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Ag-enriched TiO$_2$ nanocoating apposite for self-sanitizing/ self-sterilizing/ self-disinfecting of glass surfaces

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**KEY POINTS**
- Anatase Ag–TiO$_2$ nanocoated self-sanitized surfaces can effectively reduce infection.
- Ag generates reactive oxygen species, induce plasmonic and Schottky effects in TiO$_2$.
- Self-disinfecting efficacy of Ag–TiO$_2$ nanocoating depends on its structural profile.

**ARTICLE INFO**

**Keywords:** COVID-19 containment, Ag–TiO$_2$ nanocoating, Self-disinfecting surfaces, Photocatalysis, Antimicrobial activity

**ABSTRACT**

The excellent strategy to mitigate the spread of the COVID-19 pandemic is to inhibit the transmission of the SARS-CoV-2. Since fomites are one of the vital routes of coronaviral transmission, disinfecting of fomites play a pivotal role in curbing its survival on the contaminated surfaces. Available commercial disinfectants cannot keep the contaminated surfaces sanitized all the time. Self-disinfecting ability of Ag-enriched TiO$_2$ nanocoating due to its superb photocatalytic efficiency can effectively reduce infections caused by spread of pathogens at public places. Anatase Ag–TiO$_2$ nanocoatings synthesized by sol-gel process at 0.5, 1.5, and 2.5% enriching concentrations were casted on glass substrates by spin-coating technique and subsequently annealed at 650 °C. The morphological shape, crystallographic structure, light absorbance, photo-luminosity, vibrational modes, and functional groups of Ag–TiO$_2$ nanocoating on glass surface were studied by FE-SEM, GIXRD, UV–Visible, Photoluminescence, Raman, and FTIR spectroscopy. The developed anatase Ag–TiO$_2$ nanocoatings manifested to improve photocatalytic disinfecting performance due to the achieved small crystallite size of 10.5–19.2 nm, diminished band gap energy of 2.56–2.60 eV, elevated surface area of 0.802–1.470 × 10$^5$ cm$^2$/g, and enhanced light absorbance. Among the enriched specimens, 0.5% Ag–TiO$_2$ nanocoatings predicted an overall exalted functionality compared to pristine one.

1. Introduction

Coronavirus disease 2019 (COVID-19) caused by severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is highly contagious viral infection in humans that has posed a global challenge for the scientific community, medical fraternity, and healthcare facility. The primary routes of coronavirus transmission are direct exchange among individuals, indirect contact via fomites, and airborne transmission through respiratory aerosols released by an infected person thru coughs, sneezes, or exhales [1,2]. Coronavirus has a spherical shape with an average diameter of 78 nm [3], and can survive on glass and other surfaces as long as 28 days depending on temperature and humidity [4].

Most common touch glass surfaces such as display touchscreens on mobile phones, bank ATMs, airport check-in kiosks, biometric attendance recorders, and self-service wending machines act as fomites for the transmission of viruses specifically SARS-CoV-2 [4]. Thus, to inhabit the transmission of deadly coronavirus, it is imperative to disinfect the contaminated surfaces. However, it is almost impossible to keep the common surfaces sanitized constantly by traditional methods. Moreover, sanitizing a contaminated surface by disinfectants can provide a temporary relief only and does not guarantee that the surface will not get contaminated again. As a matter of fact, the microbial contamination level on the cleaned surface returns to the state of precleaned surface within 2.5 h [5]. In such a vexed scenario, there has been a pressing
demand to develop self-disinfecting surfaces to contain the propagation of this disease.

Surface nanocoating technology has been recognized as one of the excellent options to disinfect pathogens (virus, bacteria, fungi) from the commonly touched surfaces. The nontoxic metal oxides are usually employed for multifunctional nanocoating which interact with light and moisture to produce the reactive oxygen species (ROS) for disinfecting airborne microbes [6]. There exist a few selective metallic oxides such as titania (TiO₂) which are superior and cost-effective in providing the antimicrobial properties through functional coatings [7,8]. When UV light shines on the TiO₂ coating, the generated electrons interact with H₂O molecules in the air, breaking them up into hydroxyl (OH⁻) radicals. These radicals break asunder chemical bonds of organic molecules converting them into CO₂ and H₂O which evaporates off or spills down the surface, rendering the material self-cleaning. Here self-cleaning involves phenomena of keeping contaminated surface self-sanitizing against dirt/germs to safer levels, self-sterilizing to get rid of all germs, and self-disinfecting for removing harmful germs by involving two diverse processes of photocatalysis and hydrophilicity. Photocatalysis is a process which results in the generation of electron-hole pairs and ROS. The photocatalytic process disintegrates the organic dirt on the glass surface when exposed to UV light and renders the hydrophobic glass a super-hydrophilic surface. The conditions for super-hydrophobicity are a very high static water contact angle greater than 160°, and a very low inclination angle lesser than 5° necessary for a spherical droplet to roll off the surface [9]. However, on a smooth surface, it is not possible to exceed 120° contact angle by means of chemical hydrophobicity [10]. Hence, super-hydrophobicity requires tuning of surface roughness on nanoscale which can be possibly achieved through sophisticated fabrication techniques but at very high production costs besides being inappropriate for large-scale production of super-hydrophobic surfaces. On the contrary, hydrophilicity reduces the contact angle to very low values, causing the water to sheet evenly on the surface to form a thin film rather than forming spherical droplets.

On the one hand, TiO₂ has emerged as one of the best photocatalysts for antimicrobial nanocoating owing to its affordability, reactivity, stability, reusability, durability, and biocompatibility [11]. The metastable anatase phase of TiO₂ is contemplated to exhibit higher photocatalytic activity and greater photovoltaic performance owing to its wider energy bandgap and larger surface energy among all the polymorphous structural phases [12]. Anatase TiO₂ being a super-hydrophilic material, its nanocoating thus acts in exactly the reverse fashion on a surface whose self-cleaning features are instituted on the superhydrophobic Lotus effect. On the other hand, Ag particles can inactivate pathogens through oligodynamic effect of metals. Moreover, in the presence of moisture, Ag particles generate highly oxidative Ag ions, which can coalesce with DNA and RNA of microorganisms and hence inhibit their replication [13]. Therefore, Ag delivers TiO₂ nanocoating a higher affinity for dissolved oxygen, and induces Surface Plasma Resonance as well as Schottky effects in TiO₂ which improve light absorption and restrain charge carrier recombination to attain the highest photocatalytic disinfection efficiency [1-3]. Thus, silver-enriched titania (Ag-TiO₂) multifunctional nanocoating with super-hydrophilic property not only keeps the hydrophobic glass surface free from clogged grime but also chemically breaks down the adsorbed hydrocarbons, disinfects pathogens, and sanitizes microorganisms. Recent studies have elucidated that Ag incorporated TiO₂ coatings are more effective to combat COVID-19 and related viral genetic RNA compared to bare TiO₂ [1,13,15-17].

Nevertheless, the antibacterial, antifungal activities of Ag-TiO₂ coating will rely upon the surface morphology, nanograins size, crystallographic phase, doping concentration, and defect structure. The tunability of these parameters can exert diverse impacts on Ag-TiO₂ nanocoated surfaces. For example, earlier investigations have shown that the morphological shape of nanorod [18], average crystal size of 10-30 nm [19], structural phase of anatase [20], Ag doping of 3.9 wt% and 0.06 mol.% [21,22], and interstitial defects of Ti³⁺ and Ti⁴⁺ [23] play a vital role for achieving superior antimicrobial efficiency in Ag-TiO₂ nanostructures. However, almost all these studies are mutually isolated where it has been unclear if the effect of one parameter bears any consequence on the other, and on the outcome of the final product. Therefore, a detailed study of synergy of these characteristic parameters is warranted that can unveil tremendous opportunities for multifunctional applications of Ag-TiO₂ nanocoating. With this perspective, in the present work a meticulous and comprehensive investigation via a cluster of experiments has been put forth for the study of anatase Ag-TiO₂ nanocoatings (NCs) casted on glass substrates. The Ag-TiO₂ NCs were developed by sol-gel method at diverse doping concentrations and casted on glass substrates by spin-coating technique followed by thermal annealing. An important advantage of sol-gel process is to achieve transparent hydrophobic and oleophobic coatings [24]. Very recently, sol-gel procedure has been widely used in the fabrication of anatase Ag-TiO₂ NCs [11,25-30]. While sol-gel process facilitates the fabrication of Ag-TiO₂ NCs thru phase purity and thermal stability; spin-coating technique provides film uniformity and thickness controllability; and thermal annealing provides superior crystallinity and defect manageability. The fabricated anatase Ag-TiO₂ specimens were characterized by using field emission scanning electron microscopy (FE-SEM) for morphological studies, glancing incident X-ray diffractometry (GIXRD) for structural investigations, ultraviolet-visible (UV-Vis) spectroscopy for light absorption analysis, PL spectroscopy for luminescence measurements, Raman spectroscopy for vibrational mode assignments, and Fourier transform infra-red (FT-IR) spectroscopy for molecular functional group recognition.

2. Materials and methods

The development of anatase Ag-TiO₂ NCs through sol-gel method began with the preparation of 0.2 M TiO₂ sol by dissolving 1.6 ml of titanium(iv) isopropoxide (Merck,99.9%) in 23.4 ml of butan-1-ol under constant stirring on a magnetic stirrer at room temperature in an inert atmosphere. 0.1 M homogenous AgNO₃ sol was obtained by dissolving 0.11 g of AgNO₃ into 10 ml of acetic acid and 10 ml of ethylene glycol under constant stirring for 1 h at room temperature. The sol-gel process allows to control the Ag content for enriching of TiO₂ by simply repeating the process with different amounts of AgNO₃ sol. Specific amounts of AgNO₃ sol (0.25, 0.15, 0.05 ml) were individually added to 10 ml of TiO₂ sol each time under constant stirring on a magnetic stirrer for 1 h at 80 °C to get required Ag-TiO₂ concentrations (2.5, 1.5, 0.5 mol %), respectively. Glass substrates were thoroughly cleaned by acetone, methanol and deionized water. The gel was deposited on the cleaned and dried glass substrates with the help of a spin coater with 3000 RPM for 30 s. Each coated specimen was pre-heated on a hot plate at 80 °C for 5 min. The same procedure was adopted by depositing directly TiO₂ sol to get pure TiO₂ NCs. Next, all the specimens were thermally annealed at 650 °C for 5 h in a muffle furnace.

3. Results and discussions

3.1. Morphological studies by FE-SEM

By tuning the surface morphologies of nanostructures, it is plausible to influence the properties that can usher to widen the domain of their applications. Surface morphological studies of anatase Ag-TiO₂ NCs developed at 0, 0.5, 1.5 and 2.5% doping concentrations were performed by using FE-SEM (ZEISS, GEMINI 500) operating at an extra-high tension (EHT) accelerating voltage of 15 kV. The micrographs filmed at magnifications of 100 KX and 200 KX are shown in Fig. 1. The surface morphological studies reveal that the Ag-TiO₂ NCs have developed into nanostructures of irregular shape and smaller size as compared to the smoother shape and larger size of TiO₂ NCs. The occurrence of larger crystal size in pristine samples may be due to the aggregation and agglomeration of nanocrystallites during the growth
and nucleation processes. While bare as well as enriched samples exhibit well-densified structures, yet the shapes and sizes of constituent nano-crystallites manifest to be dissimilar. By contrast, there seem to have cropped up marginal alterations in surface morphologies of Ag–TiO$_2$ samples amongst 0.5, 1.5, and 2.5% enriching concentrations. Moreover, the NCs encompass voids all over the surface that may have occurred during the pre- and post-synthetic heat treatment procedures. It can be keenly observed that the voids increase with the increase of Ag content in Ag–TiO$_2$.

3.2. Structural investigations by GIXRD

Glancing or grazing incident X-ray diffractometry (GIXRD) from a nanostructure involves small angle of incidence for the inward X-ray so that diffraction can be made surface sensitive. The fixed angle is generally chosen to be slightly above the critical angle in order to achieve the total reflection of the surface material. Owing to its limited penetration (~nm), GIXRD is effectively used to investigate the NCs. Crystallographic structural studies and polymorphic phase identification of the synthesized anatase Ag–TiO$_2$ NCs were performed over a rotating angle of $2\theta = 20–80^\circ$ by employing the Rigaku Smart-Lab X-ray diffractometer (Cu-K$_\alpha$, $\lambda = 1.5406$ Å), fitted with HyPix-3000 detector and loaded with analysis software PDXL (9240J702, 9240J703, 9240J710). The diffractometer operated at an accelerating voltage of 40 kV, current of 30 mA, scan speed of 5°/min, and a scan step of 0.04°. The GIXRD patterns of the anatase Ag–TiO$_2$ specimens developed at 0, 0.5, 1.5, and 2.5% Ag-doping concentrations are presented in Fig. 2.

The diffraction data revealed that the specimens have grown into nanocrystallites of TiO$_2$ of anatase phase with space group 14: I41/amd coinciding with standard ICDD 41–1426, and Ag crystalline phase with space group 225: Fm-3m matching well with standard ICDD 01-071-4613. The diffraction patterns of Ag–TiO$_2$ NCs exhibit no other peaks related to any other phase (brookite or rutile) which confirmed that the specimens have crystallized into pure anatase phase. Moreover, the anatase Ag–TiO$_2$ NCs presented qualitatively the same patterns of the TiO$_2$ NC indicating that the anatase structure does not get affected upon Ag enriching. The existence of anatase structural phase of Ag–TiO$_2$ NCs corroborated well with the anatase phase reported for Ag–TiO$_2$ nanostructures in the scientific literature [26–30].

GIXRD patterns of anatase Ag–TiO$_2$ NCs fabricated at different Ag contents.
38.0°, 48.0°, and 55.0° indexed to the crystal planes (101), (004), (200), and (211), respectively. The most pronounced diffraction peak appeared about 25.0° corresponding to the (101) crystal plane in all the samples which confirmed the occurrence of anatase phase of Ag–TiO$_2$ [31]. The angular location of almost all the peaks remained invariant in respect of different concentrations except the occurrence of a shift towards lower 20 value (from 55.0° to 54.0°) in the peak positions observed at 1.5% and 2.5% concentrations. Therefore, silver enriching has not shifted the peak positions noticeably, signifying that there was no drastic impact of Ag enriching on the TiO$_2$ structure. Moreover, the intensity of diffraction peaks first increased from 0 to 0.5% and then upsurged to its climax at 1.5% which demonstrated that the crystallinity slightly increased with the increase in enriching concentration up to 1.5%. However, the intensity of all the diffraction peaks eventually declined at 2.5% enriching content which indicated the diminished crystallinity due to defects.

The diffraction peak and crystal structural parameters of angular peak position (20), interplanar spacing (d), peak height (h), full width half maximum (β), integrated intensity (I), integrated spectral distribution (W), asymmetric factor (F), lattice constants (a, b, c), unit cell volume (V), average crystallite size (D), lattice strain (ε), mass density (ρ) and specific surface area (S) corresponding to the anatase Ag–TiO$_2$ NCs are compiled in Table 1. The unit cell parameters obtained for the anatase Ag–TiO$_2$ NCs were quite consistent with the corresponding values reported in the literature [26,27,30]. However, the observed unit cell parameters vary among themselves to some extent for different enriching concentrations among the casted NCs.

The crystallite sizes distribution data of the fabricated anatase Ag–TiO$_2$ NCs is plotted in Fig. 3. The XRD peak profile analysis results based on Williamson-Hall method corresponding to most pronounced diffraction peak (101) in all the enriched samples exhibited $D$ in the ascending order of 10.5, 16.0, and 19.2 nm at 0.5, 1.5 and 2.5 % concentrations, respectively against agglomerated nanoparticles of pristine one reaching size of 414.16 nm. That is, with the increase in Ag content, the average diameter within enriched NCs was found to increase. This escalation in $D$ with the increase of enriching content was an anticipated behaviour because the Ag$^+$ ions dissolve into TiO$_2$ matrix. Since the ionic radii of Ag$^+$ (0.126 nm) is greater than that of Ti$^{4+}$ (0.068 nm) which permits only a little amount of Ag to dissolve into the periodic crystal lattice of TiO$_2$ by replacing the Ti$^{4+}$ ions [26]. This is due to reason that particles with smaller atomic radii than Ti atom act as intersticals to dissolve into Ti lattice as solid solution without substituting for Ti atoms [32]. These ionic radii mismatch also caused increase in $d$, $ρ$, and $S$ as well as decrease in 20, $β$, $W$, $a$, $c$, and $V$ with increase in enriching concentration. Corresponding trends were experienced in $I$, $F$, and $ε$, with trivial variations amid different concentrations.

3.3. Absorption analysis by UV–Visible spectroscopy

The optical properties such as absorbance, transmittance, and reflectance of NCs are determined by a powerful analytical technique recognized as UV–Vis spectroscopy. The UV–Vis absorption spectra of anatase Ag–TiO$_2$ NCs fabricated at 0, 0.5, 1.5 and 2.5% enriching concentrations were measured by using Analytijena SPECORD S-600 spectrometer in the absorption wavelength range of 300–1000 nm as shown in Fig. 4. Anatase Ag–TiO$_2$ NCs have shown appreciable enhancement in wavelength absorption leading to superior photocatalytic disinfecting activity as compared to the pristine TiO$_2$ films. The observed UV–Vis absorption spectra revealed that the enriching content has pushed the UV absorption range (300 nm) of anatase TiO$_2$ NCs towards the violet (380–390 nm), and red (680–725 nm) ranges of anatase Ag–TiO$_2$ NCs. The Ag–TiO$_2$ NCs thus exhibited an obvious red-shift in absorbance edge and a significant enhancement of light absorption in the region 300–1000 nm. This shift has been assigned to charge transfer transition between the electrons of Ag and TiO$_2$ at the interface via the surface plasmon resonance (SPR) effect of Ag because the Fermi level of Ag is located below the conduction band of TiO$_2$ [14,25]. It resulted in

| Doping Content | Structural parameters corresponding to (101) peak of anatase Ag–TiO$_2$–NFs developed at different Ag contents. |
|----------------|----------------------------------------------------------------------------------------------------------|
| %              | Peak angle position (20) | Interplanar spacing (d) | Peak height (h) | Full width half maximum (β) | Integrated intensity (I) | Integrated spectral distribution (W) | Asym. factor (F) | Lattice constants | Crystal size | Lattice strain | Mass density | Specific Surface area |
| 0              | 25.28° | 0.352 nm | 458 cps | 0.49° | 294 deg | 0.64 (deg) | 488 nm | 0.49 | 204 nm | 0.6 | 3785 cm$^{-2}$ | 0.53 |
| 0.5            | 25.35° | 0.351 nm | 712 cps | 0.48° | 253 deg | 0.70 (deg) | 732 nm | 0.48 | 252 nm | 0.6 | 3785 cm$^{-2}$ | 0.53 |
| 1.5            | 25.32° | 0.351 nm | 1332 cps | 1.05° | 827 deg | 0.62 (deg) | 1322 nm | 0.6 | 3785 cm$^{-2}$ | 0.53 |
| 2.5            | 25.28° | 0.351 nm | 1098 cps | 1.06° | 1098 deg | 0.62 (deg) | 1098 nm | 0.6 | 3785 cm$^{-2}$ | 0.53 |
| 2.5            | 25.28° | 0.351 nm | 1098 cps | 1.06° | 1098 deg | 0.62 (deg) | 1098 nm | 0.6 | 3785 cm$^{-2}$ | 0.53 |
| 2.5            | 25.28° | 0.351 nm | 1098 cps | 1.06° | 1098 deg | 0.62 (deg) | 1098 nm | 0.6 | 3785 cm$^{-2}$ | 0.53 |
Fig. 3. Crystal size distribution of anatase Ag–TiO$_2$ NCs enriched at different Ag contents.

Fig. 4. UV–Vis patterns of anatase Ag–TiO$_2$ NCs casted at different Ag contents.

Table 2
Absorbance spectra and bandgap energy of anatase Ag–TiO$_2$ NCs developed at different Ag contents.

| Percentage | I-peak Absorption wavelength (nm) | I-peak Absorbance (a.u.) | II-Peak Absorption wavelength (nm) | II-Peak Absorbance (a.u.) | $E_g$ (eV) |
|------------|----------------------------------|--------------------------|-----------------------------------|----------------------------|------------|
| 0          | 300                              | 06.00                    | 690                               | 14.23                     | 2.6        |
| 0.5        | 300                              | 20.83                    | 690                               | 14.23                     | 2.57       |
| 1.5        | 385                              | 32.59                    | 725                               | 16.89                     | 2.59       |
| 2.5        | 380                              | 23.96                    | 680                               | 13.30                     | 2.56       |
the formation of Schottky barrier acting as electron-trapping centre thereby escalating absorption wavelength, plunging bandgap energy, improving photocatalytic performance, and enhancing antibacterial activity [33]. Anatase TiO$_2$ and anatase Ag–TiO$_2$ NCs fall under indirect bandgap semiconductors and hold bandgap energies from 3.20 to 3.35 eV. After incorporation of Ag into TiO$_2$, the band gap energy reduced to 2.57, 2.59, and 2.56 eV for 0.5, 1.5 and 2.5% concentrations, respectively. Absorbance spectra and bandgap energy of anatase Ag–TiO$_2$ NCs developed at different Ag contents are displayed in Table 2.

3.4. Luminescence measurements by PL spectroscopy

Photoluminescence (PL) spectroscopy has become a measurement of choice for determining the luminescent properties of materials thru photoexcitation, non-radiative relaxation, and radiative emission processes taking place among different electronic states in a material. PL spectra are recorded by measuring the intensity of emitted radiation as a function of either the excitation wavelength or the emission wavelength. The PL spectra of anatase Ag–TiO$_2$ NCs were recorded by a time resolved fluorescence spectrophotometer (Horiba Yuvon Fluorocube-01-NL). The excitation and emission spectra of TiO$_2$ structure have been generally attributed to different photoexcited surface electron-hole pair recombination mechanisms such as self-trapped excitons and surface defects. The most common types of defects found in almost all anatase TiO$_2$ nanostructures comprise of oxygen vacancies associated with Ti$^{3+}$ species obtained via reduction of Ti$^{4+}$ cations by the UV irradiation [34].

An excitation spectrum is obtained by monitoring emission at a fixed wavelength while varying the excitation wavelength. The excitation spectrum offers expedient means for choosing the best excitation wavelength for a quantitative or qualitative analysis. Absorption of light is of tremendous importance for improving the luminescence efficiency in TiO$_2$ materials via creating electron-hole pairs and effective charge separation. However, owing to the large band gap of anatase TiO$_2$ semiconductor (~3.2 eV), its optical absorption is greatly limited in the UV region. Therefore, efforts have been mad to tune the band structure of TiO$_2$ semiconductor by doping with Ag metal in order to boost the photon utilization efficiency.

![Excitation and Emission Spectra](image_url)

**Fig. 5.** PL spectra of anatase Ag–TiO$_2$ NCs grown at different Ag contents:
(a) excitation spectra @ emission $\lambda_{em} = 285$ nm
(b) emission spectra @ excitation $\lambda_{ex} = 430$ nm
(c) emission spectra @ excitation $\lambda_{ex} = 480$ nm
(d) emission spectra @ excitation $\lambda_{ex} = 410$ nm.
visible-light absorption without diminishing photocatalytic efficiency [26,28,35–38]. The excitation spectra of anatase Ag–TiO$_2$ NCs were achieved by detecting photons emitted from the atoms in the excited state at an emission wavelength of 285 nm in the TiO$_2$ emission-range while scanning the excitation for different wavelengths in the TiO$_2$ absorption-range. The excitation spectra of anatase Ag–TiO$_2$ NCs developed at 0, 0.5, 1.5, and 2.5% enriching concentrations recorded at room temperature in the excitation wavelength range of 300–700 nm observed at an emission peak of 285 nm are shown in Fig. S5(a). The corresponding excitation parameters are displayed in Table 3(A). With the emission at 285 nm, anatase Ag–TiO$_2$ NCs exhibit PL excitation peaks in the visible spectral range and the four prominent excitation peaks stem out around $\lambda_1 = 388$–389 nm (violet), $\lambda_2 = 400$–402 nm (violet), $\lambda_3 = 478$–480 nm (blue), and $\lambda_4 = 530$–531 nm (green) in all the samples. The first two peaks corresponding to $\lambda_1$ and $\lambda_2$ may be attributed to the direct and indirect intra-band transitions of electrons as the corresponding excitation photon energies of 3.196–3.187 eV and 3.100–3.085 eV, respectively were intimate to the standard value (3.2 eV) of band gap energy of bulk anatase TiO$_2$ structure. The other two peaks belonging to $\lambda_3$ and $\lambda_4$ corresponding to energies 2.594–2.58 eV and 2.399–2.335 eV, respectively were assigned to presence of oxygen vacancies associated with Ti$^{3+}$ ions in anatase Ag–TiO$_2$ NCs [26]. The PL excitation spectra of anatase TiO$_2$ NCs showed non-monotonous variations with excitation photon absorption. The absorption edges determined from the low photon energy insets cropped up around 497–399 nm (3.12–3.11 eV), 399–406 nm (3.11–3.05 eV) and 455–458 nm (2.72–2.71 eV) for $\lambda_1$ to $\lambda_4$, respectively.

The intensity varied unsystematically but marginally for 0, 1.5, and 2.5% anatase Ag–TiO$_2$ NCs. The highest intensity occurred at peak 1 for all the samples and maximum excitation intensity arose for 0.5% content among the enriched samples. This surge in intensity can be explained on the basis of self-trapped exciton recombination stemming out of dual vacancies associated with Ti$^{3+}$ and 2.339% anatase Ag–TiO$_2$ NCs. This excitation in intensity leads to increase in luminence centres participating in this band and could be associated with self-trapped exciton recombination. These results clearly indicate that the horizon of luminence activities of anatase Ag–TiO$_2$ NCs have widened in the UV spectral range as a result of the decline in the carrier recombination rate of electrons and holes.

### 3.5. Vibrational mode assignments by Raman spectroscopy

Raman spectroscopy involves the phenomenon of inelastic scattering between incident photons and vibrational modes of scattering molecules. As a result, a unique Raman spectrum is produced that acts as a chemical fingerprint specific to the molecule. The molecular symmetry in conjunction with the group theory stipulate the selection rule for interpretation of Raman spectra. Each Raman mode conforms to the irreducible representation of a symmetry specie in the point group of the molecule. The Raman spectra of synthesized anatase Ag–TiO$_2$ NCs were recorded with a Renishaw inVia Raman microscope fitted with 325, 442 and 514 nm lasers as excitation sources. The Raman spectra of the fabricated samples are depicted in Fig. 6, and the corresponding Raman shifts, peak intensities and mode symmetries are presented in Table 4.

There exist three types of characteristic Raman active modes represented by A, B, and E symmetry groups fundamentally associated with the symmetric stretching, symmetric bending, and asymmetric bending vibrations of O–Ti–O bonds, respectively in the TiO$_2$ structure [39]. The characteristic Raman modes pertaining to Ag–TiO$_2$ anatase phase assigned to $E_g$ mode symmetries transpired around 143–144, 196–197, and 638–639 cm$^{-1}$ bands corresponded to the symmetric stretching vibration of O–Ti–O bonds whereas vibrational modes observed around 396–398 and 515–516 cm$^{-1}$ bands ascribed to B$_2$ and A$_g$ mode symmetries corresponded to asymmetric and symmetric bending vibrations of O–Ti–O bonds, respectively [40]. The Raman mode emerging around 790–797 cm$^{-1}$ band attributed to B$_{2g}$ mode as the first overtone of the B$_g$.

### Table 3

PL spectra parameter of anatase Ag–TiO$_2$ NCs prepared at different Ag contents.

| Enriching Percentage | Excitation Peak 1 (Violet) | Excitation Peak 2 (Violet) | Excitation Peak 3 (Blue) | Excitation Peak 4 (Green) |
|----------------------|---------------------------|---------------------------|--------------------------|--------------------------|
|                      | $\lambda_1$ (nm) | $I_1$ (a. u.) | $\lambda_2$ (nm) | $I_2$ (a. u.) | $\lambda_3$ (nm) | $I_3$ (a. u.) | $\lambda_4$ (nm) | $I_4$ (a. u.) |
| 0%                   | 388           | 493          | 400           | 471          | 480           | 263          | 530           | 199          |
| 0.5%                 | 389           | 868          | 401           | 799          | 480           | 408          | 530           | 344          |
| 1.5%                 | 389           | 566          | 402           | 535          | 478           | 298          | 530           | 231          |
| 2.5%                 | 389           | 497          | 400           | 471          | 479           | 265          | 531           | 200          |

| Enriching Percentage | $\lambda_{em} = 410$ nm | $\lambda_{em} = 430$ nm | $\lambda_{em} = 480$ nm |
|----------------------|--------------------------|--------------------------|--------------------------|
|                      | $\lambda_{ex}$ (nm) | $I_1$ (a. u.) | $\lambda_{ex}$ (nm) | $I_2$ (a. u.) | $\lambda_{ex}$ (nm) | $I_3$ (a. u.) |
| 0%                   | 335           | 163          | 321           | 728          | 352           | 463          |
| 0.5%                 | 335           | 370          | 320           | 285          | 353           | 194          |
| 1.5%                 | 333           | 186          | 320           | 830          | 354           | 540          |
| 2.5%                 | 336           | 161          | 321           | 714          | 353           | 465          |
mode is caused by the symmetric stretching of the O–Ti–O bond in the TiO$_2$ lattice [26]. The two specific bands arising about 564–566 and 1095-1098 cm$^{-1}$ corresponded to Si–O stretching vibration bond of the glass substrate [41].

Analysis of the Raman spectra revealed that the Ag-enriching percentage and thereby the crystallite size marginally influenced the peak positions of the Raman modes of anatase TiO$_2$ NCs by swinging discordantly without exhibiting any illustrious shift pattern on the wavenumber scale. The triviality of the shifts may be recognized by the invariant nature of anatase crystal structure observed in all prepared samples. However, the significant impact of Ag-enriching upon intensity of the characteristic Raman peaks of the anatase Ag–TiO$_2$ NCs manifested variations for various symmetry modes among different Ag contents. The elevated intensities existed for all fundamental modes of 1.5% Ag–TiO$_2$ NCs and the maximum value of intensity was achieved for E$_g$(1) mode. Such pronounced intensity shifts may be attributed to concentration and location of crystalline defects such as the presence of oxygen vacancies associated with Ti$^{3+}$ ions in the anatase lattice structure [34].

### 3.6. Functional groups recognition by FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a versatile experimental technique used to generate an infrared spectrum for the qualitative identification of the distinctive atomic arrangement of each dissimilar sample. FTIR studies were performed to observe the molecular functional groups by using Thermo-Nicolet 6700 FTIR spectroscope and the spectra of anatase Ag–TiO$_2$ NCs were recorded in the spectral range of 4000 to 500 cm$^{-1}$, as shown in Fig. 7. The FTIR spectra of anatase Ag–TiO$_2$ NCs absorbance bands appeared at different peak locations for different enriching contents. The dual bands observed at 618–638 and 655-692 cm$^{-1}$ epitomize the characteristic Ti–O bonds of anatase TiO$_2$ NCs [42]. The presence of band around 718-748 cm$^{-1}$ was attributed to vibrations of the Ti–O–Ti stretching bond [43]. The band existing at 1339 cm$^{-1}$ was ascribed to Ag–Ti–O bond [44,45]. A band appearing at 1456 cm$^{-1}$ relates to asymmetric bending vibration of C–H bond and may be explicated as some residual/pollutant organic matter present in the NCs [46]. The cluster of five peaks emerging out between 1500-1700 and 3500-3900 cm$^{-1}$ broad bands affirmed the presence of asymmetric stretching bond due to physisorbed and/or chemisorbed of H$_2$O molecule on the surface of TiO$_2$ from the environment [47].

The twin peaks at 1747 and 2343 cm$^{-1}$ occurred due to the symmetric and asymmetric stretching of C–O bond of the CO$_2$ molecule adsorbed from the atmospheric air [48–50]. The absorption intensity at 650 cm$^{-1}$ has been observed to remain constant for 0.5% and surged to higher wavenumber (blue shift) at 1.5% and finally plunged to lower wave numbers (red shift) with the upsurge at 2.5%. Functional group recognition, peak location, and absorption intensity of anatase Ag–TiO$_2$ NCs casted at different Ag contents are presented in Table 5.

### 4. Conclusions

The COVID-19 pandemic has highlighted the need of self-disinfecting...

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**Table 4**

| Enriching Percentage | Mode Symmetry | Shift (cm$^{-1}$) | Intensity (l.a.u.) | Shift (cm$^{-1}$) | Intensity (l.a.u.) | Shift (cm$^{-1}$) | Intensity (l.a.u.) | Shift (cm$^{-1}$) | Intensity (l.a.u.) |
|----------------------|---------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 0.0%                 | Eg(1)         | 144.49            | 55408             | 144.49            | 39723             | 143.35            | 69019             | 143.04            | 55501             |
|                      | Eg(2)         | 197.61            | 1281              | –                 | –                 | 196.48            | 1217              | 196.17            | 1090              |
| 0.5%                 | Ig(1)         | 398.75            | 2932              | 397.66            | 2493              | 397.66            | 3320              | 396.26            | 2958              |
|                      | Ag(1)         | 516.23            | 4250              | 516.22            | 4656              | 516.23            | 4851              | 515.93            | 3048              |
|                      | Eg(3)         | 564.62            | 6242              | 566.76            | 7523              | 564.62            | 4697              | 565.40            | 2288              |
|                      | B2g           | 638.20            | 8245              | 639.27            | 6956              | 639.27            | 8792              | 637.92            | 6522              |
| 1.5%                 | –             | 794.60            | 1487              | 790.44            | 1176              | 792.52            | 1171              | 797.42            | 1165              |
|                      | Eg(1)         | 1095.38           | 11940             | 1097.36           | 12906             | 1098.36           | 9498              | 1098.08           | 4006              |
| 2.5%                 | –             | 144.49            | 55408             | 144.49            | 39723             | 143.35            | 69019             | 143.04            | 55501             |
antimicrobial coatings to protect common surfaces from the propagation of infections and to control the ability to mutate. Silver enriched titania nano-coated self-sterilizing surfaces possess the unique property of inhibiting microbes by inducing redox stress and photocatalytic obliteration of the microbial cells. These self-sterilizing surface coatings offer tremendous opportunities in effectively containing the spread of aerosolized viral droplet infection settled on the fomites at public places serving as reservoirs for virus transmission; thereby preventing the propagation of COVID-19. The coatings diminish the diameter of the particles and restrain the activating of cytotoxic effects of reactive oxygen species on the cellular host, thus accomplishing effective anti-serviring as reservoirs for virus transmission; thereby preventing the tremendous opportunities in effectively containing the spread of aero-

### Table 5

| Molecular Functional Group | 0.0% | 0.5% | 1.5% | 2.5% |
|----------------------------|------|------|------|------|
| Ti-O-Ti asymmetric stretching | 620.63 | 0.9969 | 620.63 | 0.9974 |
| Ti-O-Ti symmetric stretching | 748.15 | 0.9973 | 718.40 | 0.9983 |
| Ag-O-Ti stretching | 1339.03 | 0.9972 | 1339.03 | 0.9985 |
| C-H asymmetric bending | 1456.63 | 0.9977 | 1456.63 | 0.9987 |
| O-H symmetric stretching | 1506.94 | 0.9949 | 1507.64 | 0.9984 |
| O–O symmetric stretching | 1747.82 | 0.9960 | 1747.82 | 0.9977 |
| C-O asymmetrical stretching | 2139.56 | 0.9973 | 2139.56 | 0.9985 |
| O-H symmetric stretching | 2554.28 | 0.9973 | 2554.28 | 0.9986 |
| 3649.38 | 0.9969 | 3649.38 | 0.9979 |
| 3745.02 | 0.9968 | 3735.10 | 0.9981 |
| 3898.76 | 0.9971 | 3867.59 | 0.9984 |
| 3909.39 | 0.9991 | 3909.39 | 0.9991 |
| 3898.76 | 0.9978 | 3898.76 | 0.9978 |

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