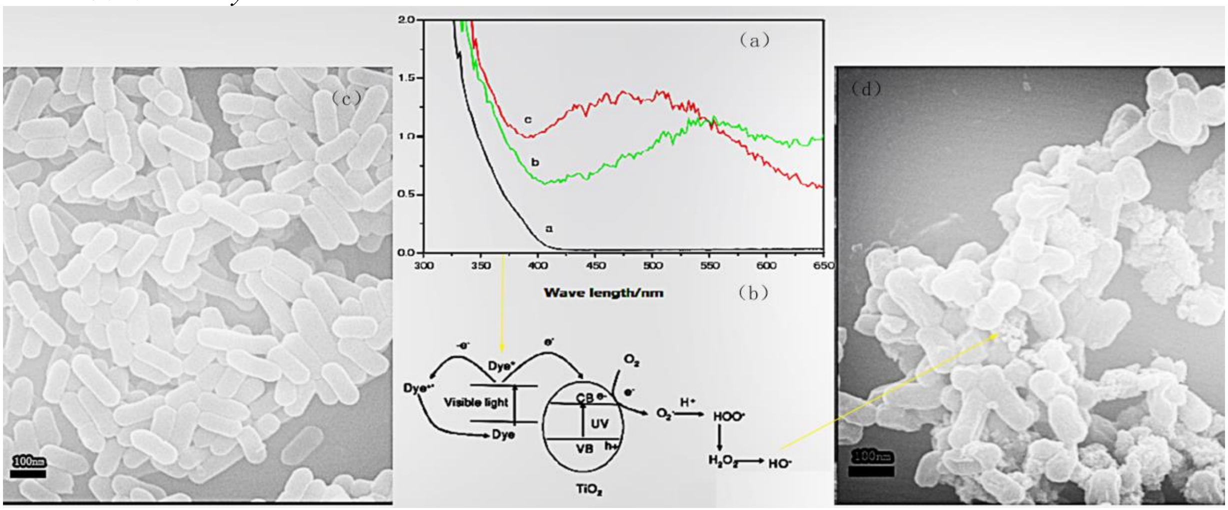


Figure 3. (a)UV-vis diffuse reflectance absorption spectra of various samples (a.Tartrazine-TiO_2, b. Alizarin red-TiO_2. Acid Fuchsin-TiO_2), (b) the sheme of dyes-sensitized Anatase photodegradation pollutants under sunlight illumination (c)

Figure 3(an Anatase, b Alizarin red modified Anatase, c Acid Fuchsin modified Anatase d Tartrazine modified Anatase) is the adsorption of Alizarin red, Acid Fuchsin, Tartrazine and the diffuse reflectance spectra. Three kinds of dyes all absorb visible light, the maximum absorption peak is located in 420nm, 542nm and 426nm. They come into contact with a large surface area of nano titanium dioxide, the molecular structure of the sulfonic Acid group in Kulun and Anatase interaction with the adsorption of titanium dioxide surface [23].The figure shows that Anatase is a wide band gap semiconductor, only absorb ultraviolet light, the adsorption of Acid Fuchsin and Alizarin red after the optical absorption edge shifted to long wave, there is a strong absorption in the visible region, which indicates that the three kinds of dyes has good effect light sensitization to Anatase. Dyes not only broaden the response range of Anatase to visible light, to overcome the insufficient use of Anatase solar rate is low, and can significantly improve its photocatalytic activity under sunlight.

Figure. 3 (a) shows that the sensitization agent is adsorbed on the Anatase surface, and the light is excited by the sensitization agent. The sensitization agent will inject electrons into the Anatase conduction band, and react with the adsorbed reactant via the Anatase surface. The reaction of the agent and the sacrificial agent back to the ground state, or its own decomposition [24].

According to Figure3. (b), compare with Tartrazine, Alizarin red and Acid Fuchsin which have more joints point than atrazine. The reaction of agents contingent on the joints, has been accepted by some reports [25]. Consequently, organic dyes sensitized with nano Anatase are more efficient for antibacterial applications according to their joints with nano Anatase.

4. Conclusion

There was no correlation between the dye concentration and the size of obtained crystallite, Size has not also correlation between bare-anatase and dye modified anatase.

The antimicrobial rate of the nano-Anatase was mainly related with assistant of the absorption which increased with the dyes and linearly with their concentrations.

Dyes modified anatase increased the antimicrobial rate under the 2Wt. % in Tartrazine group significantly. However, it has not significantly increased above 1Wt. % in Alizarin red and Acid Fuchsin group.

After 24h, all dyes- Anatase possessed a higher significant different ZI value than pure-Anatase. At 2Wt. % level, the best was Acid Fuchsin group, it increased 2.97 times than pure-Anatase, and

Alizarin red group increased 2.91times than pure-anatase, Tartrazine group increased 1.63 times than pure-anatase.

Anatase is a wide band gap semiconductor, only absorb ultraviolet light, the adsorption of Acid Fuchsin and Alizarin red after the optical absorption edge shifted to long wave, there is a strong absorption in the visible region, which indicates that the three kinds of dyes has good effect light sensitization to Anatase.

Acknowledgments
This work was supported by funding from NSFC (Modern agricultural industry technology system vegetable innovation team of Shandong Province SDAIT-05-14).

References
[1] D.A.H. Hanaor, C.C. Sorrell, Review of the anatase to rutile phase transformation, J. Mater. Sci. 46 (2011) 855.
[2] K. Nakata, A. Fujishima, Anatase photocatalysis: design and applications, J. Photochem. Photobiol. C: Photochem. Rev. 13 (2012) 169.
[3] J. Gangwar, B.K. Gupta, S.K. Tripathi, A.K. Srivastava, Phase dependent thermal and spectroscopic responses of Al2O3 nanostructures with different morphogenesis, Nanoscale,7 (2015) 13313.
[4] X. Bai, L. Lv, X. Zhang, Z. Hua, Synthesis and photocatalytic properties of Palladium-loaded three dimensional flower-like anatase Anatase with dominant 00 1 facets, J. Colloid Interface Sci. 467 (2016) 1.
[5] T. Kamegawa, D. Yamahana, H. Yamashita, Graphene coating of Anatase nanoparticles loaded on mesoporous silica for enhancement of photocatalytic activity, J. Phys. Chem. C 114 (2010) 15049.
[6] T. Aarthi, G. Madras, Photocatalytic degradation of rhodamine dyes with nano- Anatase, Ind. Eng. Chem. Res. 46 (2007) 7.
[7] Y.R. Smith, A. Kar, V. Subramanian, Investigation of physicochemical parameters that influence photocatalytic degradation of methyl orange over Anatase nanotubes, Ind. Eng. Chem. Res. 48 (2009) 10268.
[8] L. Alibabaei, B.H. Farnum, B. Kalanyan, M.K. Brennaman, M.D. Losego, G.N.Parsons, T.J. Meyer, Atomic layer deposition.
[9] J.Y. Ahn, J.H. Kim, K.J. Moon, S.D. Park, S.H. Kim, Synergistic effects of the aspect ratio of Anatase nanowires and multi-walled carbon nanotube embedment for enhancing photovoltaic performance of dye-sensitized solar cells, Nanoscale 5 (2013) 6842.
[10] L. Yu, J. Xi, M.D. Li, H.T. Chan, T. Su, D.L. Phillips, W.K. Chan, The degradation mechanism of methyl orange under photo-catalysis of Anatase, Phys. Chem. Chem. Phys. 14 (2012) 3589.
[11] C.Y. Flores, C. Diaz, A. Rubert, G.A. Benitez, M.S. Moreno, M.A.F.L. De Mele, R.C. Salvarezza, P.L. Schilardi, C. Vericat, Spontaneous adsorption of silver nanoparticles on Ti/Anatase surfaces. Antibacterial effect on Pseudomonas aeruginosa, J. Colloid Interface Sci. 350 (2010) 402.
[12] R. Verma, B. Mantri, Ramphal, A.K. Srivastava, Shape control synthesis, characterizations, mechanisms and optical properties of large scaled metal oxide nanostructures of ZnO and Anatase, Adv. Mater. Lett. 6 (2015) 324.
[13] F. Turci, E. Peira, I. Corazzari, I. Fenoglio, M. Trotta, B. Fubini, Crystalline phase modulates the potency of nanometric Anatase to adhere to and perturb the stratum corneum of porcine skin under indoor light, Chem. Res. Toxicol. 26 (2013) 1579.

[14] A. Jaroenworaluck, W. Sunsaneeyametha, N. Kosachan, R. Stevens, Characteristics of silica-coated Anatase and its UV absorption for sunscreen cosmetic applications, Surf. Interface Anal. 38 (2006) 473.
[15] N.Sobana,M.Muruganadham,M.Swaminathan, Nano-Ag particles doped TiO2 for efficient photodegradation of Direct azo dyes, Journal of Molecular Catalysis A Chemical, 2006 , 258 (1-2) :124-132.
[16] Maatoug A M, Peter A, et al. Role of pigments in the stability of polyethylene systems. Macromol. Mater. Eng., 2000, 282: 30-36.
[17] Cho S M, Choi W Y. Solid-phase photocatalytic degradation of PVC-Anatase polymer composites. J. Photochem. Photobil. A, 2001, 143: 221-228.
[18] Zhu Y F, Shang J, Chai M. Photocatalytic degradation of polystyrene plastic under fluorescent light. Environ. Sci. Techol., 2003, 37: 4494-4499.
[19] T. Zhang, T. Oyama, S. Horikoshi, H. Hidaka, J. Zhao, N. Serpone, PhotocatalyzedN-demethylation anddegradation of methylene blue in titania dispersions exposed to concentrated sunlight, Sol. Energy Mater. Sol. Cells 73 (2002)287–303.
[20] Z.Ling,W.Songlin,F.Wenjun.Solid-phase photocatalytic degradation of polystyrene with modified nano-Ti O2 catalyst[J].Polymer,2006,47:8155-8162.
[21] Zhao W, Chen C C, Li X Z, et al. Photodegradation of sulforhodamine-B dye in platinized titania dispersions under visible light irradiation: Influence of platinumas a functional co-catalyst. J. Phys. Chem. B, 2002, 106(19): 5022-5028.
[22] Methods for dilution antimicrobial susceptibility tests for bacteria that grow aerobically, Clinical and Laboratory Standards Institute, 2000.
[23] Zhu Y F, Shang J, Chai M. Solid-phase photocatalytic degradation of polystyrene plastic with Anatase as photocatalyst. J. Solid. State. Chem.,2003, 174: 104-109.
[24] G. M. Liu, X. Z Li, J. C. Zhao, et al., Photooxidation mechanism of dye AlizarinRed in Anatase dispersions under visible illumination:an experimental and theoretical examination[J]. Journal of Molecular Catalysis A: Chemical, 2000, 153:221-229.
[25] MIHINDUKU, LASURIYA et al., Nanotechnology Development in Food Packaging: A Review[J]. Trends in FoodScience & Technology,2014,40(2):149—167.