Analysis of sol aging effects on self-cleaning properties of TiO$_2$ thin film

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Abstract
This study investigated the effect of aging TiO$_2$ Sol on the final thin film performance using the heat-assisted sol-gel synthesis method. The sol was aged 24 h, 48 h, and 72 h respectively before being spin-coated on glass substrates. The annealing of the coated thin films occurred at 600 °C. The scanning electron microscope, x-ray diffraction (XRD), and UV–vis spectrophotometer characterized the thin films to ascertain morphological, structural, and optical properties. Also, methylene blue degradation characterized the thin films to confirm the self-cleaning properties. The result revealed that aging time influences the ability of the electrons to gather or transit. The light absorption experienced an increasing shift in value. Also, light absorption optimized with absorption bands with peak intensities becoming strong as aging time increased. Aging the TiO$_2$ Sol caused micro and macro-structural transformations. The structural analysis showed anatase with possible transitioning to rutile as aging time increased. Crystallite size from the most prominent peak range from 3.61 nm to 21.77 nm as aging time increased from 24 h to 72 h and 19.31 nm for rutile at 72 h. The optical bandgap dropped from 3.51 eV to 3.26 eV as aging time increased from 24 h to 72 h. The morphology showed increasingly uniformly distributed shapes of TiO$_2$ particles scattered over the surface of the substrate as aging time increased. The self-cleaning test showed the thin film has a high degradation efficiency of methylene blue dye in the range of 72.50 to 92.90% confirming substantial, self-cleaning property.

1. Introduction
Titanium dioxide (TiO$_2$) is gaining increasing attention owing to its self-cleaning properties. As a semiconductor material, it is responsible for photogeneration activity on surfaces of photovoltaic panels. It induces photocatalytic action once it absorbs light and gets excited to affect electrons and holes movement that degrades the contaminant by creating hydrogen molecules that seek to combine with oxygen ions to produce water molecules [1]. It is one of the semiconducting oxide materials that have attracted considerable interest in the recent decade. Other materials include tin oxide, zinc oxide, and indium oxide with a wide bandgap [2]. It has also earned diverse applications due to its chemical stability, photocatalytic activity, and non-toxicity. The wide bandgap (3.00–3.20 eV) and close refractive index to glass (2.10 to 2.20) make it suitable for application as a thin film on photovoltaic panels. The bandgap is essential as it dictates the range of light in a solar spectrum that a solar cell can absorb. The use of TiO$_2$ thin films as self-cleaning coatings on photovoltaic panels has reduced soiling effects caused by environmental pollution. The material usage also increases the power conversion efficiency of the photovoltaic panel [3]. Self-cleaning of a surface is the ability of that surface to fight off dirt and contaminants without assistance from any external source such as humans or robots.

The ability of TiO$_2$ coating to self-clean a surface is governed by several parameters, as shown in figure 1. Each of these parameters influences the final performance of the TiO$_2$ thin film [4]. Several authors investigated some of these parameters to understand their effects on synthesizing the thin film on the final product's...
performance. A. Guillén-Santiago et al 2010 [5] investigated the effects of aging time and film thickness of TiO₂ through a methylene blue degradation process after doping it with Silver for use in water cleaning.

D Regonini et al 2014 [6] studied the effect of aging time and film thickness of TiO₂ sol to understand its photoelectrochemical characteristics. Wong et al 2013 [7] looked at the precursor concentration and time of aging and observed that crystallinity was improved for a longer aging time. Other research works focus on parameters such as annealing temperature, molarity, the acidity of the solution, doping, and more on the prepared TiO₂ thin films have also been carried out [8–11]. Titanium dioxide thin-film depositions have been achieved through atomic layer deposition [12], sol-gel spin coating process [13], chemical vapor deposition [14], and dip-coating [15]. Among these methods, the sol-gel spin coating method is favorable due to its ease of control, simplicity, and quick affordability [16]. The sol-gel spin coating process has been used to investigate several parameters affecting TiO₂ thin films and their self-cleaning properties. Intensive literature search has revealed that several authors have employed the method to investigate the effects of sol aging on the TiO₂ thin films. Still, no studies have been done to understand the impact of aging TiO₂ Sol on its self-cleaning properties, especially for photovoltaic application. The self-cleaning properties of TiO₂ thin films in photovoltaic panels can be optimized by a proper investigation of the TiO₂ precursor solution. Aging a prepared solution has the potential to cause micro and macro-structural changes on the TiO₂ particles, which might influence its final self-cleaning performance.

TiO₂ thin films coated on the surfaces of PV panels facilitate the decomposition and dissemination of dust and contaminants from the surface through its photocatalytic activity induced when it absorbs energy from sunlight. Once illuminated by light, electrons in the valence band of TiO₂ get excited and move to the conduction band, creating a negative-electron hole (− e) in the valence band. This photoexcitation leads the positive electron-hole (h +) in TiO₂ to separate water molecules to form hydrogen and hydroxyl radicals. In contrast, the negative electron (− e) forms double oxide anions by combining with oxygen molecules. The process will keep repeating so long as there is light, an essential feature of TiO₂ that can be exploited for self-cleaning in photovoltaic applications.

This paper examines the influence of TiO₂ sol aging on its self-cleaning properties for photovoltaic application using the sol-gel spin coating method. The morphology, elemental composition of the prepared film from the solutions aged 24 h, 48 h, and 72 h, and the structural, optical, and self-cleaning abilities of the spin-
coated TiO₂ thin films were analyzed. The paper is arranged to discuss the introduction and background of the material, technique, and process. After that, the methodology discussed substrate cleaning, sol-gel synthesis, and thin film deposition using spin coating. After that, the characterization of deposited samples is presented. A detailed discussion of the results of the characterization is performed, and a conclusion is drawn.

2. Methodology

TiO₂ thin films were obtained through a heat-assisted sol-gel spin coating method.

2.1. Materials
All chemicals were obtained as analytical grade and used without further purification for the synthesis and deposition process. Glass plates obtained from Sigma Aldrich were used as substrates for the thin film coating. Also, 97.00% Titanium Isopropoxide (TTIP) and 99.90% ethanol, all from Sigma Aldrich (Germany) was used as the precursor for TiO₂ and solvent, respectively. Deionized (DI) water was used as a hydrolyzing agent, and nitric acid used as a stabilizer was obtained from Merck chemicals, South Africa.

2.2. Substrate preparation
The glass substrates were first cut into size (25 mm × 20 mm × 1 mm) before being cleaned. The glass substrates were washed with detergent and further cleaned with deionized water, acetone, and ethanol for 15 min, respectively, after that dried in an Ecotherm oven for 30 min at 100 °C. It is essential to properly prepare and clean the substrate to improve material-to-substrate bonding and reduce impurities within the deposited thin film.

2.3. Preparation of the TiO₂ Sol
The TiO₂ sol was obtained by dissolving titanium (IV) Isopropoxide 97% in 99.90% ethanol in the ratio of 1: 5 volumes while stirring. Acid stock, prepared by mixing nitric acid with deionized water in the ratio of 1: 50 volume, was added dropwise after 30 min of stirring into the whitish precursor solution while under continuous stirring at 500 rpm using a magnetic stirrer to form a transparent film as shown in figure 2. The solution was stirred for another 2 h at 60 °C temperature under atmospheric pressure to ensure proper hydrolysis. After which, it was aged in a desiccator for different periods (24 h, 48 h, and 72 h) at room temperature.

2.4. TiO₂ thin films preparation
The TiO₂ thin films were coated using the spin coater. The aged sol was dispensed onto the glass substrates in a static dispensing manner and then spanned at a lower speed of 1000 rpm for 6 seconds and a higher rate of 3000 rpm for 30 seconds, respectively, using the CHEMAT TECHNOLOGY KW-4A Spin Coater. The lower speed helped spread the solution fully onto the surface of the substrate, while the higher speed thins off the solution into a thin film. All spin-coated films were calcined at 600 °C for 2 h to improve the crystal structure and then allowed to cool at room temperature before being characterized.
2.5. Characterization of the deposited film

Morphologies were examined using a Scanning Electron Microscope TESCAN VEGA3 (OXFORD). The elemental composition was confirmed with an Energy Dispersive x-ray Spectrometer Aztec instrument (OXFORD). The Figure 3. SEM micrographs and EDX percentage composition of various elements existing in the TiO₂ films deposited after aging for; (a) 24 h, (b) 48 h, and (c) 72 h.

Figure 3. SEM micrographs and EDX percentage composition of various elements existing in the TiO₂ films deposited after aging for; (a) 24 h, (b) 48 h, and (c) 72 h.
structural properties were studied with a Philips XPERT-PRO x-ray for 2θ angles from 5° to 90°. The optical properties of the deposited films were studied in wavelengths of 200 to 600 nm using a UV-2450 (SHIMADZU) Spectrochometer with a scan rate of 600 nm min⁻¹. The nanoparticles’ molecular bonding and absorption bands were characterized with a Perkin Elmer Spectrum 100 FT-IR spectrometer in the spectrum range of 4000 cm⁻¹ to 300 cm⁻¹.

All deposited films were tested for self-cleaning activity by staining each film with methylene blue as a form of contamination. Then the stained film was illuminated under UV irradiation for 30 min before being washed with deionized water. An empty glass without TiO2 deposited was stained with methylene blue, illuminated simultaneously, and washed afterward. The films coated with TiO2 were compared to that of empty glass to observe the self-cleaning abilities of the deposited thin films.

The results of characterized samples are now discussed.

3. Results and discussion

3.1. Morphological and elemental composition of the deposited films
The EDX analysis showed in figures 3(a)–(c) show Titanium (Ti) and Oxygen (O) strongly present and having higher weight percentages. Silicon (Si), Calcium (Ca), and Sodium (Na) are visible because they are components of the glass substrate. They have a lower weight percentage than (Ti) and (O), thus confirming the significant presence of the constituents of TiO2 in good proportion. It is also observed from the elemental composition that the (Ti) and (O) percentage dropped as sol aging time was increased. This observation could be caused partially by the diffusion of sodium and silicon into the TiO2 thin films at averaged annealing temperatures and the disappearance of oxygen atoms with water molecules due to evaporation during sol aging [17]. However, the (Ti) and (O) are still present in higher percentage weights providing necessary details concerning the purity of the TiO2 thin films. The uniformly distributed TiO2 thin films are desired in self-cleaning applications as they expose the surface for higher photon absorption from sunlight, leading to higher photocatalytic activity [18].

The morphologies of the spin-coated TiO2 thin films for 24 h, 48 h, and 72 h observed under the scanning electron microscopy are shown in figure 3. For 24 h, the cloudy films are seen to be dense and continuous. The peak intensities indicate Ti, O, Si, Na, and Ca with visible cracks due to moisture presence, as shown in figure 3(a). The film deposited after 48 h of aging is shown in figure 3(b) to have snowflakes structures scattered with some chain links, which is characteristic of well-spread film on the glass substrate. After 72 h of sol aging, the deposited film showed more agglomerated flakes scattered over the substrate with larger shapes. The shapes looked more uniform, as seen in figure 3(c).

3.2. Structural composition (XRD)
The crystal structures and phase composition of the deposited TiO2 were evaluated using Philips XPERT-PRO X-ray diffractometer from 2Theta degree equal 5 to 90 on Gonio scan-axis with Cu-Kα radiation (λ = 1.54060). Figure 4 shows x-ray diffraction patterns for 24 h, 48 h, and 72 h aged sol, respectively deposited and annealed at 600 °C.

Figure 4. XRD diffraction pattern of the deposited TiO2 thin films after aging sol for 24 h, 48 h, and 72 h.
It was observed that a tetragonal anatase structure was formed after 24 h with cell volume 137.24 Å³ and 2 theta angles of 25.22, 37.81, 47.84, 53.87, and 54.84 with corresponding (h k l) planes of (101), (004), (200), (105), and (211), which matches ICSD collection code 154602 and ICDD card–01–075–2545. The peaks were weak, with the most significant appearing at 2Theta 25.22. The XRD pattern for the TiO₂ thin film deposited from sol aged for 48 h matched ICSD code 82082 and ICDD card 01–086–1156 having tetragonal anatase structures with the volume of cell equal 135.88 Å³. The anatase peaks appeared at 2Theta degrees 25.34, 37.81, 48.10, 53.92, 55.13, corresponding to (h k l) planes of (101), (004), (200), (105), and (211). It was observed that as the aging increased to 72 h, anatase and rutile tetragonal crystal structures were formed with cell volumes of 136.93 Å³ and 62.89 Å³ respectively. The anatase phase had prominent peaks at 2Theta degrees 25.27, 37.69, 47.98, 53.76, 54.99, and 62.57 correspondings to (h k l) crystal planes of (101), (004), (200), (105), (211), and (204) respectively (ICSD code 9853 and ICDD card 01–071–1167). The rutile phase had peaks appearing at 2Theta degree 27.37, 35.97, 41.13, and 56.49 with miller indices (110), (101), (111), and (220) matching reference code 01–080–2531 and ICSD code 169625. All three samples had their most intense peak around the 2Theta value of 25.3 degrees, with the peak intensities becoming stronger as aging time increases. Also, as the aging time increases coupled with the long annealing time at 600 °C, the transition to anatase phase appeared on XRD patterns of the thin from 72 h aging. Rutile affects the particle size to reduce [19]. This observation could be attributed to aging the precursor solution to allows its particles to react adequately, bond, and form a stable homogeneous solution that improves crystal structure and particle size [20]. The delicate nature of the film also attracted the visibility of amorphous glass in the XRD patterns; Chu et al observed a similar effect in 2016 [21].

The average particle size for each of the three different patterns was calculated using the Debye–Scherrer formula [22] shown in equation (1).

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

(1)

Where β is the full width at half maximum (FWHM) peak intensity (in Radian), λ is the wavelength, θ represents Bragg’s diffraction angle, and k is 0.94, respectively. The average particle size was calculated using three different peak values for each sample for accuracy, and the average is reported in table 1 for the three different samples.

From table 1, it was observed that the sample aged 24 h had the smallest crystallite size, which is in agreement with the x-ray diffraction peak intensities. Smaller grain sizes are known to form cavities that expose the greater surface area for free radical absorption [23]. The sample that was aged for 72 h showed phase transition with the formation of rutile tetragonal structures. This observation could lead to a smaller crystallite size. Rutile structures are usually smaller than those of anatase. So as grain size decreases, their photocatalytic ability increases.

### 3.3. Optical studies

The optical properties of the three different samples as analyzed using UV–2450 SHIMADZU spectrophotometer in 200 to 600 nm wavelength range are shown in figure 5. The three samples for 24 h, 48 h, and 72 h displayed high absorption within the visible light region, as seen in figure 5(a). The percentage absorption value increased with an increase in aging time. Also, as the aging time increased, absorption shifted to higher wavelengths. High absorption is suitable for self-cleaning applications as higher absorption increases photocatalytic activity since more energy leads to more photon excitation [24]. The value of hν and (αhν) were evaluated from the absorbance data obtained from the UV–vis spectrophotometer. Then the Tauc and David Mott relation [25] given in equation (2) was used to create a plot from which the optical bandgap of the prepared TiO₂ thin films was obtained.

$$\left( \alpha h\nu \right)^n = K (h\nu - E_g)$$  

(2)

Where hν is the incident photon energy, α is the absorption coefficient, K being an energy-independent constant, and $E_g$ is the optical band gap value of the thin film. At the same time, n is a value dependent on the nature of transition (n = 2 for direct allowed transition, 1/2 for indirect allowed transition, and 2/3 for direct forbidden transition. The bandgap of each sample was established from the linearity of the graph of (αhν)² versus photon energy (hν). It was evaluated by extrapolating a straight line from the straight-line section of the curve to intersect the hν-axis, as shown in figure 5(b). The direct bandgap of the coated TiO₂ thin film was evaluated and recorded as shown in table 2 for the different aging times. The result showed bandgap energy dropping as aging time increased. The observed reduction in bandgap energy may be attributed to increased crystallinity arising from increased aging time [26]. The increase in crystallite size and the transition from tetragonal anatase to rutile phase as aging time increased [27].

The drop in bandgap as crystallite size increases is due to the densification caused by larger crystallite size and a decrease in porosity [29]. The larger the crystallite sizes, the more the atoms and atomic orbitals overlap under the quantum size effect. This overlap increases the number of occupied molecular orbitals that are highest in
Figure 5. Optical properties of the deposited thin films (a) Absorption spectrum of deposited after aging sol for 24 h, 48 h and 72 h (b) Tauc’s Plot of ($\alpha h\nu$)$^2$ versus h$\nu$ with direct bandgap energy of sample 24 h, 48 h, and 72 h indicated are due to more excellent crystallinity associated with longer aging time [28]. The configurations of the absorption bands are similar except for the fact.

Table 1. Crystallite size of the TiO$_2$ thin films deposited after aging sol for 24 h, 48 h, and 72 h.

| Sample (Aging time) | 2 Theta Position (°) | (h k l) | FWHM (°) | Crystallite size D | Structure/Crystallinity |
|---------------------|----------------------|---------|----------|--------------------|-------------------------|
| 24 h                | 25.20                | 101     | 2.3564   | 3.61 nm            | Anatase/Tetragonal      |
| 48 h                | 25.34                | 101     | 0.5651   | 15.05 nm           | Anatase/Tetragonal      |
| 72 h Anatase        | 25.26                | 101     | 0.3906   | 21.77 nm           | Anatase/Tetragonal      |
| 72 h Rutile         | 27.39                | 110     | 0.4423   | 19.31 nm           | Rutile/Tetragonal       |

Table 2. Observation of changes in crystallite size and bandgap with changing aging time.

| Aging time | Crystallite size | Bandgap | Phase |
|------------|------------------|---------|-------|
| 24 h       | 3.61 nm          | 3.51 eV | Anatase |
| 48 h       | 10.05 nm         | 3.36 eV | Anatase |
| 72 h       | 21.77 nm         | 3.26 eV | Anatase |
energy and the unoccupied molecular orbital that is lowest in energy. It reduces the gaps between them, which are band gaps or energy gaps [30]. When two atomic orbitals mix, they produce two molecular orbitals. As the number of nodes decreases, the energy of the orbital also decreases. The closer in energy are two orbitals, the greater the amount of mixing that occurs. The amount of mixing is dependent upon the amount of overlap between the mixing orbitals. Therefore, a larger crystallite size increases the bonding and antibonding effect. A resultant decrease in the bandgap because of increased overlaps [31, 32]. A sol-gel mesh is formed as the reaction and hydrolysis occur, during aging, to form a homogenous and stable structure. This sol-gel meshing influences crystallinity and electron transportability.

3.4. FTIR analysis
Molecular bonds and absorption bands of the deposited TiO2 thin films were examined with a SHIMADZU 2450 spectroscopy from a wavenumber of 4000 cm⁻¹ to 400 cm⁻¹ with a resolution of 16 cm⁻¹ as shown in figure 6. The weak decreasing peak bands at 3725.66 cm⁻¹, 2321.41 cm⁻¹ and 842.30 cm⁻¹ are disappearing hydroxyl, carboxyl, and alkane groups [33]. This observation can be associated with the long annealing time and higher annealing temperature of 600 °C. The band from 2979.43–2807.49 is attributed to C–H stretching vibration, while at 1731.70 cm⁻¹ C=O stretching vibration appears. The sharp band from 1458.96 to 1372.58 cm⁻¹ represents the C–H bending vibrations. The C–O stretching vibration from the alcohol group appears at 1158.86 cm⁻¹. The T–O–O band appears at 1015.72 cm⁻¹ while the band at 851.00 cm⁻¹ is attributed to the O–Ti bending vibration. The band at 439.99 cm⁻¹ is attributed to O–T–O bending vibration due to the crystallization of the Titania particles showing the presence of Ti and Oxygen molecules. The absorption bands and peak intensities became very strong as the aging time increased from 24 h to 72 h.

3.5. Self-cleaning test
The samples were stained with methylene blue (10 ppm) as a form of contaminant to confirm the self-cleaning ability of the deposited thin film. An empty glass piece without TiO2 coating was also stained with methylene blue as a control sample. A quick observation revealed the samples with TiO2 coatings absorbing and dissolving the dye while empty glass remained still, indicating TiO2 self-cleaning function. Thus, the methylene blue covered a more significant portion of the coated glass sample than bare glass. Contact angle measurement using

![Figure 6. FTIR analysis of the different TiO2 thin films deposited after aging the sol for 24 h, 48 h, and 72 h.](image)

| Table 3. Contact angle measurement for an empty glass (control sample) and coated films. |
|---|---|---|---|---|---|
| Sample | Run one | Run two | Run three | Run four | Average value |
| Empty glass | 31.10 | 31.13 | 40.35 | 28.86 | 32.86 |
| 24 h film | 54.17 | 48.71 | 51.46 | 55.94 | 52.57 |
| 48 h film | 46.86 | 49.83 | 49.54 | 40.95 | 46.79 |
| 72 h film | 32.75 | 37.04 | 49.20 | 42.11 | 40.27 |

They become more intense and more robust as the aging time increases. Strong molecular bonds are essential for self-cleaning thin films as they are required to withstand adverse environmental conditions during application in solar panels.
DataPhysics optical contact angle goniometer revealed the contact angle of empty glass remained lower than those of the TiO$_2$ coatings after four test runs, as recorded in table 3. These contact angle values confirmed that TiO$_2$ is hydrophilic and exhibits self-cleaning by absorbing and degrading the contaminant through the spread of the water molecules.

All the samples were then subjected to visible light illumination for one hour to observe their photocatalytic degradation of the methylene blue. It was observed after the lighting illumination that the dye was still more on the empty glass sample than on the samples coated with TiO$_2$, as shown in figure 7. Thus, indicating that TiO$_2$ was retrieving self-purity, thus affirming that the TiO$_2$ had a self-cleaning ability.

The UV absorption readings of the three samples were taken to compare the self-cleaning ability of the different deposited films. The samples were then stained with 10 ppm (2.5 mg l$^{-1}$) methylene blue solution and subjected to UV-light illumination (40 W and 40 cm in length) for two hours for photodegradation to take place. The samples were mounted 5 cm below the UV lamp throughout the test. After the UV illumination, the UV absorbance readings of the samples were retaken. The percentage degradation of each sample was calculated using the formula in equation (2), and the results were recorded in table 4.

Table 4. Photodegradation of methylene blue under UV-light by various thin films.

| Sample | Absorbance Value before | Absorbance value after | MB degradation value (%) |
|--------|--------------------------|------------------------|--------------------------|
| 24 h   | 0.23                     | 0.06                   | 72.50%                   |
| 48 h   | 0.58                     | 0.04                   | 92.90%                   |
| 72 h   | 0.64                     | 0.05                   | 92.50%                   |
\[
\%D = \frac{A_0 - A_t}{A_0} \times 100\%
\]

Where \(\%D\) is the percentage degradation of methylene blue, \(A_0\) is the initial absorbance of the thin film, and \(A_t\) is the thin-film absorbance value after UV-light illumination time.

It was observed that all the TiO\(_2\) thin films degraded the methylene blue by absorption in differing percentages. This observation led to significant drops in UV absorbance value after the UV light illumination. The decrease could be attributed to the breakage of bonds that produce vacancy where lighting could not penetrate and the cluster of microporous structures that inhibit penetration of light and self-suction of the dye. The percentage degradation of methylene blue by thin-film ranged from 72.50 to 92.90%, showing that the coated thin film will self-clean with the thin film of 48 h displaying the highest value. The results are shown in figure 8.

4. Conclusion

TiO\(_2\) thin films were prepared from Sol and aged 24 h, 48 h, and 72 h, respectively. After that, the influence of aging the sol on the self-cleaning properties of TiO\(_2\) was examined by analyzing the morphology, structure, optical, and self-cleaning tests. It was observed that as the aging time increased, more uniformly distributed shapes of TiO\(_2\) particles distributed over the substrates were formed. XRD revealed mainly anatase structures with the tendency of rutile transition as aging time increased. Crystallite size from the most prominent peak range from 3.61 nm to 21.77 nm as aging time increased from 24 h to 72 h. The optical bandgap dropped from 3.51 eV to 3.26 eV as aging time was increased from 24 h to 72 h. As the aging time increased from 24 h to 72 h, absorption bands and peak intensities became very strong. The self-cleaning test showed the prepared film’s high degradation efficiency of methylene blue dye from 72.50 to 92.90%, confirming strong, self-cleaning property. No precipitation was observed during the aging of the TiO\(_2\) Sol for the times.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Conflict of interest

The authors declare that there is no conflict of interest.

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