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ORIGINAL ARTICLE

Augmentation of functional properties on Cotton Fabric using milled TiO_2 nanopowders

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Abstract

The effect of the milling process on TiO_2 nanopowders and the functional properties of TiO_2 coated cotton fabric was investigated. The XRD analysis reveals that the milled TiO_2 nanopowders reduce its size in Nano scale when milling time increases. SEM analysis reveals that the milled TiO_2 powder shows a seed-like structure. FTIR spectra show the presence of the functional groups in milled TiO_2 nanopowders and TiO_2 coated cotton fabric. The hydrophobic test exhibits that the 100 and 125 hours of milled TiO_2 nanopowders coated cotton fabric has 70% water repellency. The bursting strength (shearing stress) of TiO_2 coated cotton fabric also indicates an appreciable value of about 503.6 Kpa. TiO_2 nano finishing of cotton fabric can eliminate up to 99.99% of Staphylococcus aureus and Klebsiella pneumonia bacterial strains, which would be suitable for sports wears and surgical clothes.

Keywords: *Antibacterial; Ball Mill; Nanostructured Materials; Surface: Wetting; X-Ray Diffraction.*

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INTRODUCTION

Nanoparticles are emerging spectacular vital tool in all scientific ranges of research, predominantly in nano scale sciences [1]. The uniqueness of nanomaterial attracts great attention in the field of textiles industry. Conventional textile processing methods are used to impart different properties, such as water repellency and stain repellency, to the fabrics often do not lead to permanent effects, and lose their functions after laundering or use. By virtue of its small size and high surface energy, nanoparticles are bound to the fabric surface by Vander Waals forces which give a reasonable wash fastness [2]. Titanium dioxide has a number of exceptional features that make it supremely matched to many different applications such as reducing harmfulness of dyes, pharmacological drugs, waste water treatment, reproduction of silkworm, hydrophobic property, and antimicrobial property and in space applications [3, 4]. From the literature it is evidenced that the low toxicity of TiO_2 nanoparticles comes from cosmetics industry, with the 20-year long history of human use in sun screen preparations.

Milling process of nanomaterial is a machine-driven procedure and hence all the organizational and chemical alterations are produced by mechanical energy [5]. This process of ball milling is done approximately 100 to 125 hours to get uniform fine powder. Hence, changeable size at micro- and nano-levels is important for new findings [6]. A very significant part of the application of nanotechnologies in the textile industry is determining the problem of binding nanoparticles to the fabric material. The dominant tricky is to promise tight binding of nanoparticles to the surface of textiles in order to increase the resilience of the preferred properties. This also confirms that nanoparticles are not released in the environment, satisfying also the natural requirements. In order to

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apply TiO_2 nanoparticles, the maximum chemical compatibility between nanoparticles and textile surface should be attained.

The literature survey specified numerous methods for this purpose. Some of the methods which are used for covalent linking agents, a layer by layer method (using electrostatic interactions) and introduction of volatile functional groups on textile materials such as RF, MW, UV plasma and hydrolytic enzymes. In the subsequent text, distinctive processes and approaches for TiO_2 nanoparticles coating on textile materials will be conferred [7-9]. The dip-pad-dry-cure process is frequently used to make bonds between TiO_2 and a fabric material. The pigment deterioration activity of TiO_2 coated cotton fabric by the dip-pad-dry-cure process, before and after 10 and 20 washings was inspected and reported [10]. This research outcome aids some novel ideas to improve TiO_2-functionalized textile materials and proposes upcoming research perceptions and guidelines in the textile Industry.

MATERIALS AND METHODS

Milling process of TiO_2 nano powders

A commercially available high-energy planetary ball milling apparatus was employed for milling process (fig. 1). TiO_2 nanopowder (Aeroxide TiO_2 P25 purity C 97%, particle size of about 100 nm) was obtained from Sigma Aldrich. A ZrO_2 milling vessel and ZrO_2 milling balls were used to grind the TiO_2 powder. Titanium dioxide and balls were taken in the ratio of 1 : 2. In this work milling was performed for two different milling times (100 &125 hours) and revolution speed at 150 rpm for obtaining uniformly crushed fine powder. In the present study no solvents were used and the complete experiment was performed at room temperature.

Testing of functional properties on Cotton Fabric

The coating experiment was carried out using fabric which is made up of pure cotton (100%). The TiO_2 coating on cotton fabric was done by the following procedure. The coating of nanopowder was accomplished via pad-dry-cure method. Add of 1 mL of HDTMS (Hexadecyltrimethoxysilane) to 99 ml of ethanol. The solution containing 1ml of HDTMS and 99ml of absolute Ethanol was mechanically stirred for 2 hours. To dilute TiO_2 as in solution, add TiO_2 of 3gm and toluene of 100ml for each test (molarity of M= 0.4 M) and stirred mechanically at 100 rpm for 4 hours. The TiO_2 coated cotton fabric was dried under vaccum at 60 degree Celsius for 12 hours.

The feature of a waterproof fabric is the low degree of air absorptivity. Spray testing method is one of the methods to measure the water repellency of textile materials. In this test the sample fabric is mounted on the embroidery hoop and fixed on the instrument at 45°. At this instant the beaker is filled with 250 mL water using funnel. The water is sprinkled through spray nozzle on the fabric. After spraying has done the sample holder is removed

Fig. 1. Milling process of TiO_2 and water repellency of untreated & TiO_2 treated cotton fabric.

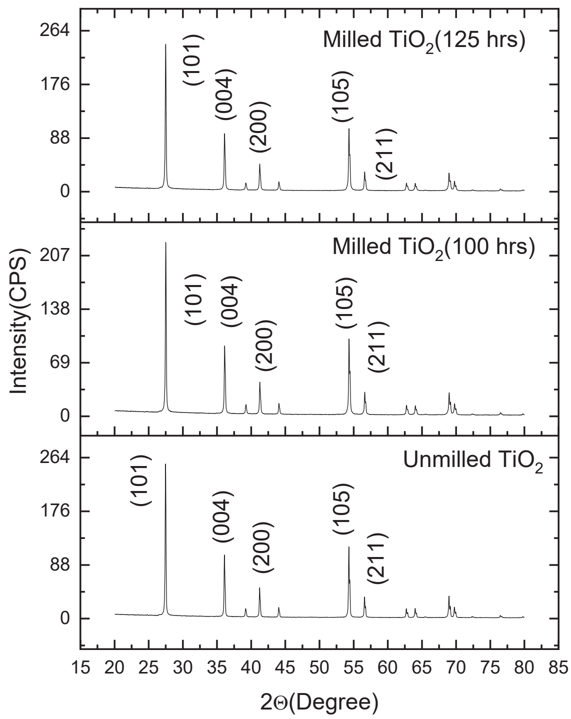

Fig. 2. XRD pattern of unmilled and milled TiO_2 nanopowders.

and the surplus water removed by tapping the frame 6 times against a solid object, with the face of the sample facing the solid object. The water repellency is evaluated from the spray rating table. The American Association of Textile Chemists and Colorists approved the use of a chart of photographs which the actual fabric appearance is matched.

One of the highly consistent monotony techniques which are used to test the fabric by holding it over a rubber diaphragm by means of a boney clamping apparatus and increasing rate of pressure is applied through a purified lab grade liquid glycerin from under the diaphragm up to the sample burst or shattered. After the assessment is done, the evaluations are verified from the display. This explains the maximum pressure that a sample can tolerate to its maximum before it ruptures. In adding to this, the next phase is to estimate the Burst Factor and Burst Index of the sample material using formulas

Burst Index = Bursting Strength (KPa) x 0.10197 / Grammage (g/m^2)

Bursting Factor = Bursting Strength (Kg/cm^2) x 1000 / Grammage (g/m^2) Where, Grammage is the base weight. 1 KPa = 101.97162 Kgf/m^2

Quantitative procedure was carried out to examine the antibacterial activity. A test and control swatch has to be inoculating with the test organisms. After growth, the bacteria are eluted from the swatches by quivering in identified amounts of neutralizing solution. Cut circular swatches, 4.8 ± 0.1 cm in diameter from the fabric using steel die. Place the swatches separately in a petri dish and determine the number of swatches required to absorb 1.0 ± 0.1 mL of distilled water without leaving free liquid in the plate. S. aureus (ATCC 6538), K. pneumonia (ATCC 4352) were used as testing organisms.

Place the determined no of cut/sterilized treated and untreated swatches separately in petri dishes and evenly distribute 1.0 ± 0.1 mL of diluted S.a and K.p inoculum separately. Stack all the swatches together and transfer aseptically to the screw cap bottle labeled as 0 and 24 h time duration. Incubate the 24 h bottle for 24 hour duration at 37 ± 2 ˚C. Immediately, in 0 h bottle, add 100 ± 1 mL of neutralizing solution to each of the bottles of inoculated treated, inoculated untreated and un-inoculated treated and shake the bottles vigorously in shaker for 1 min. Keep the plates in incubator (37 ± 2˚C) and incubate for 24 to 48 h. Examine 0 h plates for the growth, count the colonies and record

Table 1. XRD parameters of TiO_2 nanopowders.

Sample	2θ degree	FWHM In radian	Interplanar Spacing 'd' A°	hkl Plane	Lattice Constant		Crystallite Size (nm)
					Observed	JCPDS	
Unmilled TiO_2 Powder	36.11	0.168	2.485	0 0 4	c=9.94135	9.18	49.755
	27.46	0.146	3.244	1 0 1	a=3.43255	3.78	56.04
100 hours milled TiO_2 Powder	36.144	0.177	2.4831	0 0 4	c=9.93251	9.18	47.231
	27.501	0.151	3.2406	1 0 1	a=3.42826	3.78	55.586
125 hours milled TiO_2 Powder	36.129	0.182	2.4841	0 0 4	c=9.36559	9.18	45.93
	27.485	0.156	3.2457	1 0 1	a=3.45633	3.78	52.445

the values.

RESULTS AND DISCUSSION

XRD Analysis

The XRD analysis of the milled TiO_2 nanopowders was done using a Bruker make diffractometer, Cu-Kα X-rays of wavelength (λ)=1.5406 Å. The observed XRD formation shows good agreement with the JCPDS card no. 21-1272. The 2θ at peak 27.4° confirms the TiO_2 anatase structure [11]. Fig. 2 shows the XRD pattern of unmilled and milled TiO_2 at 100 hours and 125 hours respectively. Average crystalline size of the TiO_2 nanoparticles was estimated using Debye Scherer formula, $D=k\lambda/\beta\cos\theta$. With the increasing milling time, the mean crystalline size of the TiO_2 particles is reduced down. During milling process, mechanical activation decreases the crystalline size of the nanoparticles. A crystalline size value D and the structural peaks were presented in Table 1.

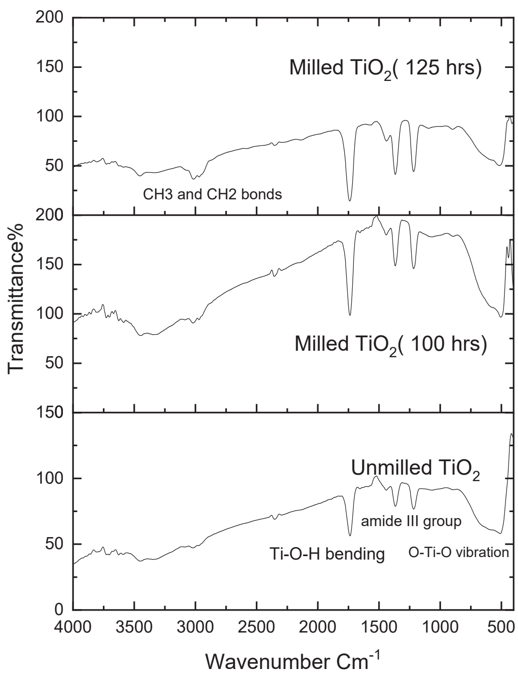

Fig. 3. FTIR spectra unmilled and milled TiO_2 nanopowders.

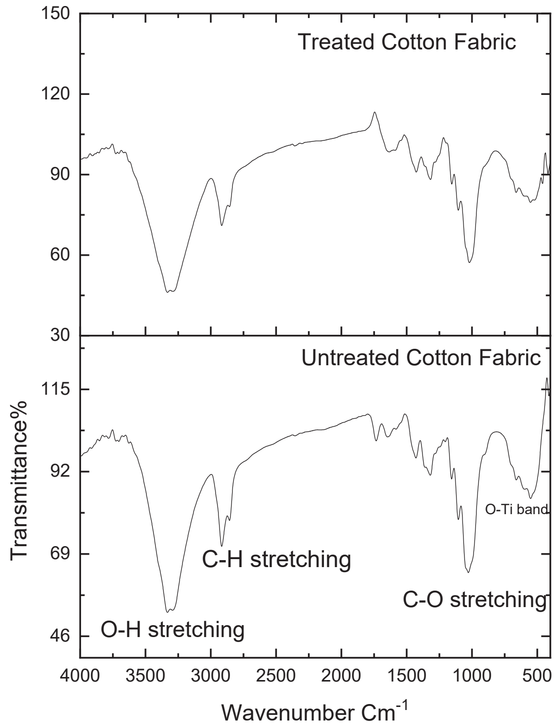

Fig. 4. FTIR spectra of untreated and treated cotton fabric.

It is clear that increasing milling time results in an increasing in frequency of collisions. Therefore the applied energy to powder is increased which leads to decrease in mean crystalline size. By increasing the milling time from 100 hours to 125 hours the intensity of peak has been increased, so that anatase one has been intensified. The calculated lattice parameters also well match with the JCPDS a, c value for the anatase phase. These effects could be assigned to the change in the crystalline size and internal structure of TiO_2 crystalline induced by the ball milling process. It has been reported by some authors that the increase in lattice strains and the reduction in crystalline size [12].

FTIR Analysis of TiO_2 Nanopowders

FTIR spectroscopy technique was carried out to assess the chemical composition and function groups of unmilled and milled TiO_2 nanoparticles in the wavenumber range of 400 cm^{-1} to 500 cm^{-1}(fig. 3). The observed absorbance bands in the range 3000 cm^{-1} to 4000 cm^{-1} indicative of the stretching vibrations of -OH or absorbed water molecules [13]. The next small peak is located at 2353.69 cm^{-1}which shows the existence of CH_3 and CH_2 bonds which indicate the presence of long chain. A sharp absorption peak appeared at 1736.58 cm^{-1} is referred to as the Ti-O-H bending mode [14] & asymmetrical CO coupled vibration of anhydride group. The strong peaks present at 1367.28 cm^{-1} & 1216.81 cm^{-1} are assigned to amide III group. The peak near 500 cm^{-1} is attributed to the O-Ti-O vibration.

Fig. 4 shows the FTIR spectra of untreated and treated cotton fabric. The spectra reveals that the high affinity of TiO_2 towards hydroxyl groups and anchoring of TiO_2 NPs exactly to these sites. FTIR peak at 2915 cm^{-1} is associated with the functional groups C─H stretching of the long hydrocarbon chains in HDTMS. Compared with the original cotton fibers, the peaks at 3332 cm^{-1} (O–H stretching) and 2915 cm^{-1} (CH_2 asymmetrical stretching) for the modified fiber are intensified to some extent, but the peak at 2915 cm^{-1} (CH_2 symmetrical stretching) is weakened. That is due to the absorbed water or surface hydroxyl groups [15]. The peak at 1027 cm^{-1} (C–O stretching at C–3 and C–C) is shifted to 1020 cm^{-1}. The peak at 551 cm^{-1} should be assigned to the O–Ti stretching band with respect to the spectrum of TiO_2 (515 cm^{-1}). This is attributed to the formation of O-Ti covalent bonds between TiO_2 and cotton fibers. Thus, it may be deduced that TiO_2 nanoparticles react with cotton fibers.

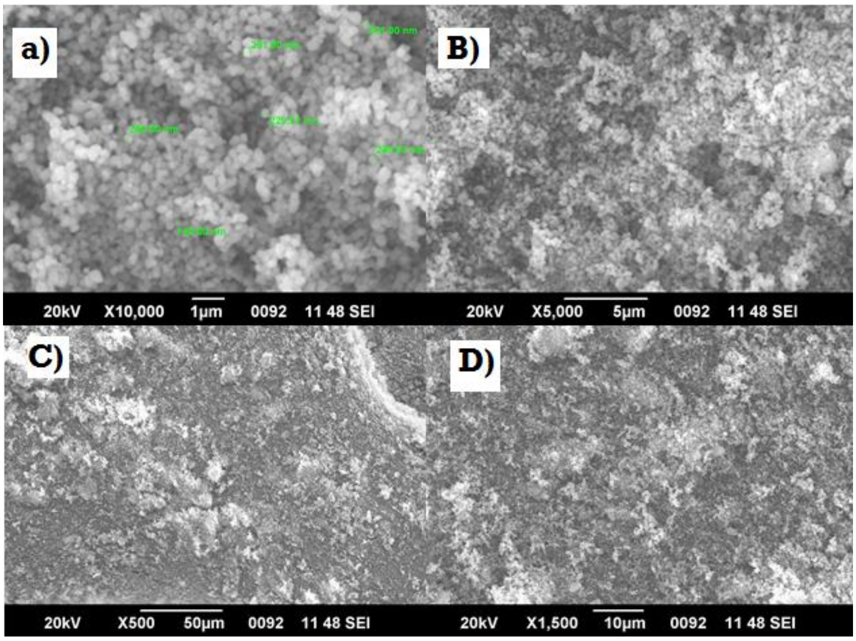

Fig. 5 (a, b, c, d). SEM images of TiO_2 nanopowders milled at 125 hours.

SEM analysis

The changes of morphology and size of the milled TiO_2 powders at 125 hours were observed under SEM. The observed SEM images are presented in figs. 5 (a, b, c, d) with different magnifications. The milled TiO_2 nano powders have a spherical shape with good dispersion. Less agglomeration of nanoparticles was also appeared, after ball milling process. Agglomeration is owing to the bond of nanoparticles to each other by weak forces and high surface energy. The observed nanoparticle size ranges from 140 nm to 240 nm is evidenced form SEM images.

Hydrophobic test on TiO_2 coated Cotton Fabric

In this research hydrophobic test was conducted for milled TiO_2 nanoparticles at 100 and 125 hours. The observed results showed that (Table 2) TiO_2 coated cotton fabric has partial wetting of whole of upper surface of the water droplet and this optimized molar ratio, the fictionalization of TiO_2 by HDTMS has better hydrophobic effect. HDTMS on the top layer of the surface lowers the surface free energy. The increase in concentration may provide even more hydrophobic effect which gives advantages in different properties such as UV-blocking and antibacterial activity. However, higher concentrations of TiO_2 and HDTMS also added some disadvantages such as poor mechanical stability, alteration of textural properties, and cost [16]. Since HDTMS imparts the hydrophobic property to the hydrophilic fabrics previously applied with TiO_2 nanoparticles. Untreated fabrics showed completely wetted by water, due to the high hydrophilic property of cellulosic textiles. Fig. 1 shows the simple laboratory testing of water

Table 2. Water repellent rating of coated fabric.

Sample	Rating of Water Repellent	Description
100 hrs milled TiO_2 coated cotton fabric	70	Partial wetting of whole of upper surface.
125 hrs milled TiO_2 coated cotton fabric	70	Partial wetting of whole of upper surface.

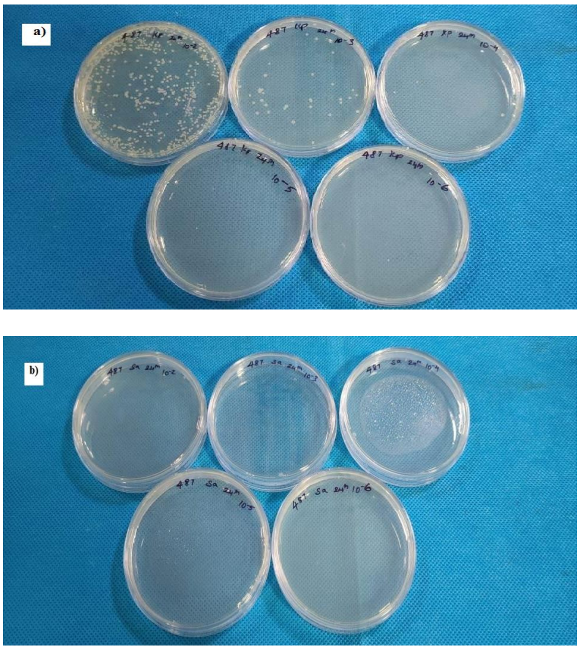

Fig. 6. a) Photograph of antibacterial activity of TiO_2 coated cotton fabric against *S.aureus* b) against *K. pneumonia*.

repellency of TiO_2 coated cotton fabric.

Bursting strength of TiO_2 nanoparticles coated Cotton Fabric

Bursting strength tests were carried out from different ten points of the fabrics by suitable inflated rate. A measurement was carried out to evaluate the bursting strength. The bursting strength was tested on cotton fabric coated TiO_2 nanopowders milled at 125 hours. The result of bursting strength represents the bursting strength improved with the incorporation of TiO_2. Bursting strength of both the treated fabric and untreated fabric was measured and compared.

The optimized bursting strength of the sample knitted fabrics changes between approximately 413 to 536 kPa. It was found that the mean bursting strength of coated cotton fabric was 503.6 Kpa [17]. Bursting strength is an innovative test that was accepted by ASTM in 2015. Therefore, it has limited history of use and was not reported in the literature reviewed for the study. Therefore, this bursting strength test will drive treasured impact to the textile industry.

Antibacterial activity

Antibacterial tests for TiO_2 coated cotton fabrics were carried out with *Staphylococcus aureus* and *Klebsiella Pneumonia* (figs. 6a & 6b). The untreated cotton fabric sample has no falling in the bacterial count against both *Staphylococcus aureus* and *Klebsiella pneumonia*. Nano- TiO_2 treated cotton fabric sample has revealed improved reduction of bacterial count and nano-TiO_2 has photo catalytic effect when exposed to light, photons with energy equal to or greater than the band gap of the titanium dioxide stimulate electrons active to the conduction band. The excited electrons inside the crystal structure retort with oxygen atoms in the air, generating free-radical oxygen. These oxygen atoms are influential oxidizing agents, which can disrupt the cell wall of microorganisms through oxidation-reduction reactions [18].

The above reported result (Table 3) confirms the concept that the nanoparticles get bound to the fabric surface on their own because of their high surface energy. The test results were clearly indicated 4 g/l concentration solution shows the 99 % reduction of bacteria colonies in *Staphylococcus aureus* and *Klebsiella pneumonia*. This is due to that anti-microbial agent gets attached to the fabric through bond formation on the surface. The attached antimicrobial agent disrupts the cell membrane of the microbes through the physical and ionic phenomenon [19].

CONCLUSION

The size of the TiO_2 nanopowders was reduced

Table 3. Quantitative antibacterial assay of TiO_2 treated cotton fabric.

Sample	Tested Bacteria	Finishing agent concentration in gpl	Bacteria Reduction after treatment in %
100 hours Milled TiO_2 Coated Cotton fabric	Staphylococcus aureus ATCC 6538	4	99.99
	Klebsiella pneumoniae ATCC 4352	4	99.83
125 hours Milled TiO_2 Coated Cotton fabric	Staphylococcus aureus ATCC 6538	4	99.99
	Klebsiella pneumoniae ATCC 4352	4	99.99

by milling process and milled TiO_2 nanopowders were coated on cotton fabric through Pad-Dry-Cure method. The important functional properties such as antimicrobial activity, bursting strength and water repellency were tested and analyzed. The XRD spectra of the TiO_2 nanoparticles were analyzed and the presence of well-defined peaks indicates the anatase crystalline structure. The FTIR spectra confirm the functional groups present in TiO_2 nanopowders and treated cotton fabric. SEM analysis showed that spherical structure of TiO_2 nanopowders. Anti-bacterial assay was carried out on nanosized TiO_2 treated cotton fabric against both *Staphylococcus aureus* and *Klebsiella pneumonia* and the observed results revealed that the superior reduction of bacterial count. Milled TiO_2 coated cotton fabric exhibits notable water repellent and bursting strength rate. Undoubtedly finishing of textile materials with TiO_2 nanoparticles brings many valuable benefits in a view of end-use properties, but many aspects must be covered in order to meet functional, economical, health safety and environmental demands.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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