Interfacial Modification of Photoanode-Electrolyte Interface Using Oleic Acid Enhancing the Efficiency of Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: Dye-sensitized solar cells (DSSCs) are useful devices in converting renewable solar energy into electrical energy. In DSSCs, the triiodide reduction at the surface of TiO₂ is one of the detrimental processes that limit the realization of high efficiencies of the device. To alleviate the active sites available on the semiconductor surface for this detrimental process, the interfacial modification of the dye-adsorbed TiO₂-electrolyte interface has been attempted by coadsorption of oleic acid (OA) over the TiO₂ surface. Thus, the modified cell exhibited a higher efficiency (η) of 12.9% under one sun illumination when compared with that of the unmodified cell (η = 11.1%). To provide an insight into the OA anchoring and dynamics of electron transport at the photoanode-electrolyte interface, molecular spectroscopic and electrochemical impedance spectroscopic analyses were carried out. A red shift in the optical absorption spectrum was observed after the addition of OA to dye-adsorbed TiO₂. The binding of OA to TiO₂ surface was found to be through bridging bidentate type. Mott–Schottky analyses of the DSSCs under dark conditions were made to probe the shift in the Fermi level of TiO₂ upon OA modification. In addition, the Förster resonance energy transfer (FRET) has been found between OA and N719 dye. Thus, the red shift in the optical absorption, enhanced electron-transfer kinetics, and FRET contributes to the observed enhancement in the efficiency of the device containing OA-modified photoanode.

INTRODUCTION

Renewable energy resources, such as wind and solar, are receiving tremendous attention as supplements in meeting the ever-increasing energy demand and in reducing the dependence on fossil fuels and alarming levels of global warming. Solar energy conversion is an economically viable choice to cater the elevating energy demands of the modern society. Among the third generation solar cells, dye-sensitized solar cells (DSSCs) have been paid substantial attention because of the ease of fabrication and cost-effectiveness as compared with the conventional silicon-based solar cells. High photoconversion efficiency (PCE) is one of the indispensable key parameters to the commercialization of DSSCs to meet the energy demands. Theoretically a high PCE of 18% has been shown possible by overcoming the $V_{OC}-J_{SC}$ trade-off by designing new sensitizers with extended light absorption till near IR region and with new red-ox couples. Multitudinous approaches have been made to improve the PCE of DSSC, viz, (i) design and synthesis of sensitizing dyes with broader absorption up to near infrared region, (ii) finding new red-ox couples with higher reduction potential than that of $I^-/I^-$ to improve the open-circuit voltage ($V_{OC}$), (iii) using coadsorbents to prevent the competitive adsorption among dye molecules and to avoid the photoexcited state quenching, and (iv) administering new additives to overcome $V_{OC}-J_{SC}$ trade-off and surface passivation of photoanodes to retard the charge recombination. Particularly, DSSCs comprising metal-free organic dyes and Co(III)/Co(II) redox electrolyte have shown a PCE of 14.7% by collaborative sensitization process. All these reveal that there is a large prospect to improve the PCE of DSSCs further.

One of the major causes for the loss in the efficiency of DSSC is the charge recombination at the photoanode-electrolyte interface. Earlier reports have shown the possibility to modify the photoanodeldye molecule interface to suppress or eliminate the loss mechanism by coating the photoanode surface with a thin layer of insulating oxides or a higher band edge semiconductors. In one such attempts, Sewvandi et al. have modified the TiO₂ photoelectrode with the organic silane molecules and studied the effects of molecular structure of silanes, alkyl chain length, and TiO₂ surface coverage by silane molecules on the back electron-transfer reaction rate. Kakiage et al. have demonstrated cosensitization using two metal-free silyl anchored dye with antireflecting film and observed the high incident photon-to-current conversion efficiency upto 88%. However, all of the efforts were made to modify the TiO₂ surface prior to the dye loading which significantly reduces the...
amount of dye adsorption and electron injection rate from the dye to TiO₂. To reduce the charge recombination at photoanode and electrolyte interface without affecting the electron-transfer rate, Son et al. have deposited a transparent silica layer on the exposed areas of the photoanode through which the adsorption of dye molecules was significantly reduced and 36% enhancement in the PCE versus uncoated devices was achieved.¹⁴ An organic silane layer was incorporated in between TiO₂ and the perovskite for printable mesoscopic perovskite solar cells to tune the interfacial electronic structure and to passivate the recombination process.¹⁵ Similarly, Zuo et al. have reported that the ZnO-based photoelectrode when modified with self-assembled monolayer of 3-aminopropanoic acid exhibited a low photogenerated charge recombination and high carrier lifetime in perovskite solar cells.¹⁶ Furthermore, the iodine binds with the thiocyanate ligand of N719 dye through its lone pair of electrons and leads to unfavorable effects on the DSSC performance. Mazloum-Ardakani and Khoshroo demonstrated that the oleic acid (OA) prevents the charge recombination and reduces the surface concentration of dye-iodine complex via saturating the π-bond of OA by iodine present in the electrolyte.¹⁷ OA-capped TiO₂ was used in DSSC along with resorcinol-based Ru(II)−Re(I) complexes and higher electron lifetimes were observed because of the resorcinol binding.¹⁸ Recently, OA has also been shown as a blue emitter and a sensitizer of rare-earth luminescent centers when anchored over different oxide surfaces.¹⁹ Thus, it is important to understand the role of OA that is anchored over dye-adsorbed TiO₂ surface and its implications on DSSC performance.

Hence, the interfacial engineering of photoanode to overcome the VOC−JSC trade-off, suppress the recombination losses, enhance the charge injection rate from sensitizer to semiconductor, and understand the mechanisms of the aforementioned phenomena will help in designing DSSCs with higher PCE. With this motivation, in this work, we have used OA, a long chain omega-9 fatty acid (Figure S1), to modify the surface of TiO₂-based photoanode after N719 dye adsorption. OA molecules are selectively adsorbed at the naked surface of TiO₂ that is free from the dye molecules. Thus, the entire exposed area of TiO₂ is covered by dye and OA molecules. These OA molecules are expected to block the recombination processes occurring at the TiO₂/electrolyte interface without affecting the charge injection from the photoexcited dye molecule to TiO₂. An enhanced PCE of 12.9% has been achieved with this approach, and a detailed understanding of the mechanism is presented here.

### RESULTS AND DISCUSSION

To illustrate the effect of OA on the photovoltaic performance, the DSSCs with unmodified and OA-modified TiO₂ photoanodes were fabricated. The fabricated devices were evaluated under the illumination of 100 mW/cm² with the optical filter of AM 1.5G. Figure 1A shows the current density−voltage (J−V) characteristics of DSSCs with the active area of 0.16 cm². The photovoltaic parameters obtained from the J−V measurements of DSSCs with unmodified and OA-modified TiO₂ photoanode are compared in Table 1. The OA concentration is found to be 1.00 mM in these results. The short-circuit current density (JSC), open-circuit voltage (VOC), and fill factor (FF) are 24.3 mA/cm², 0.769 V, and 0.69, respectively, which led to the PCE of 12.9% for the DSSC with OA-modified TiO₂ photoanode. The high JSC is a combined result of the reduced recombination of injected electron with oxidized electrolyte, enhanced optical absorption, altered electronic structure, effective charge injection from the dye to TiO₂, and improved charge transport kinetics.

![Figure 1. J−V characteristics of the DSSCs with unmodified and OA-modified TiO₂ photoanodes (A) under 100 mW/cm² and AM 1.5G illumination and (B) under dark conditions. The OA concentration in the OA-modified TiO₂ photoanode is 1.00 mM.](image)

![Table 1. J−V Characterization of the DSSCs under AM 1.5G Simulated Sun Light (100 mW/cm²)](table)

| device       | VOC (V) | JSC (mA/cm²) | FF | η (%) |
|--------------|---------|--------------|----|-------|
| TiO₂/dye     | 0.779   | 20.7         | 0.69 | 11.1  |
| TiO₂/dye/OA  | 0.769   | 24.3         | 0.69 | 12.9  |

The optimized OA concentration of 1.00 mM was arrived at by carrying out experiments with DSSCs comprising TiO₂ photoanodes modified with different OA concentrations (0.25, 0.50, 1.00, and 1.50 mM). The J−V curves and their characteristics of these DSSCs (other than the one shown here) are presented in Figure S2 and Table S1 (Supporting Information), respectively. With increasing OA concentration, a systematic decrease in VOC was observed, and this can be attributed to the downward shift in the quasi-Fermi energy (EFL) level of TiO₂. The DSSC with the lowest concentration of OA (0.25 mM) exhibited a PCE of 10.7%. Upon increasing OA concentration to 0.5 mM, the PCE also increased to 11.3% and further increase in OA concentration to 1.5 mM decreased the PCE to 10.0%. Thus, the optimum concentration of OA was found to be 1.00 mM in this work. To find the influence of OA on the morphology of TiO₂, the field emission scanning electron microscopic (FE-SEM) and atomic force microscopic (AFM) analyses of the unmodified and OA-modified TiO₂ (with OA concentration of 1.00 mM) film coated on fluorine doped tin oxide (FTO) substrates were carried out. The FE-SEM images of unmodified and OA-modified TiO₂ films (Figure S3, Supporting Information) show the porous...
structure formed by the uniform spherical nanoparticles of the size ∼30 nm and the added OA did not make any distinct difference in the morphology. Similarly, not much difference in the morphology and topography was found in the AFM images as well (Figure S4). The transmission electron microscopic (TEM) analyses of the unmodified and OA-modified TiO₂ powders showed an identical morphology and crystallinity (Figure S5) of the samples. Thus, there is no influence of OA on the morphology of TiO₂ nanoparticles and this could be due to the low concentration of OA.

In general, the recombination of photoinjected electrons in the conduction band (CB) of TiO₂ with oxidized electrolyte I₃⁻ occurs when it is in contact with TiO₂ surface where no dye molecules are present. The blocking of this recombination can be understood by comparing the dark current measurements, and Figure 1B shows the results obtained for the devices with unmodified and OA-modified TiO₂ anodes. Under dark conditions, the dye molecules are inactive to act as sensitizer. Instead they act as a blocking layer on TiO₂ surface preventing the interaction of I₃⁻ with the surface. From Figure 1B, it is clear that the dark current density of the device with OA-modified TiO₂ anode is lower than that of the cell with unmodified anode. As the TiO₂ surface is covered with OA molecules in addition to dye, the dye-modified TiO₂/electrolyte interface is altered. This inhibits the I₃⁻ to contact the TiO₂ surface resulting in the lower dark current density. These results indicate that the OA molecules anchored on the TiO₂ surface block the active sites for the charge recombination process, that is, the electron transfer from the transparent conducting oxide to I₃⁻ via TiO₂.

In DSSC, the extended light absorption by the single sensitizer till the near IR region is critical in realizing a good photovoltaic performance. The standard N719 dye was used in this work because of its high molecular stability and promising photovoltaic performance in the presence of I₃⁻/I⁻ redox couple. The aggregation of excessively adsorbed dye molecules showing a blue shift in the optical absorption limits the PCE of DSSC. Hence, preventing the dye aggregation with additives like cholic acid, chenodeoxycholic acid, and their derivatives enhanced the PCE. The optical absorption spectra of dye-adsorbed photoanode with and without OA modification are compared in Figure 2A. It is observed that upon OA modification, there is a significant red shift in the absorption spectrum. There could be a rearrangement of already anchored dye molecules over TiO₂ surface during OA adsorption. The formation of J-aggregates of dye can result in the red shift in its optical absorption and this is favored by the presence of an additive, for example, OA in the present study, or the acidic pH of the solution during OA addition. This is possible by leaching out of excessively aggregated dye molecules from the TiO₂ surface upon OA treatment. The amount of N719 dye present in the unmodified and OA-modified TiO₂ photoanodes was measured by washing with NaOH (0.1 M in ethanol and water solution, 1:1 vol %). The amounts of desorbed dye from the unmodified and OA-modified TiO₂ photoanode were 5.9 × 10⁻⁵ and 5.1 × 10⁻⁵ mol/cm², respectively, indicating the lower concentration of dye in OA-modified TiO₂ which can be attributed to the leaching out of dye molecules during immersion of the TiO₂/dye photoanode in OA solution. Thus, the red shift observed in the optical absorption of dye molecule resulted in the enhanced PCE for the cell with OA-modified photoanode.

To understand further the red shift in the optical absorption spectrum upon OA coadsorption, we recorded the diffuse reflectance UV (DRUV)–vis absorbance spectra of pristine and OA-modified TiO₂ powders. As shown in Figure 2B, the absorbance shows a slight increase in the entire visible region of the spectrum in the case of OA-modified TiO₂. This enhanced absorbance can be attributed to the creation of surface states as observed in the case of OA-anchored ZnAl₂O₄:Eu³⁺ and BiPO₄:Eu³⁺ phosphors. To clearly observe this, the DRUV–vis spectrum of OA-modified TiO₂ was recorded using pristine TiO₂ as baseline reference. The spectrum obtained is the difference spectrum and shows only the absorbance from the surface states created because of anchoring of OA over TiO₂ surface. The inset in Figure 2B clearly reveals an increased absorbance from 800 to 330 nm with a maximum at ∼360 nm. This result clearly shows the creation of new surface energy states upon OA coadsorption over TiO₂, and these states that form the mid-gap energy levels could play a role in enhancing the electron transport.

To obtain more insights into the binding of OA molecules over TiO₂ surface, we recorded the Fourier-transform infrared (FT-IR) spectra (Figure 3A) of pure OA and OA-anchored TiO₂ (TiO₂/OA). The spectrum of pure OA shows the characteristic peak at 1707 cm⁻¹ which is assigned to the carbonyl stretching mode of the carboxylic acid group. In the FT-IR spectrum of TiO₂/OA, the absorbance due to carbonyl stretching mode of OA at 1711 cm⁻¹ disappeared and a new absorption band at 1604 cm⁻¹ is observed. This shift indicates that the OA molecules are chemically bonded over TiO₂ surface rather than by simple physisorption. Furthermore,
The metal-carboxylate band in the region 1300−1700 cm\(^{-1}\) can be used to deduce the binding mode of the carboxylic acid on metal centers. The carboxylate anion (\(-\text{COO}^\text{-}\)) shows asymmetric and symmetric stretching bands because of its coordination with the “Ti” centers. The binding nature of the carboxylate anion on the TiO\(_2\) surface can be deduced from the difference in the wavenumbers between the asymmetric and symmetric stretching modes of carboxylate group, respectively. The calculated difference (\(\Delta\)) is 144 cm\(^{-1}\) which reveals that the OA molecules are anchored over TiO\(_2\) surface through bridging bidentate mode.\(^{27}\) The absorptions at 1418 and 723 cm\(^{-1}\) are assigned to the umbrella stretching mode of \(-\text{CH}_3\) group and rocking mode of \(-\text{CH}_2\) groups, respectively, of OA.\(^{28}\)

Further to infer the binding mode of OA molecules on TiO\(_2\) surface, the X-ray photoelectron spectra (XPS) of TiO\(_2\) and TiO\(_2\)/OA were recorded. Figure 3B shows the C 1s spectrum of TiO\(_2\)/OA that was deconvoluted into four distinct bands indicating four different carbon species derived from OA. The most intense band centered at 285.5 eV corresponds to the aliphatic carbon atoms while the band at 284.8 eV is assigned to ethylene carbon atoms (\(-\text{C}==\text{C}\)) of OA. The peaks at 287.0 and 289.8 eV are assigned to the monodendate and bidentate carboxylate carbon atoms of OA upon binding over TiO\(_2\).\(^{26}\) The absence of peak at 290 eV is an indication for the absence of free \(-\text{COOH}\) group.\(^{29}\) Thus, OA capping over TiO\(_2\) surface through the bridging bidentate coordination is confirmed from these results. The XPS spectrum of Ti 2p level (Figure S6) has shown two distinct peaks at 459.7 and 465.5 eV corresponding to \(2p_{1/2}\) and \(2p_{1/2}\) levels, respectively. The bands upon OA modification has broadened and shifted toward lower binding energy, indicating a change in the electronic environment of Ti upon OA anchoring over TiO\(_2\) surface.

To elucidate the charge transport mechanisms of the DSSCs, electrochemical impedance spectroscopic (EIS) analyses of illuminated DSSCs were carried out under open-circuit voltage conditions. The experimental data (Figure 4) were fitted using an equivalent circuit model as shown in inside. (B) Bode plots for the DSSCs with unmodified and OA-modified TiO\(_2\) photoanodes under similar conditions.
Illumination of 100 mW/cm² with the Optical Filter of AM 1.5G modiﬁcation (see Table 2). A higher value of the charge accumulation in TiO₂. The increased resistance is lower in the entire range of the bias potentials for transport to the electrolyte. In addition, the electron transport of the interfacially modiﬁed TiO₂ becomes conductive and the electrons are allowed to diﬀuse through the TiO₂ network and reach the external circuit in an eﬃcient manner without any impediment.

Further, to elucidate the inﬂuence of OA modiﬁcation on the charge transfer mechanisms of the DSSCs, EIS experiments were carried out under dark conditions with diﬀerent applied bias potentials, and the results are presented in Figures 5 and 6. Figure 5A shows that the cell comprising OA-modiﬁed TiO₂ photoanode has a higher electron density of 6.12 × 10¹⁸ cm⁻³ than that of the unmodiﬁed device (5.51 × 10¹⁸ cm⁻³). This result further supports the high PCE of the interfacially modiﬁed DSSCs. In addition, it can be seen from Table 2 that the post modiﬁcation of OA on TiO₂/dye photoanode decreased the electron transport resistance (Rₑ) of the TiO₂ film. Hence, the photoinjected electrons are transported through the TiO₂ network and reach the external circuit in an eﬃcient manner without any impediment.

The intercept of the straight line at the abscissa in Figure 6B for the OA-modiﬁed device is higher than that of the unmodiﬁed device (6.08 mF) results in the increased electron density in TiO₂. Steady-state electron density (nₑ) was calculated for the fabricated DSSCs. The device with OA-modiﬁed photoanode has a higher electron density of 6.12 × 10¹⁸ cm⁻³ than that of the unmodiﬁed device (5.51 × 10¹⁸ cm⁻³). This result further supports the high PCE of the interfacially modiﬁed DSSCs. In addition, it can be seen from Table 2 that the post modiﬁcation of OA on TiO₂/dye photoanode decreased the electron transport resistance (Rₑ) of the TiO₂ film. Hence, the photoinjected electrons are transported through the TiO₂ network and reach the external circuit in an eﬃcient manner without any impediment.

The charge recombination process in DSSCs can be enhanced by either shifting the reduction potential of the red-ox couple (I₃⁻/I⁻) or using a red-ox electrolyte with more positive potential. Table 1 shows that upon interfacial modiﬁcation of cell with OA, the V_OC of the device decreased when compared with the unmodiﬁed device with a diﬀerence of 10 mV. A similar trend was observed with diﬀerent OA concentrations (Table S1) as well. To establish the role of OA modiﬁcation over the charge-transfer resistance and conductivity of TiO₂, the EIS Nyquist plots are shown in Figure S8 and the diﬀerence in the semicircular arcs shows that the charge-transfer resistance and conductivity of TiO₂ have improved with OA modiﬁcation. The charge-transfer resistance (R_CT) at the electrode-electrolyte interface for the OA-modiﬁed TiO₂ is smaller (1.24 kΩ) than that of the unmodiﬁed TiO₂ (29.8 kΩ). Thus, OA modiﬁcation is favorable in improving the charge-transfer kinetics of TiO₂ and enhancing the DSSC performance.

Table 2. EIS Data of the DSSCs Comprising Unmodiﬁed and OA-Modiﬁed TiO₂ Photoanode Measured under the Illumination of 100 mW/cm² with the Optical Filter of AM 1.5G

| device         | Rₑ (Ω) | R_CT (Ω) | Cₑ (mF) | τ (ms) | Kₑ (s⁻¹) | Rₛ (Ω) | nₑ (cm⁻³) |
|----------------|--------|----------|---------|--------|----------|--------|-----------|
| TiO₂/dye       | 15.2   | 11.12    | 5.49    | 61.08  | 16.37    | 0.22   | 5.51 × 10¹⁶ |
| TiO₂/dye/OA    | 17.7   | 10.04    | 6.08    | 61.12  | 16.36    | 0.09   | 6.12 × 10¹⁶ |

marginaly lower than that of the unmodiﬁed device suggesting that the OA moieties slow down the kinetics of back electron-transfer process.

Furthermore, the electron lifetime (τ) was calculated for both the devices and the values are listed in Table 2. The device with OA-modiﬁed TiO₂ shows a τ value of 61.12 ms which is slightly higher than that of the unmodiﬁed device (61.08 ms). Bode phase plots are presented in Figure 4B and it can be seen that the frequency is lowered for the OA-modiﬁed device, suggesting a slower electron lifetime. The electron lifetime has been calculated at various bias potentials and presented in Figure 5D. The electron lifetime of DSSC with OA-modiﬁed TiO₂ is slightly higher while increasing the bias potential (>0.75 V) and this strongly suggests that the OA moieties prevent the charge recombination process and thus improve the overall device performance. To establish the role of OA modiﬁcation over the charge-transfer properties of TiO₂, EIS measurements were carried out in a three-electrode setup for unmodiﬁed and OA-modiﬁed TiO₂ ﬁlms using I₃⁻/I⁻ electrolyte in acetonitrile. Lithium perchlorate (0.1 M) was used as a supporting electrolyte. The EIS Nyquist plots are shown in Figure S8 and the diﬀerence in the semicircular arcs shows that the charge-transfer resistance and conductivity of TiO₂ have improved with OA modiﬁcation. The charge-transfer resistance (R_CT) at the electrode-electrolyte interface for the OA-modiﬁed TiO₂ is smaller (1.24 kΩ) than that of the unmodiﬁed TiO₂ (29.8 kΩ). Thus, OA modiﬁcation is favorable in improving the charge-transfer kinetics of TiO₂ and enhancing the DSSC performance.

Figure 6A shows that the steady-state electron density of the OA-modiﬁed device is higher than that of the unmodiﬁed device in the entire range of the applied bias potential. This can be due to the increased chemical capacitance as well as the downward shift of the CB of TiO₂ after OA modiﬁcation over the naked surface of TiO₂. At lower bias potentials, TiO₂ behaves as an electrical insulator and under this condition the recombination takes place predominantly at the uncovered FTO surface. While increasing the bias potential, the TiO₂ becomes conductive and the electrons are allowed to diﬀuse through the TiO₂ ﬁlm, and now the recombination takes place at the TiO₂ surface. Figure 5B shows an increase in the charge recombination resistance at photoanode-electrolyte interface for the OA-modiﬁed device while forwarding the bias potential from 0.80 to 0.85 V, suggesting that the adsorbed OA molecules over the naked surface of TiO₂ passivate the exposed TiO₂ surface and prevent the electron transport to the electrolyte. In addition, the electron transport resistance is lower in the entire range of the bias potentials for the OA-modiﬁed DSSC (Figure 5C) and these results are in good agreement with the calculated Rₑ values under illumination (see Table 2). A higher value of R_CT/Rₑ is required for the low charge recombination rate, a high charge collection efficiency, and high photovoltaic performance of a DSSC. The ratio R_CT/Rₑ for OA-modiﬁed device was calculated to be 111.5, which is higher than that of unmodiﬁed device (50.05) and hence the photoinjected electrons are collected eﬀectively via TiO₂ network upon OA modiﬁcation. These results further support the increased PCE of the OA-modiﬁed device. Electron lifetime has been calculated at various bias potentials and presented in Figure 5D. The electron lifetime of DSSC with OA-modiﬁed TiO₂ is slightly higher while increasing the bias potential (>0.75 V) and this strongly suggests that the OA moieties prevent the charge recombination process and thus improve the overall device performance.
the $V_{OC}$ that is, the energy difference between $E_f$ and $E_{\text{redox}}$. The surface modification of TiO$_2$ with acid results in a positive shift of the quasi-Fermi level while the treatment with a base results in the shift of the $E_f$ toward negative potential. Consequently, a decrease in $V_{OC}$ ($\sim 10$ mV) has been observed upon OA modification in the present study. However, this shift toward positive direction is favorable for the efficient charge injection from the dye molecule to TiO$_2$ CB (Scheme 1). In addition, the built-in-potential (difference between the $E_f$ value of OA-modified and unmodified TiO$_2$ photoanodes) in the device upon OA modification of TiO$_2$ was found to be 10 mV and it is the main driving force for the enhanced charge separation and minimized back electron transfer from TiO$_2$ to I$_3^-$.

Scheme 1. Effect of OA Modification in Tuning the $E_f$ of TiO$_2$: (A) Unmodified Photoanode and (B) Modified Photoanode with the $E_f$ Shifting toward the Red-ox Potential of the I$_3^-/I^-$; $E_{\text{VB}}$—the Valence Band Maximum; $E_{\text{CB}}$—the Conduction Band Minimum; $E_f$—Quasi-Fermi Energy; $E_{\text{redox}}$—Red-ox Potential of the Electrolyte; $V_{OC}$—Open Circuit Voltage

Figure 6. (A) Variation in the electron density with respect to the applied bias potentials under dark condition. (B) $M-S$ plots measured at a frequency of 1 kHz of the DSSCs with unmodified and OA-modified TiO$_2$ photoanodes under dark condition.
the energy required to promote an electron from $E_g$ to vacuum. This difference is partially attributed to the electron withdrawing nature of the $-\text{COOH}$ group of OA moiety that directs the dipole away from the TiO$_2$ surface. Hence, upon interfacial modification of photoanode using OA not only prevents the charge recombination process but also augments the facile charge injection from the dye to CB of the TiO$_2$.

As mentioned earlier, OA also acts as an emitter and a sensitizer. Hence, understanding the optical properties of OA and its interaction with N719 dye will provide further insights into the observed enhancement in the PCE. The photoluminescence (PL) emission spectrum of OA while being monitored using 365 nm excitation wavelength falls in the blue region of visible spectrum (Figure 7A) where N719 dye absorbs. Thus, there could be an electronic interaction between OA and N719 through energy transfer. Förster resonance energy transfer (FRET) involves a dipole–dipole interaction between two chromophores, called the donor and the acceptor. Upon excitation of the donor (OA), the excited energy can be transferred nonradiatively to the acceptor molecule (N719) if there is a spectral overlap between the absorption spectrum of acceptor and the emission spectrum of donor. Here, the absorption spectrum of N719 dye effectively overlaps with the emission spectrum of OA (Figure 7A) and contributes to the FRET in an efficient manner. The coadsorption of OA on TiO$_2$ along with N719 dye ensures that the FRET donor can strongly interact with the FRET acceptor N719 dye, thus introducing an in situ FRET system.

Further evidence for this FRET was obtained from the quenching of the emission of OA upon addition of N719 dye (Figure 7B). Consequently, the $J_{SC}$ of the OA-modified device was greatly improved because of the enhanced light harvesting ability of N719 along with OA. A comparison of reported efficiencies in the literature for DSSC and perovskite solar cells using different coadsorbents (Table S2, Supporting Information) shows that the obtained efficiency of 12.9% in the present work is higher than the ones reported. Our results show the promising nature of OA modification of TiO$_2$ surface to enhance the PCE of DSSC through the combined effects of the enhanced optical absorption and minimizing the photoinjected electron recombination at the TiO$_2$|electrolyte interface.

### CONCLUSIONS

In summary, the interfacial engineering of the N719 dye-anchored TiO$_2$ photoanodes using OA has allowed us to achieve a high PCE of 12.9% when coupled with I$_3$|I$^-$/I$^-$ redox couple under one sun illumination. The OA molecules anchored over TiO$_2$ surface through a bridging bidentate coordination altered the optical absorption of dye-anchored TiO$_2$ film. The red shift in the optical absorption of dye-anchored TiO$_2$ film is due to the rearrangement of dye aggregates and leaching out of excess dye molecules. Also, OA anchoring over TiO$_2$ surface introduces surface electronic states that could help the facile charge-transfer process. Upon OA modification, $E_g$ of TiO$_2$ shifted toward the positive potential, and this favors the effective charge injection from the highest occupied molecular orbital level of dye molecule to the CB of TiO$_2$. The dipole formed at the dye-TiO$_2$/OA|electrolyte interface passivates the charge recombination process without affecting the charge injection from the dye to TiO$_2$. The mechanism of the enhanced PCE with OA as elucidated using EIS analyses suggests that OA molecules not only suppress the back electron-transfer rate but also facilitate the charge injection process and improve the charge transport kinetics. In addition, we found that the in situ FRET occurring between OA and dye is also responsible for the observed high PCE. This work further stimulates the search for new organic or organic-inorganic hybrid surface modifiers to realize high efficiencies of DSSCs.

### EXPERIMENTAL SECTION

**Chemicals and Reagents.** All chemicals used in this study were of analytical grade. TiO$_2$ (P25), chloroplatinic acid hexahydrate, OA (99%), 1,3-dimethyl-3-propyl-imidazolium iodide (DMPII, 98%), lithium iodide (LiI, 99.9%), iodine (I$_2$, 99.9%, metal basis), tertiary butyl pyridine (TBP, 96%), and guanidine thiocyanate (GSCN, 99%) were purchased from Sigma-Aldrich India Pvt. Ltd. FTO-coated glass (FTO glass, 3.2 mm thickness, sheet resistance 15 Ω/$\square$) was purchased from Xin Yan Technology Ltd., Hong Kong. N719 dye was purchased from Solaronix S.A. (Switzerland). Other reagents were purchased from TCI India Pvt. Ltd., India, and used as received.

**Device Fabrication.** The detailed procedure for the fabrication of DSSCs is as follows: FTO glasses were cut into plates of dimension 2.0 × 1.5 cm$^2$ and were cleaned in detergent solution, distilled water, acetone, and ethanol in an ultrasonic bath, and the glasses were subjected for UV/O3 treatment. The blocking layer of TiO$_2$ was deposited by spin-coating the acidic solution of titanium(IV) isopropoxide (Sigma-Aldrich, 97%) and sintered at 450 °C for 30 min. The pure anatase phase was extracted from the commercial titania TiO$_2$–P25 by the method reported in the literature.

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*Figure 7. (A) Optical absorption spectrum of N719 and PL emission spectrum of OA in dimethylformamide, excited using 365 nm wavelength. Concentrations of OA and N719 were fixed as 0.02 mM. (B) Quenching of the PL emission (decreasing intensity) of OA upon addition of increasing concentrations of N719 is observed.*
To an ice-cooled aqueous solution of H2O2 (30%, 200 mL), aqueous NH3 (2.5%, 32 mL) was added under magnetic stirring. P25 powder (2.0 g) was added to the H2O2−NH3 mixed solution and stirred for 12 h. The pale yellow colored reaction mixture was centrifuged at 6000 rpm for 30 min, washed several times with distilled water, and dried at 80 °C in air. The dried powder was calcined at 500 °C in air for an hour to obtain the pure anatase TiO2. The anatase phase formation was confirmed by powder X-ray diffraction (XRD) analysis (Figure S9). Then, a film of TiO2 whose thickness was found to be 12 μm (see Figure S10 for the cross-sectional FE-SEM image) was coated by doctor blade method using the paste prepared by grinding isolated anatase TiO2 nanoparticles (0.5 g) with 0.15 g of polyethylene glycol (MW—35 000), 0.10 g of polyethyleneoxide (MW—100 000), Triton-X-100 (two drops), and 3.5 mL of 0.1 M glacial acetic acid for an hour. The whole content was allowed to stir for 24 h. The obtained paste was coated on to a cleaned FTO glass and sintered at 500 °C for 30 min. The TiO2-coated glasses were cooled to 70 °C and immersed in 0.3 mM solution of N719 in tert-butyl alcohol—acetonitrile mixture (1:1) for overnight. The dye-coated film was washed copiously with absolute ethanol to remove the unadsorbed dye molecules and dried over the N2 flow. For OA modification, the TiO2/dye-coated films were immersed in ethanolic solution of OA (1.00 mM) for 3 h and washed thoroughly with absolute ethanol and dried under nitrogen flow.

The counter electrode was prepared by drop-casting a solution of chloroplatinic acid (5 mM) in isopropyl alcohol over FTO glass and heated at 420 °C for 15 min in air. The dye-coated TiO2 or OA-modified TiO2/dye film was sandwiched with a predrilled platinum-coated FTO counter electrode. The two electrodes were separated by hot melt polymer film (thickness 60 μm, Meltonix-1170-60). The red-ox electrolyte consists of 0.6 M DMPFI, 0.05 M LiI, 0.03 M I2, 0.5 M TBPA, and 0.1 M GSCN in the mixture of acetonitrile and valeronitrile (85:15), was injected into the device, and sealed. The active area of the fabricated DSSCs is 0.16 cm2.

**Characterization.** Optical absorption spectra of the films of unmodified and OA-modified TiO2/dye coated FTO glasses were obtained using an UV−vis−NIR spectrophotometer (Cary 5000, Varian). The optical absorption spectrum of N719 dye solution was recorded using a spectrophotometer (UV-3600 Plus SHIMADZU). DRUV−vis absorption spectra were recorded using a spectrometer (Cary 5000, Varian) with an integrating sphere attachment. Spectralon diffuse reflectance standard was used as baseline reference. The morphologies of TiO2 and OA-modified TiO2 in the films coated over FTO glass and its cross section were analyzed using FE-SEM (Supra 55VP, Carl Zeiss). The AFM (Agilent Technologies 5500) images of unmodified and OA-modified TiO2-coated FTO glasses were analyzed to find the topographies. The TEM images of TiO2 and OA-modified TiO2 powder samples were obtained using an FEI Technai 20-GZ microscope. FT-IR spectra of OA and OA-modified TiO2 were recorded using a spectrometer (TENSOR 27, Bruker). Powder XRD patterns of TiO2 (P25) and anatase TiO2 were obtained using Cu Kα radiation (1.5418 Å, D8 ADVANCE, Bruker). The X-ray photoelectron spectroscopic analysis (ESCA Lab 250Xi, Thermo Scientific) was carried out with a Al Kα source (1486.6 eV) to obtain information about the chemical states of TiO2 and OA-modified TiO2. All of the electrochemical experiments were carried out using a potentiosstat–galvanostat (SP-150, Bio-Logic). The photovoltaic performances of fabricated devices were tested at 100 mW/cm2 with the optical filter of AM 1.5G using a solar simulator (Scientechtech-AAA) coupled with Keithley-2400 voltmeter. EIS measurements were carried out under alternating current amplitude of 10 mV and in the frequency range from 106 to 10−2 Hz. M−S analyses were carried for the DSSCs under dark conditions at 1 kHz of frequency. Room-temperature PL spectra were recorded using a spectrofluorometer (FP-8500, JASCO).

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