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Photocatalytic Effects of Nanoparticles of TiO_2 in Order to Design Self-Cleaning Textiles

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Titanium dioxide nanoparticle shows photo catalytic effect. It can decompose organic structures (pollution) with touch its surface also. It shows superhydrophilic effect. According to lotus leaf model, we provided textiles with withstanding penetration of liquids without using any resin. So, the textiles firstly withstand pollution and if they pollute, they can decompose the pollution structure under UV radiation. In this work, we studied the effect of nano silver and enhancement of electron-hole separation by the electron trapping and reduction of energy gap of titania. In addition to that, adding nano silica to titania, demonstrated higher photocatalytic and superhydrophilc activity in comparison to pure TiO_2.

Key Words: Self cleaning, Nanoparticles, TiO_2, SiO_2, Ag.

INTRODUCTION

The photocatalyst is composed of two parts of photo and catalyst, which refers to the semiconductors stimulated by light energy. When TiO_2 (e^-) and the holes (h^+) resulted from the electron layers energy, then the electron deficiency are formed. The electrons react to a reduction reaction with molecular oxygen and produce superoxide anion radical ($^{\bullet}O_2^-$). The holes produced react during a oxidation reaction with water (and the moisture in the air) and produce $^{\bullet}OH$ radicals. The produced radicals are quite energetic and react with different organic and contaminants to decompose them. Due to decomposition of the organic materials bonds, their poisonous and dangerous characteristics are removed and the produced materials are less hazardous and less poisonous with respect to the initial materials[1-3].

Titanium dioxide has three main phases which include anatase, rutile and brookite. Energy gap of titania in anatase *ca.* 3.2 ev and in rutile 3.05 ev. The higher photocatalytic activity of anatase is attributed to the energy level of a positive hole in the valency band which is 210 mV lower than that of rutile. Therefore, the oxidation potential of a positive hole in an anatase crystal is higher than a comparable hole in a rutile crystal[2].

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$$TiO_2 + hv \rightarrow h^+ + e^-$$
$$e^- + Ti^{4+} \rightarrow Ti^{3+}$$
$$Ti^{3+} + O_{2(g)} \rightarrow Ti^{4+} + O_2^-(ads)$$
$$O_2^-(ads) + h^+ \rightarrow O_{2(g)} \uparrow$$

Fig. 1. Photocatalytic mechanism of TiO_2

The level of photocatalytic operations is dependent on the following three factors: (1) level of light absorption by photocatalyst (2) oxidation- reduction reaction rate of electron-hole (3) electron-hole re-compound rate[4].

TiO_2 has a big energy gap, which is only active within the UV range, which includes less than 5 % of the sun spectrum.

The noble metals such as Pt and Au deposited or doped on TiO_2 have the high Schottky barriers among the metals and thus act as electron traps, facilitating electron-hole separation and promotes the interfacial electron transfer process[5].

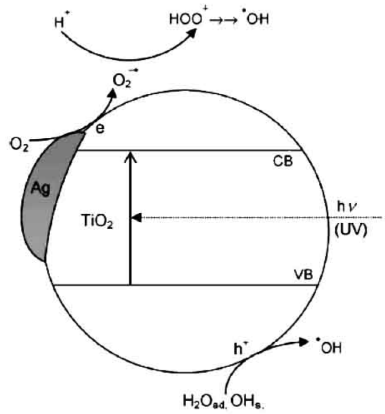


Fig. 2. Enhancement the photocatalytic characteristic of TiO_2 by silver

The water drop contact angle with TiO_2 is at the beginning tens of degrees, which after radiation of UV this angle decreases seriously and such surface become hydrophilic.

As mentioned earlier, due to UV radiation with wavelengths less than 387.5 nm, which is the same as the TiO_2 energy gap, the electrons will find the required energy to transfer from the valence band to conduction band and the electron-hole pair is formed. The electrons tend to convert the Ti^{4+} cations to Ti^{3+}. The latter reacts with the molecular oxygen in the air and is converted to O_2^- and then absorbed into the surface. Due to such reaction, the Ti^{3+} cations are converted to Ti^{4+}. In holes, the oxide (O_2^-) anions absorbed on the surface and the molecular oxygen exits the external surface in gas format and eventually, oxygen appeared empty surfaces. In case if the sample is exposed to the moisture, then the water molecule fills these spaces and the OH absorbed on the TiO_2 surface are appeared, which make the surface hydrophilic.

A water layer which is absorbed chemically because of the film hydrophilic nature of the film may absorb more layers of water due to the vander Waals force and hydrogen bonds and these layers make the contact between the surface and the absorbed containments. Thus, the absorbed materials are easily removed from the surface by the distributed water and the self- cleaning effect is observed[1].

The use of TiO_2 as a photocatalyst for the decomposition of organic compounds and microbial organisms including viruses, bacteria and cancer cells has been reported, as well as its potential use in sterilization of medical devices, food preparation surfaces, air-conditioning filters, *etc.*[6].

When trying to formulate photocatalytic coatings a way has to be found to incorporate the titania into the resin matrix without covering all of its surface with binder. Of course its important to compromise between film integrity and photocatalytic activity. The next thing to consider is that the resin itself will inevitably be oxidized provided that is vulnerable for this type of attack. The only exemptions are to some extent fluorinated polymers. It seems that the C-F bond is strong enough to withstand oxidation by titania photocatalysts[2].

This study focuses on the introduction of a spacer onto a cotton textile by chemical means. This spacer needs to have at least two free carboxylic groups to be able to bind both the cotton and the TiO_2. The spacer should also have an acceptable chemical and thermal stability. It will be introduced by formation of a covalent ester bond. This implies esterification of one carboxylic group of the spacer by a hydroxyl group of cellulose. The second spacer carboxylic group is meant to anchor TiO_2 by electrostatic interaction.

As the proper spacer the polycarboxylic acids such as succinic acid, may be exemplified. The catalyst used to perform this reaction is sodium hypophosphite.

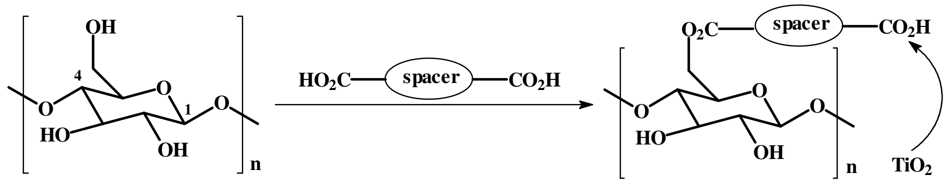


Fig. 3. Method of succinic acid and TiO_2 bond with cotton

Mielert and Laub[7] reported that the highest TiO_2 were obtained with succinic acid in comparison with BTCA and PTCA. This result shows that the highest TiO_2 loading was not always obtained with the spacers that have the most carboxylic groups[7]. In a study performed by Chen and Wang[8], they used the nanoparticles with succinic acid to make cotton fabrics wrinkle resistant.

EXPERIMENTAL

Cotton fabrics were obtained with density of 124.5 g/m^2, succinic acid, sodium hypophosphite, TiO_2 (Plasachem Co), Ag (Lotus Co), SiO_2 (Degussa Co).

First of all the desized, bleached and fully washed fabrics are immersed in a bath of succinic acid of 50 g/L accompanied with 30 g/L sodium hypophosphite and timing is set for 1 h.

After treatment of the samples of the bath, they are dried for 5 min under a temperature of 70 ºC and then the acid curing step and formation of the bonds is done for 2-10 min under a temperature of 120-140 ºC. Then the fabrics are washed with water to remove the materials on the surface which have not participated in the reaction.

The fabrics prepared in the previous step are dipped into the nano TiO_2 bath having density of 5 g/L and the same is left for 1 h. After treatment, the excessive solution was removed from the fabric surface. The drying step is done under 60 ºC for 10 min and the curing step under a temperature of 100 ºC for 1 h.

Another part of the test and with the purpose of mixing the nano-particles, we cross out the basis making step and similar to the foregoing, the fabrics was dipped into a bath mixture of TiO_2, SiO_2 (5 g/L) and Ag nano particles (100-300 ppm) and the process continued. The nano particles present in bath were set in two different temperatures (ambient and at 60 ºC) and the results were compared.

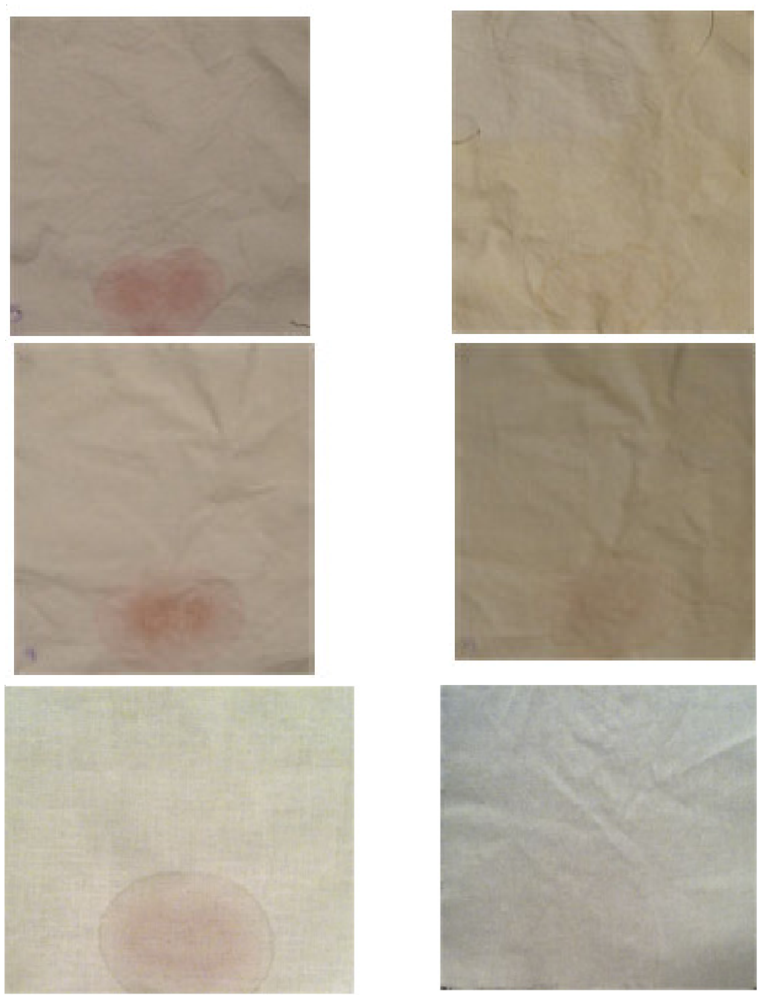
TABLE-1
INFORMATION OF SOME TREATED SAMPLES

Samples	Acid	TiO_2 (g/L)	SiO_2 (g/L)	Ag (ppm)
1	Yes	5	–	–
2	No	5	–	–
3	Yes	5	–	100
4	No	5	–	100
5	No	5	–	300
6	No	5	5	–
7	No	5	5	300

RESULTS AND DISCUSSION

Photocatalytic characteristic: Comparing the processed samples, it was observed that in case if basis is made prior to enter the fabrics into the nano bath, then the pick up level of the nano particles by the fabric will increase.

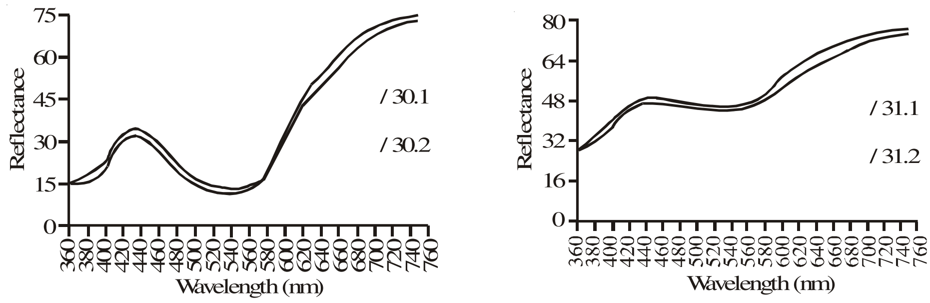
Also in case if the Ag nano particles are used with TiO_2, then due to the explained mechanism, it results in an improvement in the TiO_2 photo-catalytic characteristic which is proved in the level of decolourizing of the stains generated on the fabric. Also in the SiO_2 containing samples, which result in enhancement of the titania Photo-catalytic characteristic accompanied with TiO_2, we observed more effectiveness in stains decolourization. In case if the temperature of 60 ºC is applied to the nano particles, then the nano particles energy to pass the electrical potential will increase and their level of absorption also increases. Fig. 4 shows stained pieces of fabric with red wine, before and after 24 h of UV radiation.



Before UV After UV

Fig. 4. Stain fabric

Also using the indosol rubinole SF-RGN colour and making a stain on raw and processed fabric and performing the calorimetric test, we performed the comparison of the two samples.



Before UV After UV

Fig. 5. Calorimetric charts of raw and treated fabrics

In Fig. 5, the upper curve is associated with the processed fabric with nano particles, which after UV radiation, the stain colour difference especially within the 570-640 mm on the two samples is quite obvious. However, the relatively high light fastness of the colour used is within the 4-5 range, results in non existence of a great difference and it seems that for the colours with lower light stabilities, such as rhodamine B and methylene blue the difference of these two curves is more identical.

Characteristic of superhydrophilic and hydrophobic: Investigation into the samples and water repellency tests (Fig. 6) and SEM images (Fig. 7) indicate that the samples processed with TiO_2, SiO_2 and Ag prevent from entrance of water and liquids into the fabric because of making rough surface like lotus leaf, which results in resistance of the cloth against entrance of contaminants. This cloth resistance to liquids penetration before UV radiation without using resins and only made by the nano particles and they will not have the problems of using resins such as the limitation generated for the cloth respiration.

But in case if these fabric are under UV radiation, after a while they are hydrophilic, but the other side of the fabric which was not directly exposed to radiation will slightly resist against liquids penetration.

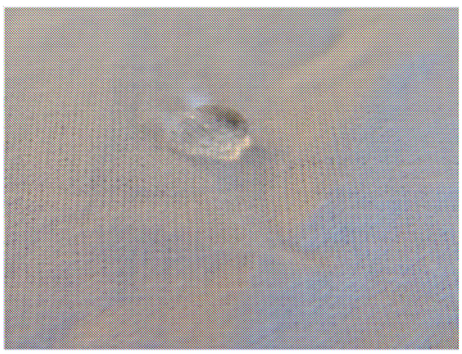


Fig. 6. Fabric resistance to liquids penetration characteristic

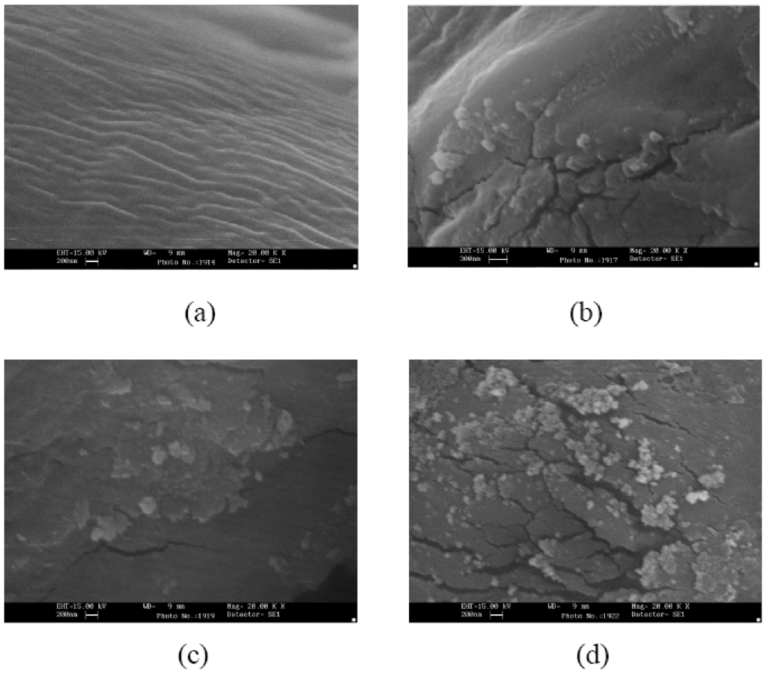


Fig. 7. SEM image: (a) raw sample, (b, c) samples covered with TiO_2, (d) sample covered with TiO_2 and silver

Conclusion

Results indicate that using the TiO_2 nano particles and the respective photo-catalytic characteristic we proceeded with designing cotton-based textiles, which are resistance against the liquids penetration and may decompose the containment structure under UV radiation. By adding the SiO_2 and Ag nano particles to TiO_2, more effectiveness of the titania photocatalytic activities may be seen.

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