Bimetallic Implanted Plasmonic Photoanodes for TiO₂ Sensitized Third Generation Solar Cells

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An auspicious way to enhance the power conversion efficiency (PCE) of third generation sensitized solar cells is to improve the light harvesting ability of TiO₂ sensitizer and inhibition of back recombination reactions. In the present work, we have simultaneously comprehended both the factors using stable bimetallic Au and Ag metal nanoparticles (Mnps) embedded in TiO₂ with ion implantation technique at lower fluence range; and explored them in third generation dye sensitized solar cells (DSSCs). The best performing Au-Ag implanted DSSC (fluence $6 \times 10^{15}$ ions cm$^{-2}$) revealed 87.97% enhancement in its PCE relative to unimplanted DSSC; due to plasmon induced optical and electrical effects of Mnps. Here, optimized bimetallic Au-Ag Mnps embedded in TiO₂ improves light harvesting of N719 dye; due to the well matched localized surface plasmon resonance (LSPR) absorption band of Au and Ag with low and high energy absorption bands of N719 dye molecules, respectively. Furthermore, Au and Ag acts as charge separation centers in TiO₂ that inhibit the recombination reactions occurring at photoanode/electrolyte interface via prolonging photo-generated electron lifetime; resulting in efficient inter-facial charge transportation in DSSCs.

In last decade, third generation sensitized solar cells have achieved tremendous consideration out of authoritative traditional silicon based photovoltaic technology in tandem cell configuration; owing to their low manufacturing cost, non-toxic nature and undeniable higher theoretical limit of power conversion efficiencies (PCE)1–3. Sensitizer plays a key role in third generation sensitized solar cells; thus should exhibit phenomenal properties like high chemical and thermal stability, high photo-catalytic activity, low-cost, high redox ability, strong absorption coefficient, biocompatibility, high specific surface area, non-toxicity, and recyclability4. TiO₂, an extrinsic n-type semiconductor, fulfills all the requirements and hence widely studied as sensitizer in third generation photovoltaic devices constituting quantum dot sensitized solar cells, dye sensitized solar cells (DSSCs), and perovskite sensitized solar cells5. However, TiO₂ appears to undergo some limitations such as random charge transportation occurring due to trapping and detrapping of photo-generated electrons in its trap levels resulting in recombination losses and light absorption confined only in UV region of solar spectrum; hence requires some modifications which can be done via incorporating different shape, size and dimensions of TiO₂, metal oxides, metal nanoparticles (Mnps), hybridized carbon materials, and coupling with semi-conducting materials6–10. Among them, inclusion of Mnps such as gold (Au) and silver (Ag) induce plasmonic optical and electrical effects in TiO₂, due to their unique localized surface plasmon resonance (LSPR) property; which effectively strengthens their light absorption and charge transportation ability and ultimately improves the PCE of sensitized third generation solar cells11–13.

Recently, we observed that the single crystalline spherical shaped Ag nps incorporated in TiO₂ via chemical reduction method, effectively improves the absorption cross-section of dye sensitizer14. Moreover, the inclusion of different single crystalline anisotropic shapes of Ag nps in TiO₂ results in improved light harvesting ability of TiO₂ as they exhibit multiple LSPR bands in the broadened region of solar spectrum ranging from 380–900 nm15. Although, bare Mnps significantly improves the light harvesting ability of TiO₂ via enhancing the absorption cross-section of dye sensitizer; they become unstable coming in contact with liquid based electrolytes and gets corroded.

Xu et al. demonstrated the utilization of Au-Ag alloy popcorn shaped core-shell nanoparticles in TiO₂ to broaden the light absorption range via using efficient excitation of LSPR modes on the popcorn nanoparticles16. However, core-shell structures improved the stability of Mnps in liquid electrolytes, but suffered from their unpronounced LSPR effect on light harvesting ability of TiO₂.

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Furthermore, ion implantation have been observed to be practically quite effective technique to embed Mnps in TiO2, which helped in resolving both the instability and unpronounced LSPR issues of bare and core-shell structures, respectively. Recently, we have explored the ion implantation method to implant Au Mnps in TiO2 and employ them as photoanodes in third generation DSSCs. The optimized Au implanting fluence provides balancing effect of LSPR of Au and effective adsorption area of TiO2 for N719 dye in DSSCs; and showed an enhancement of 44.7% in its PCE relative to unimplanted TiO2 based DSSCs. Similarly, Ag Mnps implantation in TiO2 showed 65.3% enhancement in PCE of DSSCs. However, their increment is not a match for its economical utilization; since efficient light harvesting in Au as well as Ag implanted DSSCs is only around single LSPR absorption wavelength; resulting in unsatisfactory PCEs.

In order to further enhance the light harvesting ability of TiO2 within the whole visible region of solar spectrum, Kim et al. demonstrated the efficient energy matching between the absorption bands of N719 dye and Au and Ag Mnps; resulting in relatively enhanced PCE of double layered plasmonic DSSCs by 19.12%. Wang et al. introduced the plasmonic cooperation of Au and Ag Mnps in TiO2 photoanodes of DSSCs using chemical reduction method and achieved 20.8% PCE enhancement; by exploiting the strong plasmonic cooperation effects due to the complementary light absorption of both the Au and Ag Mnps via their respective LSPR absorptions at ~550 and 400 nm. Yun et al. demonstrated the incorporation of core shell Au@Ag Mnps in TiO2 hollow spheres leading to synergetic effects of improved light harvesting and widening of absorption band, appearing due to effective light scattering effects of core-shells; which raised the PCE by 25%. Dong et al. proclaimed 40% increment in PCE of DSSCs comprising Ag-encapsulated Au nanorods prompting enhanced light harvesting and efficient one dimensional charge transportation. Al-Awazi et al. showed the optimal concentration of Au-Ag alloys (4:1) introduced into TiO2 via pulsed laser ablation, emanating PCE by 52.1%; arising from the broader optical absorption of dye molecule. Au and Ag Mnps generating larger number of photo-generated charge carriers. A seed mediated growth of Ag shells on Au Mnps incorporated in TiO2 photoanodes have been investigated by Salimi and his co-workers, and noted 125% enhancement in PCE of DSSCs due to their prominent light absorption as well as enhanced inter-facial charge transportation through Mnps minimizing the charge recombination processes. Till now, maximum 230% enhancement in PCE of DSSCs, having modified TiO2 photoanodes with Au-Ag nanocomposites, have been achieved by Lim et al. that originates from LSPR synergistic interactions between Au and Ag Mnps resulting in the improved light harvesting; and efficient separation and transportation processes.

Above reported literature mentioned the simultaneous inclusion of Au and Ag Mnps in photoanodes of DSSCs using chemical methods, and their PCEs enhancement is not at par with the theoretical maximum value; resulting from the uncontrolled growth and concentration of Mnps which leads to their non-linear conglomerations in TiO2; hence deteriorating their long term stability and sustainability. In this direction, we have investigated the use of ion implantation technique to embed Au and Ag Mnps inside TiO2 semiconductor of DSSCs; resulting in efficient enhancement in the PCE of highly stable plasmonic DSSCs via extending the region of light harvesting within UV-Vis-NIR, by utilizing LSPR absorptions of Au and Ag Mnps as well as improving the charge transfer processes by reducing recombination rate of photo-generated charge carriers, owing to their charge storage ability.

**Results and Discussion**

**Concept visualization.** Bimetallic Au and Ag implantation in TiO2 will significantly improve its light harvesting ability and inhibit back recombination reactions, resulting in better electron transportation; that positively influences the photovoltaic performance of DSSCs. Figure 1 represents the schematics of electron transportation processes occurring in DSSCs using bimetallic Au-Ag implanted TiO2 photoanodes. When light falls on the photoanode of DSSCs, enormous photo-generated electrons are produced from excited N719 dye molecules, especially from the ones present in the vicinity of Au and Ag Mnps. Rapid accumulation of photo-generated electrons on Au and Ag Mnps takes place due to their charge storage ability (Fig. 1(1)); which in turn induces an upward shift in the Fermi energy level ($E_F$) of photoanode; resulting in efficient transportation of accumulated photo-generated electrons to the conduction band (C.B.) of TiO2 (Fig. 1(2)). Moreover, the trap levels of TiO2 are filled by the electrons generated from the plasmonically excited Au and Ag Mnps, which reduces the random charge distribution of photo-generated electrons in TiO2; hence inhibits the recombination reactions occurring at photoanode/ electrolyte interface (Fig. 1(3)). Further, the photo-generated electrons from the C.B. of TiO2 get transported to the external circuit via TiO2, compact layer deposited FTO and are collected at Pt CE. Thus, Au and Ag Mnps in TiO2 would efficiently enhance the charge transportation processes throughout DSSC via elongating electron lifetime as well as transport path length. The above mentioned concept exhibiting higher light harvesting ability as well as better charge transportation processes in bimetallic Au and Ag implanted photoanode based DSSCs has been fully supported by the underlying investigations.

**Structural and Optical characterization of photoanodes.** XRD diffraction patterns of unimplanted and Au-Ag implanted TiO2 on FTO substrates are depicted in Fig. 2. TiO2 exists in both the anatase (A) and rutile (R) phase with peaks appearing at 26.08°, 27.22°, 38.42°, 48.66°, 54.96°, 64.48°, and 66.18° Bragg’s angle relating to (110)-R, (110)-A, (004)-A, (200)-A, (211)-A, (116)-A, and (204)-A crystal planes, respectively (ICPDS Card No. 21–1272 and 04-0551). In case of Au-Ag implantation in TiO2, two new crystal planes (200) and (311) at 44.04° and 77.58° Bragg’s angle, respectively appeared along with slight increase in the intensity of (004), (211), and (116) plane of TiO2; which is due to the overlapping of Au, Ag and TiO2 crystal planes; as they exhibit very similar lattice constants that further confirms their metallic face centered cubic crystal structure (ICPDS Card No. 04-0784 for Au and 04-0783 for Ag). The peak intensities with overlapped Au, Ag and TiO2 crystal planes enhanced initially with increasing Au-Ag implantation fluence, that results in the formation of large number of metal nanoparticles (Mnps); but then suddenly decreases which is due to the suppression of TiO2 planes as they
get covered with Au and Ag Mnp as well as thin TiO₂ melt. Thus, the crystallinity of Au-Ag implanted TiO₂ increases particularly along (200) and (311) crystal planes; leading to better charge carrier mobility which is necessity for improved DSSCs.

The elemental composition as well as chemical state of unimplanted and Au-Ag implanted TiO₂ at varying fluence are analyzed from the XPS survey spectra demonstrated in Fig. 3; which shows four peaks of Ti-2p, O-1s, Au-4f and Ag-3d elements. The high resolution Ti-2p spectra of TiO₂, present in all the samples (Fig. 4); exhibited two peaks centered at binding energies 458.3 and 464.3 eV corresponding to Ti-2P3/2 and Ti-2P1/2, respectively; which indicates the presence of Ti⁴⁺ oxidation state.⁵ O-1s peak observed at binding energy 529.9 eV corresponds to the lattice oxygen atoms (O²⁻) in the TiO₂; present in the form of oxides, −COO⁻ and >C=O in each sample (Fig. 5). No significant change in the binding energies of Ti-2P3/2, Ti-2P1/2 and O-1s is observed in Au-Ag implanted TiO₂, which is a clear manifestation of unaffected nano-crystalline structure of TiO₂.

After the implantation of Au-Ag in TiO₂; very weak Au and Ag peaks present in Au 4f₇/₂, Au 4f₅/₂ and Ag-3d₅/₂, Ag-3d₃/₂ states appeared at binding energies 83.3, 87.0 eV (Fig. 6) and 367.0, 373.0 eV (Fig. 7), respectively; whose intensity increases with increasing fluence and becomes measurable at A4 and A5 samples. The difference between two states of Au (~3.7 eV) and Ag (~6.0 eV) clearly suggests their presence in zero valent metallic state i.e. Au⁰ and Ag⁰.⁶ Moreover, the binding energies of Au-4f₅/₂ and Ag-3d₅/₂ are slightly smaller than their metallic state; which arises due to the electron transfer processes taking place from TiO₂ to Au and Ag Mnp. The immeasurable Ag and Au atomic %age in A1, A2 and A3 samples indicates Au and Ag content lesser than the 0.5 atomic %age; which is confirmed through decreasing Ti element content. The atomic %age of Ti-2P₃/₂, Ti-2P₁/₂, O-1s, Au-4f₅/₂, Au-4f₇/₂, Ag-3d₅/₂ and Ag-3d₃/₂ elements are summarized in Table 1; showing an increased atomic %age of Ag and Au as well as decreased content of Ti with increased fluence in TiO₂.

The FESEM images demonstrating the existence of Au and Ag Mnp embedded in TiO₂ via modifying their surface morphology are depicted in Fig. 8. TiO₂ surface depicts unequal as well as inter-connected nano-pores morphology; which gets flattened with Au-Ag implantation and the flattening increases with increasing fluence; along with the increasing pore size distribution.⁷ The uniform embedment of Au-Ag Mnp over flattened surface has been observed at Au-Ag implanted TiO₂ and their number increases with increasing fluence.

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**Figure 1.** Proposed concept visualization. Schematic diagram of bimetallic Au and Ag implanted plasmonic DSSC.
The UV-visible absorption spectra of TiO₂ and Au-Ag embedded TiO₂ at different fluence are depicted in Fig. 9(A). TiO₂ represents prominent absorption around 310 nm arising due to their intrinsic electronic excitation; with negligible absorption in the visible region of solar spectrum. The range of absorption has been observed to be extended to the visible light region with the implantation of Au and Ag Mnps in TiO₂; attributable to the characteristic LSPR absorption peak of Au and Ag lying around 530 nm and 400 nm, respectively stimulated by optical excitation. Also, the LSPR phenomenon of Au and Ag Mnps enhances the absorbance of TiO₂ in UV region. The absorbance peak shows a continuous increase with increased fluence up to A3; then a sudden decrement is observed along with the sharp decrease in TiO₂ absorbance around 310 nm. It is related to the excessive flattening of TiO₂ surface that reduces its absorption cross-sectional area; which is in consonance with FESEM images.

Similar trend has been observed in the absorbance spectra of N719 dye loaded TiO₂, A1, A2, A3, A4 and A5 photoanodes and is shown in Fig. 9(B). After dye loading, TiO₂ photoanode exhibited strong absorption peaks centered at 400 and 530 nm; which corresponds to the metal to ligand charge transfer interactions within N719 dye molecules. Higher absorbance around 400 nm is due to the merged absorption peaks of TiO₂ as well as dye molecules. Broad absorption region extending from UV to NIR light region (300–750 nm) has been observed with the Au-Ag implantation; which is attributed to the synergistic effects of LSPR peaks at 400 and 530 nm associated with Ag and Au Mnps, respectively; that efficiently interacts with dipole moment of dye molecules within a certain minimal spatial range.

The relative change in the absorbance of different Au-Ag implantation fluence based TiO₂ photoanodes with respect to unimplanted TiO₂ (Fig. 10(A)) for understanding their effective contribution in absorption enhancement in the entire wavelength range; has been estimated from Eq. (1) [25];

$$\frac{\Delta A}{A} = \frac{A_{TiO₂, N719, Au/Ag Mnps}(\lambda) - A_{TiO₂, N719}(\lambda)}{A_{TiO₂, N719}(\lambda)}$$

where, $A_{TiO₂, N719, Au/Ag Mnps}(\lambda)$ is the absorbance of dye loaded Au-Ag implanted TiO₂ photoanodes and $A_{TiO₂, N719}(\lambda)$ represents the absorbance of unimplanted dye loaded TiO₂ photoanodes. It confirmed the continuous enhancement in the relative absorbance up to A3 photoanode, which reflects the sole contribution of Au-Ag Mnps embedment in improving the light harvesting ability of TiO₂ photoanodes. Although Au and Ag synergistically affect optical absorption of TiO₂ photoanodes, the parallel decrease in the amount of dye loading starts to dominate at higher fluence; that leads to smaller relative absorbance change. Figure 10(B) depicts the dye
desorption spectra of all the prepared photoanodes which shows absorbance peak around 400 and 530 nm related to N719 dye. The amount of dye loaded on the photoanodes can be estimated from Eq. (2) \[ \text{Dye Loading (molecules cm}^{-2}\] = \[\frac{[\text{Dye Concentration (in M) } \times \text{ Volume (ml)}]}{\text{Electrode Area (cm}^2)} \] where, dye concentration is calculated using Beer Lambert’s law at absorbance value around 535 nm, 10 ml volume is taken and effective area is 0.25 cm\(^2\). The variation of dye loading for TiO\(_2\), A1, A2, A3, A4 and A5 photoanodes, respectively shown in the inset of Fig. 10(B); suggests that at lower fluence, the dye loading is almost similar but at A4 and A5 fluence it is considerably small; hence confirming lower relative absorbance change in them. Hence, the plasmonic optical effects of Au and Ag Mnps optimally influence the light harvesting ability of TiO\(_2\) at A3 fluence based photoanode.

**Photovoltaic characteristics of DSSCs.** Unimplanted and Au-Ag implanted TiO\(_2\) films are used as photoanodes in the fabrication of DSSCs to test their photovoltaic performance under 1 sun illumination conditions (Intensity 100 mW cm\(^{-2}\)). The photo-current density – voltage (J-V) curves of various DSSCs are shown in Fig. 11; and the obtained short circuit current-density (J\(_{SC}\)), open circuit voltage (V\(_{OC}\)), fill factor (FF) and PCE are tabulated in Table 2. PCE of Au-Ag implanted DSSCs are observed to be higher (A1 (4.69%), A2 (5.49%), A3 (6.56%), A4 (4.18%) and A5 (3.95%)) in comparison to unimplanted DSSC (3.49%); which is due to the enhanced...
J_{SC}, V_{OC}, and FF values. Momentous enhancement in J_{SC} of implanted DSSCs (A1 (10.26), A2 (11.90), A3 (14.75), A4 (9.59), and A5 (9.09) mA cm\(^{-2}\)) relative to unimplanted DSSC (8.78 mA cm\(^{-2}\)) originates not only from the enhanced light harvesting ability of TiO\(_2\), generating enormous amount of photo-excited electrons; but also from the plasmonic electrical effects induced by Au and Ag Mnps embedded in TiO\(_2\) photoanodes. The plasmonically excited Mnps also generate hot charge carriers i.e. electrons and fill the trap levels of TiO\(_2\), which helps in reducing the charge extraction barrier at C.B. of TiO\(_2\) and LUMO level of dye interface that stimulates the transfer of photo-generated electrons to the C.B. of TiO\(_2\); hence contributes to the enhanced J_{SC} values in plasmonic DSSCs. Furthermore, Au and Ag Mnps accumulate photo-generated electrons from dye molecules that eventually leads to the upward shifting of Fermi energy level (E_F) of TiO\(_2\); and has been investigated from Kelvin-Probe work function (\(\phi\)) measurements shown in Fig. 12. It has been observed that \(\phi\) values decreases in Au-Ag implanted TiO\(_2\) relative to unimplanted TiO\(_2\). Since, \(\phi\) is defined as the difference between vacuum energy (EV) and EF level; and EV is constant, EF shifts towards C.B. of TiO\(_2\) photoanode; which, further is an indication of increased V_{OC} of implanted TiO\(_2\) based DSSCs (A1 (0.66 V), A2 (0.67 V), A3 (0.68 V), A4 (0.65 V) and A4 (0.65 V)) than unimplanted DSSC (0.63 V), as V_{OC} is the difference of E_F and redox potential of electrolyte; resulting in higher F.F. values. Moreover, it has been observed that PCE, J_{SC}, V_{OC} and F.F. suddenly decreases at A4 and A5 based DSSC; due to the combined effect of lesser dye loading, generating lesser photo-generated charge carriers as well as higher recombination rate as Au and Ag start acting as charge recombination centers, preventing their transportation to TiO\(_2\) C.B. The variations in the photovoltaic parameters of the fabricated DSSCs are presented in Fig. 13. Hence, A3 based DSSC exhibited highest PCE with an augmentation of 87.97% in comparison to the unimplanted DSSCs.

The increased J_{SC} and V_{OC} via upward shifting of E_F level due to photo-generated electrons accumulation at Mnps supports the reduction in recombination rate of photo-generated charge carriers in Au-Ag implanted TiO\(_2\) photoanodes and is demonstrated by recording PL emission spectra. Since, PL emission arises due to the photons emitted during the recombination of photo-generated electron-hole pairs; offering lesser recombination rate for lower PL intensity. Figure 14 shows broad emissions around 330–550 nm in all the photoanodes; attributable to transitions involving singly ionized oxygen vacancies present in TiO\(_2\). A significant decrease is observed in PL intensity of Au-Ag implanted photoanodes; which further decreases with increased fluence up to A3 photoanodes; suggesting effective suppression of recombination rate, as now the photo-generated electrons gets stored at Au and Ag Mnps and hence prolongs the electron lifetime at photoanode, which is later confirmed through EIS.
Figure 5. Oxygen composition. High resolution O-1s XPS spectra of unimplanted and Au-Ag implanted TiO$_2$ at varying fluence (A1–A5).

Figure 6. Au composition. High resolution Au-4f XPS spectra of Au-Ag implanted TiO$_2$ at varying fluence (A1–A5).
measurements. A slight increase at A4 and A5 photoanodes arises due to the agglomeration of Au and Ag in TiO₂ letting them act as charge recombination centers.

Figure 15 depicts the Nyquist plots fitted with equivalent circuit model, measured for the unimplanted and Au-Ag implanted DSSCs; to understand their interfacial charge transfer mechanism. It exhibited two semicircles; at higher frequency fitted to resistance offered by reduction reactions at C.E./electrolyte interface (R₁); and at intermediate frequency fitted to the charge transfer process at photoanode/electrolyte interface given by charge transfer resistance (R₂) and charge transfer capacitance (C) along with a constant phase element (Q). The intercept along X-axis of high frequency semicircle represents equivalent series resistance (Rₛ) having the contribution of FTO, unimplanted and Au-Ag implanted TiO₂, Pt CE, and electrolyte of DSSCs; which slightly increases with increasing fluence of Au-Ag Mnps in TiO₂ owing to the additional resistance induced by Au and Ag Mnps relative to unimplanted DSSC. R₁ is observed to be analogous in all the fabricated DSSCs; because of the usage of same type of Pt CE in them. Substantial increase in R₂ values is noticed with the embedment of Au-Ag in TiO₂ based DSSCs; with continuous increment for increasing fluence from A1 to A5. It is referred to the hot carrier generation and charge storage ability of Au and Ag Mnps; that lead to decrease in the recombination rate of photo-generated charge carriers; resulting in increasing the electron lifetime at photoanode as well as its transport path length, which leads to efficient charge transportation in DSSCs.

The electron lifetime calculations at TiO₂ for all the fabricated DSSCs are investigated through Bode plots (Fig. 16(A)). Fabricated DSSCs exhibited a characteristic frequency maxima, indicating the transient processes occurring at photoanode/electrolyte interface, which shifts towards the lower frequency region with increasing Au-Ag embedment in TiO₂; resulting in longer electron lifetime (τ) calculated from the Eq. (3);

![Figure 7. Ag composition. High resolution Ag-3d XPS spectra of Au-Ag implanted TiO₂ at varying fluence (A1–A5).](image)

| Sample | Atomic %age of Ti | Atomic %age of O | Atomic %age of Au | Atomic %age of Ag |
|--------|------------------|-----------------|------------------|------------------|
| TiO₂   | 44.84            | 55.15           | —                | —                |
| A1     | 44.84            | 55.15           | —                | —                |
| A2     | 41.90            | 58.10           | —                | —                |
| A3     | 34.67            | 65.32           | —                | —                |
| A4     | 27.35            | 39.38           | 19.68            | 13.7             |
| A5     | 6.92             | 66.87           | 10.43            | 15.7             |

**Table 1.** Elemental composition. Atomic %age composition of Ti, O, Au and Ag elements present in unimplanted and Au-Ag implanted TiO₂.
Figure 8. Morphology of TiO₂. FESEM images of unimplanted and Au–Ag implanted TiO₂ at varying fluence (A1–A5).

Figure 9. Absorption spectra. UV-Vis absorption spectra of (A) without and (B) with N719 dye loaded unimplanted and Au–Ag implanted TiO₂ photoanodes at varying fluence (A1–A5).
where, $f_{\text{max}}$ is the frequency maxima corresponding to phase shift peak in Bode plots. Moreover, the elongated electron lifetime at photoanode further confirmed the increase in their transport path length. Further, the value of capacitance ($C$) at C.B. of TiO$_2$ are measured from the expression, $C = \frac{\tau}{2\pi f_{\text{max}}}$, which indicates the increased charge storage ability of Au-Ag implanted DSSCs and this capacity enhances with increased fluence of Au-Ag Mnp's, as the photo-generated electrons get accumulated on them. Figure 16(B) shows the variation of $\tau$ and $C$ with the different fluence of Au-Ag implantation on TiO$_2$ based DSSCs. The EIS parameters such as $R_s$, $R_2$, $C$, and $\tau$ for all the fabricated DSSCs are tabulated in Table 3. Although, Au-Ag embedment in TiO$_2$ facilitates the charge transportation in DSSCs via reducing the recombination, enhancing the electron lifetime as well as charge storage

Figure 10. Relative absorbance change and dye deloading spectra. (A) Relative absorbance change in the Au-Ag implanted TiO$_2$ photoanodes w.r.t. unimplanted TiO$_2$ and (B) UV-Vis absorption spectra of N719 dye deloaded from different photoanodes (inset – represents the variation of amount of dye loading at different photoanodes).

Figure 11. Device performances. Current-density – Voltage (J-V) curves of unimplanted and Au-Ag implanted TiO$_2$ at varying fluence (A1–A5).

Table 2. Photovoltaic and Work function parameters. Photovoltaic and work function parameters of unimplanted and Au-Ag implanted TiO$_2$ photoanodes at varying fluence based DSSCs.

| Sample Name | $J_{\text{SC}}$ (mA cm$^{-2}$) | $V_{\text{OC}}$ (V) | PCE (%) | FF | $\varphi$ (eV) |
|-------------|-------------------------------|--------------------|---------|----|---------------|
| TiO$_2$     | 8.78                          | 0.63               | 3.49    | 0.63| 5.49          |
| A1          | 10.26                         | 0.66               | 4.69    | 0.68| 5.07          |
| A2          | 11.90                         | 0.67               | 5.49    | 0.68| 4.92          |
| A3          | 14.75                         | 0.68               | 6.56    | 0.65| 4.82          |
| A4          | 9.59                          | 0.65               | 4.18    | 0.67| 4.73          |
| A5          | 9.09                          | 0.65               | 3.95    | 0.67| 4.46          |
Figure 12. Work function measurements. Kelvin Probe work function images of unimplanted and Au-Ag implanted TiO₂ at varying fluence (A1–A5).

Figure 13. Variation in photovoltaic parameters. Variation of photo-voltaic parameters with different implantation fluence based photoanodes of DSSCs.
ability; even at highest fluence (A5 based DSSC), still its PCE value is lower which confirmed the sole effect of lower dye loading.

Furthermore, A3 based DSSC exhibiting highest PCE, has been tested for photo-voltaic performance after an interval of 5 days for overall 40 days. Figure 17 shows a slight decrease in the PCE of A3 DSSC within initial days and then becomes negligibly constant; which indicates the long-term stability of Au and Ag Mnps in TiO2 protected with thin TiO2 melt from corrosion; hence representing long run durability of Au-Ag implanted DSSC.

Figure 14. Emission spectra. PL emission spectra of unimplanted and Au-Ag implanted TiO2 at varying fluence (A1–A5).

Figure 15. EIS characteristics. Nyquist plots obtained for unimplanted TiO2 and Au-Ag implanted TiO2 based DSSCs at different fluence (A1-A5) and fitted with equivalent circuit model $R_s + C/[R_1 + Q/R_2]$.

Figure 16. Bode plots, electron lifetime and capacitance calculations. (A) Bode plots obtained for unimplanted TiO2 and Au-Ag implanted TiO2 based DSSCs at varying fluence (A1-A5) and (B) Variation of electron lifetime ($\tau$) and capacitance (C) with different photoanodes based DSSCs.
Hence, optimized fluence representing maximum PCE enhancement of highly stable DSSC by 87.97%, due to balanced synergistic interactions involving plasmonic optical and electrical effects of Au and Ag Mnps, is $6 \times 10^{15}$ ions cm$^{-2}$.

**Conclusions**

In conclusion, we were able to successfully optimize the bimetallic Au-Ag implantation in TiO$_2$ photoanodes for the fabrication of highly efficient third generation DSSCs. Significant enhancement of 87.97% in PCE was achieved for Au-Ag implanted DSSC (Fluence - $6 \times 10^{15}$ ions cm$^{-2}$) with $J_{SC}$ and $V_{OC}$ of $14.75$ mA cm$^{-2}$ and $0.68$ V, respectively in comparison to unimplanted DSSC ($J_{SC} = 8.78$ mA cm$^{-2}$, $V_{OC} = 0.63$ V and PCE = 3.49%). It is attributed to (i) the enhanced and broadened absorbance of N719 dye sensitizer via simultaneous LSPR property of Au and Ag Mnps along with the hot carrier generation, which improves the light harvesting ability of TiO$_2$ photoanodes; (ii) the reduced recombination reaction rate as Au and Ag Mnps in TiO$_2$ exhibits charge storage ability, leading to increased charge transfer resistances at photoanode/electrolyte interface; (iii) improved interfacial charge carrier transfer processes via increased charge storage capacitance as well as photo-generated electron lifetime.

**Materials and Methods**

**Materials procurement.** Materials used for the fabrication of DSSCs such as Fluorine doped tin oxide (FTO), absolute ethanol, zinc powder, hydrochloric acid (HCl), titanium (IV) isopropoxide (TTIP), platinum (Pt) paste and Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719) dye with analytical grade quality were purchased from Sigma Aldrich. Titanium dioxide (TiO$_2$) paste and redox electrolyte (iodide-tri iodide $I^-/I_3^-$ in 3-methoxypropionitrile (EL-HSE)) were procured from Dyesol, Australia.

**Ion Implantation on TiO$_2$ and DSSCs fabrication.** Patterned and pre-cleaned FTO substrates, were spin coated with TTIP solution forming a compact layer and were annealed at 450°C for 30 min. TTIP solution was prepared by adding a solution mixture of 5 ml ethanol and 200 μl HCl into 5 ml ethanol; kept under continuous stirring for 3 hours, along with the drop wise addition of 50 μl TTIP. Further, TiO$_2$ paste was doctor bladed onto the compact layer deposited FTO with effective thickness and area of 3 μm and 0.25 cm$^2$, respectively; followed by thermal annealing at 450°C for 30 min. The prepared TiO$_2$ films were implanted firstly with Ag ion beam (Energy-120 KeV) at room temperature under high vacuum conditions using low energy negative ion implanter (Inter University Accelerator Centre (IUAC), New Delhi, India) at different fluence of $10^{15}$–$10^{16}$ions cm$^{-2}$. Secondly, Au ion beam was implanted with energy 80 KeV onto Ag implanted TiO$_2$ at respective similar fluence.

**Table 3.** EIS parameters. $R_s$, $R_2$, $C$, and $\tau$ parameters of unimplanted and Au-Ag implanted TiO$_2$ photoanodes at varying fluence based DSSCs.

| Sample Name | $R_s$ ($\Omega$ cm$^2$) | $R_2$ ($\Omega$ cm$^2$) | $\tau$ (ms) | $C$ (μF) |
|-------------|-------------------------|-------------------------|-------------|-----------|
| TiO$_2$     | 4.45                    | 9.3                     | 0.87        | 23.38     |
| A1          | 4.93                    | 10.41                   | 1.12        | 26.89     |
| A2          | 5.29                    | 12.91                   | 8.44        | 163.43    |
| A3          | 6.00                    | 15.08                   | 10.59       | 175.56    |
| A4          | 6.36                    | 21.83                   | 13.25       | 151.74    |
| A5          | 7.07                    | 34.54                   | 23.90       | 172.98    |

**Figure 17.** Long term stability test. Stability of PCE of Au-Ag implanted DSSC (Fluence $6 \times 10^{15}$ ions cm$^{-2}$) under 1 sun illumination (Intensity 100 mW cm$^{-2}$).
The Au-Ag implanted TiO₂ films are named as A1, A2, A3, A4 and A5 for 1 × 10⁻¹⁵, 3 × 10⁻¹⁵, 6 × 10⁻¹⁵, 9 × 10⁻¹⁵ and 1.2 × 10⁻¹⁶ ions cm⁻², respectively. Au and Ag penetrated up to 22 and 17 nm depth in TiO₂ and are calculated using the stopping and range of ions in matter (SRIM) software. The unimplanted and Au-Ag implanted TiO₂ were immersed in the N719 dye (0.3 mM concentration) for 24 h. Pt was deposited on pre-cleaned FTO substrates and were annealed at 450 °C for 30 min. for the preparation of counter electrode (CE). DSSCs were assembled by sandwiching different photoanodes and Pt CE using redox electrolyte in them as an intermediate to complete the circuit.

Characterizations. Crystal structure of unimplanted and Au-Ag implanted TiO₂ films were determined with X-ray diffraction (XRD) using D8 FOCUS, Bruker Ettlingen with Cu Kα radiation (λ = 1.5418 Å, Current = 30 mA and Voltage = 40 kV) from 5–80° Bragg’s angle. X-ray photoelectron spectroscopy (XPS) was done for elemental analysis via MAC2 electron analyzer system interconnected with MBE machine (EVA-32 Riber, France) at an excitation energy of 1253.3 eV using Mg Kα X-ray beam; within binding energy (E.B.) range 10–1500 eV. System was initially calibrated using Au 4f7/2 line with 84.0 eV B.E. Surface morphology of the prepared films were investigated using field emission scanning electron microscope (FESEM-Carl Zeiss, Supra 55). UV-Vis measurements were done using SHIMADZU, UV-VIS NIR 3600 spectrometer within 250–800 nm wavelength range. To perform the desorption experiments, the N719 dye was desorbed from unimplanted and Au-Ag implanted TiO₂ using 0.1 M aqueous solution of potassium hydroxide (KOH) and further, the absorbance spectra of deloaded dye solutions were recorded. Photovoltaic parameters of fabricated DSSCs were studied using Keithley source meter (Model 2400) under 1 sun illumination at 1.5 G AM of intensity 100 mW cm⁻² with OAI, TriSOL solar simulator; which was initially calibrated with standard silicon cell prior to the measurements. The work function measurements of unimplanted and Au-Ag implanted TiO₂ were recorded using Kelvin Probe technique (SKP, Kelvin Probe 4.5). The photoluminescence (PL) spectra was obtained at an excitation wavelength of 310 nm using PerkinElmer, LS 55 Fluorescence Spectrometer. Electrochemical impedance spectroscopy (EIS) was performed using frequency response analyzer (FRA) connected with Autolab potentiostat/galvanostat (PGSTAT12) within the frequency range of 0.1 Hz to 1.0 MHz19,20.

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**Acknowledgements**

One of the authors, Navdeep Kaur, is grateful to UGC, New Delhi, India for providing financial support to do the present research work. The authors acknowledge Inter University Accelerator Centre, New Delhi for providing beam times through Project No. UFR-60331. The authors are sincerely thankful to BARC, Mumbai for providing XPS and Kelvin Probe Measurements.

**Author contributions**

All the authors conceived the concept and designed the experiments; N.K. and V.B. performed the experiments, A.M. analyzed the results; N.K. wrote the paper. D.P.S. and A.M. reviewed the manuscript.

**Competing interests**

The authors declare no competing interests.

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