Synthesis of TiO_2 doped selenium nanoparticles using herbal turmeric powders coating on cotton fabric for antibacterial

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Abstract. Nano materials based on the titanium dioxide doping selenium oxide and turmeric coated fibers of gauze pad cotton. The titania hydrosol was successfully prepared at low temperature by a microwave facilitated sol-gel method. The study also explored the efficiency of this sample to inhibit the growth of *Escherichia coli* and *Staphylococcus aureus* with various samples of titanium dioxide, titanium dioxide doped selenium oxide and titanium dioxide doped selenium oxide with turmeric powder. The morphology and composition of the surface pure and titanium dioxide coated gauze pad cotton fibers were investigated by the Scanning electron microscopy. The physical properties result showed the smaller size of selenium oxide dope compound crystal (11.06 nm.) than undoped crystal (15.80 nm.) by X-ray spectroscopy. The antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* under ambient temperature showed that cotton coated with titanium dioxide, titanium dioxide doped selenium oxide and titanium dioxide doped selenium oxide with Turmeric nanoparticles enhance bacterial inactivation efficiency completed 100% within AATCC test method 2004-100 standard.

1. Introduction

Infectious diseases can be the result of the colonization of the body by various bacteria. Our bodies are populated by an extremely large number of bacteria. Although most bacteria are harmless or often beneficial, several are pathogenic. The significance of this human pathogen, apart from its ability to cause life threatening infections, is its remarkable possible to develop antibacterial resistance. *Staphylococcus aureus* (*S. aureus*) is one of the main causes of community and hospital received infections which can result in high effect. *S. aureus* infections affect the soft tissues, skin and lower respiratory tracts. *S. aureus* can be a cause of central venous catheter-associated bacteremia and ventilator-assisted pneumonia. It also causes serious deep-seated infections, such as endocarditis and osteomyelitis. [1] Nowadays fabrics are used in different parts and diverse intentions beyond imagination. Hygienic and clean fabric, an urgent need for production of antibacterial textile fabric has appeared. Medical part is one of them. An important and emerging part of the fabric industry is medical, health and hygiene part. The development is taking place due to the simultaneous growth and enhancement of technology in both fabric as well as medical part. [2]

In the recent years, Titanium dioxide (TiO_2) was also investigated for photocatalytic degradation of organic contaminants. Three crystal of TiO_2 has forms namely, rutile, anatase and brookite. Efficient photocatalytic activity of TiO_2 depended on a wide variety of factors are crystallite size, surface area, and crystal structure. [3] As widely reported, anatase and mixture phases of anatase and rutile display highest photocatalytic activities. [4] Anatase, with large surface area, high crystallinity and nano-scaled crystallite size, exhibits high effective photo catalytic activity. In the process, oxygen atoms are ejected, and oxygen vacancies are created in the ground state. These holes can oxidize the O anions. Water molecules can then occupy these oxygen vacancies to produce adsorbed OH groups. For the past thirty years, the novel antimicrobial activities of TiO_2 through a photocatalytic reaction over *Escherichaia coli* (*E. coli*), *S. aureus* [5], cancer cells and virus [6] have been reported. Furthermore, the application of TiO_2 photocatalytic disinfection for drinking water production has been explored, and the development of incorporating TiO_2-coated for packaging and preparation equipment has also received attention. Nowadays, coated textiles are being widely used in clothing and garment industry.

The aim of this work is to study the, TiO_2 doped selenium dioxide (Se) mixed with Tu powders were finally obtained by coating onto cotton fabrics at room temperature. The antimicrobial capacity of this coated cotton against *E. coli* and *S. aureus* exposed in vitro tests has been determined.

2. Materials and Methods

2.1. Preparation of TiO_2 Doped Se Nanoparticles

Titanium (IV) isoproxide (TTIP, 99.95%, Fluka Sigma-Aldrich) and selenium dioxide (SeO_2) were used, and Hydrochloric acid (HCl) was added in this mixture as a peptizer. Distilled water (125 ml) was used in the TiO_2 sols, TTIP (10 mL), ethanol (90 mL) (99.9%; Merck Germany) and SeO_2 (1.0 mol%). Then it was stirred for 5 min at room temperature. Hydrochloric acid (2 M) was added drop wise to the solution to adjust the pH~2. The solution was then refluxed for 2 h by a domestic microwave oven at low working power (about 180 W). TiO_2 powders were formed. Finally, the powders were ground using a mortar in order to reduce the agglomerate grains. To make a TiO_2 doped Se solution, Se was added to TiO_2 sols, while further processes were similar to those of pure TiO_2 preparation.

2.2. Preparation of Cotton Fabric Coated with TiO_2 Doped Se using Herbal Tu Powders.

Before the coated Tu modification, the raw cotton was boiled in 200 mL of distilled water solution at 100°C for 2 h for the removal of most of the non-cellulosic constituents. After this, the pre-treated cotton fibers were thoroughly washed with distilled water and dried in air. Cotton fabric samples were dipped in Tu solutions for 30 min. The coated fibers were heated at 100°C for 30 min for water removal. Then, the coated cotton fabrics immersed in TiO_2 doped Se solutions for 30 min then dried at 100°C for 30 min. The obtained cotton coated samples using Tu, TiO_2, TiO_2 doped Se, TiO_2 doped Se and Tu were denoted as Tu, TiO_2, TiO_2/Se, TiO_2/Se/Tu, respectively.

2.3. Materials Characterization

The X-ray spectroscopy (XRD) patterns were characterized in terms of phase compositions and crystallite size by using Phillips X'pert MPD diffractometer. The crystallite size was characterized by XRD peaks using the Scherer equation [7],

$$D = 0.9\lambda / \beta \cos\theta_B \qquad (1)$$

Where D is crystallite size, λ is the wavelength of the x-ray radiation (CuK_α = 0.15406 nm), and β is the angle width at half maximum height, and θ_B is the half diffraction angle of the center of the peak. The hydroxyl function group (TiO_2-OH bonds) of the films was analyzed by FTIR transmittance spectrophotometer. UV-Vis spectrometer, ShimadzuISR-3100, were analyzed the band gap energy of all powder. The surface morphology and element analysis of films was characterized by scanning electron microscopy (SEM) with EDX.

2.4. Antibacterial Activity of Cotton Fabric Coated with TiO_2 Doped Se using Herbal Tu Powders

AATCC Test Method 100-2004 is specifying a qualitative and relatively easily executed method to determine residual antibacterial activity of textile materials. Typical gram positive micro-organisms are *S. aureus* (ATCC 6538) and gram negative organisms are *E. coli* O157:H7 (ATCC 43895). The trypticase soy agar was from Difco Laboratories, Detroit, MI. The initial bacterial concentration was kept about 10^5 CFU/ml used for all experiments. The equation:

$$100(B - A)/B = R \quad (2)$$

was used to calculate the percentage reduction in the number of colony forming units between the untreated and treated fabrics after incubation for 24 h at 37 ± 1°C. R is the percentage reduction in bacteria, and *B* and *A* are the numbers of CFU/ml of bacteria measured for the untreated and the treated cotton fabrics respectively.

3. Results and Discussion

3.1. XRD patterns and energy gap measurement

Fig. 1a show the XRD pattern, the anatase peaks were found at 25.50, 37.59, 48.01, and 54.16 degrees. TiO_2 brookite traces were observed a small broad peak at 30.64 degrees. TiO_2 anatase phase are usually found at high calcination temperature, at least at 300°C, additionally, it was found that Se doping seems to retard anatase crystal growth, especially at low temperature synthesis.

The efficiently inhibit the anatase crystal growth due to effects confirm that Se doped. The undoped TiO_2 has a band gap energies at around 3.20 eV from Fig. 1b. The doped TiO_2 shifted towards the visible region of the spectrum. In contrast to the undoped TiO_2, a narrow band gap from 3.20 eV extending down to 2.80 eV was obtained, which is consistent with the color of the samples. It can be seen that Se dopants have an effect on the UV–vis spectra due to an inhibition of the recombination of electron hole pairs. [8, 9] The calculated band gap energies and the corresponding wavelengths are presented in Fig. 1b. This consequently results in the smaller grain size of TiO_2 (15.8 nm) film compared to those of TiO_2 doped Se (11.06 nm).

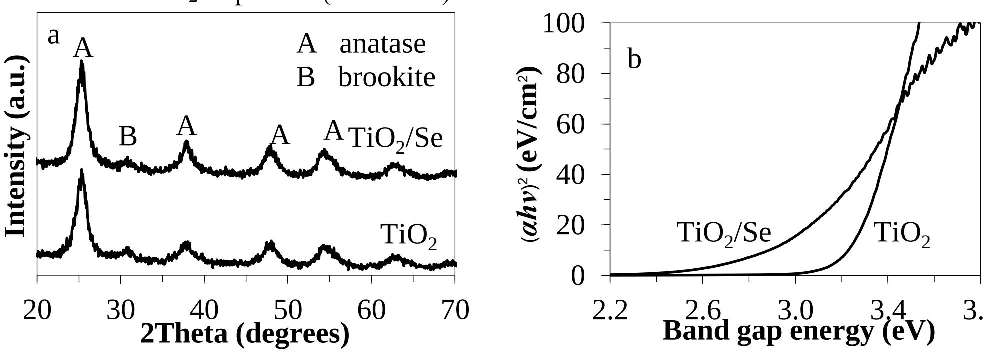


Fig. 1. (a) XRD patterns and (b) UV–vis diffuse reflectance spectra of pure TiO_2 and TiO_2 doped Se powders.

3.2. Morphology of Cotton Coated TiO_2 Doped Se Surface

The surface morphologies of the pure cotton and composite TiO_2 coated cotton fibers are shown in Fig. 2c-f. It can be seen from Fig. 3c that the pure cotton fibers do not contain any contaminations. The cotton fibers in the CF/TiO_2 (cotton fibers coated TiO_2) Fig. 2d. are unevenly covered by TiO_2 nanoparticles after coated by TiO_2 hydrosol. Fig. 2e. TiO_2/Se displayed the TiO_2 doped Se nanoparticle aggregates are unevenly covered. TiO_2/Se/Tu were unevenly covered by Tu powders after coated by TiO_2 doped Se solution (Fig. 2f.). Moreover, details of EDX analysis of samples doped by Se, The elements Ti and Se were clearly detected and the quantitative analysis estimated weight fractions in this order were about 30.02 and 30.40 wt% for Ti, 3.63 and 3.27 wt%, for Se on TiO_2/Se and TiO_2/Se/Tu cotton surface, respectively

3.3. FTIR analysis

Fig. 2a. In the range of 3200-3600 cm^{-1} usually confirm that photo generated hydroxyl groups on TiO_2 surface. Stretching vibration of the -OH groups linking with Ti atoms (TiO_2-OH) are appearing at 3400-3468 cm^{-1} in TiO_2 doped Se which arise from the hydrolysis reaction in the sol-gel process. The bending vibration of the OH group of free water or absorbed water found broad and strong peaks at 1630-1640 cm^{-1}. [10] The enhancement of the photocatalytic activity since they can interact with photo generated holes of the electron due to larger surface hydroxyl group density. These results confirm that the surface -OH group density of TiO_2 doped Se is better than pure TiO_2. The absorption bands of Ti-O and O-Ti-O flexion vibration found at 600 cm^{-1}. Fig. 2a. revealed FTIR spectra of Tu powder from different regions along with functional groups responsible for IR absorption. The bands in the region of 813-888 cm^{-1} were assigned to the aromatic hydrocarbon bending. The bands at 1543 and 1655 cm^{-1} can be assigned to the binding vibrations of amide I and amide II bands of proteins respectively. The bands at 3342, 3299 and 3083 cm^{-1} were assigned to the O-H stretching, amide-A and amide-B respectively. [11, 12]

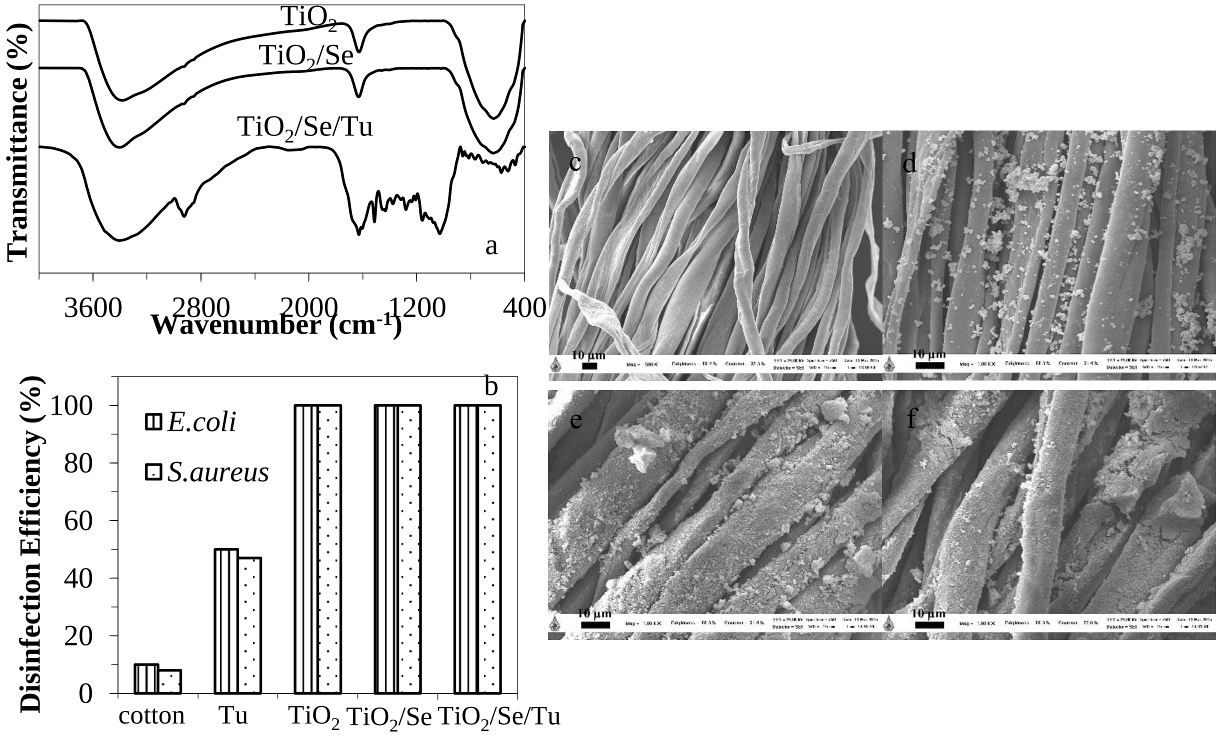


Fig. 2. (a) FTIR, (b) The disinfection efficiency of *E. coli* and *S. aureus* and SEM of (c) cotton and cotton coated with (d) TiO_2, (e) TiO_2/Se and (f) TiO_2/Se/Tu

3.4. Antibacterial Activity of Cotton Coated TiO_2 Doped Se using Tu Powders

Antibacterial activity of cotton coated with TiO_2, TiO_2/Se, and TiO_2/Se/Tu (Fig. 3.) occurred at completely destroyed *E. coli* and *S. aureus* bacteria. Fig. 2b. show only 50% and 47% destroyed *E. coli* and *S. aureus* respectively, of bacteria were killed with CF/Tu sample. In addition, TiO_2, TiO_2/Se and TiO_2/Se/Tu shows a disinfection caculated from equation (2) about 100% which *E. coli* (gram negative bacteria) higher than that of the *S. aureus* (gram positive bacteria). This is possibly due to the higher concentration of OH radicals in TiO_2 and Tu which are very strong oxidant species against microbial on its surfaces. The bactericidal effect of TiO_2 generally has been attributed to the decomposition of bacterial outer membranes by reactive oxygen species (ROS), primarily hydroxyl radicals (-OH), which leads to phospholipid peroxidation and ultimately cell death. [13-15] These results confirmed that the symbiotic effect of reduced graphene oxide (RGO) and TiO_2 was responsible for the observed strong bactericidal efficiency. The O-H groups and curcumin from herbal powder showed significant antibacterial activity. [16]

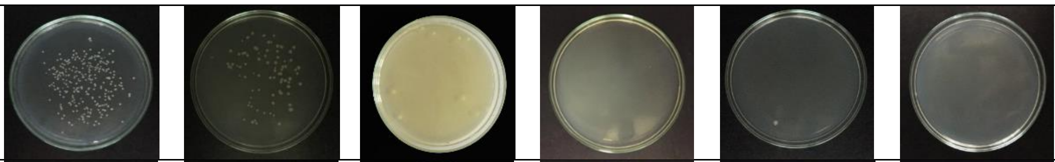
sample	control	cotton	Tu	TiO_2	TiO_2/Se	TiO_2/Se/Tu
E. coli						
S. aureus						

Fig. 3. Images of *E. coli* and *S. aureus* test with composite coated cotton fabric.

4. Conclusion

The cotton fabrics were coated by the nanocrystalline TiO_2 doped Se and Tu sol-gel. The TiO_2 doped Se nanoparticles using Thai herbal, Turmeric powders have been successfully synthesized at low temperature sol–gel method in an aqueous solution. These cotton based coatings have good compatibility. The bactericidal efficiency tests show that TiO_2 doped Se nanoparticles using Turmeric has a higher photocatalytic bactericidal efficiency than pure cotton.

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