

The efficiency development of TiO₂ and Henna dye-coated solar wafers by Pulsed Nd: YAG laser treatment

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This work describes the Dye-sensitized solar material (DSSM) incorporating titanium dioxide (TiO₂) with natural henna dye (*Lawsonia inermis*) as the photosensitizer. The changes in dye adsorption, light absorption, and solar cell effectiveness are estimated with henna dye. The pulsed Nd:YAG laser texturing of TiO₂ thin films enhances surface roughness, porosity, area and hence improves the dye adsorption and light absorption. The XRD analysis confirms the TiO₂ phase. The open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), maximum voltage (V_m), and maximum current (I_m) are measured through current-voltage (I–V) characterisation to assess the DSSM. The enhancements in dye adsorption and efficiency through the texturing process by the modification of surface roughness were confirmed through speckle photography. The use of henna dye offers a sustainable alternative to synthetic dyes by means of increasing the efficiency for future solar energy applications.

Keywords: Efficiency, Henna DSSM, Nd: YAG pulsed laser, Solar wafer, TiO₂ thin film

The improvement in photon absorption and charge transport gains in DSSM efficiency in sensitizers selection and thin-film engineering. These progresses are supported by the studies of natural dyes like Henna (*Lawsonia inermis*) which can equal or even outperform synthetic dyes in dye-sensitised solar materials¹. In large scale applications, dyes are suitable due to the ease of extraction, biodegradability and low impact on the environment². Light absorption and efficiency improvement is attained due to optimisation of the extraction process, which enhances the sensitisation ability³. Many plant-based dyes have been described and support their relevance for justifiable development⁴. More uniform and stable photoactive films are obtained by refined spin coating speed, precursor concentrations and post deposition treatment⁵. Enhanced dye uptake and reduced light reflectivity were achieved by Nd:YAG Laser textured film⁶. The solar energy harvesting is achieved by better charge carrier mobility through the laser-induced photon absorption⁷ and the XRD study confirms the structural TiO₂ suitability⁸. Q-switched nanosecond pulsed Nd: YAG laser texturing is employed to refine the exterior morphology of TiO₂

thin films⁹. The texturing process increases the surface roughness and absorbency, resulting in greater dye adsorption and reduced light reflectivity¹⁰. The laser-treated films demonstrate enhanced photon absorption and improved charge transport, leading to higher DSSM efficiency¹¹. Studies show that Nd: YAG lasers create precise nanostructures on thin-film surfaces, offering significant advantages across various material systems, including TiO₂¹². The enhancement in charge-carrier mobility is a crucial factor for effective solar energy gathering as reported¹³.

This work demonstrates that the henna dye added to the textured specimen improves the efficiency. Nd:YAG pulsed laser texturing through the modification of surface roughness after coating TiO₂ nanoparticles onto the solar wafers.

Materials and Methods

The uniform and smooth TiO₂ paste is consummate by adding 0.06 mL of Triton X-100 surfactant. After 30 minutes of grinding process followed by dilute the mixture with 5 mL of distilled water. Before dilution, 4 g of TiO₂ powder is combined with 2 mL of distilled water and 0.1 mL of acetic acid to prevent agglomeration. The cleaning process of the solar wafers took place in an ultrasonic bath comprising

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acetone, distilled water, and ethanol, followed by drying.

The doctor blade method is used for coating on the substrate and SEM image of TiO₂ nanoparticles displays agglomerated particles with an average diameter of 7 microns and the existence of TiO₂ in the thin film is confirmed by X-ray diffraction (XRD) with peaks matched with the JCPDS reference data. The energy band gap (E_g) is computed by:

$$E_g = hc/\lambda \quad \dots (1)$$

where, E_g is the energy band gap, *h* is Planck's constant, *c* is the velocity of light and *λ* is the absorption wavelength. Henna dye extract is obtained after the mixture is maintained at a controlled temperature with continuous stirring for 15 hours. Fine powder of *Lawsonia inermis* leaves is blended with distilled water and citric acid (pH between 5 and 5.5) to ensure optimal extraction. The photocatalytic activity of TiO₂ enhanced by means of Nd:YAG laser texturing, a well-established technique. Its band gap value 3.2eV shows the laser-based surface modification process.

The dye-sensitised solar wafer performance improvement is understood by the higher photon-to-current conversion. This happens because enhanced light absorption allows more dye to load onto the TiO₂ surface. This enhanced dye adsorption occurs because the laser causes nanostructures like nanopores and nanoparticles to expand the effective surface area of the TiO₂ film. These nanostructures are created through precise ablation or etching when the TiO₂ thin films undergo pulsed Nd: YAG laser texturing. Effective adsorption is subject to the concentration of the dye solution, which must remain stable and be used within 15 hours after preparation. Stability is maintained by storing the dye in an airtight container, and its intensity is adjusted beforehand by adding extra powder or solvent to obtain the required concentration.

Experimental setup

A laser with a power of 5 W, wavelength of 532 nm, pulse duration of 4 ns, and pulse energy of 1200 mJ helps to generate micro-pores on the top layer of the material, and these micro-pores were formed by directing the laser accordingly. The 1 mm diameter spot was formed by focusing the pulsed laser, and an area of 0.0785 cm² was uniformly scanned at a frequency of 50 kHz. A red diode laser with a 650nm wavelength is projected onto a TiO₂-coated wafer,

creating speckle patterns, so that the effects of the treatment can be observed. The CCD camera captures the scattered interference images identify the structural changes on the treated surfaces. Light interaction is influenced by the irregularity of the material, and higher roughness increases light trapping and scattering, thereby enhancing absorption. The variations in the roughness of the specimen was evaluated by the speckle patterns.

Mathematical relations illustrate how pulse energy, repetition frequency, the count of pulses, and related factors affect surface parameters like roughness. The pulse repetition rate can be modified, while the peak power adheres to the specified expression.

$$P_p = \left(\frac{P_a}{\Delta T}\right) \quad \dots (2)$$

Where P_p is peak power, P_a is average power, ΔT is time for one pulse.

The laser pulse width multiplied by pulse repetition frequency is shown in the following:

$$\Delta T = (PRF) \times (t) \quad \dots (3)$$

Where PRF is the pulse repetition frequency, and t is the pulse width.

Substituting for ΔT from Eq. 4 into Eq. 5, hence, the highest power is given in Eq. 6:

$$P_p = \left(\frac{P_a}{PRF \times t}\right) \quad \dots (4)$$

The laser energy (E_L) evaluation depends on the laser irradiation area described in Eq. 7:

$$E_L = P_p \times t \quad \dots (5)$$

We assume that the Nd: YAG laser system power output is constant.

$$\text{Energy Density} = \frac{1.2J}{0.0785\text{cm}^2} = 15.27J/\text{cm}^2 \quad \dots (6)$$

The efficiency is determined by the number of pulses, laser mode, and resulting micro-pore shape and size. The total energy delivered to the surface can be calculated as:

$$E_{\text{total}} = (E_{\text{pulse}}) \times N \quad \dots (7)$$

Where E_{total} = Total energy delivered

E_{pulse} = Energy per pulse.

The number of pulses can be expressed as PRF:

$$N = (PRF) \times (t) \quad \dots (8)$$

where PRF = Pulse repetition frequency (in pulses per second)

t = Total processing time (in seconds)

while a specific mathematical connection among these with surface roughness (Ra or Rz) can be expressed as a general empirical relationship (subjected to material and process):

$$R = k E_{total}^m N^m \quad \dots (9)$$

R is the Surface roughness parameter (average roughness, Ra)

k, m, n are the empirical constants determined through experimentation. Another important parameter is the energy density, which can impact the treatment results. The energy density (D) can be calculated as:

$$D = \frac{E_{total}}{A} \quad \dots (10)$$

A is laser spot area and for circular spot,

$$A = \pi \left(\frac{d}{2}\right)^2$$

Where *d* is the illuminated spot diameter.

The empirical relationships that connect energy density to surface roughness are $R \propto D^p$.

Where, *p* is another empirical constant.

Absorption Intensity = 255 - Reflecting Intensity

Applied to surface roughness data, Principal Component Study (PCS) helps identify key factors driving variance. Changes in curve spacing affect surface features' periodicity and amplitude, influencing roughness metrics like average roughness (Ra) and root mean square roughness (Rq). Usually, larger or more irregular curb spacing leads to increased roughness, as it affects the surface's texture and pattern, ultimately altering the roughness characteristics of the material. The laser speckle image-histogram-profile plots for different timings of laser fluence are displayed in (Fig. 1).

Figure 2 depicts that ND: YAG Laser fluence modifies the sample surface. Average surface roughness (Ra) values are used to quantify the texture of a surface. The higher values indicate rougher surfaces. The white pixel values show the reflecting intensity corresponds to the amount of light reflected by the surface, which is recorded as white pixel values.

Table 1 shows that as fluence time rises, the surface roughness (Ra) also upturns. As the fluence time upsurges from 50 μ s to 250 μ s, the surface roughness grows from 15.69 μ m to 21.46 μ m. This shows a perfect positive correlation between fluence time and roughness. A small drop is seen between 200 μ s (Ra = 21.54 μ m) and 250 μ s (Ra = 21.46 μ m).

This slight decline may be due to experimental variations or material behaviour.

Table 2 shows a reverse relationship amid the roughness (Ra) and reflecting intensity. As the roughness increases from 15.69 μ m to 21.54 μ m, the reflecting intensity decreases from 262142 to 261025. This advocates that coarser layer scatter more light, resulting in lower reflecting intensity.

The absorption intensity of the dye influences the efficiency of TiO₂ films in dye-sensitised solar cells. After Nd: YAG laser texturing, the TiO₂ film is immersed in the henna dye for six hours, allowing dye molecules to infiltrate pores and adhere to the roughened surface. The laser treatment develops the porosity and roughness and hence the penetration of dye on the substrate. This leads to greater absorption intensity. The maximum absorption occurs when the immersion time taken by the sample is more for higher uptake within the first hour at room temperature. To achieve adhesion stability, excess solvent is removed from the dye solution by drying the TiO₂ film within an oven. Heat treatment by fluence of laser optimises interaction of dye with TiO₂ to improve the light absorption and charge transfer. The laser-induced roughness ensures uniform dye adsorption, enhancing photon-to-electron conversion efficiency.

The UV-Vis absorption spectrum, depicted in (Fig. 3A & b), best part the absorption characteristics of TiO₂ and henna-coated films, endorsing improved light-harvesting proficiencies.

The relationship between absorption intensity and efficiency is analysed through power computation, as shown in (Fig. 4), highlighting the direct effect of dye absorption on DSSM performance.

Results and Discussion

Light-trapping capabilities of TiO₂ coatings are significantly improved by the application of a pulsed Q-switched laser of 200 mJ energy with varying durations, as micro- and nano-scale features such as spikes, grooves, and cavities are created on the surface. Increased surface roughness is generated by these features, causing the surface area to expand and producing greater light scattering and an extended optical path, which in turn raises photon absorption within the TiO₂ layer. Internal reflections are promoted by the increased roughness, and light absorption in the UV range, where TiO₂ is most efficient. The adsorption of henna dye molecules is facilitated by the modified surface energy of TiO₂,

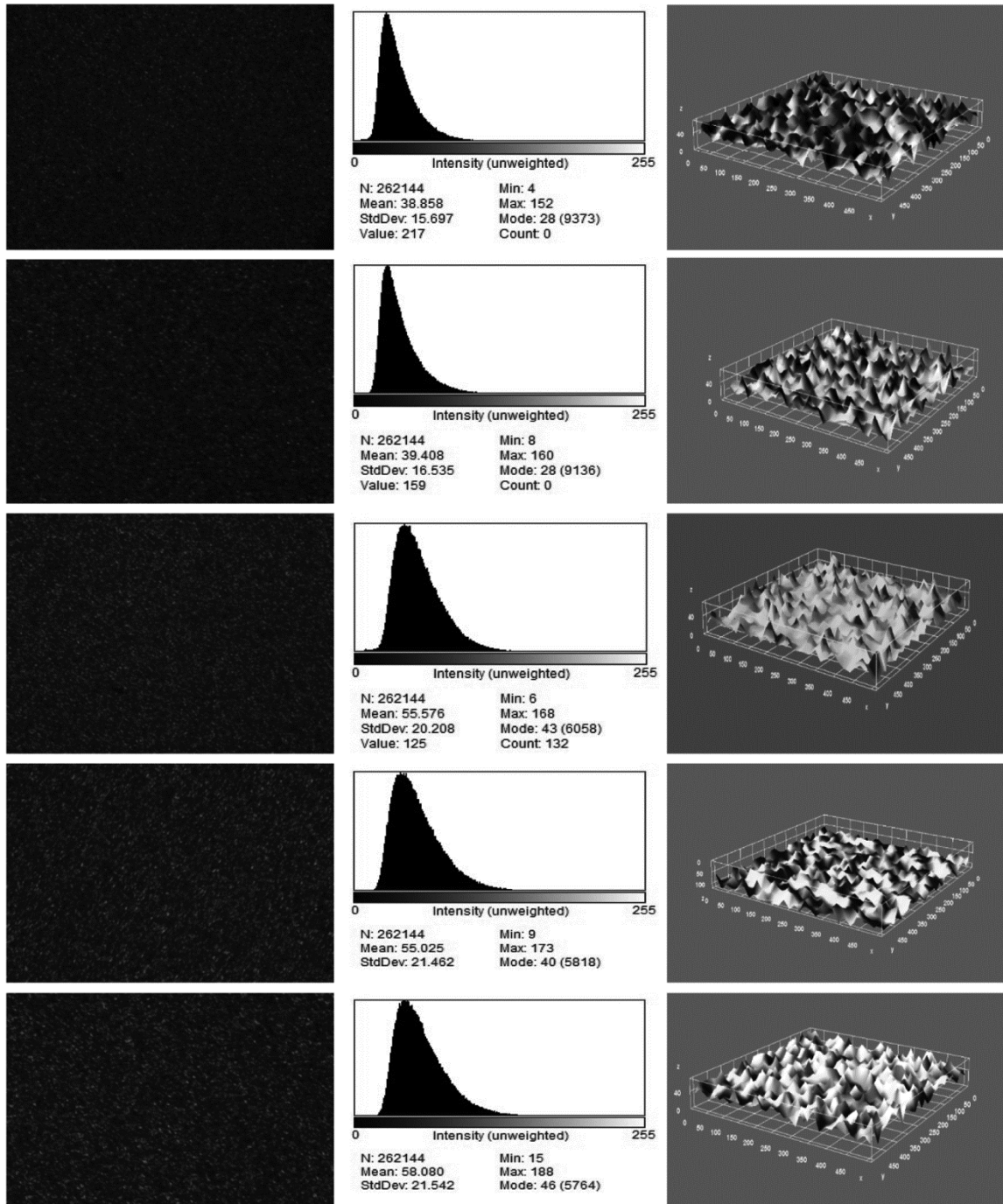


Fig. 1 — Speckle image with Histogram and Surface profile (from top to bottom) for (A) 50 microseconds' fluence. [Ra - 15.697 microns]; (B) 100 microseconds' fluence. [Ra - 16.535microns]; (C)150 microseconds' fluence. [Ra - 20.208 microns]; (D) 200 microseconds' fluence. [Ra - 21.462 microns]; and (E) 250 microseconds' fluence.[Ra - 21.542 microns]

and the interaction of the dye with TiO₂ is enhanced, optimising light absorption and electron transfer. Henna dye molecules are excited by the pulsed Nd:YAG laser, which emits in the infrared and visible ranges, and this excitation assists in generating the electron-hole pairs required by dye-sensitized solar

materials (DSSMs). Sunlight absorption and electron transfer to the TiO₂ surface are both increased by this stimulation. After the TiO₂ surface has been roughened, lawsone-rich henna dye is applied, and visible light in the 450–550 nm range is absorbed by the henna, extending the absorption range into the

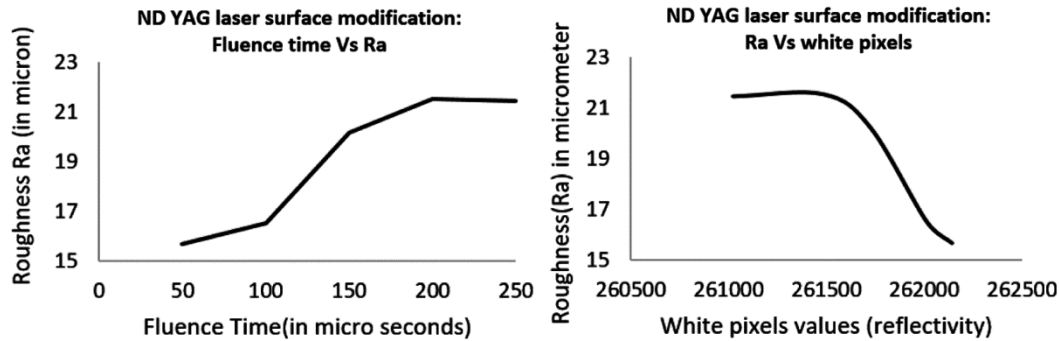


Fig. 2 — Surface modification of the sample – Nd YAG laser Fluence

Table 1 — Solar sample parameters Fluence Time and Roughness

S No.	Fluence Time (in microseconds)	Roughness Ra (in micron)
1	50	15.69
2	100	16.53
3	150	20.20
4	200	21.54
5	250	21.46

Table 2 — Solar sample parameters: Roughness (Ra) and White pixels (Reflection).

S No.	Roughness Ra (in micron)	Reflecting Intensity (White pixels values)
1	15.69	262142
2	16.53	262013
3	20.20	261728
4	21.54	261488
5	21.46	261025

visible spectrum that TiO₂ alone cannot capture. Additional adsorption sites are provided by the roughened TiO₂ surface, thereby improving dye absorption efficiency.

The henna dye-coated TiO₂ surface acts as an effective light trap, capturing scattered and reflected light within the rough TiO₂ structure, converting visible light into absorbed energy. Henna's absorption properties, such as $\pi \rightarrow \pi$ transitions in the UV range (250–300 nm)* and $n \rightarrow \pi$ transitions between 300–400 nm*, allow it to absorb high-energy UV and visible light. The weak absorption starting from 500nm and ending in 600 nm range, which gives the dye its reddish-brown colour, results from the dye's conjugation and charge transfer effects. The absorption intensity varies depending on the concentration of henna and the solvent used. The mixture of rough TiO₂ and henna dye significantly enhances light trapping, particularly for applications in solar energy and photocatalysis. While TiO₂ captures UV light, the henna dye absorbs

visible light, effectively broadening the absorption spectrum.

The increased roughness enhances light scattering and internal reflection, thereby trapping light within the TiO₂/henna composite and improving photocatalytic performance and energy conversion efficiency. The choice of solvent, such as ethanol or water, can change high absorption due to solubility effects, while non-polar solvents like hexane may alter or reduce absorption properties. The pulsed Nd:YAG laser treatment of TiO₂-henna composites enhances dye adsorption, charge transport, and electron injection, improving TiO₂ efficiency and leading to enhanced DSSM performance and optimised photovoltaic technology. Henna is chosen for its stability, non-toxicity, and rich chemical properties, but other natural dyes face challenges such as fading, inconsistency, and difficulties in extraction. The performance of the Henna dye-sensitised photovoltaic (PV) cell was evaluated by measuring Voc, Isc, maximum voltage (V_{max}), and maximum current (I_{max}). The Fill Factor (FF) works as a vital constraint, computing the ability of the solar material to convert sunlight into electrical power. A higher Fill Factor indicates capable charge transport with negligible losses, resulting in better overall performance. The procedure was accompanied by sunlight exposure of 100 mW/cm².

$$FF = \frac{I_{mp}V_{mp}}{V_{oc}I_{sc}} \quad \dots (11)$$

Where,

I_{mp}: Current at the highest power position (from the I-V curve); V_{mp}: Voltage at the top power position (from the I-V curve); V_{oc}: Open-circuit voltage (measured when the circuit is open); I_{sc}: Short-circuit current (measured when the cell is short-circuited).

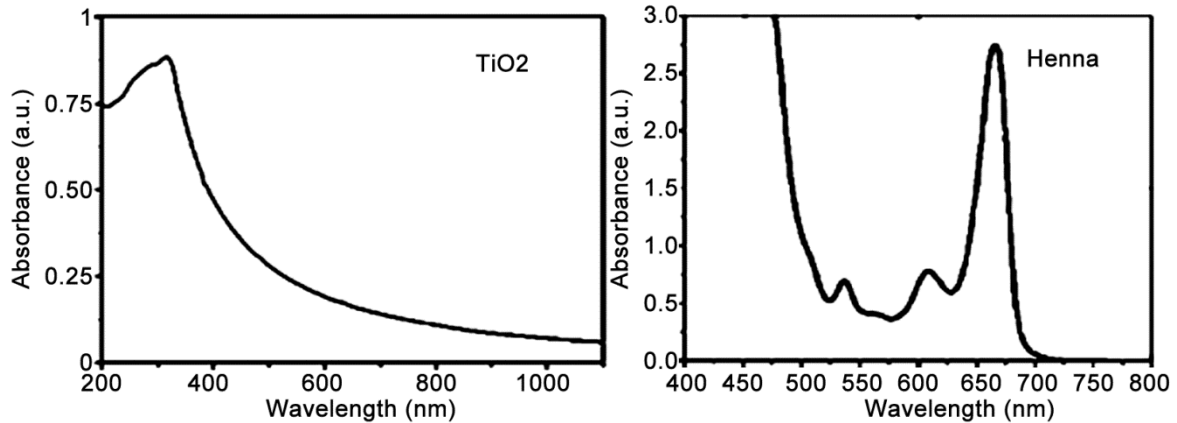


Fig. 3 — UV-Vis spectrum consists of a) TiO₂ and b) Henna dye

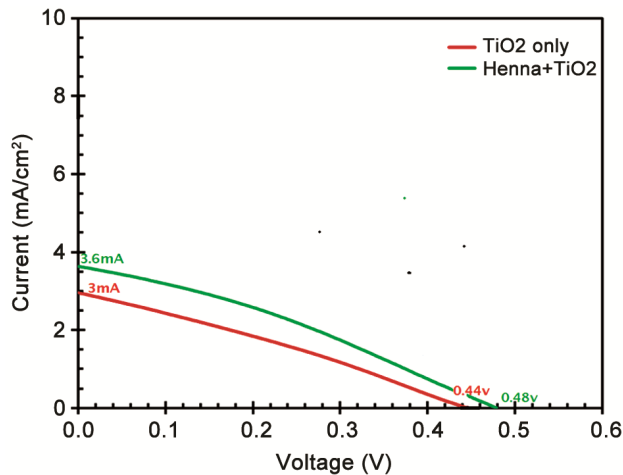


Fig. 4 — Efficiency of TiO₂(Red line) and TiO₂+Henna dye (Green line) solar wafer

Table 3 — Efficiency parameters for the DSSM.

Parameters	I _s	V _{oc}	I _{mp} (mA/cm ²)	V _{mp} (V)	Fill Factor	Efficiency (%)
TiO ₂	3.0	0.44	1.58	0.24	0.28	0.36
Henna+TiO ₂	3.6	0.48	2.56	0.25	0.37	0.64

$$\eta = \frac{I_{sc}V_{oc}FF}{P_{in}} \dots(12)$$

The data from the graph and the computations using fill factor and efficiency are existing in (Table 3).

Pulsed laser texturing and henna dye coating develop TiO₂-coated solar wafers. This optimisation results in a 10% escalation in the fill factor. Laser roughened TiO₂ improves light scattering and lengthens the optical path. Thus, more light gets trapped, improving UV absorption. Henna dye absorbs visible light effectively, covering TiO₂'s weak absorption range. Together, they broaden the usable light spectrum and boost overall solar cell performance.

Conclusion

The TiO₂ surface roughness and henna dye absorption together increases solar energy harvesting. The pulsed Nd: YAG laser treatment enhances the roughness and porosity of the TiO₂ layer. This allows better dye adhesion, stronger light absorption, and electron transfer becomes more efficient. Thus optimising the laser parameters boosts DSSM efficiency. The structural reliability of the sample remains well-maintained.

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Conflict of interest

All authors declare no conflict of interest.

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