

Effect of various dopants on titanium dioxide nanorod arrays: A review

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Abstract

In recent years, titanium dioxide (TiO₂) has emerged as one of the most exceptional nanomaterials, attracting interest from experts throughout the globe. In addition to having a band gap of 3.2 eV, TiO₂ has outstanding optical, structural, electrical, and photocatalytic capabilities that may be used in the semiconductor industry. However, because of its weak conductivity and capacitance, TiO₂ has not been able to reach its full potential. In order to realise its full potential, researchers have devised a variety of methods, including hydrothermal deposition, sol-gel-assisted template deposition, chemical vapor deposition, electrochemical anodisation, hydrothermal deposition, and metal oxide doping. Doping TiO₂ with metal oxides has been shown to significantly enhance its properties, which may improve its qualities. The primary goal of this study is to provide an overview of various research studies on the influence of the metal oxide dopant on the final properties of titanium dioxide (TiO₂) nanorod arrays.

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1.0 Introduction

Nanotechnology is a fascinating new area of study with numerous potential applications in a variety of domains. Nanotechnology can be defined as technology on the nanoscale, which encompasses 1–100 nm, or more succinctly as atomically precise technology. It can also be defined as engineering with atomic-level precision. As a result, nanotechnology has expanded to encompass a wider range of technologies, including those with medical, catalytic, sensor, and electrical applications, as well as environmental and biological applications (Salamanca, 2005). In recent years, research into metal and metal oxide nanoparticles (NPs) have increased significantly due to the unique properties and capabilities of these materials in a variety of fields. Numerous research projects have

been conducted in related disciplines, resulting in the development of various types of photovoltaic cells. Titanium dioxide (TiO₂) is an inorganic semiconductor with a broad energy band of 3.2 eV (İkizler & Peker, 2016). Due to the fact that TiO₂ is a potential semiconductor, it possesses exceptional optical, structural, electrical, and photocatalytic properties. There are three distinct forms of TiO₂: anatase, brookite, and rutile. In comparison to other forms, anatase TiO₂ is the form of TiO₂ that researchers around the world are most interested in researching due to its high photocatalytic efficiency. It is a preferred material for solar cells, fuel cells, sensors, wastewater treatment, self-cleaning coatings, and disinfecting materials due to its physical and chemical stability, low toxicity, high refractive index, high reactivity, ease of

synthesis, low cost, high catalytic activity, and high energy conversion efficiency (Kusior et al., 2018). TiO_2 may be found in a variety of 1D, 2D, and 3D forms. When it comes to one-dimensional (1D) structures, the most common are nanowires (NWs), nanorods (NRs), and nanotubes. 1D NRs, have a high aspect ratio and are confined in the radial direction when seen from the side. Large surface areas and efficient electron transport in these structures make them favourable for reducing the recombination process to the bare minimum. TiO_2 NRs have clear quantum confinement, an exceptionally ordered structure, and a large explicit surface area, which allow them to significantly improve the photoinduced charge carrier separation rate and provide a high charge transport efficiency (Mokhtar et al., 2018). This is one of the reasons why TiO_2 NRs are well-known all over the world for their superior performance. Fig. 1 shows the field emission scanning electron microscope (FESEM) morphology of TiO_2 NRs.

TiO_2 NRs have been made by researchers all over the globe by using novel techniques such as sol-gel-assisted template, chemical vapour deposition, electrochemical anodisation, hydrothermal, and solvothermal procedures (Khanna et al., 2020). A technique known as the hydrothermal method, which has the capacity to improve the form and size of the produced nanostructure, has piqued the interest of a large number of researchers. The hydrothermal technique is a simple and uncomplicated procedure to use. It was discovered that doping TiO_2 with a variety of elements is an easy way to circumvent this limitation. Doping TiO_2 with other elements result in improved electronic properties, reduced charge recombination, increased electron transport, faster electron injection, and a band-edge shift that is more favourable (Katta et al., 2021). When doping TiO_2 , a downward shift in the location of the conduction band (CB) leads in an increased amount of electron injection, whereas an upward shift results in a higher

amount of open-circuit voltage (V_{oc}). Doping also plays a significant part in the modification of oxygen vacancies, which is vital in a wide range of technological applications. Doping plays a major role in several technological applications.

2.0 Synthesis of doped-titanium dioxide nanorod arrays

Doping with metal oxide is a frequent way to improve the TiO_2 structure. Various metal oxide can be used as dopant such niobium (Nb), calcium (Ca), yttrium (Y), gallium (Ga), antimony (Sb), and tellurium (Te) to obtain doped-metal oxide NRs.

Yang et al. (2014) used 1D rutile TiO_2 NRs as a photoanode for dye-sensitive solar cells (DSSCs) to investigate the influence of Nb-doping on the electrical band structure and microstructure of these NRs (Yang et al., 2014). It is directly grown on top of fluorine doped tin oxide (FTO) substrates where the NRs with varying Nb concentrations are assembled into DSSCs. Nb-doping is reported to significantly improve the energy conversion efficiency of NRs-based DSSCs by more than 70%, compared to their untreated counterparts. At the dye-NRs interface, as well as at the NRs-FTO interface, this improvement in the photon-electron conversion process may be ascribed to increased electron injection and reduced carrier recombination. Nb-doping increases the surface potential of the NRs in a positive direction, allowing electron injection from the dye sensitiser to the NRs to be facilitated. This is shown by flat band potential analysis. The researchers also discovered that the high carrier concentration of the Nb-doped NRs enhances electron tunnelling at the NRs-FTO interface, which was discovered by nanoscale conductive atomic force microscopy (c-AFM) measurements of individual NRs. According to the findings of this work, the introduction of Nb doping into the NRs changes the surface states of the NRs as well as the interface resistance between TiO_2 and FTO. As a result, carrier transport from the excited dye to the FTO layer is made easier by decreasing carrier recombination and increasing electron collecting efficiency.

Ca-doped TiO_2 nanorod arrays can be made using the one-step hydrothermal process, and the research discusses in detail the influence of Ca ions concentration on the photovoltaic conversion efficiency of dye-sensitised solar cells (Li et al., 2014). However, despite the fact that no obvious changes in the microstructure and morphology of the Ca-doped

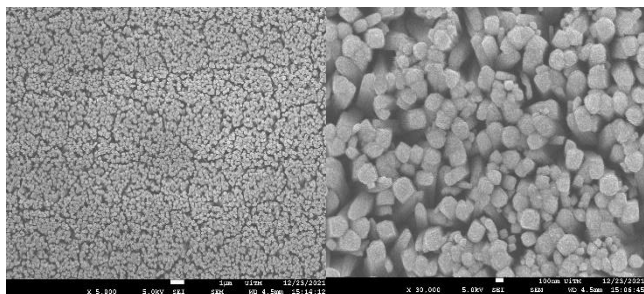


Fig. 1: FESEM top morphology of TiO_2 NRs at (a) 5k, and (b) 30k magnification

samples were observed using the field emission scanning electron microscope and transmission electron microscope, the results of X-ray diffraction and X-ray photoelectron spectroscopy confirmed that Ti^{4+} was successfully substituted with Ca^{2+} . The findings of the UV-Vis spectroscopy indicated that the flat band edge was positively displaced because of the Ca ions doping. Compared to the undoped electrode, the photovoltaic conversion efficiency of the dye-sensitised solar cells based on the 2% Ca-doped TiO_2 electrode was 43% higher, indicating that there was less chance of recombination between the dye and the electrode.

The fabrication of undoped and barium doped TiO_2 (Ba- TiO_2) nanoparticles (NPs) were made simple using the sol-gel process (Mugundan et al., 2022). The amorphous NPs were calcined at 500 degrees Celsius in order to transform them into crystalline NPs after they were manufactured. The SEM and TEM analyses of TiO_2 NPs following Ba doping revealed that the size of the NPs had grown. With the use of EDS and ICP-MS, the presence of Ti, O, and Ba elements in Ba- TiO_2 NPs was established. In the case of Ba- TiO_2 nanoparticles, the XRD profile revealed the existence of anatase phase and barium titanate phase. By using a BET surface area analyser, it was possible to determine the specific surface area and porosity of pure TiO_2 and Ba- TiO_2 NPs. FTIR was used to determine the functional groups of the Ba- TiO_2 nanoparticles. The UV-Vis spectrum was used to investigate the E_g of pure TiO_2 and Ba- TiO_2 nanoparticles. According to the NLO investigations, pure TiO_2 NPs had a greater second harmonic generation (SHG) efficiency when compared to Ba- TiO_2 NPs under the same conditions. In this study, the photocatalytic activity of pure TiO_2 and Ba- TiO_2 nanoparticles were examined in relation to the degradation of methylene blue (MB) dye when exposed to sunlight. The TOC analyser was used to investigate the mineralisation of methylene blue dye.

A simple one-step hydrothermal process was used to create Y-doped TiO_2 nanorod arrays, which were then effectively used as the photoanode in photovoltaic solar cells (Lv et al., 2018). The rutile structure of TiO_2 was preserved after Y doping, and the strength of several diffraction peaks was increased, suggesting that Y-doped TiO_2 NRs crystallised more efficiently. Doping with Y also raised the electron concentration, which resulted in an even greater increase in electron conductivity. Furthermore, the flat band edge of Y-doped NRs moves positively, which contributes to the

improvement of the electron-injection efficiency, which in turn results in a rise in the current density of the device. It was discovered that the PSC based on Y-doped TiO_2 could achieve an overall power conversion efficiency of 7.95%. When compared to the non-doped counterpart, this represents a 24% gain in performance. The increased electron injection and transfer efficiency generated by a positive shift in V_{fb} , as well as a decrease in charge recombination, were described to the improve of performance. The findings of this work pave the way for the enhancement of photocurrent density in perovskite solar cells by the use of element doping.

TiO_2 with varied morphologies were developed and synthesised with ease by manipulating the seeding concentration and subsequent nitridation, which were done in a simple and straightforward manner (Su et al., 2020). While it is possible to generate TiO_2 microflowers in the lack of TiO_2 seeds, it is also possible to form TiO_2 nanorod arrays in the presence of TiO_2 seeds. A variety of TiO_2 seeding concentrations were used in the preparation procedure in order to determine the most favourable synthesis conditions for TiO_2 production. Consequently, N- TiO_{2-3} synthesised using 0.2 g L1 TiO_2 seeds exhibits higher areal capacitance than N- TiO_{2-3} synthesised using 0.2 g L1 TiO_2 seeds, which is attributed to the rapid charge transfer and improved hybrid structure of free-standing NRs and nanoflowers. The highest areal capacitance of the optimised N- TiO_{2-3} electrode was 177.1 mF cm^2 , which is much greater than the maximum areal capacitance of the no seeding sample (16 mF cm^2). Through the manipulation of the concentration of the seed solution, this approach offers a broad way for improving the areal capacitance of nanomaterials.

They reported the TiO_2 NAs with varying molar ratios of zinc doping were employed as electron transport layers (ETLs) for carbon-based perovskite solar cells with improved photovoltaic performance, and the ETLs were shown to be effective (Lv et al., 2021). By using a one-step hydrothermal process, the zinc-doped TiO_2 NAs were produced directly on the conductive fluorine-doped tin oxide (FTO) substrate using zinc-doped TiO_2 NAs. It can be seen from the XRD patterns that the addition of Zn dopant improves the vertical growth orientation of TiO_2 NAs as well as the crystallinity of perovskite films. The measurements of the space-charge-limited current (SCLC) demonstrate that Zn-doped TiO_2 NAs have better electrical conductivity and lower trap-state density than

pure TiO₂, resulting in an increase in J_{sc}. The Mott-Schottky measurement determines the location of the conduction band, which implies more electron injection into the perovskite layer, resulting in an improvement in the J_{sc} of the material. By optimising the zinc doping concentration, the PCE increased from 12.99% to 14.45%, a significant improvement (2.5 mol %). Furthermore, according to stability tests conducted over a 30-day period, the best-performing cell without encapsulation retains 85% of its initial efficiency.

A straightforward hydrothermal approach was used to create Ce-doped TiO₂ NRs (Chen et al., 2021). The length and diameter of Ce doped NRs, as determined by FESEM, are around 500 nm and 80 nm, respectively (Chen et al., 2021). The XRD results show that Ce⁴⁺ has taken the position of Ti⁴⁺ in the crystal lattice without affecting the TiO₂ crystal structure at all. The doping of Ce⁴⁺ in TiO₂ NRs, as shown by SEM, reduces the grain size of the NRs. The effective integration of Ce ions is shown by the XRD and EDS patterns. The UV-Vis absorption spectra and PL emission spectra of the down-conversion centre Ce⁴⁺ ions demonstrate that the ions can effectively use ultraviolet light and that the perovskite functional layer can enhance the light-harvesting ability of the perovskite functional layer to the ultraviolet region. The photoelectric performance varies depending on the concentration of Ce doping used. When the Ce-doping concentration is 0.05 (Ce: Ti molar ratio), the hole-transport-free and carbon electrode-based perovskite solar cells achieve the greatest performance, the hole-transport-free and carbon electrode-based perovskite solar cells reach the highest performance. The power conversion efficiency (PCE) of the optimised Ce-doped device was 10.1%, a 24.6% improvement over the efficiency of the undoped device. The dark current density and hysteresis effect of the Ce-doped cells are both less than those of the undoped cells, indicating that they are more efficient. Upon Ce doping, the band gap of TiO₂ is increased from 2.92 to 3.00 eV, and the flat band potential is de-shifted by 50 mV to the negative side, leading to a higher Fermi level and a reduction in the surface defect density, all of which contribute to boosting the V_{oc} of the PSCs. The electron lifespan is extended by the Ce (0.05)-TiO₂ device, as seen by the V_{oc} decay curve. According to the results of the impedance study, more carriers are created. Additionally, the UV stability has been greatly increased. Even after 12 hours of exposure to light at room temperature in an optimised Ce-doped device,

PCE maintains 90% of its original value. The value of the undoped gadget, on the other hand, declines to 55% of its starting value.

Spin coating was used to create high grade nanocrystalline Fe doped TiO₂ films (Komaraiah et al., 2019). Research on the structural, optical, and photocatalytic activity (PCA) effects of Fe doping has been conducted. TiO₂ crystallite size shrank as Fe doping concentrations increased. Table 1 shows by using HRTEM images, it was determined that the average particle size of 1% and 7% Fe doped TiO₂ films were 14 nm and 8 nm, respectively. As Fe doping concentration increased, the crystallite size decreased, and the Raman blue shift was ascribed to it. The bandgap of TiO₂ is reduced from 3.32 eV to 2.57 eV when the concentration of Fe dopant is increased. As Fe³⁺ is added to doped TiO₂ thin films, the PL emission intensity drops. An increased PCA was attributed to Fe-TiO₂ films because of their large specific surface area, decreased bandgap energy, and increased absorption of visible light. MB dye photodegradation maximised when exposed to light via, fluorine doped-tin oxide sample 7, FTO7 film. The PCA of TiO₂ thin films shows that the photodegradation efficiencies for the disintegration of MB under visible light irradiation decrease as the content of Fe-precursors increases.

Sol-gel spin coating successfully applied Ag⁺ doped TiO₂ thin films on glass substrates (Komaraiah et al., 2020). Table 1 states the average Ag-TiO₂ crystallite size was 6.2 to 18.0 nm. Ag doping reduced crystallite size. TEM images show that pure TiO₂ is 23.8 nm and Ag⁺ doped TiO₂ is 11.6 nm. Due to a decrease in crystallite size, the vibrational Raman modes in Ag-doped titania films moved towards higher energy. Increasing Ag-precursor concentration decreases TiO₂ bandgap from 3.32 to 2.75 eV. The high PCA during visible light irradiation is due to oxygen vacancies and Ti³⁺ sites in Ag-TiO₂, as shown by EPR spectra. Silver ion doping reduces luminescence emission. Silver-doped titanium dioxide at 5%, ATO5 film causes dye degradation. Degradation efficiencies rise with Ag⁺ doping concentration, reaching a maximum at 5% Ag and decreasing at higher concentrations for visible light dye breakdown. Smaller crystallite and particle size, narrow bandgap, and optimum doping concentration may improve degradation efficiency. Given their good PCA and easy deposition, coated Ag-TiO₂ films may have photocatalytic applications.

Moreover, the spin coating process was used to make the KI-doped TiO₂ film, and the optical

absorbance of the TiO₂ film was increased by doping alkali halide (Shanthi et al., 2022). The presence of an anatase phase structure in the grown film was shown by Raman spectrum and X-ray diffraction studies, respectively. A shift from the ultraviolet to the visible range was observed using UV-Vis spectroscopy, and an increase in particle size of the anatase crystal resulted in a lower energy band gap when measured using FESEM. Both studies demonstrate that the optical absorbance of the alkali halide doped film is ensured by the alkali halide doped film. Energy dispersive X-ray spectroscopy (E-DAX) was used to demonstrate the presence of a dopant, and the created film was confirmed to be free of contaminants after being processed. Thus, the doped film may be employed as an excellent optical absorber for photovoltaic cells as a consequence of its enhanced absorption properties.

An acidic sol-gel technique was used to fabricate both pure TiO₂ and TiO₂ nanoparticles that had been doped with varying amounts of Zn and Mg (Javed et al., 2022). Table 1 states pure samples were calcined at 400 °C for 4 hours. Pure TiO₂, Mg-doped TiO₂, and ZnO-doped TiO₂ were examined for their surface morphology, crystal dimensions, bandgap size, and visible light absorption. X-ray diffraction analysis confirmed the presence of the anatase phase in both undoped TiO₂ and Zn/Mg-doped TiO₂ nanoparticles. According to the scanning electron micrographs, both pure TiO₂ and Zn/Mg-doped TiO₂ nanoparticles were aggregated into particles of about the same size and shape during preparation. Pure TiO₂ was found to have a mean particle size of 5 nm, whereas Mg-doped TiO₂ nanoparticles were found to be 30 nm and Zn-doped TiO₂ nanoparticles were found TiO₂ has a wide PL spectrum because of its indirect energy bandgap, which can be seen in UV-Vis spectra as an expansion of the valence band. The data also shows that the peak intensity increases with Mg doping due to a greater recombination rate. ZnO doping, however, was crucial in preventing this narrowing. By using the sol-gel spin coating method, it was possible to create TiO₂ thin films that were doped with varying concentrations of Fe³⁺ (Carotta et al., 1999). Analysis using X-ray diffraction and Raman spectroscopy demonstrate that, depending on their concentration, the Fe ions either restrict the crystallisation process or appear to stabilise the amorphous phase of the TiO₂ material. As stated in Table 1, the concentration of Fe in thin films was

increased, the edge of absorption moved farther out to longer wavelengths, moving from 356 to 416 nm. The band gap of TiO₂ may be shrunken via Fe-doping in the material. The photocatalytic activity in the visible spectrum functions more effectively as a result of this impact. The crystallinity of the material dropped as the amount of Fe³⁺ in it climbed from 0 to 20%. Despite the addition of Fe³⁺ to a concentration of 20%, the amorphous condition of the TiO₂ thin film did not change. The grain size determined from the XRD patterns ranges anywhere from 29.3 to 22.6 nm.

Hydrothermal synthesis has been used to produce TiO₂ as well as N-GO-doped TiO₂ (M. Sharma and Nihal, 2019) The FESEM and XRD techniques have been used so that the structure may be characterised. The NRs type morphology is seen for TiO₂ by FESEM, but the spherical morphology is observed for N-GO doped TiO₂. Techniques such as FTIR, UV-Vis, and PL spectroscopy are used in order to investigate the optical characteristics. Referring to Table 1, there is a red shift in energy in the band gap of both pure TiO₂ and N-GO-doped TiO₂. The current-voltage (I-V) characteristics have been used in carrying out the electrical measurements. The electrochemical approach was used to compute the value of the specific capacitance, and the results turned out to be 16.41 Fg⁻¹ for TiO₂ and 121.40 Fg⁻¹ for N-GO doped TiO₂, respectively.

Next, they investigated the photovoltaic performance of dye-sensitised solar cells based on undoped and Sr-doped TiO₂ photoanodes with TiO₂ scattering layers and TiCl₄ treatment, in order to summarise their findings (Rajamanickam and Ramachandran, 2020). With the addition of Sr doping and treatment with TiCl₄, the efficiency increased from 2.74% for the bare undoped TiO₂ photoanode to 9.6% for the finished product. Several variables have contributed to the greater efficiency. The dielectric, electrochemical impedance spectroscopy (EIS), and incident photon-to-current efficiency (IPCE) tests on the Sr-doped TiO₂ sample reveal that the material exhibits rapid charge separation. Furthermore, IPCE measurements revealed that TiCl₄-treated and scattering layer-coated TiO₂ photoanodes had high photon energy for charge transport as well as decreased charge recombination. Aside from that, the TiCl₄-treated photoanode has the lowest charge transfer resistance, which results in a high photocurrent density and efficiency in the Sr-doped TiO₂ photoanodes.

Table 1: Comparison on the preparation of element doped TiO₂ NRAs by various research groups

No.	Starting Materials	Deposition Method	Parameter Involved	Findings	Ref.
1.	<ul style="list-style-type: none"> • Titanium isopropoxide • Chloride of iron (III) • Isopropanol • Acetic acid 	Sol-gel spin coating technique	<ul style="list-style-type: none"> • Iron (5%, 10% and 20%) 	<ul style="list-style-type: none"> • Fe³⁺ concentration from 0% to 20% reduced crystallinity • TiO₂ thin film remained amorphous after 20% Fe³⁺ addition • Grain sizes between 29.3 and 22.6 nm • Increasing Fe³⁺ lowered the optical bandgap 	(Carotta et al., 1999)
2.	<ul style="list-style-type: none"> • Ammonia (NH₃) • Sodium Hydroxide • Titanium dioxide 	Hydrothermal	<ul style="list-style-type: none"> • Pristine TiO₂ and 0.2g of N-GO Doped TiO₂ 	<ul style="list-style-type: none"> • TiO₂ and N-GO Doped TiO₂ band gap energy display red shift. • Specific capacitance values for TiO₂ and N-GO doped TiO₂ were 16.41 Fg⁻¹ and 121.40 Fg⁻¹, respectively. 	(Sharma & Nihal, 2019)
3.	<ul style="list-style-type: none"> • Titanium(IV) propoxide • Acetylacetone 	Sol-gel spin coating technique	<ul style="list-style-type: none"> • Iron (0, 1, 3, 5, 7 and 10%) 	<ul style="list-style-type: none"> • The average particle size of 1% and 7% Fe-doped TiO₂ films was determined to be 14 and 8 nm. • As Fe doping concentration increased, the Raman blue shift was seen. 	(Komaraiah et al 2019)
4.	<ul style="list-style-type: none"> • Titanium tetra isopropoxide • Magnesium chloride • Zinc nitrate hexahydrate • Ethanol • Deionized water 	Facile sol-gel technique	<ul style="list-style-type: none"> • Zinc (0.25 M, 0.5 M, and 1 M) • Magnesium (1 M and 2 M) 	<ul style="list-style-type: none"> • Good thermal stability and fewer surface flaws than ZnO-doped TiO₂. • Mg-doped TiO₂ nanoparticles limit recombination processes to display visible absorption. 	(Javed et al., 2022)
5.	<ul style="list-style-type: none"> • Titanium(IV) propoxide • Acetyl acetone • Nitric acid 	Sol-gel spin coating technique	<ul style="list-style-type: none"> • Silver concentration (0, 1, 3, 5, 7, and 10%) 	<ul style="list-style-type: none"> • Ag⁺ doped TiO₂ films outperformed undoped TiO₂ in photocatalysis. • PL emission efficiency was poor in Ag-doped TiO₂ compared to TiO₂ thin film. • The Raman bands showed anatase phase development. 	(Komaraiah et al., 2020)

3.0 Conclusions

This work gives an overview of the metal oxide element that is employed in the manufacture of TiO₂ NRs, as well as the influence of doping on the characteristics of the NRs. There are several more techniques that may be employed to improve the characteristics of TiO₂ NRs. Because of the unique qualities that TiO₂ material has, it has the potential to be the optimal solution with a great deal of promise in a broad range of applications. Since the usage of

dopants have a substantial impact on the characteristics of TiO₂ NRs, this will be a fantastic chance to learn about the new technology that it delivers. As a result, more research is necessary to improve the properties of TiO₂ NRs and to maximise their potential for use in larger-scale applications. According to the findings of this research, TiO₂ NRs have the potential to become one of the most important semiconductor materials, as well as having additional uses.

Contribution statement

Mohd Firdaus Malek, Mohd Khairul Ahmad & Mohamad Rusop Mahmood: Conceptualisation and supervision; **Mohd Rasydan Mustapha, Mohd Firdaus Malek and Musa Mohamed Zahidi:** Methodology; **Mohd Rasydan Mustapha & Mohd Firdaus Malek:** Formal analysis and investigation; **Mohd Firdaus Malek, Asiah Mohd Nor, Mohd Khairul Ahmad & Mohamad Rusop Mahmood:** Resources; **Mohd Rasydan Mustapha & Mohd Firdaus Malek:** Writing-original draft; **Musa Mohamed Zahidi, Asiah Mohd Nor, Ruziana Mohamed, Noor Asnida Asli:** Writing-review and editing; **Mohd Firdaus Malek & Mohamad Rusop Mahmood:** Project administration.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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