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Primary Colors (Red, Yellow, and Blue) Use as Self-Cleaning Paints with Layer of Titanium Dioxide

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Abstract

Transparent nano- coating was prepared by Sol-Gel method from titanium dioxide TiO_2 which has the ability to self-cleaning coating used for hospitals, laboratories, and places requiring permanent sterilization. Three primary colors are selected (red, blue, and yellow) as preliminary study to the effect of these colors on the nano-coating. Three traditional oil paints color were used as base, then coated by a layer of TiO_2-Sol and deposited on the paints. The optical properties of TiO_2-Sol were measured; the maximum absorption wavelength at (λ_{max}=387 nm), the refractive index (n=1.4423) and the energy band gap (E_g=3.2 eV). The structure properties found by X-ray diffraction of TiO_2-Sol illustrated that TiO_2-Sol is polycrystalline nanoparticle have anatase phase also the morphological properties measured by Scanning Electron Microscopy (SEM) obetained the average grain size of TiO_2-Sol was (50.427 nm). Self-cleaning properties measured by tensiometer dives. The best color gave the highest response to self-cleaning is the yellow color where the contact angle before exposure to UV (θ_c= 101.47º ,at t = 0 min) and after exposure over time (θ_c= 1.75º ,at t = 50 min), thus the water sheet of the surface and remove all contaminants.

Key words: Contact angle, Optical properties of TiO_2, Primary color, Self-cleaning process, TiO_2 –Sol.

Introduction:

Self-cleaning paint has the ability to clean itself. The phenomenon of self-cleaning is taken from lotus flower which always seen clean even if its grows in muddy medium (1). The self-cleaning depend on: surface roughness of TiO_2 photocatalysis, chemical composition of the surface and dirt particle adhesion (2). TiO_2 photocatalysis material which illumination in UV-irradiation and has a strong oxidation in low energy for removing the organic and inorganic compounds on the surface (3). Contact angles (θ_c) are measurement properties of self-cleaning which have two cases: θ_c <90° hydrophilicity and θ_c >90° hydrophobic (4). TiO_2 is widely used as a photocatalyst, De Jesus et al in 2015 worked on TiO_2/SiO_2 composites films compared with pure TiO_2 films in relation to adhesion, hydrophilicity and transparency. Both films have been deposited over low iron float glass substrates by sol-gel dip-coating method and different calcination temperatures (5). Sangchay, (2016) prepared TiO_2/SnO_2 thin films by the sol-gel method.

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The films were deposited onto glass substrate and calcination at 700 °C and investigated that films enhance the photocatalytic and self-cleaning property (6). Mufti et al.in 2017 prepared different thickness coating of TiO_2 anatase phase using sol-gel spin–coating method and found the thin film surface possess a hydrophilic nature (7). Gherardi et al. in 2018 treated the natural stones by using a layer of nano-TiO_2 and Tetraethylorthosilicate (TEOS) have the ability to photocatalytic and self-cleaning properties. Two treatments use (wet-on-dry and wet-on-wet) were compared in the results. A strong interactions between (titanium-oxygen-silicon) Ti-O-Si formed the key factor of the successful treatment and this layer shows depolluting and self-cleaning durable activity (8).

TiO_2 is a white, highly stable and unreactive metal oxide, present in nature in three different crystalline forms: anatase, rutile and brookite. Titanium dioxide prepared by variety precursors : titanium (IV) isopropoxide (TTIP) – $Ti[OCH(CH_3)_2]_4$, titanium (IV) butoxide – $Ti(OCH_2CH_2CH_3)_4$ and titanium (IV) chloride $TiCl_4$. TiO_2 is an indirect semiconductor with an energy gap of about 3.2 eV for anatase phase (9).

The different structures of absorbing edge were described and energy band gap was identified by suitable absorbing edge utilized from models direct and indirect use linear fitting in the area concerned with a plot of $(\alpha h\upsilon)^r$ against $(h\upsilon)$. Energy band gap E_g is calculated by equation below (10).

$$\lambda = \frac{hc}{E_g} = \frac{1240}{E_g}$$

where:-

λ: Wavelength in (nm).

h: Planck′s constant.

c: Speed of light.

r : Transition coefficient.

In this work, three primary colors are used to the first test to this product. While the color is known as brains reaction to specific visual stimulus also colors are ordinarily divided into primary, secondary, and tertiary colors. Primary colors are the most fundamental colors in the RYB model (red, yellow and blue) (11).

The aim of the work is converting the traditional paints to self-clearing paints by using TiO_2-Sol and primary colors paints. Thus, these self-cleaning paints can be used for hospitals, laboratories, and places requiring permanent sterilization.

Materials and methods:

The materials and the method Sol –gel was used to prepare TiO_2-Sol by drop wise 4 ml titaniumteteraisopropoxide (TTIP), chemical symbol is Ti $[OCH(CH_3)_2]_4$, purity 99%, from Sigma-Aldrich with mixing 45 ml deionization water (DW). Then 0.4 ml of nitric acid (HNO_3) we added to the solution until reached the pH to 2.1. The solution was put on a magnetic stirrer for 72 hrs. then the sol was aged for 24 hrs. at 55 C̊ yielding a transparent sol. Preparation self-cleaning coating TiO_2- Sol as shown in Fig. 1.

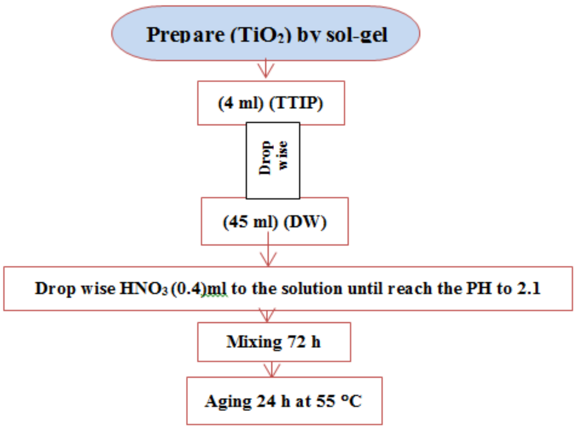

Figure 1. Diagram of preparation TiO_2.

Twenty one samples were prepared by painting the glass slide in different color of paint (red, blue and yellow) as shown in Fig. 2 each color has 7 samples. The paints dried in room temperature at 25° for three days.

Figure 2. The image for all slide coated by (red, blue and yellow) paints.

The 21 samples were coated by TiO_2-SoL using brush as shown in Figs. 3, 4 and 5 respectively and the samples dried at room temperature for three days.

Figure 3. The image for paint red slides coated by TiO_2-SoL then dry at room temperature for three days.

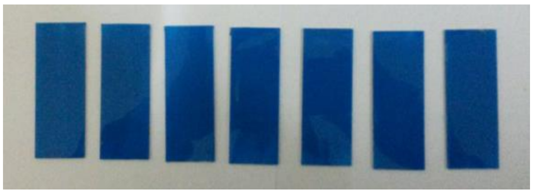

Figure 4. The image for paint blue slides coated by TiO_2-SoL then dry at room temperature for three days.

Figure 5. The image for paint yellow slides coated by TiO_2-SoL then dry at room temperature for three days.

While the optical properties measured by using double beam (No. CE7200 from Aquarius company) spectrophotometer have wavelength range of (200-1100)nm and the refractive index measured by Refractometer AR4 from Germany.

The crystalline phase was obtained by using diffractometer instrument from [(PANALYTICAL), model X'Pert Pro MPD]. X-ray diffractometer operated at 40kV and 30mA, which used (CuKα) radiation source at wavelength (λ= 0.15418 nm). The SEM was used to get the morphology of TiO_2. It was performed from "Hitachi", model (MIR3A TESCAN). Thus, self-cleaning properties were achivied by measuring the contact angle of water droplet injected on the surface of the paints.

Contact Angle (θ_c) Measurements

Wettability behavior was evaluated by measuring the contact angle of a water droplet on the surfers of paint using (Optical Tensiometer), Company model (Theta Lite/TL100 and TL 101. A water droplet is injected on the surface using micro-injector (5µL) syringe pointed vertically down onto the sample surface, light source monochromatic LED, contact angle range (0º-180º) and high resolution (60 fps) video camera which is built-in the system, captures the image of the water droplet, and then analyzes using image analysis software.

Results and Discussion:

Three primary colors were used as a paint and developed to self-cleaning paints by coating the paint surface in TiO_2-Sol. The optical properties, structure, morphological and self-cleaning properties are studied. Self-cleaning properties measured by contact angle which determine the best paint color. These film were fabricate by 21 coated samples of glass slides, each color has 7 samples. The samples were left to dry completely for three days and then coated by TiO_2-Sol photocatlysis under ultraviolet radiation that makes the surface self-cleaning as pollutants turn into water (H_2O) and carbon dioxide (CO_2) and are emitted into the atmosphere, which is similar to photosynthesis in plants.

Optical Properties

The optical properties {absorption (A), refractive index (n) and energy band gap (E_g)} for TiO_2-sol are measured. The absorption spectrum of TiO_2–sol NPs is shown in Fig. 6. The maximum absorption wavelength in (λ_{max}=387 nm). This result is good agreement with the other researchers (12).

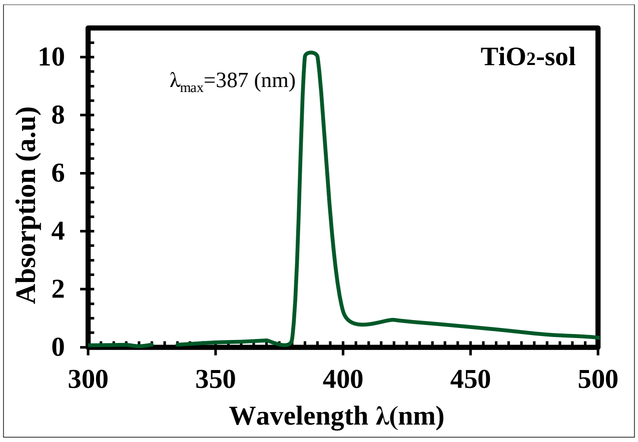

Figure 6. Absorption spectrums of TiO_2–sol.

The refractive index was measured by refractometer-AR4 (n=1.4423) for TiO_2 –sol. The energy band gap was calculated by applying previous equation is (E_g=3.2 eV) and this is in agreement with searchers (13).

Structure Properties Found by X-Ray Diffraction (XRD) of TiO_2.

The diffraction pattern analysis of TiO_2 as shown in Fig.7. Comparing the result of XRD spectra with American Society of Testing and Materials (ASTM) data card (# o21-1236) for anatase (14), the materials formed was polycrystalline nanoparticles in anatase phase (15). The reflection forms (110), (021), (200), (102) (022) and (122) planes at 2θ values 25.42°, 37.50°, 39.81° , 41.94°, 49.78° and 53.98° for sample fabricated by sol-gel path.

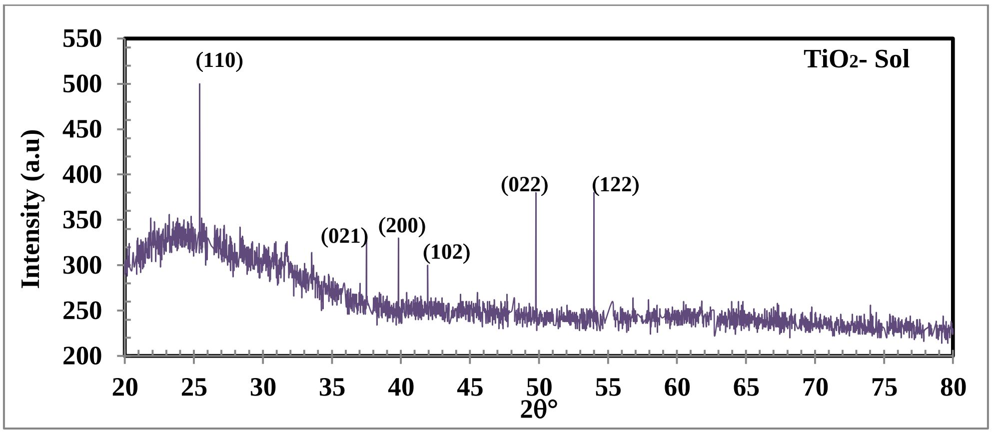

Figure 7. XRD analysis for TiO_2 at 2θ = 25.42°, 25°C.

Scanning Electron Microscopy (SEM) of TiO_2.

The morphologic properties were studied by using SEM of TiO_2. A layer was analyzed using SEM which gave characterize of the shape and size of TiO_2. Figure 8 refers to SEM image of TiO_2-sol and the magnification of image is (5000) and the scale in (500 nm) and the average crystallite size (50.427 nm) it means that TiO_2-sol was nanoparticles size (NPs) solution and the shape was uniformly distributed.

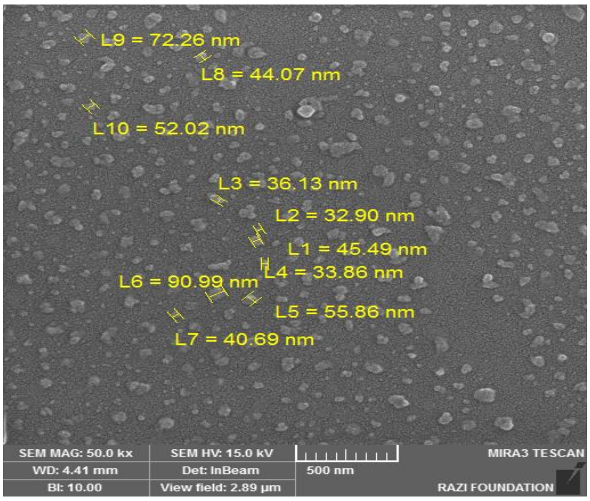

Figure 8. SEM image for surface profile and the average crystallite size for TiO_2-sol =50.427 (nm).

Self-Cleaning Properties

The contact angle was measured by optical tensiometer device containing digital camera which measured the angle between water drop and the surface of the paint with variation of time exposure to UV-irradiation. The results were presented first by calculating the relation between contact angle (θ_c°) and UV-irradiation time in minutes. Second, monitoring the drop water with increasing time of UV-irradiation and taking different images to contact angle from the highest value stat "hydrophobic" to the lowest value stat "hydrophilic" until the angle became (5°-0) which represented wettability stat "superhydrophilicity" so that the self-cleaning occurring to the surface of the paint.

Initial measures to all samples were taken directly to the TiO_2-sol NPs after released from dark container, at time UV-irradiation equal zero, to get the highest contact angle to the drop which referred to "hydrophobic"(16).

Figures 9 and 10 shows the contact angle of water droplet on the surface of TiO_2-Sol on the red and blue paints respectively.

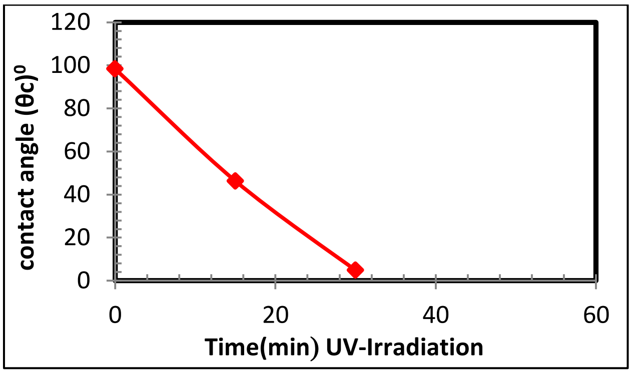

Figure 9. The contact angle measurement with time UV-irradiation for red paint.

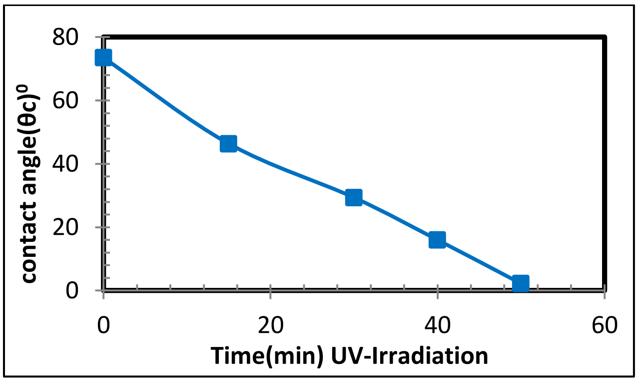

Figure 10. The contact angle measurement with time UV-irradiation for blue

The highest contact angle on the red paint at (θ_c= 98.34°) and for blue paint at (θ_c= 73.49°) the angle decrease with increasing the time exposure to UV-irradiation until it reaches to superhydrophilicity (17) in red paint (θ_c= 4.82°) at (t = 30 min) and for blue paint (θ_c= 2.23°) at (t = 50 min), mean that the surface of this samples complete wetting. The contact angle images in different time exposuer to the sample red and blue paint as shown in Figs. 11 and 12 respectively.

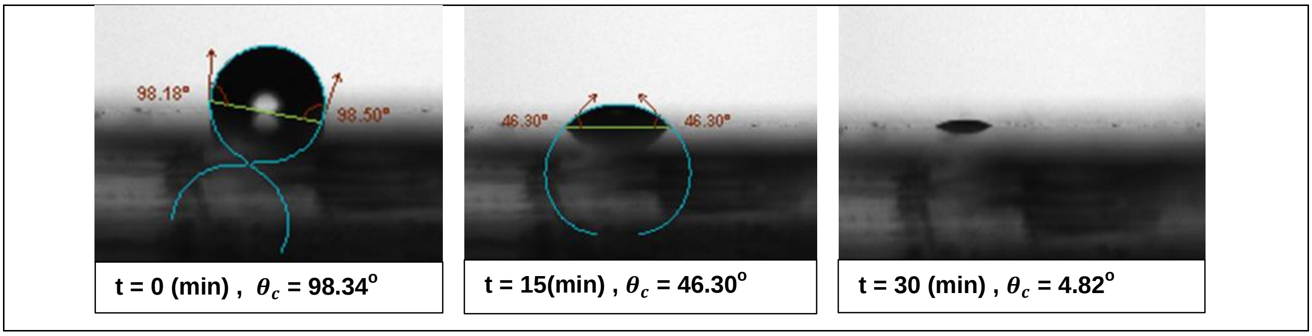

Figure 11. The image of contact angle with time for red paint.

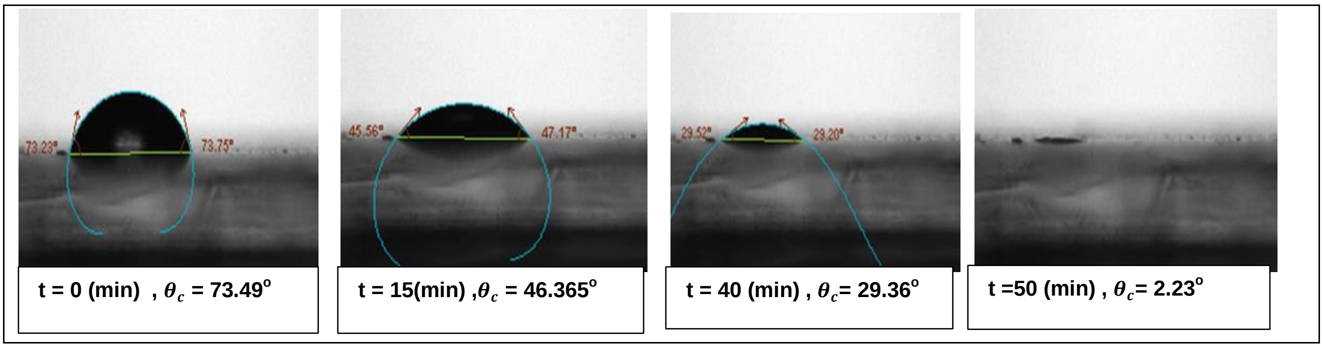

Figure 12. The image of contact angle with time for blue paint.

Figure 13 show the contact angle measurement for yellow paint. The optimum sample has a highest contact angle which is (θ_c= 101.47°) at (t = 0), it means good hydrophobic water droplet (18) in yellow paint. Also, the drop has a large size from (red and blue) TiO_2-sol NPs which (θ_c=98.34° ,θ_c= 73.49°) respectively.

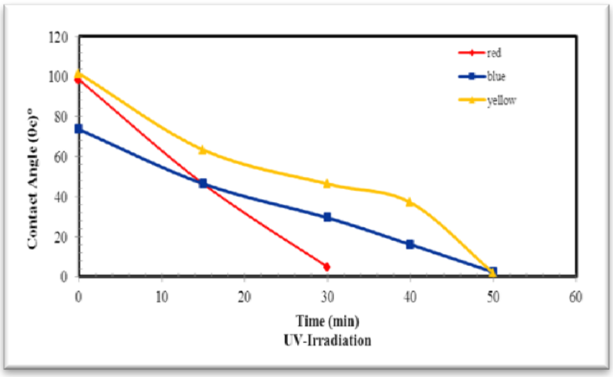

Figure 13. The contact angle measurement with time UV-irradiation for all three paints.

Figure 14 shows that the images of contact angle for yellow paint after exposure over time (θ_c= 1.75° ,at t = 50 min) it means that the contact angle is converted from the "hydrophobic" highest value to the lowest value "hydrophilic" , so the water sheet the surface and thus removes all contaminants on the surface of the paints and this in agreement with Rios et al. (19). The drop on the yellow painted surface has larger amount of water than another colors, which will contribute to self-cleaning better than droplets on red and blue paints.

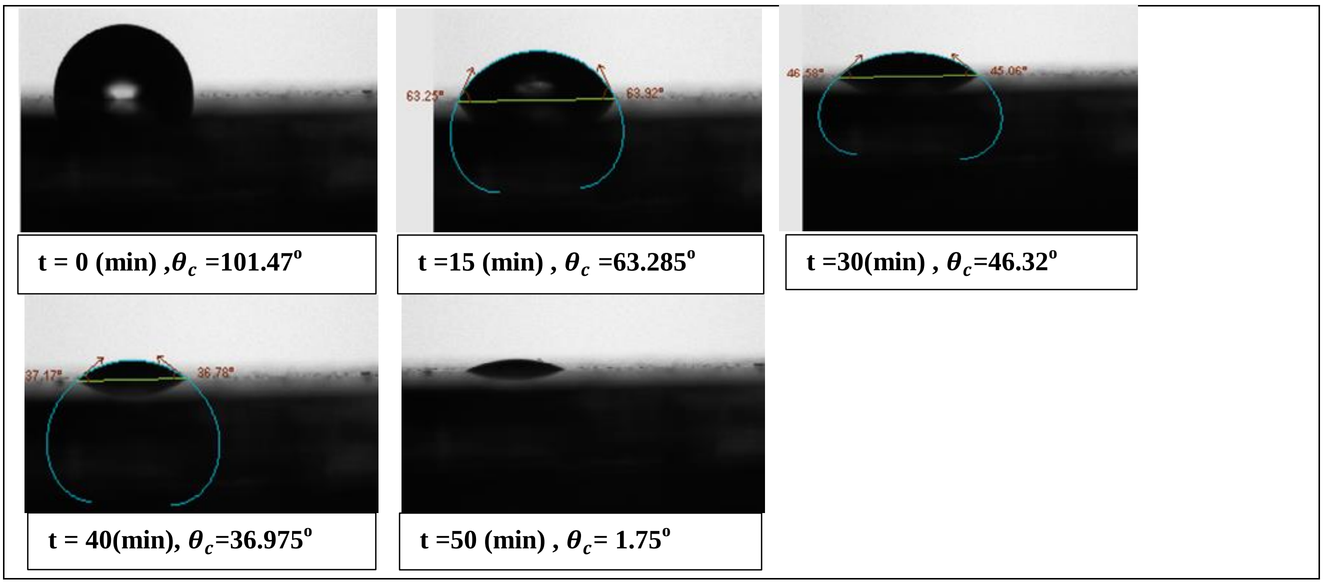

Figure 14. The image of contact angle with time for yellow paint.

Therefore, the droplet on the yellow paint takes more time to dissociate on the surface prolonging wettability time of the surface due to extended water droplet adhesion on the yellow painted surface compared to other color.

Conclusions

From the results obtained in this work, it can concluded that:-

1- The characterizations of TiO_2-Sol are the maximum absorption wavelength at (λ_{max}=387 nm), the refractive index (n=1.4423) and the energy band gap (E_g=3.2 eV). TiO_2 formed was polycrystalline nanoparticles in anatase phase and the crystallite size (50.427 nm).

2- The best paint color uses is a yellow.

3- The self-cleaning yellow paint has a highest contact angle θ_c= 101.47º at zero time (hydrophobic water droplet), also has a lowest contact angle θ_c= 1.75º after exposure time at 50 min (hydrophilic water droplet), thus the water sheet of the surface and remove all contaminants.

4- TiO_2 –Sol nano-coating have self-cleaning properties were prepared by liquid phase deposition, which is a low-cost and simple method that can be used at a low deposition temperature and suitable for coating over a large area.

Conflicts of Interest: None.

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الالوان الاساسية (الاحمر، الاصفر والازرق) تستعمل كاصباغ تنظيف ذاتي مع طبقة من ثنائي اوكسيد التيتانيوم

سُمّا حكمت آل شيخ حسين

قسم الفيزياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق.

الخلاصة:

حُضر طلاء نانوي شفاف بطريقة السول جل من ثنائي اوكسيد التيتانيوم (TiO_2) له القابيلية على التنظيف الذاتي يستعمل كطلاء للمستشفيات والمختبرات والاماكن التي تتطلب التعقيم. اختيرت الالوان الاساسية الثلاثة (الاحمر, الازرق, الاصفر) كدراسة اولية لتأثير اللون على هذا الطلاء النانوي. استعملت ثلاث الوان من الاصباغ الدهنية كاساس ثم تم طلائها بطبقة من ثنائي اوكسيد التيتانيوم (TiO_2) السول –جل و رسبت على الاصباغ. الخصائص البصرية لثنائي اوكسيد التيتانيوم-السول TiO_2-Sol قيست, فكانت قمة الامتصاص تقع عند الطول الموجي (λ_{max}=387 nm) ومعامل الانكسار (n=1.4423) وفجوة الطاقة (E_g=3.2 eV) . الخصائص التركيبية وجدت باستعمال جهاز حيود الاشعة السينية (XRD) واظهرت ان TiO_2-Sol هو متعدد التبلور بجسيمات نانوية في طور الاناتايز وايضا الخصائص الشكلية قيست بواسطة المجهر الاكتروني الماسح SEM وبينت ان معدل الحجم الحبيبي الى TiO_2-Sol هو (50.427 nm). خصائص التنظيف الذاتي قيست بجهاز الشد السطحي (tensiometer). افضل لون اعطى اعلى استجابة للتنظيف الذاتي هو الالون الاصفر حيث كانت زاوية الاتصال له قبل التعريض للاشعة القوق البنفسجية عند زمن يساوي صفر (θ_c= 101.47º ,at t = 0 min) وبعد التعريض بمرور الزمن يساوي (θ_c= 1.75º ,at t = 50 min) , وهكذا الماء يزاح من سطح و يزيل كل الاوساخ.

الكلمات المفتاحية: زاوية الاتصال، الخصائص البصرية لثنائي اوكسيد التيتانيوم، الالوان الاساسية، عملية التنظيف الذاتي، TiO_2-السول.