



Synthesis and Characterization of Cu, Nd, Ce, Chitosan-Codoped TiO₂ Nanoparticles by Sol-Gel Method for Stain Resistance Cotton Fabric Application

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In this study, Nd³⁺, Cu²⁺ and Ce³⁺ doped TiO₂ and chitosan masked TiO₂, TiO₂/Nd³⁺, TiO₂/Nd³⁺/Cu²⁺, TiO₂/Nd³⁺/Ce³⁺ was synthesized by sol-gel method using tetra *n*-butyl orthotitanate (TBT) as a precursor. The prepared nanoparticles characterized by FT-IR, XRD, SEM-EDS, TEM, TGA. The XRD showed that the major phase of nanocomposite was anatase. The morphology of the TiO₂/Nd³⁺/Cu²⁺ and TiO₂/Nd³⁺/Ce³⁺ microsphere was investigated using SEM. The TEM shows that the size of TiO₂/Nd³⁺/Cu²⁺ and TiO₂/Nd³⁺/Ce³⁺ were 8-10 nm. IR spectrum and TGA showed that the existence of chitosan. IR spectrum indicated that Ti-O bond formed in the chitosan-TiO₂ nano composite. One of the most important applications of nano particle TiO₂ in textile industry product of stain resistance cotton fabric. We studied about this effect of nano particle TiO₂ on cotton fabric. The results show that cotton fabric treatment with nano particle TiO₂ has this property.

Key Words: Doped TiO₂, Sol-gel, Chitosan.

INTRODUCTION

Titanium dioxide (TiO₂) has many interesting physical properties¹, which make it suitable for various thin film application which had many application in photo catalyst, solar energy cell, gas sensor, cell cancer, degradation of pollutants in wastewater *etc.* There are three main types of TiO₂ structures: rutile, anatase and brookite. The size dependence of the stability of various TiO₂ phase has recently been reported². Copper is less costly as compared to noble metals and Cu-TiO₂ has been studied extensively in the treatment of gaseous pollutant³.

It is highly effective, saves energy without further pollution and is a low-cost photocatalyst. Other applications, however, are limited by its large band gap (3.2 eV), which captures less than 3 % of solar energy (< 387 nm) and the fast recombination of photo-generated electron-hole pairs both on the surface and in the bulk of TiO₂. Thus, current research efforts in this fields are directed at improving its efficiency in sunlight irradiation⁴.

Chitosan, a cationic bio-polymer, is biodegradable and non-toxic. Chitosan, (1 → 4)-2-amino-2-deoxy-β-d-glucose, is derived by the alkaline deacetylation of chitin, a polysaccharide found in the exoskeletons of shrimps and crabs⁵.

The metal doping process can be homogenous, using the sol-gel method (more common) or restricted to the surface by metal deposition⁶. Three critical variables in sol-gel coating

preparations are (i) the temperature of the heat treatment used to crystallize the titania⁷; (ii) the presence of metal ion dopants on the semiconductor net work⁸ and (iii) the pH of the synthesis and coating suspensions⁹. Various methods are available for the preparation of TiO₂-based photocatalysts, such as electrochemical¹⁰⁻¹⁵, continuous reaction¹⁶, multi-gelation^{17,18}, supercritical carbon dioxide¹⁹, thin films and spin coating²⁰⁻²² and thin film by vacuum arc plasma evaporator²³, combining inverse micelle and plasma treatment^{24,25}, dip coating^{26,27} and SILAR²⁸, two-step wet chemical²⁹, precipitation³⁰⁻³², thermal (ethanol thermal, hydrothermal and solvothermal)³³⁻³⁷, chemical solvent decomposition and chemical vapour decomposition³⁸⁻⁴⁰, ultrasonic irradiation⁴¹, extremely low temperature^{42,43} and aerogel and eerogel^{44,45}, other methods different from sol-gel⁴⁶⁻⁴⁹, modified sol-gel^{50,51}, two-route sol-gel^{52,53} and methods similar to sol-gel⁵⁴ and sol-gel⁵⁴⁻⁷⁶.

In the present paper we try to improve the photocatalytic activity of TiO₂ by doping and masked chitosan doping species.

EXPERIMENTAL

Rare earth ion-doped TiO₂ catalyst prepared with raw materials of analytical grade. The raw materials included tetra-*n*-butyl orthotitanate [Ti(O-Bu)₄], Ce(NO₃)₃·6H₂O, Cu(NO₃)₂·3H₂O, HNO₃, Nd(NO₃)₃·6H₂O, absolute ethanol which purchased from Romil. Chitosan purchased from Sigma.

The crystal structure and the phase transformation of membrane top layer during the calcinations process were using X-ray diffraction technique with a X-ray diffractometer, Bruker, D and Advance, Germany and a X-ray diffractometer Philips using CuK_α radiation $k = 0.15405$. The microstructure of the top layer was examined for any defect or cracks using the scanning electron microscope (Phillips XL30) and a transmission electron microscope (TEM 900 ZEISS). The elemental analysis of the film was performed using energy dispersive spectroscopy (EDS). FT-IR spectra were obtained by BRUKER.

Preparation of nanoparticle TiO_2 : In the present study polymeric sol was obtained *via* tetra-*n*-butyl orthotitanate $[\text{Ti}(\text{O-Bu})_4]$ as a titana precursor. Tetra-*n*-butyl orthotitanate was dissolved in absolute ethanol and then the tetra-*n*-butyl orthotitanate solution was added dropwise under vigorous stirring to the mixture solution containing ethanol, Deionized water, HNO_3 and the resulting transparent colloid suspension was stirred before being aged for 2 day till the formation of gel. The gel was calcined at 600°C for 2 h. Finally, the preparation of TiO_2 powder catalyst. The molar ratio for tetra-*n*-butyl orthotitanate/ $\text{H}_2\text{O}/\text{HNO}_3/\text{C}_2\text{H}_5\text{OH}$ of the final sol was 1/0.9/0.6/6, respectively.

Preparation $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ nanoparticle: This nanoparticles were prepared by the sol-gel method with the following procedure: Nanoparticles polymeric sol were obtained *via* tetra-*n*-butyl orthotitanate $[\text{Ti}(\text{O-Bu})_4]$ as a titana precursor. Tetra-*n*-butyl orthotitanate was dissolved in absolute ethanol and then the tetra-*n*-butyl orthotitanate solution was added dropwise under vigorous stirring to the mixture solution containing ethanol, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ratio molar (1:1), deionized water, HNO_3 and the resulting transparent colloid suspension was stirred, before being aged for 2 day till the formation of gel. The gel was calcined at 600°C for 2 h. Finally, the preparation of $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ powder catalyst. The molar ratio for tetra-*n*-butyl orthotitanate/ $\text{H}_2\text{O}/\text{HNO}_3/\text{ethanol}$ of the final sol was 1/0.9/0.6/6, respectively.

Preparation $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ nanoparticle: This nanoparticles were prepared by the sol-gel method with the following procedure: Nanoparticles polymeric sol were obtained *via* tetra-*n*-butyl orthotitanate $[\text{Ti}(\text{O-Bu})_4]$ as a titana precursor. Tetra-*n*-butyl orthotitanate was dissolved in absolute ethanol and then the tetra-*n*-butyl orthotitanate solution was added dropwise under vigorous stirring to the mixture solution containing ethanol, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ratio molar (1:1), deionized water, HNO_3 and the resulting transparent colloid suspension was stirred for 2 h, before being aged for 2 day till the formation of gel. The gel was calcined at 600°C for 2 h. Finally, the preparation of $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ powder catalyst. The molar ratio for tetra-*n*-butyl orthotitanate/ $\text{H}_2\text{O}/\text{HNO}_3/\text{ethanol}$ of the final sol was 1/0.9/0.6/6, respectively.

Preparation chitosan- TiO_2 , chitosan/ $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$, chitosan/ $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$, chitosan/ $\text{TiO}_2/\text{Nd}^{3+}$ nanocomposite: Chitosan was dissolved in 2 wt % acetic acid at 80°C . TiO_2 nano particle was added in chitosan solution under mechanical stirring for 1 h and then annealed at 120°C for 2 h.

RESULTS AND DISCUSSION

Crystallization of the TiO_2 , Chitosan- TiO_2 , $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$, $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ nanoparticles: The $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ nanoparticles were prepared *via* sol-gel process from a $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ sol followed by heat treatment at high temperature. To study the crystalline structure of nanoparticles, the XRD pattern of nanoparticles of TiO_2 , chitosan/ TiO_2 , $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ were recorded. The powder XRD patterns of the TiO_2 and $\text{TiO}_2/\text{chitosan}$, $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$, $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$, prepared by homogeneous hydrolysis of tetra-*n*-butyl orthotitanate are shown in Fig. 1, which can be indexed as a single phase of anatase. No other polymorph of titania observed and no metal ion-doped peaks are found in the XRD patterns. It can be observed that the major peak of pure nano TiO_2 chitosan/ TiO_2 , $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ is anatase ($2\theta = 25.281, 25.295, 25.375, 25.381$) observed in the spectrum.

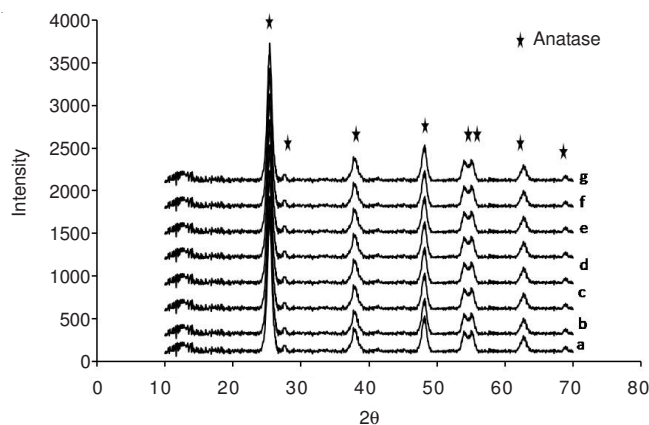


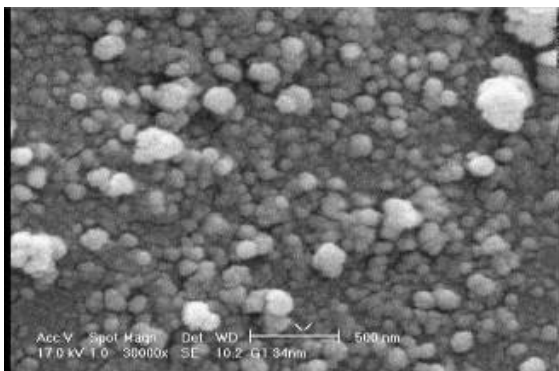
Fig. 1. XRD patterns (a) TiO_2 (b) $\text{TiO}_2/\text{Nd}^{3+}$ (c) $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ (d) $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ (e) chitosan/ TiO_2 (f) chitosan/ $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ (g) chitosan/ $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ nanoparticles after the calcination for 2 h at 600°C

From full width at half maximum (FWHM) of the peak at the TiO_2 , $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ (0.1591, 0.906, 0.871), respectively and using Sherrer's equation, the average crystal size of about 8-10 nm, can be calculated. The average particle size D_c of crystallites in the film was also estimated from the peak half-width β by using the Sherrer's equation:

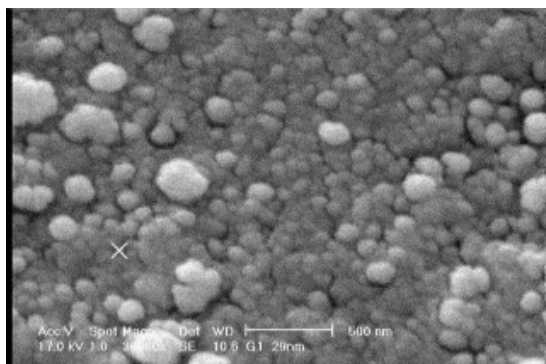
$$D = \frac{K\lambda}{\beta \cos\theta}$$

where K is a shape factor of particles (normally chosen as 0.89), λ is the wavelength of X-ray nanometer (0.1541 nm for CuK_α in this study) and θ is the incident angle of X-ray, respectively.

Microstructure, morphology of the $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ nanoparticles: The morphology of the $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ microspheres were investigated using SEM. Fig. 2 shows an optical micrograph of $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ (Fig. 2a) $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ (Fig. 2b) microspheres and it can clearly be seen that a very homogenous distribution of nanoparticles was achieved in the microspheres. SEM images show the particle sizes of $\text{TiO}_2/\text{Nd}^{3+}/\text{Ce}^{3+}$ and $\text{TiO}_2/\text{Nd}^{3+}/\text{Cu}^{2+}$ nanoparticle are the same.



(a)



(b)

Fig. 2. SEM photographs showing patterns: (a) TiO₂/Nd³⁺/Ce³⁺, (b) TiO₂/Nd³⁺/Cu²⁺ nanoparticle morphology after heat treatment for 2 h at 600 °C

In order to identify the element composition of the TiO₂/Nd³⁺/Cu²⁺ and TiO₂/Nd³⁺/Ce³⁺ nanoparticles, the EDS analysis element was performed (Figs. 3 and 4).

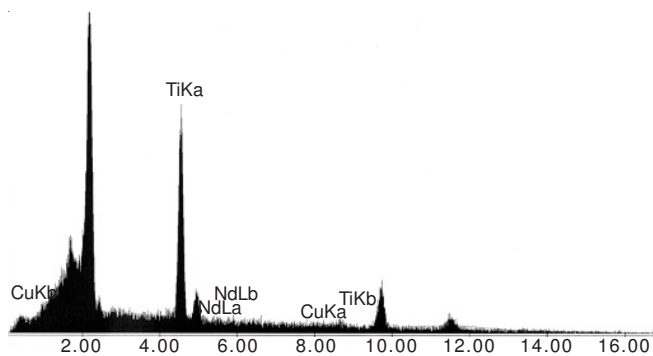


Fig. 3. EDS analysis of element composition of the TiO₂/Nd³⁺/Cu²⁺

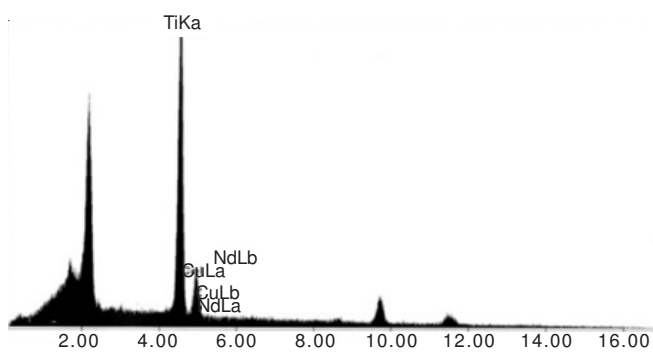
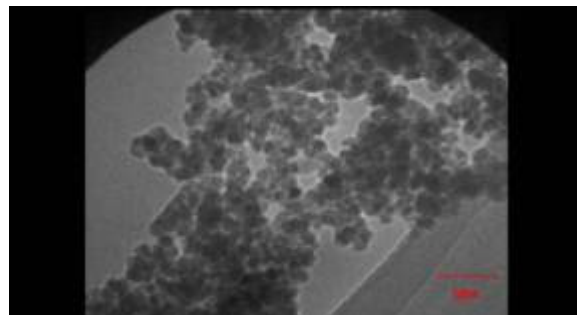
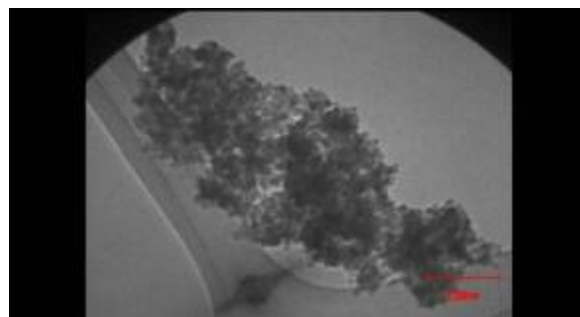


Fig. 4. EDS analysis of element composition of the TiO₂/Nd³⁺/Ce³⁺ nanoparticles

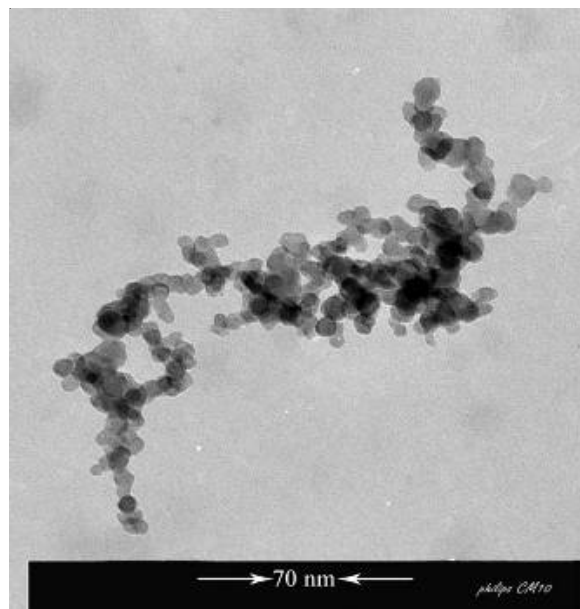
The TEM images indicate that the TiO₂/Nd³⁺/Cu²⁺, TiO₂/Nd³⁺/Ce³⁺ and TiO₂/Nd³⁺/Cu²⁺/chitosan nanoparticles are shown in Fig. 5a-c. The average particle size of the nanoparticles was about 8-10 nm. It was found that TiO₂/Nd³⁺/Cu²⁺, TiO₂/Nd³⁺/Ce³⁺ and TiO₂/Nd³⁺/Cu²⁺/chitosan nanoparticle were distributed homogeneously and they were spherical in shape.



(a)



(b)



(c)

Fig. 5. TEM image of (a) TiO₂/Nd³⁺/Cu²⁺, (b) TiO₂/Nd³⁺/Ce³⁺ (c) TiO₂/Nd³⁺/Cu²⁺/chitosan nanoparticle after calcined for 2 h at 600 °C

Thermal gravimetric analysis: Thermal stability of the pure chitosan/TiO₂/Nd³⁺/Cu²⁺ nanocomposite was measured using a thermal gravimetric analysis (Fig. 6). In the TGA curve of the nanocomposite, the small weight loss at lower temperature blow is probably due to evaporation of residual alcohol

and physically absorbed water. There are three steps (at 100-280 °C, 280-520 °C, 520-620 °C, respectively) in the TGA curve of nanocomposite. The three steps was ascribed to the decompose chitosan in the chitosan/TiO₂/Nd³⁺/Cu²⁺ nanocomposite. The pure chitosan exhibited a weight loss starting at about 25 °C and a rapid weight loss at 100-500 °C. When the gets 700 °C, the chitosan decomposed completely.

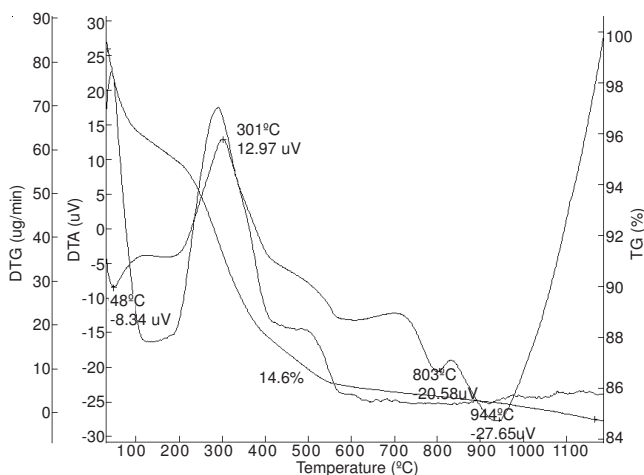


Fig. 6. TGA analysis chitosan/TiO₂/Nd³⁺/Cu²⁺ nanocomposite

FT-IR spectrum for chitosan-TiO₂ nanocomposite: IR spectrum of chitosan/TiO₂ nanocomposite is shown in Fig. 7. The characteristic bands at 3424 and 1627 cm⁻¹ are assigned for the stretching vibration of the OH group and molecular H₂O, respectively. The band at 2931 cm⁻¹ are attributed to symmetric stretching of -CH₂- of chitosan. The band at 465 cm⁻¹ is due to the ν(Ti-O). The band at 1080 cm⁻¹ attributed to the bond of Ti-OH on three -OH group and five -CH₂-OH of chitosan. The band 1410 cm⁻¹ is due to hydrogen bond and protonation of the amino group.

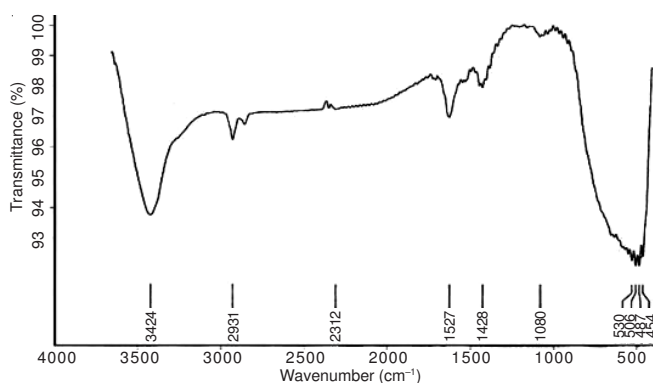


Fig. 7. IR spectrum of chitosan/TiO₂ nanocomposite

Preparation of TiO₂ sols: Titanium tetraisopropoxide was added drop-wise into water, ethanol and nitric acid under vigorous stirring. The mixtures were heated at different temperatures, 25 and 60 °C and kept vigorous for 16h. The prepared TiO₂ sols were named as S25 and S60 respectively.

Coating process: The as -prepared sols were used to prepare TiO₂ thin coating on substrates (woven white cotton fabric) by a dip-pad-dry-crue process. The substrates were scoured by nonionic detergent to remove the wax, grease and

other finishing chemicals from the fabrics before coating. The scouring process was performed at 80 °C for 0.5 h. The cleaned substrates were dipped in TiO₂ sols for 1 min and pressed with an automatic padder at a nip pressure of 2.75 kg cm⁻² to keep the same amount of TiO₂ on each of the cotton substrates. After 5 min, the padded fabrics were put in ammonia gas for neutralization until a pH 7 of the fabric surface is achieved. The substrates were dried at 80 °C for 5 min in a preheated oven and finally cured at 120 °C for 3 min in a preheated curing oven.

Colorant decomposition activities: The self-cleaning effect of TiO₂ coated white cotton fabrics could also be evaluated by the decomposition of colorants in aqueous solution under UV light irradiation (Table-1). The decrease in the concentration of the blue colorant Neolan blue 2G was observed in the following descending order, in aqueous solution containing S60 (sol 60 °C) coated substrates, S25 (sol 25 °C) coated substrates, here S25 has the highest photocatalytic activity which is considered to be attributed to the highest anatase crystallinity as demonstrated by its sharpest anatase peaks with greatest intensities from XRD.

Sample	1*	a*	b*
Blank	57.59	-9.10	-24.72
TiO ₂ at 25 °C	87.240	-0.058	-1.086
TiO ₂ at 60 °C	86.072	-0.102	-1.314

Conclusion

In the present study the TiO₂/Nd³⁺/Ce³⁺, TiO₂/Nd³⁺/Cu²⁺, TiO₂, TiO₂/Nd³⁺ and chitosan/TiO₂ and doped chitosan/TiO₂ nanoparticles sample were prepared *via* sol-gel process. The film characterization through XRD, SEM, EDS, TGA, TEM indicated that the prepared powders TiO₂/Nd³⁺/Cu²⁺, TiO₂/Nd³⁺/Ce³⁺ had a particle size approximate 8-10 nm. It was found that TiO₂/Nd³⁺/Cu²⁺ and TiO₂/Nd³⁺/Ce³⁺ nanoparticles were distributed homogenously and they were spherical in shape. The SEM technique proved that the nanoparticle size TiO₂/Nd³⁺/Cu²⁺ equals TiO₂/Nd³⁺/Ce³⁺. IR spectrum and TGA showed that the existence of chitosan. It result shows from Stain Resistance Cotton Fabric S25 has the highest photocatalytic activity which is considered to be attributed to the highest anatase crystallinity as demonstrated by its sharpest anatase peaks with greatest intensities from XRD.

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