Cu Doped TiO₂: Visible Light Assisted Photocatalytic Antimicrobial Activity and High Temperature Anatase Stability

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Indoor surface contamination by microbes is a major public health concern. A damp environment is one potential sources for microbe proliferation. Smart photocatalytic coatings on building surfaces using semiconductors like titania (TiO₂) can effectively curb this growing threat. Metal-doped titania in anatase phase has been proved as a promising candidate for energy and environmental applications. In this present work, the antimicrobial efficacy of copper (Cu) doped TiO₂ (Cu-TiO₂) was evaluated against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) under visible light irradiation. Doping of a minute fraction of Cu (0.5 mol %) in TiO₂ was carried out via sol-gel technique. Cu-TiO₂ further calcined at various temperatures (in the range of 500 °C – 700 °C) to evaluate the thermal stability of TiO₂ anatase phase. The physico-chemical properties of the samples were characterised through X-ray diffraction (XRD), Raman spectroscopy, X-ray photo-electron spectroscopy (XPS) and UV-visible spectroscopy techniques. XRD results revealed that the anatase phase of TiO₂ was maintained well, up to 650 °C, by the Cu dopant. UV-DRS results suggested that the visible light absorption property of Cu-TiO₂ was enhanced and the band gap is reduced to 2.8 eV. Density functional theory (DFT) studies emphasises the introduction of Cu⁺ and Cu²⁺ ions by replacing Ti⁴⁺ ions in the TiO₂ lattice, creating oxygen vacancies. These further promoted the photocatalytic efficiency. A significantly high bacterial inactivation (99.9%) was attained in 30 mins of visible light irradiation by Cu-TiO₂.

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Cu doped TiO₂: Visible light assisted photocatalytic antimicrobial activity and high temperature anatase stability

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Abstract: Indoor surface contamination by microbes is a major public health concern. A damp environment is one potential sources for microbe proliferation. Smart photocatalytic coatings on building surfaces using semiconductors like titania (TiO₂) can effectively curb this growing threat. Metal-doped titania in anatase phase has been proved as a promising candidate for energy and environmental applications. In this present work, the antimicrobial efficacy of copper (Cu) doped TiO₂ (Cu-TiO₂) was evaluated against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) under visible light irradiation. Doping of a minute fraction of Cu (0.5 mol %) in TiO₂ was carried out via sol-gel technique. Cu-TiO₂ further calcined at various temperatures (in the range of 500 °C – 700 °C) to evaluate the thermal stability of TiO₂ anatase phase. The physicochemical properties of the samples were characterised through X-ray diffraction (XRD), Raman spectroscopy, X-ray photo-electron spectroscopy (XPS) and UV-visible spectroscopy techniques. XRD results revealed that the anatase phase of TiO₂ was maintained well, up to 650 °C, by the Cu dopant. UV-DRS results suggested that the visible light absorption property of Cu-TiO₂ was enhanced and the band gap is reduced to 2.8 eV. Density functional theory (DFT) studies emphasises the introduction of Cu⁺ and Cu²⁺ ions by replacing Ti⁴⁺ ions in the TiO₂ lattice, creating oxygen vacancies. These further promoted the photocatalytic efficiency. A significantly high bacterial inactivation (99.9%) was attained in 30 mins of visible light irradiation by Cu-TiO₂.

Keywords: Cu doped TiO₂; Doping; Phase transition; Escherichia coli; Staphylococcus aureus; Photocatalysis; Antibacterial coatings;

1. Introduction

Indoor air pollution has been a major public health concerns worldwide in recent days [1, 2]. A study by the National Human Activity Pattern Survey (NHAPS) found that people in U.S.A and Canada spends most of their time (more than 80% of their time) inside enclosed buildings and 6% inside enclosed vehicles [3]. According to World Health Organization (WHO), a significant share of world population is suffering from indoor air pollutants and microbial contamination. The formation of microbial colonies inside the wet or damp indoor environments is one of the major contributing elements to the deterioration of indoor air quality [4, 5]. These microorganisms have the potential to produce contaminants like spores, allergens and toxins affecting the health of the occupants [6, 7]. This kind of continuous exposure can lead to various health concerns like respiratory or skin diseases [8, 9].
Several studies in the past few decades have looked at alteration of building materials and paints to overcome the challenges of indoor air pollution [10, 11]. Most of the physico-chemical techniques and usual cleaning procedures are inactive to completely eliminate the microbes. TiO$_2$ photocatalysis is one of the most promising, simple and economically viable technology to address the indoor air pollution/microbial contamination. TiO$_2$ has been recognized as a traditional semiconductor photocatalyst which has been widely reported for its anti-microbial coatings [12, 13]. The formation of uniform aqueous slurry and the feasibility of deposition on the various substrates make TiO$_2$: a lucrative candidate [14, 15]. However, this material suffers from its own set of limitations. Low visible light absorption because of the wide band gap of TiO$_2$ (3.2 eV) is incompatible to receive visible light for practical applications. Moreover, the low temperature stability of photocatalytically active anatase phase also makes them vulnerable with regards to application as a potential material for coating [16].

Elemental doping, morphological tailoring in the form of nanotubes and fibers, making composites out of new 2-D materials like graphene, C$_n$N$_x$ are some of the efficient techniques to overcome these limitations [17-19]. Elemental doping is an effective strategy to tune the band gap of TiO$_2$: by introducing new energy levels in between and by alteration of conduction band minima(CBM) and valence band maxima(VBM) [20, 21]. In this regard, cationic dopants served to extend the visible light absorption and also enhanced the high temperature stability of the anatase phase TiO$_2$. Copper is one of the interesting dopants added to TiO$_2$: at different mole and weight percents. Cu doped TiO$_2$: was evaluated for various photocatalytic applications like Hydrogen production [22-25], CO$_2$: conversion[26], degradation of dyes and organic contaminants. Several studies demonstrating the photocatalytic anti-bacterial efficiency were also reported [27-29]. However, in most of the cases, a high concentration of Cu was used to display the antimicrobial activity. Additionally, Cu dopants were deposited on morphologically tuned TiO$_2$: nanotubes and nanofibers. This involves with a series of cumbersome synthesis techniques.

In this present study, we demonstrate a facile one-step sol-gel technique to prepare 0.5 mol % of Cu-TiO$_2$: The as prepared samples were calcined at different temperatures ranging 500 °C-700 °C. Simultaneously, the samples were analyzed by Density Functional Theory (DFT) to understand the band gap alteration occurring inside of TiO$_2$: lattice. The anatase phase of TiO$_2$: was maintained (55%) up to 650 °C. The sample calcined at 650 °C illustrated high visible light absorption and Cu doping resulted in lowering of TiO$_2$: band gap from 3.2 eV (for anatase TiO$_2$) to 2.8 eV. Cu-TiO$_2$: was further assessed for the photocatalytic disinfection efficiency towards Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) bacterial strains. A Log 2 reduction by the Cu-TiO$_2$: was attained at a very short time span of 30 mins.

2. Materials and Methods

2.1 Chemicals and Reagents

All the materials used were of analytical grade. The materials were used as received, without further purification. Titanium isopropoxide (97%), copper sulphate pentahydrate (≥98.0%) and isopropanol (≥99.5%) were purchased from Sigma-Aldrich. Strains of Staphylococcus aureus (ATCC-25923) and Escherichia coli (ATCC-25922) were purchased from LGC Standards. Nutrient broth No.2, Agar and all other consumables were bought from Cruinn Diagnostics. Deionized water was used in all experiments.

2.2 Synthesis of Cu-TiO$_2$: 

Cu-TiO$_2$: was synthesized using a sol-gel method as follows: Titanium isopropoxide (TTIP) was stirred in isopropanol (200 ml) for 15 min (solution A). The required amount of copper sulphate was taken separately in deionized water and the mixture was stirred for 15 min (solution B). Then, Solution B was added drop wise to solution A under constant stirring. The resulting gel was dried in an oven at 100 °C for 12 h. The powder was then calcined at various temperatures (500 °C, 600 °C,
650 °C and 700 °C) at a ramp rate of 10 °C/min for 2 h. Pure TiO\textsubscript{2} was also synthesized by the same procedure without the addition of copper sulphate.

2.3 Density functional theory (DFT) computations

DFT calculations were performed using the VASP5.2 [30, 31] code with projector augmented wave (PAW) [32, 33] potentials to account for the core-valence interaction and a kinetic energy cut-off of 400 eV. Cu was substitutionally doped onto a Ti site in rutile (2 ×2×3) and anatase (2 ×2×2) supercells. This gives dopant percentages of 4.2 % and 3.1 % for rutile and anatase respectively, which are consistent with the experimental concentrations of Cu in TiO\textsubscript{2} [22, 34, 35]. The k-point sampling was used a Monkhorst-Pack (4×4 ×2) grid for both bulk polymorphs. Structures were relaxed until forces were less than 0.01 eV Å\textsuperscript{-1}.

Calculations were performed taking into account spin polarisation and no symmetry constraints were imposed. In the initial DFT + U calculations, U = 4.5 eV was applied to the Ti 3d states and U = 7 eV was applied to the Cu 3d states, arising from the inability of DFT to describe consistently the Cu\textsuperscript{2+} oxidation state of Cu and U = 7 [36, 37]. These choices for U are based on the previous studies [38-42]. The starting geometries were manually distorted from the symmetric bulk geometry in order to examine relaxation to distorted geometries, which can be compared with undistorted geometries. To study the charge compensation that arises as a result of the difference in the Cu\textsuperscript{2+} and Ti\textsuperscript{4+} oxidation states, one oxygen ion was removed from different sites of the most stable Cu-doped structures and the energy of formation was calculated by the following equation:

\[ E_{\text{vac}} = E(CuxTi1-xO2-y) + \frac{1}{2E(O2)-E(CuxTi1-xO2)} \] (Equation 1)

Where \( E(CuxTi1-xO2-y) \) is the total energy of Cu doped TiO\textsubscript{2} with a charge compensating oxygen vacancy and \( E(CuxTi1-xO2) \) is the total energy of Cu-doped TiO\textsubscript{2}. The formation energy is referenced to half the total energy of O\textsubscript{2}.

Copper ions were initially in the 2+ oxidation state and calculations were therefore performed with 1 and 3 unpaired spins taking into account the electron deficit due to substitutional doping of Cu\textsuperscript{2+} for Ti\textsuperscript{4+} and the d9 configuration of Cu\textsuperscript{2+}. The oxidation states of Cu dopant, lattice Ti and O ions were determined from Bader charge analysis [43].

2.4 Characterization

The as-synthesized samples were characterized by various techniques. The crystallinity of the samples was analysed by X-ray diffraction (XRD). The diffractograms were produced using Cu Ka radiation (\( \lambda = 0.15418 \) nm) in a Siemens D500 X-ray powder diffractometer. The diffraction was examined in the range of 10°- 80°. Anatase and rutile percentages of TiO\textsubscript{2} were measured by the Spurr equation [44].

\[ F_R = \frac{1}{1+0.8(I_A(101)/I_R(110))} \] (Equation 2)

Where \( F_R \) is the quantity of rutile phase; \( I_A(101) \) and \( I_R(110) \) are the intensity of anatase peak and rutile peak respectively. The crystallinity of the samples was calculated using the Scherrer equation[45].

\[ \Phi = \frac{K\lambda}{\beta \cos \theta} \] (Equation 3)
Where $\Phi$ is the crystallite size; $K$ is the shape factor with a value close to unity; $\lambda$ is the wavelength of X-rays; $\beta$ is the full width half-maximum (FWHM) of the main intensity peak; and $\theta$ is the Bragg angle.

The phase transformation was also analyzed using Raman spectroscopy (Horiba Jobin Yvon LabRAM HR 800) with a grating of 300 gr/mm. A 660 nm solid state diode laser standard bandwidth version with double edge filter upgrade was the laser used. The acquisition time was 3 seconds.

The bonding interactions and oxidation state of elements were studied with the help of X-ray photoelectron spectroscopy. Samples were analyzed on a XPS, Thermo Fisher Scientific, (East Grinstead, UK) K-Alpha spectrometer, which has an XR3 twin anode X-ray source ($\text{AlK}_\alpha/\text{MgK}_\alpha$) and an Alpha 110 analyser. The twin anodes AlK$_\alpha$ X-ray source ($\text{hv} = 1486.6$ eV) was used at 300 W ($15 \text{ kV} \times 20 \text{ mA}$) for analysis of all samples. For all survey spectra, a Pass Energy of 200 eV and a step size of 0.4 eV were used. In order to acquire C 1s, O 1s and Ti 2p high resolution spectra a Pass Energy of 20 eV and a step size of 0.2 eV were used.

The optical properties of the as prepared samples were measured using Perkin-Elmer UV-Vis Spectrophotometer. Barium sulphate (BaSO$_4$) was used as a reference, and slit width was set to 1 nm. Additionally, band gap was calculated from the UV DRS spectrum by using Kubelka-Munk function $F(R)$ [46].

$$F(R) = \left(\frac{1-R^2}{2R}\right)^2 \quad \text{(Equation 4)}$$

Where $R$ is the absolute reflectance of the sample.

The photocatalytic experiments were performed inside weathering and corrosion photo-reactor from Q-Labs (Q-sun Xe-1-S).

2.4 Measurement of antimicrobial activity:

All the glassware used was autoclaved before carrying out the photocatalytic experiments. *Escherichia coli* (gram-negative bacterium) and *Staphylococcus aureus* (gram-positive bacterium) were used to study the antibacterial activity of the Cu-TiO$_2$. Nutrient broth culture medium was prepared by dissolving 25 g of nutrient broth No.2 (10 g peptone, 5.0 g NaCl, 10 g beef extract) in 1 L of distilled water followed by sterilization at 121 °C using an autoclave. The 90 mm agar plates were prepared by dissolving 28 g nutrient agar (5 g peptone, 8.0 g NaCl, 3.0 g Beef extract, Agar No.2) in 1 L distilled water, then autoclaved at 121 °C for 15 mins and poured into petri dishes. The strains were inoculated in 20 ml of nutrient broth and incubated for 24 h at 37 °C. A definite amount of the grown culture was transferred to the cylindrical glass vessel to make the working solution of $10^4$ CFU/ml (colony forming unit/ml). The reaction mixture was kept inside the photo test chamber for visible light irradiation. The photocatalyst concentration was fixed at 1 g/L and irradiated for 3 h. Aliquots of 1 ml were extracted out from the reaction mixture at a regular time interval of 10 mins. In order to attain a countable CFU, the bacterial solution was diluted in a PBS solution once and later 100 µl of diluted solution was plated. Finally, the plates were incubated at 37 °C for 24 h. The colonies formed on the agar plates were counted and recorded as CFU/ml. A control experiment was also conducted in the absence of the photocatalyst. The same set of samples was tested simultaneously under dark conditions.

3. Results

3.1. Density Functional Theory Simulations

There have been some theoretical papers on the topic of Cu-doped anatase TiO$_2$ [47-50]. A DFT + U study [49] of anatase doped with Cu at a concentration of 6.25%, applied $U = 8$ eV to the Ti 3d states; this recovers the bulk TiO$_2$ energy gap but is not to be recommended for other properties. No +U correction is applied to the Cu 3d states, despite issues with describing these electronic states. A
reduction in the band gap was reported in all studies and this is attributed to a combination of Cu 3d and O 2p states above the valence band maximum (VBM). Navas et al provided a comprehensive study [48] of Cu-doping in anatase which combined both experiment and theory including DFT + U calculations with the +U correction on Ti 3d orbitals only. However, inclusion of a +U correction for Cu 3d states is particularly important in correctly describing the Cu$^{2+}$ oxidation state [38, 39, 51]. They reported greater band gap reduction with increases in dopant concentration due to the covalent character of the Cu-O interaction leading to new states at the VBM. A theoretical account of Cu-doping in rutile, in the context of the effect of oxygen vacancies on the magnetic moment of Cu-doped TiO$_2$ [52], reported that oxygen vacancies are most stable near the Cu impurity.

Figure 1. (a) Relaxed atomic structure of bulk anatase TiO$_2$ in the vicinity of the Cu dopant and (b) excess spin density plot for Cu-doped anatase TiO$_2$. Spin isosurfaces enclose densities of up to 0.02 eV/Å$^3$. In this and subsequent figures Ti is represented by a grey sphere, O by a red sphere and Cu by an orange sphere.

Figure 1(a) shows the local atomic structure in the vicinity of the Cu dopant. The geometry around the dopant is symmetric in which apical Cu-O and equatorial Cu-O distances are 2.01 Å and 1.99 Å; these can be compared with corresponding Ti-O distances of 2.02 Å and 2.00 Å for undoped anatase. Figure 1(b) displays the excess spin density plot and shows that the hole states are spread over the oxygen sites neighbouring the dopant. The computed spin magnetizations are 0.13 $\mu_B$ for both apical sites and 0.2 $\mu_B$ for the four equatorial sites. The Bader charge of the Cu dopant is 9.6 electrons and the spin magnetization is 0.97 $\mu_B$, consistent with the d$^9$ configuration of the Cu$^{2+}$ oxidation state.

For the solution with the +U correction applied to the O 2p states, the local atomic structure near the dopant site is distorted asymmetrically; this set up results in localization of the hole states predominantly on the apical oxygen sites and the resulting Cu-O$_{Ap}$ distances are 2.27 Å and 2.42 Å. These elongated bonds are consistent with formation of an oxygen polaron as has been observed in other materials [36, 37, 53-57]. The computed spin magnetizations for these O sites are 0.78 $\mu_B$ and 0.73 $\mu_B$ and the Bader charges are reduced by 0.5 electrons after hole localization, from 7.3 to 6.8 electrons. The four equatorial Cu-O$_{Eq}$ distances are 1.99-2.00 Å. For the remainder of the calculations the differences arising from U(O) = 0 eV vs. U(O) = 7 eV are quantitative in nature and the general characteristics of Cu-doped anatase are consistent, in particular charge compensation. Thus, for brevity we include only the results arising from calculations for which U(O) = 0 eV.
In response to the charge imbalance which arises when replacing Ti\(^{4+}\) with lower valent Cu\(^{2+}\), the system compensates through formation of an oxygen vacancy. The most stable site for this compensating oxygen vacancy is the O site neighbouring the Cu dopant in the equatorial position and this has a computed formation energy of -0.35 eV.

The top panels of Figure 2 show the geometry of the charge compensated system in the vicinity of the Cu dopant; the oxygen vacancy site is indicated by a black circle. After formation of the charge compensating oxygen vacancy, the Cu and Ti ions to which the removed O atom was bound have five-fold coordination. The Ti ions move off their lattice sites and outwards from the vacancy site and this distortion leads to the shortening of metal-oxygen bonds opposite the vacancy by 0.13-0.16 Å. After oxygen vacancy formation, four of the Cu-O bonds contract by 0.01-0.06 Å. The fifth Cu-O distance, involving the O\(_{eq}\) atom opposite the vacancy site, increases by 0.07 Å. In this configuration the Bader charge on the dopant is 9.7 electrons and the spin magnetization is 0.75 μ\(_B\), indicating a Cu\(^{2+}\) oxidation state.

For the formation of a second, reducing oxygen vacancy, the most stable site is a second equatorial site neighbouring the dopant and adjacent to the first vacancy. This oxygen vacancy forms with an energy cost of 3.27 eV and the local geometry about the dopant is shown in the bottom panels of Figure DFT_2, with the oxygen vacancies indicated by black circles. This energy cost is similar to undoped bulk anatase so that Cu doping has no significant effect on the reducibility of anatase.

Both Cu-O\(_{eq}\) distances contract to 1.93 Å, while the two remaining Cu-O\(_{eq}\) distances are 2.08 Å and 2.10 Å. After formation of the second oxygen vacancy two electrons are released and we analyse computed Bader charges and spin magnetizations to determine where these electrons are localized.
For the Cu dopant the Bader charge increases from 9.7 to 10.3 electrons and the spin magnetization is 0 $\mu_B$, consistent with reduction from Cu$^{2+}$ to Cu$^+$. The second electron localizes at a Ti site which is five-fold coordinated due to formation of the second oxygen vacancy. This site has a Bader charge of 1.7 electrons and a spin magnetization of 0.95 $\mu_B$, indicating reduction to Ti$^{3+}$. For comparison, the Ti$^{4+}$ ions in TiO$_2$ have computed Bader charges of 1.29-1.34 electrons.

Figure 3. Projected electronic density of states (PEDOS) plots for (a) undoped anatase, (b) Cu-doped anatase with no oxygen vacancies and (c) after formation of a single, charge compensating oxygen vacancy and (d) after formation of a second, reducing oxygen vacancy.

The projected electronic density of states (PEDOS) plots for pure TiO$_2$ anatase is shown in Figure 3(a), highlighting the typical O 2p dominated valence band region and the Ti 3d dominated conduction band region. Figure 3(b) shows the PEDOS for Cu doping where a clear Cu$^{2+}$ derived state is present in the TiO$_2$ energy gap.

For the ground state of Cu-doped anatase, with a single, compensating oxygen vacancy, and the reduced system, with two oxygen vacancies, the PEDOS are shown in the bottom panels of Figure 3. For the ground state system (Figure 3(c)) the empty 3d state of the Cu$^{2+}$ ion lies above the conduction band minimum (CBM) of the TiO$_2$ host, so that the dopant has no impact on the magnitude of the band gap. However, states emerge in the band gap after formation of the second oxygen vacancy, as shown in Figure 3(d). These states are derived from the reduced Ti$^{3+}$ and Cu$^+$ ions which may act as recombination centres, thereby reducing photocatalytic activity. In the reduced system, Cu-derived states also emerge at the VB edge and extend the VBM to higher energies leading to a decrease in the band gap.

3.2. X-ray Diffraction (XRD)

XRD is utilized to study the impact of Cu doping on the anatase to rutile phase transition of TiO$_2$ at various calcination temperatures. Figure 4 (a) shows the XRD profiles of pure anatase TiO$_2$ and 0.5% Cu-TiO$_2$ (calcined at 500 °C, 600 °C, 650 °C and 700 °C). XRD spectrum of rutile TiO$_2$ is also
provided for reference. The anatase and rutile peak intensities are generally observed at 25.4° and 27.3° respectively, (101 and 110) [44]. These values were used to calculate the percentage of anatase and rutile of TiO₂ in all samples using Spurr equation (Equation 2). Cu-TiO₂ at 500 °C and 600 °C exhibited 100% of anatase while the sample at 700 °C showed 100% of rutile. Interestingly, calcined at 650°C yielded a mixture phase constituting 55% of anatase and 45% of rutile TiO₂ (Figure 4 (b)).

![Figure 4](image.png)

**Figure 4.** (a) XRD profiles of pure anatase TiO₂, pure rutile TiO₂, Cu-TiO₂ samples (calcined at 500 °C, 600 °C, 650 °C and 700 °C) and (b) XRD profiles of pure anatase TiO₂, pure rutile TiO₂ and the Cu-TiO₂ calcined at 650 °C.

The diffractogram also illustrates the increase in the intensity of the signature peaks of both anatase and rutile phases with increase in calcination temperature. The Scherrer equation (Equation 3) is used to calculate the average crystalline size. The decrease in the FWHM values helped in exhibiting the increase in average crystallite size from 8.83 nm for anatase TiO₂ to 28.8 nm for the mixed phase sample (calcined at 650°C). This is attributed to the thermally promoted crystallite growth [58]. For any photocatalytic application the need for improved visible light activity and high temperature stability are two fundamental desirable properties. In this study, the XRD results shows the presence of mixed phase at a high calcination temperature of 650 °C by doping a very minute fraction of Cu. This prime reason makes this sample an interesting candidate for further studies and hence, hereafter the mixed phase sample was used for further characterizations and application. Additionally, anatase (TiO₂ – 500 °C) and rutile (TiO₂– 700 °C) samples are taken as the controls.

| Sample          | Calcined Temperature (in degree C) | Particle size (in nm) |
|-----------------|------------------------------------|-----------------------|
| Control         | 500                                | 8.83                  |
| 0.5% Cu-TiO₂    | 500                                | 11.34                 |
| 0.5% Cu-TiO₂    | 600                                | 22.35                 |
| 0.5% Cu-TiO₂    | 650                                | 28.84                 |
| 0.5% Cu-TiO₂    | 700                                | 32.93                 |
| Control         | 700                                | 33.80                 |
3.3. Raman Spectroscopy

The anatase to rutile transition of Cu-TiO$_2$ was further examined using Raman spectroscopy. A typical Raman spectrum shows characteristic modes at different wavenumbers, corresponding to Raman shifts. The active modes for anatase are $\text{A}_{1g}$, $2\text{B}_{1g}$ and $3\text{E}_g$ at 147, 197, 396, 516 and 638 cm$^{-1}$ respectively. For rutile the Raman active modes are $\text{A}_{1g}$, $\text{B}_{1g}$, $\text{B}_{2g}$ and $3\text{E}_g$ at 144, 238, 446 and 612 cm$^{-1}$ [44]. Raman spectra displayed the presence of the titania peaks and did not exhibit the occurrence of copper/copper oxides or other impurities. The Raman results are consistent with the data observed in XRD analysis. However, as observed in the figure below, the doped sample shows a small decrease in frequency of 2.35 cm$^{-1}$ (red shift as illustrated in the inset of the image). Decrease in frequency is the resultant of the Cu insertion in the TiO$_2$ lattice, which subsequently weakens the bond between the O-Ti-O bond, therefore leading to a higher lattice constant.

![Raman Spectra](image)

**Figure 5.** Raman spectra of anatase, rutile and 0.5% Cu-TiO$_2$ calcined at 650 °C.

3.4. X-ray Photoelectron Spectroscopy (XPS)

The X-ray Photoelectron Spectroscopy (XPS) quantifications were performed to analyze the elemental composition of anatase TiO$_2$ and Cu doped samples. Figure 6(a) provides the survey spectrum of anatase TiO$_2$ and 0.5% Cu doped TiO$_2$ calcined at 650 °C. It illustrates the presence of titanium, oxygen and additionally copper for the doped sample. A small amount of carbon peak also emerged, which is acquired during synthesis and calcination process. In introduction of Cu into TiO$_2$ lattice resulted in substitution of Ti$^{4+}$ by the Cu$^{2+}$ ion [59]. Hence, instead of O-Ti-O bonds new bonds of Cu-O are established. Figure 6(b) provides the high resolution spectra of Ti 2p, which exhibits very sharp, symmetric and intense peaks, indicating the presence of Ti$^{4+}$ state. The deconvoluted Ti 2p peaks of anatase appears at 457.4 eV and 463.06 eV, which is ascribed to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ (Ti-O bond) respectively. In the case of Cu-TiO$_2$ 650 °C, a significant shift of around 1.7 eV is observed for both Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ (459.06 eV and 464.83 eV)[60, 61]. The shift in the peak is attributed to the introduction of Cu in the lattice. The Ti 2p peaks of Cu-TiO$_2$ 650 °C does not show any indication of Ti$^{3+}$ or Ti$^{2+}$ states. Similarly, Figure 6(c) illustrates the high resolution spectra of O 1s, where peaks at 528.59 eV constitutes to the crystal lattice oxygen (O-Ti$^{4+}$) and 530.40 eV for adsorbed hydroxyl or...
oxygen molecules. Whilst, the O 1s spectrum of doped sample showed a similar shift as observed for Ti 2p spectrum attributed to the introduction of copper atom in the lattice [62]. The Cu 2p3 spectrum (Figure 6(d)) on deconvolution exhibits an intense peak at 933.13 eV and a shorter peak at 934.60 eV, ascribed to Cu+ and Cu2+ states [60].

Figure 6. (a) Survey spectrum of anatase and 0.5 % Cu-TiO2; (b) high resolution Ti 2p spectra of anatase and 0.5 % Cu-TiO2 650 °C; (c) high resolution O 1s spectra of anatase and 0.5 % Cu-TiO2 650 °C; (d) high resolution Cu 2p3 spectra of 0.5 % Cu-TiO2 650 °C.

Figure 7 illustrates the high resolution spectra of 0.5 % Cu-TiO2 samples calcined at different temperatures. It is observed that with increase in temperature from 500 °C to 700 °C the Cu+ state observed at 933.1 eV gradually decreases. While the Cu2+ state at 934.3 eV only observed at 650 °C and 700 °C. Additionally, two satellite peaks of Cu2+ were also observed at 941.3 eV and 944.2 eV for 700 °C [60, 63]. The intensity of the peak at 934.3 eV gradually increases with the increase in calcination temperature [60, 64]. Usually, the TiO2 exhibits stable anatase phase in the range of 500 °C to 600 °C and converts to rutile with increase in temperature. However, the change in oxidation states with increase in calcination temperature in our Cu doped samples (change in oxygen vacancies) contributes to the high temperature stability of the oxygen rich anatase phase at 650 °C [20, 28].
3.5. UV-Vis absorption and bandgap estimation

The electronic band structures of the as prepared samples were analyzed by UV-Vis absorption (Figure 8). The pristine TiO$_2$ at anatase phase shows an intense absorption in the Ultra-Violet region (around 350 nm). While the rutile sample exhibits at 380 nm, on the other hand the Cu doped sample indicated a red shift extending up to 600 nm. This is attributed to the characteristic surface plasmon resonance of Cu nanoparticles. The successful doping of Cu is also evident from the change in the colour observed in the samples, shifting from pure white to light yellow (as shown in the inset of Figure 8 b). The band gap value of the samples was estimated using the Kubelka-Munk equation (Equation 4) [46]. The band gap values of pristine TiO$_2$ at anatase and rutile phases was observed to be 3.17 eV and 3.03 eV respectively. The Cu doped sample showed a significant dip in the band gap value up to 2.8 eV.
3.6. Photocatalytic antibacterial activity

To demonstrate the visible light efficiency of the doped Cu samples, the photocatalytic antibacterial experiments were carried out under dark and visible light irradiation respectively. The following data was also compared with the pristine TiO$_2$ in anatase and rutile phases (Figure 9). The samples were evaluated in relation to two different bacterial strains (*E. coli* and *S. aureus*). In the absence of photocatalyst, the growth of both the strains persisted under light and dark condition. On the other hand, on exposing the bacterial cells with catalyst (1 g/L) under visible light and dark conditions yielded different results.

In dark atmosphere no significant change in bacterial growth was observed even after 90 mins. While, the bacterial growth significantly decreased within 30 mins of visible light irradiation (Log 2 reduction). 99.9% bacterial reduction was achieved in the presence of Cu doped samples in a time span as short as 30 mins (Figure 10). Moreover, the anatase and rutile TiO$_2$ samples showed complete disinfection within 60 and 90 mins of irradiation respectively. This indicates the stability of the cell structure and the importance of light in the inactivation process. However, the inactivation observed is a synergetic effect of TiO$_2$, as well as Cu ions in presence of visible light. None of the test samples in dark atmosphere exhibited any bactericidal property. Therefore, the cease in the cell proliferation is a photo induced inactivation rather than chemo-toxic killing of bacterial cells. The introduction of Cu significantly improved the visible absorption efficiency which effectively contributed to the enhanced bacterial inactivation kinetics as observed compared to the control samples.
4. Discussion

From the DFT analysis, it is assumed that the creation of single vacancy by Cu in Cu\(^{2+}\) state only exists on the surface which does not contribute to the alteration of the band gap of the material at a very small mole percentage. On the other hand, dual vacancy created by the Cu dopant (Cu\(^+\) state) does change the band gap of the material, as well as introducing various trap sites in between. This reduces the overall band gap, but the trap sites potentially serve as recombination centers. The XPS analysis exhibited the co-existed presence of both Cu in +1 and +2 oxidation states. Where Cu\(^+\) is the major species in the sample which necessarily committed in the variation of the optical property of the sample which is also evident in the UV-vis absorption plot (Figure 8a). It is suggested that the coexistence of both the states of Cu improves the photocatalytic efficiency. The Cu\(^{2+}\) states act as a trapping sink for the excited electrons while the Cu\(^+\) serves as the electron donor for the adsorbed oxygen on the catalyst surface. This effectively aids to the interfacial electron transfer.

\[
\text{Cu}^+ + O_{ads} \rightarrow \text{Cu}^{2+} + O^\text{ads}_{ads} \quad \text{(Equation 5)}
\]

\[
\text{Cu}^{2+} + e_{cb} \rightarrow \text{Cu}^+ \quad \text{(Equation 6)}
\]

On visible light irradiation, the electron hole pair generated on the TiO\(_2\) surface reacts with the oxygen and water adsorbed on the catalyst surface to produce superoxide radicals and holes respectively. These reactive oxygen species (ROS) further interact with the bacterial cell wall which results in membrane disruption and outflow of intracellular materials, this results in cell lysis (Figure 11). In addition to this, the ROS produced has the ability to interact with the sugar phosphate groups present in the DNA of the bacteria to cause gene alteration. Further altering the protein expression responsible for cellular functioning which leads to cell damage [12, 67].
5. Conclusions

In this present work, a 0.5 mol% Cu doped TiO₂ visible light active semiconductor material has been synthesized. The introduction of small mole percent of Cu inside the TiO₂ lattice has led to an improved cationic doped TiO₂ sample. These doped samples contributed to the enhanced stability of the anatase phase up to a temperature of 650 °C and also exhibited improved visible light antimicrobial efficiency.

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Cu doped TiO₂: Visible light assisted photocatalytic antimicrobial activity and high temperature anatase stability

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Abstract: Indoor surface contamination by microbes is a major public health concern. A damp environment is one potential sources for microbe proliferation. Smart photocatalytic coatings on building surfaces using semiconductors like titania (TiO₂) can effectively curb this growing threat. Metal-doped titania in anatase phase has been proved as a promising candidate for energy and environmental applications. In this present work, the antimicrobial efficacy of copper (Cu) doped TiO₂ (Cu-TiO₂) was evaluated against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) under visible light irradiation. Doping of a minute fraction of Cu (0.5 mol %) in TiO₂ was carried out via sol-gel technique. Cu-TiO₂ further calcined at various temperatures (in the range of 500 °C – 700 °C) to evaluate the thermal stability of TiO₂ anatase phase. The physico-chemical properties of the samples were characterised through X-ray diffraction (XRD), Raman spectroscopy, X-ray photo-electron spectroscopy (XPS) and UV-visible spectroscopy techniques. XRD results revealed that the anatase phase of TiO₂ was maintained well, up to 650 °C, by the Cu dopant. UV-DRS results suggested that the visible light absorption property of Cu-TiO₂ was enhanced and the band gap is reduced to 2.8 eV. Density functional theory (DFT) studies emphasises the introduction of Cu⁺ and Cu²⁺ ions by replacing Ti⁴⁺ ions in the TiO₂ lattice, creating oxygen vacancies. These further promoted the photocatalytic efficiency. A significantly high bacterial inactivation (99.9%) was attained in 30 mins of visible light irradiation by Cu-TiO₂.

Keywords: Cu doped TiO₂; Doping; Phase transition; Escherichia coli; Staphylococcus aureus; Photocatalysis; Antibacterial coatings;
1. Introduction

Indoor air pollution has been a major public health concern worldwide in recent days [1, 2]. A study by the National Human Activity Pattern Survey (NHAPS) found that people in U.S.A and Canada spend most of their time (more than 80% of their time) inside enclosed buildings and 6% inside enclosed vehicles [3]. According to World Health Organization (WHO), a significant share of world population is suffering from indoor air pollutants and microbial contamination. The formation of microbial colonies inside the wet or damp indoor environments is one of the major contributing elements to the deterioration of indoor air quality [4, 5]. These microorganisms have the potential to produce contaminants like spores, allergens and toxins affecting the health of the occupants [6, 7]. This kind of continuous exposure can lead to various health concerns like respiratory or skin diseases [8, 9].

Several studies in the past few decades have looked at alteration of building materials and paints to overcome the challenges of indoor air pollution [10, 11]. Most of the physico-chemical techniques and usual cleaning procedures are inactive to completely eliminate the microbes. TiO$_2$ photocatalysis is one of the most promising, simple and economically viable technology to address the indoor air pollution/microbial contamination. TiO$_2$ has been recognized as a traditional semiconductor photocatalyst which has been widely reported for its anti-microbial coatings [12, 13]. The formation of uniform aqueous slurry and the feasibility of deposition on the various substrates make TiO$_2$ a lucrative candidate [14, 15]. However, this material suffers from its own set of limitations. Low visible light absorption because of the wide band gap of TiO$_2$ (3.2 eV) is incompatible to receive visible light for practical applications. Moreover, the low temperature stability of photocatalytically active anatase phase also makes them vulnerable with regards to application as a potential material for coating [16].

Elemental doping, morphological tailoring in the form of nanotubes and fibers, making composites out of new 2-D materials like graphene, C$_3$N$_4$ are some of the efficient techniques to overcome these limitations [17-19]. Elemental doping is an effective strategy to tune the band gap of TiO$_2$ by introducing new energy levels in between and by alteration of conduction band minima(CBM) and valence band maxima(VBM) [20, 21]. In this regard, cationic dopants served to extend the visible light absorption and also enhanced the high temperature stability of the anatase phase TiO$_2$. Copper is one of the interesting dopants added to TiO$_2$ at different mole and weight percents. Cu doped TiO$_2$ was evaluated for various photocatalytic applications like Hydrogen production [22-25], CO$_2$ conversion[26], degradation of dyes and organic contaminants. Several studies demonstrating the photocatalytic anti-bacterial efficiency were also reported [27-29]. However, in most of the cases, a high concentration of Cu was used to display the antimicrobial activity. Additionally, Cu dopants were deposited on morphologically tuned TiO$_2$
nanotubes and nanofibers. This involves a series of cumbersome synthesis techniques.

In this present study, we demonstrate a facile one-step sol-gel technique to prepare 0.5 mol % of Cu-TiO$_2$. The as prepared samples were calcined at different temperatures ranging 500 °C-700 °C. Simultaneously, the samples were analyzed by Density Functional Theory (DFT) to understand the band gap alteration occurring inside of TiO$_2$ lattice. The anatase phase of TiO$_2$ was maintained (55%) up to 650 °C. The sample calcined at 650 °C illustrated high visible light absorption and Cu doping resulted in lowering of TiO$_2$ band gap from 3.2 eV (for anatase TiO$_2$) to 2.8 eV. Cu-TiO$_2$ was further assessed for the photocatalytic disinfection efficiency towards *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) bacterial strains. A Log 2 reduction by the Cu-TiO$_2$ was attained at a very short time span of 30 mins.

2. Materials and Methods

2.1 Chemicals and Reagents

All the materials used were of analytical grade. The materials were used as received, without further purification. Titanium isopropoxide (97%), copper sulphate pentahydrate (≥98.0%) and isopropanol (≥99.5%) were purchased from Sigma-Aldrich. Strains of *Staphylococcus aureus* (ATCC-25923) and *Escherichia coli* (ATCC-25922) were purchased from LGC Standards. Nutrient broth No.2, Agar and all other consumables were bought from Cruinn Diagnostics. Deionized water was used in all experiments.

2.2 Synthesis of Cu-TiO$_2$

Cu-TiO$_2$ was synthesized using a sol-gel method as follows: Titanium isopropoxide (TTIP) was stirred in isopropanol (200 ml) for 15 min (solution A). The required amount of copper sulphate was taken separately in deionized water and the mixture was stirred for 15 min (solution B). Then, Solution B was added drop wise to solution A under constant stirring. The resulting gel was dried in an oven at 100 °C for 12 h. The powder was then calcined at various temperatures (500 °C, 600 °C, 650 °C and 700 °C) at a ramp rate of 10 °C/min for 2 h. Pure TiO$_2$ was also synthesized by the same procedure without the addition of copper sulphate.

2.3 Density functional theory (DFT) computations

DFT calculations were performed using the VASP5.2 [30, 31] code with projector augmented wave (PAW) [32, 33] potentials to account for the core-valence interaction and a kinetic energy cut-off of 400 eV. Cu was substitutionally doped onto a Ti site in rutile (2 ×2×3) and anatase (2 ×2×2) supercells. This gives dopant percentages of 4.2 % and 3.1 % for rutile and anatase respectively, which are consistent with the experimental concentrations of Cu in TiO$_2$ [22, 34, 35]. The k-
point sampling was used a Monkhorst-Pack (4×4 ×2) grid for both bulk polymorphs. Structures were relaxed until forces were less than 0.01 eV Å⁻¹.

Calculations were performed taking into account spin polarisation and no symmetry constraints were imposed. In the initial DFT + U calculations, U = 4.5 eV was applied to the Ti 3d states and U = 7 eV was applied to the Cu 3d states, arising from the inability of DFT to describe consistently the Cu²⁺ oxidation state of Cu and U = 7 [36, 37]. These choices for U are based on the previous studies [38-42]. The starting geometries were manually distorted from the symmetric bulk geometry in order to examine relaxation to distorted geometries, which can be compared with undistorted geometries. To study the charge compensation that arises as a result of the difference in the Cu²⁺ and Ti⁴⁺ oxidation states, one oxygen ion was removed from different sites of the most stable Cu-doped structures and the energy of formation was calculated by the following equation:

\[
Evac = E(CuxTi1−xO2−y) + \frac{1}{2E(O2)−E(CuxTi1−xO2)}
\]  

(Equation 1)

Where \(E(CuxTi1−xO2−y)\) is the total energy of Cu doped TiO₂ with a charge compensating oxygen vacancy and \(E(CuxTi1−xO2)\) is the total energy of Cu-doped TiO₂. The formation energy is referenced to half the total energy of O₂.

Copper ions were initially in the 2+ oxidation state and calculations were therefore performed with 1 and 3 unpaired spins taking into account the electron deficit due to substitutional doping of Cu²⁺ for Ti⁴⁺ and the d⁹ configuration of Cu²⁺. The oxidation states of Cu dopant, lattice Ti and O ions were determined from Bader charge analysis [43].

2.4 Characterization

The as-synthesized samples were characterized by various techniques. The crystallinity of the samples was analysed by X-ray diffraction (XRD). The diffractograms were produced using Cu Kα radiation (\(\lambda = 0.15418\) nm) in a Siemens D500 X-ray powder diffractometer. The diffraction was examined in the range of 10°- 80°. Anatase and rutile percentages of TiO₂ were measured by the Spurr equation [44].

\[
F_R = \frac{I_R(110)}{I_A(101)} / \frac{I_R}{1 + 0.8 I_R} \quad \text{(Equation 2)}
\]
Where $F_R$ is the quantity of rutile phase; $I_A(101)$ and $I_R(110)$ are the intensity of anatase peak and rutile peak respectively. The crystallinity of the samples was calculated using the Scherrer equation [45].

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

(Equation 3)

Where $\Phi$ is the crystallite size; $K$ is the shape factor with a value close to unity; $\lambda$ is the wavelength of X-rays; $\beta$ is the full width half-maximum (FWHM) of the main intensity peak; and $\theta$ is the Bragg angle.

The phase transformation was also analyzed using Raman spectroscopy (Horiba Jobin Yvan LabRAM HR 800) with a grating of 300 gr/mm. A 660 nm solid state diode laser standard bandwidth version with double edge filter upgrade was the laser used. The acquisition time was 3 seconds.

The bonding interactions and oxidation state of elements were studied with the help of X-ray photoelectron spectroscopy. Samples were analyzed on a XPS, Thermo Fisher Scientific, (East Grinstead, UK) K-Alpha spectrometer, which has an XR3 twin anode X-ray source (AlKα/MgKα) and an Alpha 110 analyser. The twin anodes AlKα X-ray source ($h\nu = 1486.6$ eV) was used at 300 W (15 kV x 20 mA) for analysis of all samples. For all survey spectra, a Pass Energy of 200 eV and a step size of 0.4 eV were used. In order to acquire C 1s, O 1s and Ti 2p high resolution spectra a Pass Energy of 20 eV and a step size of 0.2 eV were used.

The optical properties of the as prepared samples were measured using Perkin-Elmer UV-Vis Spectrophotometer. Barium sulphate (BaSO$_4$) was used as a reference, and slit width was set to 1 nm. Additionally, band gap was calculated from the UV DRS spectrum by using Kubelka-Munk function $F(R)$ [46].

$$F(R) = \frac{(1 - R)^2}{2R}$$

(Equation 4)

Where $R$ is the absolute reflectance of the sample.

The photocatalytic experiments were performed inside weathering and corrosion photo-reactor from Q-Labs (Q-sun Xe-1-S).

2.4 Measurement of antimicrobial activity:

All the glassware used was autoclaved before carrying out the photocatalytic experiments. E. coli (gram-negative bacterium) and S.aureus (gram-positive bacterium) were used to study the antibacterial activity of the Cu-TiO$_2$. Nutrient broth culture medium was prepared by dissolving 25 g of nutrient broth No.2 (10 g peptone, 5.0 g NaCl, 10 g beef extract) in 1 L of distilled water followed by sterilization at 121 °C using an autoclave. The 90 mm agar plates were prepared by dissolving 28 g nutrient agar (5 g peptone, 8.0 g NaCl, 3.0 g Beef extract, Agar No.2)
in 1 L distilled water, then autoclaved at 121 °C for 15 mins and poured into petri dishes. The strains were inoculated in 20 ml of nutrient broth and incubated for 24 h at 37 °C. A definite amount of the grown culture was transferred to the cylindrical glass vessel to make the working solution of $10^4$ CFU/ml (colony forming unit/ml). The reaction mixture was kept inside the photo test chamber for visible light irradiation. The photocatalyst concentration was fixed at 1 g/L and irradiated for 3 h. Aliquots of 1 ml were extracted out from the reaction mixture at a regular time interval of 10 mins. In order to attain a countable CFU, the bacterial solution was diluted in a PBS solution once and later 100 µl of diluted solution was plated. Finally, the plates were incubated at 37 °C for 24 h. The colonies formed on the agar plates were counted and recorded as CFU/ml. A control experiment was also conducted in the absence of the photocatalyst. The same set of samples was tested simultaneously under dark conditions.

3. Results

3.1. Density Functional Theory Simulations

There have been some theoretical papers on the topic of Cu-doped anatase TiO$_2$ [47-50]. A DFT + U study [49] of anatase doped with Cu at a concentration of 6.25%, applied $U = 8$ eV to the Ti 3d states; this recovers the bulk TiO$_2$ energy gap but is not to be recommended for other properties. No +U correction is applied to the Cu 3d states, despite issues with describing these electronic states. A reduction in the band gap was reported in all studies and this is attributed to a combination of Cu 3d and O 2p states above the valence band maximum (VBM). Navas et al provided a comprehensive study [48] of Cu-doping in anatase which combined both experiment and theory including DFT + U calculations with the +U correction on Ti 3d orbitals only. However, inclusion of a +U correction for Cu 3d states is particularly important in correctly describing the Cu$^{2+}$ oxidation state [38, 39, 51]. They reported greater band gap reduction with increases in dopant concentration due to the covalent character of the Cu-O interaction leading to new states at the VBM. A theoretical account of Cu-doping in rutile, in the context of the effect of oxygen vacancies on the magnetic moment of Cu-doped TiO$_2$ [52], reported that oxygen vacancies are most stable near the Cu impurity.
Figure 1. (a) Relaxed atomic structure of bulk anatase TiO$_2$ in the vicinity of the Cu dopant and (b) excess spin density plot for Cu-doped anatase TiO$_2$. Spin isosurfaces enclose densities of up to 0.02 eV/Å$^3$. In this and subsequent figures Ti is represented by a grey sphere, O by a red sphere and Cu by an orange sphere.

Figure 1(a) shows the local atomic structure in the vicinity of the Cu dopant. The geometry around the dopant is symmetric in which apical Cu-O and equatorial Cu-O distances are 2.01 Å and 1.99 Å; these can be compared with corresponding Ti-O distances of 2.02 Å and 2.00 Å for undoped anatase. Figure 1(b) displays the excess spin density plot and shows that the hole states are spread over the oxygen sites neighbouring the dopant. The computed spin magnetizations are 0.13 μ$_B$ for both apical sites and 0.2 μ$_B$ for the four equatorial sites. The Bader charge of the Cu dopant is 9.6 electrons and the spin magnetization is 0.97 μ$_B$, consistent with the d$^9$ configuration of the Cu$^{2+}$ oxidation state.

For the solution with the +U correction applied to the O 2p states, the local atomic structure near the dopant site is distorted asymmetrically; this set up results in localization of the hole states predominantly on the apical oxygen sites and the resulting Cu-O$_{\text{Ap}}$ distances are 2.27 Å and 2.42 Å. These elongated bonds are consistent with formation of an oxygen polaron as has been observed in other materials [36, 37, 53-57]. The computed spin magnetizations for these O sites are 0.78 μ$_B$ and 0.73 μ$_B$ and the Bader charges are reduced by 0.5 electrons after hole localization, from 7.3 to 6.8 electrons. The four equatorial Cu-O$_{\text{Eq}}$ distances are 1.99-2.00 Å. For the remainder of the calculations the differences arising from U(O) = 0 eV vs. U(O) = 7 eV are quantitative in nature and the general characteristics of Cu-doped anatase are consistent, in particular charge compensation. Thus, for brevity we include only the results arising from calculations for which U(O) = 0 eV.
Figure 2. Atomic structure of Cu-doped anatase TiO$_2$ after formation of a charge compensating oxygen vacancy (top panels) and after formation of a second, reducing oxygen vacancy (bottom panels). Panels (a) and (d) xy-plane geometry; (b) and (e) yz-plane geometry; (c) and (f) lattice distortions around the dopant site. The black circles represent the O vacancy sites.

In response to the charge imbalance which arises when replacing Ti$^{4+}$ with lower valent Cu$^{2+}$, the system compensates through formation of an oxygen vacancy. The most stable site for this compensating oxygen vacancy is the O site neighbouring the Cu dopant in the equatorial position and this has a computed formation energy of -0.35 eV.

The top panels of Figure 2 show the geometry of the charge compensated system in the vicinity of the Cu dopant; the oxygen vacancy site is indicated by a black circle. After formation of the charge compensating oxygen vacancy, the Cu and Ti ions to which the removed O atom was bound have five-fold coordination. The Ti ions move off their lattice sites and outwards from the vacancy site and this distortion leads to the shortening of metal-oxygen bonds opposite the vacancy by 0.13-0.16 Å. After oxygen vacancy formation, four of the Cu-O bonds contract by 0.01-0.06 Å. The fifth Cu-O distance, involving the O$_{eq}$ atom opposite the vacancy site, increases by 0.07 Å. In this configuration the Bader charge on the dopant is 9.7 electrons and the spin magnetization is 0.75 $\mu_B$, indicating a Cu$^{2+}$ oxidation state.

For the formation of a second, reducing oxygen vacancy, the most stable site is a second equatorial site neighbouring the dopant and adjacent to the first vacancy. This oxygen vacancy forms with an energy cost of +3.27 eV and the local geometry
about the dopant is shown in the bottom panels of Figure DFT_2, with the oxygen vacancies indicated by black circles. This energy cost is similar to undoped bulk anatase so that Cu doping has no significant effect on the reducibility of anatase.

Both Cu-O Ap distances contract to 1.93 Å, while the two remaining Cu-O Eq distances are 2.08 Å and 2.10 Å. After formation of the second oxygen vacancy two electrons are released and we analyse computed Bader charges and spin magnetizations to determine where these electrons are localized. For the Cu dopant the Bader charge increases from 9.7 to 10.3 electrons and the spin magnetization is 0 μB, consistent with reduction from Cu$^{2+}$ to Cu$. The second electron localizes at a Ti site which is five-fold coordinated due to formation of the second oxygen vacancy. This site has a Bader charge of 1.7 electrons and a spin magnetization of 0.95 μB, indicating reduction to Ti$^{3+}$. For comparison, the Ti$^{4+}$ ions in TiO$_2$ have computed Bader charges of 1.29-1.34 electrons.

The projected electronic density of states (PEDOS) plots for pure TiO$_2$ anatase is shown in Figure 3(a), highlighting the typical O 2p dominated valance band region and the Ti 3d dominated conduction band region. Figure 3(b) shows the PEDOS for Cu doping where a clear Cu$^{2+}$ derived state is present in the TiO$_2$ energy gap.
For the ground state of Cu-doped anatase, with a single, compensating oxygen vacancy, and the reduced system, with two oxygen vacancies, the PEDOS are shown in the bottom panels of Figure 3. For the ground state system (Figure 3(c)) the empty 3d state of the Cu\(^{2+}\) ion lies above the conduction band minimum (CBM) of the TiO\(_2\) host, so that the dopant has no impact on the magnitude of the band gap. However, states emerge in the band gap after formation of the second oxygen vacancy, as shown in Figure 3(d). These states are derived from the reduced Ti\(^{3+}\) and Cu\(^+\) ions which may act as recombination centres, thereby reducing photocatalytic activity. In the reduced system, Cu-derived states also emerge at the VB edge and extend the VBM to higher energies leading to a decrease in the band gap.

3.2. X-ray Diffraction (XRD)

XRD is utilized to study the impact of Cu doping on the anatase to rutile phase transition of TiO\(_2\) at various calcination temperatures. Figure 4 (a) shows the XRD profiles of pure anatase TiO\(_2\) and 0.5% Cu-TiO\(_2\) (calcined at 500 °C, 600 °C, 650 °C and 700 °C). XRD spectrum of rutile TiO\(_2\) is also provided for reference. The anatase and rutile peak intensities are generally observed at 25.4° and 27.3° respectively, (101 and 110) [44]. These values were used to calculate the percentage of anatase and rutile of TiO\(_2\) in all samples using Spurr equation (Equation 2). Cu-TiO\(_2\) at 500 °C and 600 °C exhibited 100% of anatase while the sample at 700 °C showed 100% of rutile. Interestingly, calcined at 650°C yielded a mixture phase constituting 55% of anatase and 45% of rutile TiO\(_2\) (Figure 4 (b)).

![Figure 4. (a) XRD profiles of pure anatase TiO\(_2\), pure rutile TiO\(_2\), Cu-TiO\(_2\) samples (calcined at 500 °C, 600 °C, 650 °C and 700 °C) and (b) XRD profiles of pure anatase TiO\(_2\), pure rutile TiO\(_2\), and the Cu-TiO\(_2\) calcined at 650 °C.](image)

The diffractogram also illustrates the increase in the intensity of the signature peaks of both anatase and rutile phases with increase in calcination temperature. The Schrerr equation (Equation 3) is used to calculate the average crystalline size.
The decrease in the FWHM values helped in exhibiting the increase in average crystallite size from 8.83 nm for anatase TiO$_2$ to 28.8 nm for the mixed phase sample (calcined at 650°C). This is attributed to the thermally promoted crystallite growth [58]. For any photocatalytic application the need for improved visible light activity and high temperature stability are two fundamental desirable properties. In this study, the XRD results shows the presence of mixed phase at a high calcination temperature of 650 °C by doping a very minute fraction of Cu. This prime reason makes this sample an interesting candidate for further studies and hence, hereafter the mixed phase sample was used for further characterizations and application. Additionally, anatase (TiO$_2$ – 500 °C) and rutile (TiO$_2$ – 700 °C) samples are taken as the controls.

Table 1. The average particle size of samples calcined at various calcination temperatures.

| Sample     | Calcined Temperature (in degree C) | Particle size (in nm) |
|------------|-----------------------------------|-----------------------|
| Control    | 500                               | 8.83                  |
| 0.5% Cu-TiO$_2$ | 500                      | 11.34                 |
| 0.5% Cu-TiO$_2$ | 600                      | 22.35                 |
| 0.5% Cu-TiO$_2$ | 650                      | 28.84                 |
| 0.5% Cu-TiO$_2$ | 700                      | 32.93                 |
| Control    | 700                               | 33.80                 |

3.3. Raman Spectroscopy

The anatase to rutile transition of Cu-TiO$_2$ was further examined using Raman spectroscopy. A typical Raman spectrum shows characteristic modes at different wavenumbers, corresponding to Raman shifts. The active modes for anatase are $A_{1g}$, $2B_{1g}$ and $3E_g$ at 147, 197, 396, 516 and 638 cm$^{-1}$ respectively. For rutile the Raman active modes are $A_{1g}$, $B_{1g}$, $B_{2g}$ and $3E_g$ at 144, 238, 446 and 612 cm$^{-1}$ [44]. Raman spectra displayed the presence of the titania peaks and did not exhibit the occurrence of copper/copper oxides or other impurities. The Raman results are consistent with the data observed in XRD analysis. However, as observed in the figure below, the doped sample shows a small decrease in frequency of 2.35 cm$^{-1}$ (red shift as illustrated in the inset of the image). Decrease in frequency is the resultant of the Cu insertion in the TiO$_2$ lattice, which subsequently weakens the bond between the O-Ti-O bond, therefore leading to a higher lattice constant.
3.4. X-ray Photoelectron Spectroscopy (XPS)

The X-ray Photoelectron Spectroscopy (XPS) quantifications were performed to analyze the elemental composition of anatase TiO$_2$ and Cu doped samples. Figure 6(a) provides the survey spectrum of anatase TiO$_2$ and 0.5% Cu doped TiO$_2$ calcined at 650 °C. It illustrates the presence of titanium, oxygen and additionally copper for the doped sample. A small amount of carbon peak also emerged, which is acquired during synthesis and calcination process. In introduction of Cu into TiO$_2$ lattice resulted in substitution of Ti$^{4+}$ by the Cu$^{2+}$ ion [59]. Hence, instead of O-Ti-O bonds new bonds of Cu-O are established. Figure 6(b) provides the high resolution spectra of Ti 2p, which exhibits very sharp, symmetric and intense peaks, indicating the presence of Ti$^{4+}$ state. The deconvulated Ti 2p peaks of anatase appears at 457.4 eV and 463.06 eV, which is ascribed to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ (Ti-O bond) respectively. In the case of Cu-TiO$_2$ 650 °C, a significant shift of around 1.7 eV is observed for both Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ (459.06 eV and 464.83 eV)[60, 61]. The shift in the peak is attributed to the introduction of Cu in the lattice. The Ti 2p peaks of Cu-TiO$_2$ 650 °C does not show any indication of Ti$^{3+}$ or Ti$^{2+}$ states. Similarly, Figure 6(c) illustrates the high resolution spectra of O 1s, where peaks at 528.59 eV constitutes to the crystal lattice oxygen (O-Ti$^{4+}$) and 530.40 eV for adsorbed hydroxyl or oxygen molecules. Whilst, the O 1s spectrum of doped sample showed a similar shift as observed for Ti 2p spectrum attributed to the introduction of copper atom in the lattice [62]. The Cu 2p3 spectrum (Figure 6(d))
on deconvolution exhibits an intense peak at 933.13 eV and a shorter peak at 934.60 eV, ascribed to Cu$^{+}$ and Cu$^{2+}$ states [60].

![Figure 6](image)

Figure 6. (a) Survey spectrum of anatase and 0.5 % Cu-TiO$_2$; (b) high resolution Ti 2p spectra of anatase and 0.5 % Cu-TiO$_2$ 650 °C; (c) high resolution O 1s spectra of anatase and 0.5 % Cu-TiO$_2$ 650 °C; (d) high resolution Cu 2p3 spectra of 0.5 % Cu-TiO$_2$ 650 °C.

Figure 7 illustrates the high resolution spectra of 0.5 % Cu-TiO$_2$ samples calcined at different temperatures. It is observed that with increase in temperature from 500 °C to 700 °C the Cu$^{+}$ state observed at 933.1 eV gradually decreases. While the Cu$^{2+}$ state at 934.3 eV only observed at 650 °C and 700 °C. Additionally, two satellite peaks of Cu$^{2+}$ were also observed at 941.3 eV and 944.2 eV for 700 °C [60, 63]. The intensity of the peak at 934.3 eV gradually increases with the increase in calcination temperature [60, 64]. Usually, the TiO$_2$ exhibits stable anatase phase in the range of 500 °C to 600 °C and converts to rutile with increase in temperature. However, the change in oxidation states with increase in calcination temperature in our Cu doped samples (change in oxygen vacancies) contributes to the high temperature stability of the oxygen rich anatase phase at 650 °C [20, 28].
Previous studies have reported that Cu\textsuperscript{2+}/Cu\textsuperscript{+} replaces Ti\textsuperscript{4+} from the TiO\textsubscript{2} lattice resulting in the formation of oxygen vacancies. This leads to creation of high absorption of visible light and narrowing of band gap, as observed in Figure 8. The TiO\textsubscript{6} octahedron has Ti in Ti\textsuperscript{4+} state with an ionic radius of 0.0605 nm. On the other hand, the ionic radii of Cu\textsuperscript{2+} and Cu\textsuperscript{+} exists as 0.073 nm and 0.077 nm respectively [65]. Moreover, the electronegativity of Ti and Cu is 1.54 and 1.90 respectively. According to Hume-Rothery principles the lattice substitution between atoms could only happen if the differences between them is less than 20% [62]. Considering the difference in the values of ionic radii and the electronegativity of the atoms, the substitution process of Ti by Cu would be challenging. Early DFT based theoretical studies have reported that maximum doping concentration for Cu should be less than 0.3 at% to cause a lattice substitution [66]. Thus, in the present study a doping of 0.5 mol% exhibits the successful doping of Cu inside the TiO\textsubscript{2} lattice. The doped copper existing in both oxidation states (Cu\textsuperscript{+} and Cu\textsuperscript{2+}) results in formation of single and double oxygen vacancies. However, the Ti 2p and O 1s spectra fails to provide any information regarding the new vacancies formed in doped sample. The presence of adsorbed O\textsubscript{2} and hydroxyl molecules is indicated in the O 1s spectra, which explains the occupancy of the adsorbed molecules at the vacancy sites.

3.5. UV-Vis absorption and bandgap estimation

The electronic band structures of the as prepared samples were analyzed by UV-Vis absorption (Figure 8). The pristine TiO\textsubscript{2} at anatase phase shows an intense absorption in the Ultra-Violet region (around 350 nm). While the rutile sample exhibits at 380 nm, on the other hand the Cu doped sample indicated a red shift extending up to 600 nm. This is attributed to the characteristic surface plasmon resonance of Cu nanoparticles. The successful doping of Cu is also evident from
the change in the colour observed in the samples, shifting from pure white to light yellow (as shown in the inset of Figure 8 b). The band gap value of the samples was estimated using the Kubelka-Munk equation (Equation 4) [46]. The band gap values of pristine TiO$_2$ at anatase and rutile phases was observed to be 3.17 eV and 3.03 eV respectively. The Cu doped sample showed a significant dip in the band gap value up to 2.8 eV.

![Figure 8](image)

**Figure 8.** (a) UV-Vis absorption spectra and (b) Tauc plots of anatase (control), rutile(control) and 0.5% Cu-TiO$_2$ at 650 °C.

3.6. Photocatalytic antibacterial activity

To demonstrate the visible light efficiency of the doped Cu samples, the photocatalytic antibacterial experiments were carried out under dark and visible light irradiation respectively. The following data was also compared with the pristine TiO$_2$ in anatase and rutile phases (Figure 9). The samples were evaluated in relation to two different bacterial strains (*E. coli* and *S. aureus*). In the absence of photocatalyst, the growth of both the strains persisted under light and dark condition. On the other hand, on exposing the bacterial cells with catalyst (1 g/L) under visible light and dark conditions yielded different results.
In dark atmosphere no significant change in bacterial growth was observed even after 90 mins. While, the bacterial growth significantly decreased within 30 mins of visible light irradiation (Log 2 reduction). 99.9% bacterial reduction was achieved in the presence of Cu doped samples in a time span as short as 30 mins (Figure 10). Moreover, the anatase and rutile TiO₂ samples showed complete disinfection within 60 and 90 mins of irradiation respectively. This indicates the stability of the cell structure and the importance of light in the inactivation process. However, the inactivation observed is a synergetic effect of TiO₂, as well as Cu ions in presence of visible light. None of the test samples in dark atmosphere exhibited any bactericidal property. Therefore, the cease in the cell proliferation is a photo induced inactivation rather than chemo-toxic killing of bacterial cells. The introduction of Cu significantly improved the visible absorption efficiency which effectively contributed to the enhanced bacterial inactivation kinetics as observed compared to the control samples.
4. Discussion

From the DFT analysis, it is assumed that the creation of single vacancy by Cu in Cu$^{2+}$ state only exists on the surface which does not contributes to the alteration of the band gap of the material at a very small mole percentage. On the other hand, dual vacancy created by the Cu dopant (Cu$^+$ state) does change the band gap of the material, as well as introducing various trap sites in between. This reduces the overall band gap, but the trap sites potentially serve as recombination centers. The XPS analysis exhibited the co-existed presence of both Cu in +1 and +2 oxidation states. Where Cu$^+$ is the major species in the sample which necessarily committed in the variation of the optical property of the sample which is also evident in the UV-vis absorption plot (Figure 8a). It is suggested that the coexistence of both the states of Cu improves the photocatalytic efficiency. The Cu$^{2+}$ states act as a trapping sink for the excited electrons while the Cu$^+$ serves as the electron donor for the adsorbed oxygen on the catalyst surface. This effectively aids to the interfacial electron transfer.

$$
2+\cdot + O_{ads}^{\cdot-} \\
+\cdot + O_{ads}^{\cdot-} \rightarrow Cu^{\cdot+} \quad \text{(Equation 5)}
$$

$$
2+\cdot + e_{cb}^{\cdot-} \rightarrow Cu^{\cdot+} \quad \text{(Equation 6)}
$$

On visible light irradiation, the electron hole pair generated on the TiO$_2$ surface reacts with the oxygen and water adsorbed on the catalyst surface to produce superoxide radicals and holes respectively. These reactive oxygen species (ROS)
further interact with the bacterial cell wall which results in membrane disruption and outflow of intracellular materials, this results in cell lysis (Figure 11). In addition to this, the ROS produced has the ability to interact with the sugar phosphate groups present in the DNA of the bacteria to cause gene alteration. Further altering the protein expression responsible for cellular functioning which leads to cell damage [12, 67].

![Figure 11. Schematic illustration of photocatalytic disinfection.](image)

5. Conclusions

In this present work, a 0.5 mol% Cu doped TiO₂ visible light active semiconductor material has been synthesized. The introduction of small mole percent of Cu inside the TiO₂ lattice has led to an improved cationic doped TiO₂ sample. These doped samples contributed to the enhanced stability of the anatase phase up to a temperature of 650 °C and also exhibited improved visible light antimicrobial efficiency.

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