Antibacterial Plasmonic Nanostructures Based on Ag Nanoparticles for Tritanopia Color Vision Deficiency (CVD) Management

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ABSTRACT— Color vision deficiency (CVD), or color blindness, is a prevalent ocular disorder that hinders the recognition of different colors, affecting many people worldwide (8−10% of males and 0.4−0.5% of females). Recently, there has been a significant focus on plasmonic nanostructures as an alternative to chemical dyes for managing color blindness due to their remarkable characteristics and the tunability of plasmonic resonances. In this work, the plasmonic glasses based on silver nanoparticles with a TiO_2 thin layer coating were fabricated using the sputtering technique and proposed for blue-yellow (tritanopia) CVD management. The proposed plasmonic glasses based on silver nanoparticles are more selective than commercial Enchroma glasses because of the tunability of plasmonic properties of silver nanoparticles by controlling their morphology, which provides insights for applications of color vision deficiency improvement. Also, the antibacterial activity of the proposed plasmonic glasses based on silver nanoparticles was investigated against E. coli and S. aureus bacteria, which have exhibited effective antibacterial properties. The results indicate that the silver nanoparticle-based glasses not only aid in tritanopia management but also offer potential for antibacterial applications such as implant coatings.

KEYWORDS: Color vision deficiency (CVD), silver nanoparticles, antibacterial, localized surface plasmon resonance.

I. INTRODUCTION

Colors play a vital role in the daily life of people because of their ability to carry information, so the ability to perceive different colors is considered one of the essential needs of humans in daily life. The phenomenon of human color vision is attributed to the presence of cone-shaped photoreceptor cells located within the ocular structure. These cone photoreceptors are classified into three categories: short (S), medium (M), and long (L) cones, which are respectively responsible for perceiving blue, green, and red colors with maximum spectral sensitivity at wavelengths around 430, 530, and 560 nm. All three types of cone cells are present in normal color vision, and their function is determined by their spectral sensitivity response.

Currently, a significant proportion of the population (ranging from 8 to 10% of males and 0.4 to 0.5% of females) experiences color vision deficiency (CVD) [1]-[5], which impedes their ability to distinguish different colors compared to individuals with normal color vision. Color blindness or CVD occurs due to the loss or defect of cone cells, and it is classified into three distinct categories: dichromacy, monochromacy, and anomalous trichromacy. Dichromacy occurs when one of the cone cells is completely lost and is known as protanopia (lacking L cone cells), deuteranopia (lacking M cone cells), and tritanopia (lacking S cone cells).

Monochromacy is the rarest type of CVD in which at least two cone cells are lost and monochromat patients are completely color blind or have only S cone cells. Finally, anomalous trichromacy occurs when one of the cone cells is defective and is divided into protanomaly (defective L cone cells), deuteranomaly (defective M cone cells), and tritanomaly (defective S cone cells).

In protanomaly, the sensitivity peak of L cones is shifted towards shorter wavelengths (blue-shift), while in deuteranomaly, the sensitivity peak of M cones has a red-shift. Therefore, CVD people cannot distinguish different colors due to the overlap between the spectral sensitivity curves of M and L cone cells. Protans (protanopia and protanomaly) and dotans (deuteranopia and deuteranomaly) are the most common color-blind groups. Protans and dotans are commonly known as red-green color blindness, while tritans (tritanopia and tritanomaly) are classified as blue-yellow color blindness.

Despite much useful research in the field of CVD treatment, including gene therapy, a definitive cure for this disorder has not yet been discovered. However, many assistive eyewear based on color filters, such as tinted glasses and contact lenses, have been developed to help color-blind people. The products and methods that have been studied and investigated to enhance the color perception of CVD patients are tinted glasses, tinted contact lenses, optical filters, optoelectronic glasses, and advanced capabilities that were developed on smartphones and computers. The idea of using color filters to block the overlapping wavelength range of cone-shaped cells was first proposed by Seebeck in 1837 [6]. Seabeck showed that color-blind people can distinguish between different shades of green and red by using red and green filters. These filters block the overlapping wavelength range of red and green cone cells (540-580 nm), so both cone photoreceptors are activated separately depending on the wavelength of incident light.

The current market leader in color-blind glasses is Enchroma, which was first introduced in 2012. These glasses employ a multi-notch filter to block the red and green overlapping wavelength range, and the coloring procedure of Enchroma glasses utilizes the concept of color filter proposed by Seebeck. Further, contact lenses based on chemical dyes were reported for CVD management [7]. Contact lenses use the same physical concept as glasses, utilizing color filters to block overlapping wavelengths of the human color vision spectrum. Various types of chemical dyes were utilized in contact lenses to filter out problematic wavelength ranges, recently rhodamine dyes were used in tinted contact lenses for CVD management [7].

Plasmonic nanostructures have recently been suggested as a potential substitute for chemical dyes to manage color blindness due to their tunable plasmonic resonance properties [8]-[12]. So far, gold and silver nanoparticles have been utilized in various fields such as biomedical imaging, sensing, and drug delivery [13]-[15]. These nanoparticles, depending on their size, can absorb light in different regions of the visible wavelength spectrum. Gold and silver nanoparticles are very efficient in resonant absorption of light due to their excellent properties of localized surface plasmon resonance (LSPR), but the synthesis of plasmonic nanoparticles inside contact lenses is challenging. Recently, plasmonic contact lenses based on gold nanoparticles were investigated to improve red-green CVD [8], [10], [16]-[19]. The performance of the plasmonic contact lenses is based on localized surface plasmon resonance (LSPR) [8], [16], [17], [19] or surface lattice resonance (SLR) [10], [18] and the plasmonic nanostructures embedded in these lenses offer an adjustable color filter to improve various types of CVD.

Among the various types of color blindness, researchers have focused more on improving deuteranopia CVD, which is the most common type of color blindness, while giving less attention to tritanopia color blindness. The research on managing tritanopia color blindness has only been explored in one study, in which Salih *et al.* reported silver nanoparticle-based contact lenses for tritanopia CVD [19]. In this work, the plasmonic glasses based on silver nanoparticles were fabricated using the sputtering technique and proposed for blue-yellow CVD management. Eyeglasses have fewer health regulations in comparison to contact lenses, and the utilization of plasmonic nanoparticles instead of chemical dyes offers numerous benefits such as stability, biocompatibility, environmental compatibility, and adjustability. Further, the antibacterial activity of the proposed plasmonic glasses based on silver nanoparticles was investigated against E. coli and S. aureus bacteria, which have exhibited good antibacterial properties.

II. Experimental Methods

The synthesis of silver nanoparticles (NPs) on a rigid glass substrate faces some challenges due to the rigidity and hardness of the glass substrate. In this research, the sputtering technique was employed to create silver nanoparticles on a glass substrate, and the proposed plasmonic glasses based on Ag NPs were investigated for blue-yellow CVD management.

The microscope slides were utilized as glass substrates, and after the cleaning procedure, the substrates were placed inside a vacuum chamber of a sputtering machine. As shown in Fig. 1(a), the experimental setup consists of a high-voltage direct current (DC) power supply, a vacuum chamber with high voltage and grounded sample holder electrodes, gas feeding, and measurement systems. The sputtering device was equipped with a silver target, and the grade 5 argon gas (Farafan gas, Iran) was injected into the chamber. Afterward, a DC voltage of 300 volts was applied to the target to activate the sputtering process, thereby ejecting the silver atoms from the surface of the target. In reality, the electric field accelerates the argon ions, and the ion bombardment results in the ejection of silver atoms from the target surface. Therefore, the ejected silver atoms will deposit onto the glass substrate and form a collection of nanoparticles. The deposition rate and gas pressure can be adjusted to control the size of the silver nanoclusters formed on a glass substrate.

It should be mentioned that DC sputtering of silver nanoparticles was carried out under the conditions of a DC voltage of 300 V, plasma current of 0.02 mA, chamber pressure of 0.005 mbar, and substrate rotation speed of 28 rpm. A real picture of the fabricated plasmonic glass based on silver NPs is given in Fig. 1(b). As seen, the color of the glass substrate was changed to yellow color, which confirms the formation of Ag nanoparticles onto the glass substrate.

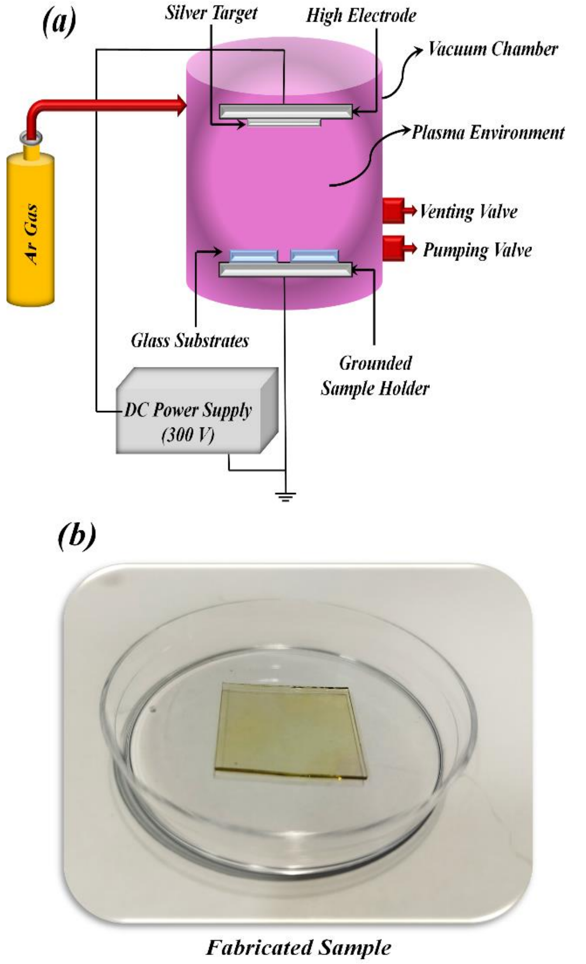

Fig. 1. (a) A schematic array of the DC sputtering mechanism of silver nanoparticles on the glass substrates, and (b) a real picture of the fabricated plasmonic glass based on Ag NPs.

Next, a thin layer of TiO_2 with a thickness of 20 nm was deposited on the fabricated plasmonic glass using the radio frequency (RF) sputtering method. This TiO_2 layer not only acts as a protective layer but can also modify the plasmonic resonance response of the sample for CVD management by changing the refractive index of the surrounding medium of the silver nanoparticles. It is worth noting that RF sputtering deposition of TiO_2 thin film was performed under the process conditions as follows: RF power of 70 W, chamber pressure of 0.004 mbar, and substrate rotation speed of 28 rpm.

In this way, a plasmonic glass based on silver nanoparticles was successfully fabricated and proposed for blue-yellow CVD management. Further, the antibacterial properties of the proposed plasmonic nanostructure based on Ag NPs were investigated, which provides new insights into antibacterial applications in addition to plasmonic glasses for color blindness management.

III. Results and Discussion

To characterize the structure of the silver NPs formed by the sputtering technique, atomic force microscopy (AFM) of the proposed plasmonic glass was performed at different magnifications (Nanosurf EasyScan 2), and the results are given in Fig. 2. As seen, the AFM images confirm the formation of silver nanoparticles on the glass substrate, and the collection of silver nanoparticles was successfully grown on the glass substrate after the sputtering process (Fig. 2(a)). For a closer look, the atomic force microscopy of the proposed plasmonic glass was recorded under higher magnification (Fig. 2(b)), and the results showed the formation of silver nanoclusters with heights ranging from 11 to 100 nm after the sputtering technique.

The real image of the fabricated plasmonic glasses based on silver nanostructure before and after TiO_2 coating is shown in Fig. 3(a). As can be seen, the plasmonic glass before TiO_2 coating shows a yellow color, which indicates the formation of silver nanoparticles on the glass substrate. While the color of the plasmonic glass has changed to gray after TiO_2 coating, the transparency of the glass is still mostly preserved, which makes it suitable for the use of plasmonic glasses for color blindness correction.

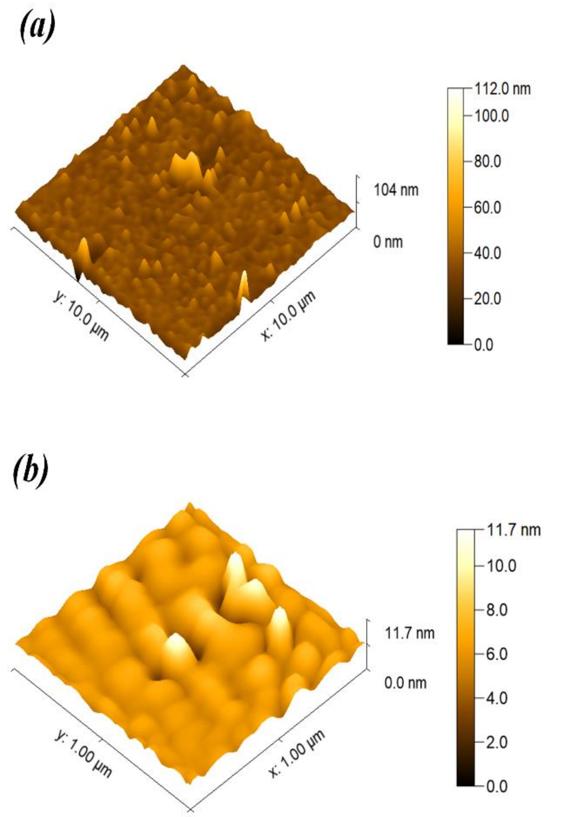

Fig. 2. (a, b) The AFM images of the silver nanoparticles distribution onto the glass substrate at different magnifications.

Absorption and transmission spectra of the proposed plasmonic glasses before and after TiO_2 coating were recorded using a UV-Vis spectrometer (RAYLEIGH UV-2601) as given in Figs. 3(b)-(c). The plasmonic response corresponding to localized surface plasmon resonances (LSPRs) of silver nanoparticles appeared as an absorption peak (or transmission dip) at the wavelength of 425 nm (Figs. 3(b)-(c)), while to improve the tritanopia color blindness, the problematic wavelength range of 450-500 nm must be blocked. Therefore, it is necessary to shift the plasmonic response towards longer wavelengths to improve blue-yellow CVD. To achieve a precise plasmonic response that is appropriate for tritanopia color blindness, a thin layer of TiO_2 with a thickness of 20 nm was deposited onto the plasmonic substrate of silver nanoparticles using the RF sputtering technique. As expected, the plasmonic response shifts to longer wavelengths (red-shift) after TiO_2 coating and covers the problematic wavelength range of tritanopia CVD (Figs. 3(b)-(c)). The TiO_2 thin film can not only modify the plasmonic resonance wavelength by changing the refractive index of the surrounding medium of silver NPs but also can act as a protective layer.

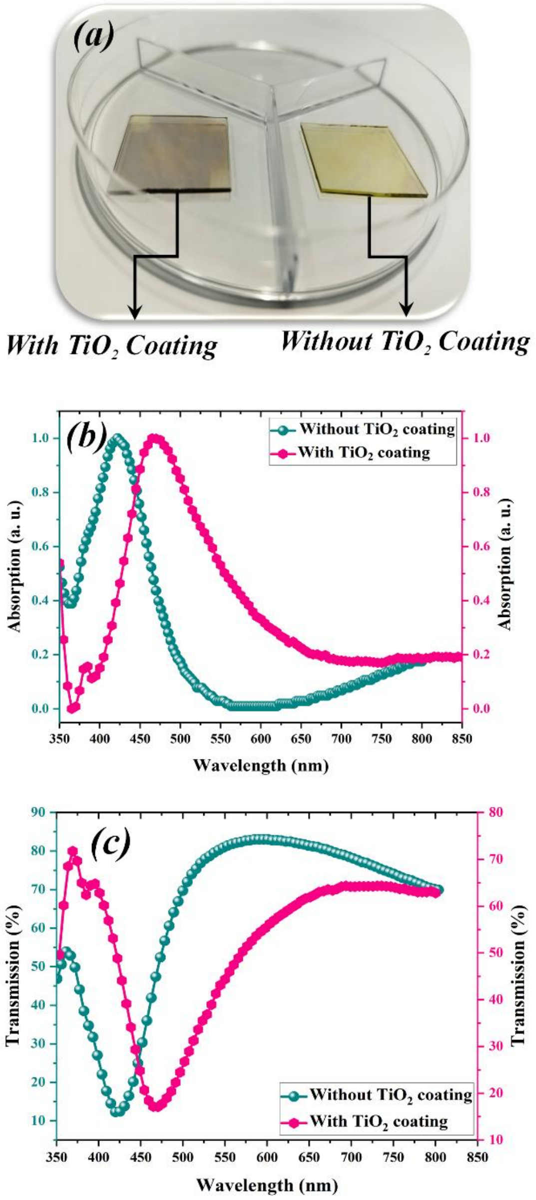

Fig. 3. (a) A real image of the fabricated plasmonic glasses based on Ag NPs before and after TiO_2 coating, the measured (b) absorption, and (c) transmission spectra of the proposed plasmonic glasses for CVD management before and after TiO_2 coating.

For a more accurate evaluation, the transmission spectra of the proposed plasmonic glasses were compared with the silver nanoparticle-loaded contact lenses reported by Salih et. al [19] and commercial Enchroma glasses (Figs. 4(a)-(b)). As seen in Fig. 4(a), the reported silver nanoparticle-based contact lens [19] exhibits a shoulder around the wavelength of about 540 nm, while no such shoulder was observed for the proposed plasmonic glass in this work. The appearance of this shoulder in the spectrum can be attributed to the formation of nanoparticles with larger diameters and a non-uniform distribution inside the contact lens. Here, apart from the main plasmonic peak, no additional peak has been observed, which indicates the uniform distribution of silver nanoparticles onto the glass substrate.

The design of assistive contact lenses or glasses for CVD management needs to take into account the wavelength location of the dip, which should be customized for the problematic wavelength range associated with each type of color blindness. Moreover, the transmission value within the problematic wavelengths also holds significance. Our proposed plasmonic glass has a red shift compared to the reported silver NPs-loaded contact lens (Silver 40) [19], which blocks the problematic wavelength region more precisely (Fig. 4(b)). Additionally, the transmission value at the problematic wavelength was reduced from 48% to 17% compared to the reported contact lens (Silver 40) [19], which confirms the better performance of the proposed silver NPs-based glass for CVD management. The proposed plasmonic glass also exhibits a better blocking rate at the problematic wavelength's center when compared to the reported contact lens (Silver 60) by Salih *et al.* (Fig. 4(b)).

Further, the transmission spectra of the fabricated plasmonic glasses were compared with the commercial Enchroma glasses (Fig. 4(b)). It is worth mentioning that Enchroma is a prominent manufacturer of eyeglasses specifically designed for color-blind people. As seen in Fig. 4(b), the Enchroma eyeglass exhibits two distinct dips in its transmission spectrum at the wavelengths of 477 and 595 nm, which can be utilized to help patients with tritanopia and deuteranopia CVD, respectively. The second transmission dip at λ=595 nm was applied to enhance color perception for red-green CVD, which was not investigated in this study. This work specifically considered the tritanopia (blue−yellow) color vision deficiency. The proposed plasmonic glass shows a lower transmission value at the problematic wavelength (17%) compared to commercial Enchroma glasses (49%) (Fig. 4(b)).

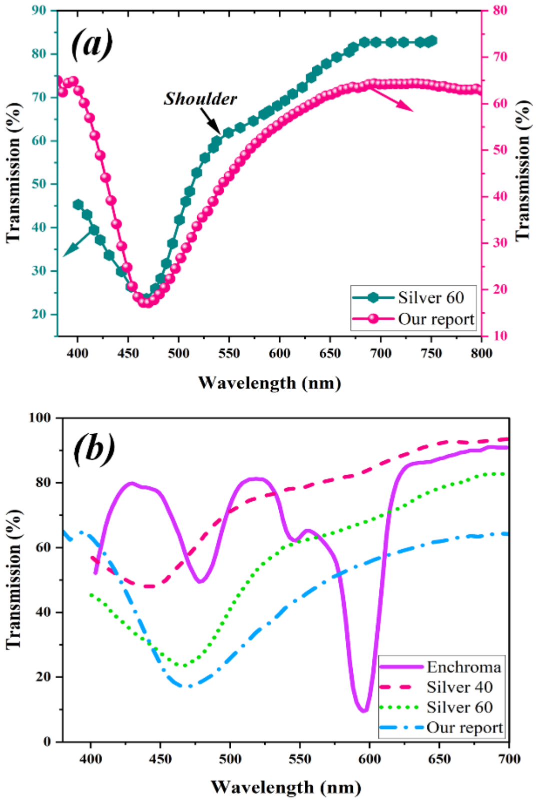

Fig. 4. (a) transmission spectra of the proposed plasmonic glasses in comparison with the transmission spectra of the reported plasmonic contact lens based on silver NPs [19], and (b) transmission spectra of the fabricated plasmonic glasses in comparison with the commercial Enchroma glasses, and plasmonic contact lenses based on Ag NPs [19].

Next, the antibacterial activity of the proposed plasmonic glasses based on silver nanoparticles was investigated against E. coli and S. aureus bacteria. These bacteria were selected due to their prevalence as ocular bacteria. Bacteria were cultured with a concentration of 0.5 McFarland on a solid culture medium and plasmonic glasses were placed onto the culture medium from the side of silver nanoparticles. The antibacterial test was investigated for plasmonic glasses before (S4, S5) and after TiO_2 coating (S3, S7), and the samples were incubated at a temperature of 37 degrees for a duration of 1 day. It should be noted that each of the fabricated plasmonic glass (with and without TiO_2 coating) is divided into four segments and positioned in various regions of the culture medium containing E. coli and S. aureus bacteria (marked areas in Fig. 5). After 24 hours, the plates containing the samples were observed under light and the results are given in Fig. 5. As can be seen, for both Ag NPs-based glasses before and after TiO_2 coating, the regions of the bacteria plate that were in direct contact with the plasmonic glass were completely cleaned and free of bacteria. While the areas of the plate that did not come into contact with the silver nanoparticles witnessed the growth of bacteria.

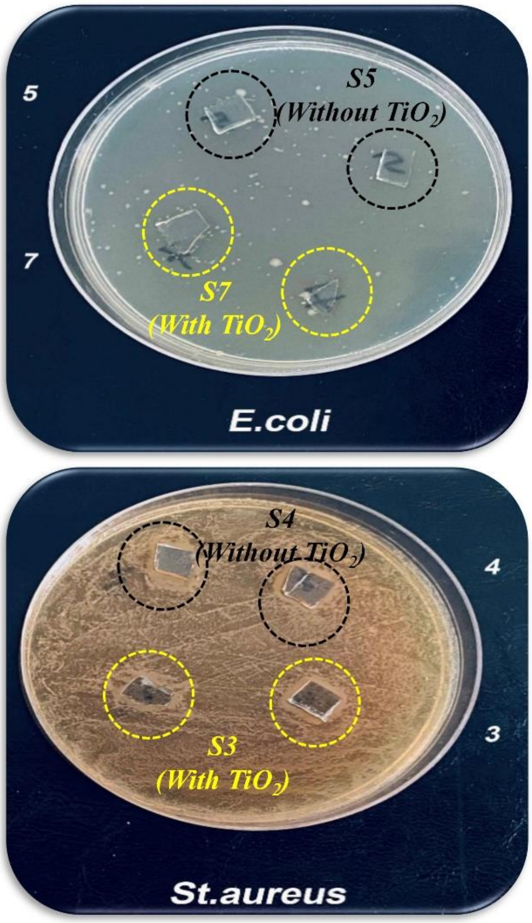

Fig. 5. Investigating the antibacterial activity of the proposed plasmonic glasses against E. coli and S. aureus bacteria. (Samples 4 and 5 are related to plasmonic glass before TiO_2 coating and samples 3 and 7 correspond to plasmonic glass after TiO_2 coating).

Titanium dioxide (TiO_2) stands out as a material with excellent biocompatibility and significant antibacterial properties, making it suitable for various biomedical and biosensing applications [20]-[25]. Its ability to facilitate cell growth while simultaneously combating bacterial infections establishes it as a valuable component in developing safer and more effective medical devices and treatments. The deposition of TiO_2 can influence the antibacterial properties of Ag nanoparticles, and the combination of TiO_2 and Ag nanoparticles can create a synergistic effect and enhance the antibacterial activity. TiO_2 can generate reactive oxygen species (ROS) under UV light, which can enhance the antibacterial effects of Ag nanoparticles. When TiO_2 is combined with Ag nanoparticles, it can enhance the production of ROS, leading to increased bacterial cell damage. Also, the presence of TiO_2 may aid in the controlled release of Ag ions, and prolong their antibacterial action. This capability is particularly beneficial for applications such as coatings or wound dressings [26]-[28]. Further, the interaction between TiO_2 and Ag nanoparticles can affect their surface properties, potentially enhancing their ability to adhere to bacterial cells and disrupt their membranes. Overall, the combination of TiO_2 and Ag nanoparticles can lead to enhanced antibacterial properties compared to either material alone, making them useful in various biomedical and environmental applications.

It can be concluded that the proposed plasmonic glasses based on silver nanoparticles offers good antibacterial activity in addition to the management of tritanopia color blindness. Further, the suggested plasmonic glass, which incorporates plasmonic nanoparticles, exhibits a higher selectivity than commercial Enchroma glasses. This is primarily due to the ability to modify and adjust the plasmonic properties of silver NPs by manipulating their morphology.

IV. CONCLUSION

The current research has proposed and fabricated plasmonic glasses based on silver nanoparticles using sputtering technique and investigated them for tritanopia CVD management. A thin coating of TiO2 is applied to tune the plasmonic response of silver nanoparticles, and in addition to adjusting the plasmonic response, this thin layer also acts as a protective layer. The performance of the proposed glass is based on the LSPR properties of silver nanoparticles, and silver nanoparticles on the glass substrate offer a good filter to improve tritanopia color blindness. Finally, the antibacterial properties of glasses based on plasmonic nanostructures have been investigated, and the results confirm their good antibacterial properties against E. coli and S. aureus bacteria. In addition to managing blue-yellow color blindness, the proposed plasmonic glasses can also provide new insights into antibacterial applications.

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