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Low cost 'green' dye sensitized solar cells based on New Fuchsin dye with aqueous electrolyte and platinum-free counter electrodes



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ABSTRACT

In this work, we present the application of a inexpensive water-soluble New Fuchsin (NF) dye as a photosensitizer for dye sensitized solar cells (DSSC). A comprehensive study including computational, spectroscopy and cyclic voltammetry measurements established the efficacy of NF as a photosensitizer. Density functional theory (DFT) modelling of NF is performed to estimate the energy levels and experimentally verified using the cyclic voltammetry measurements. For the spectroscopy characterization time-resolved absorption and fluorescence studies are employed on NF in ethanol solution and as thin film deposited on glass and mesoporous TiO₂. Femtosecond transient absorption measurements revealed ultrafast electron injection within < 1 ps at the interface of NF and TiO₂. NF sensitized solar cells were fabricated and optimised using various liquid electrolytes and carbon-based counter electrodes. The fabricated devices were further characterized using electro-impedance spectroscopy and Mott-Schottky measurements. The best-performing device with photo-conversion efficiency of 2.9% was obtained using aqueous Fe^{3+}/Fe^{2+} electrolyte and CoS treated carbon fabric. These components are non-toxic and economical resulting in the fabrication of low cost and eco-friendly "green"solar cells.

1. Introduction

Tremendous success of the dve-sensitized solar cell technology, notwithstanding, during the last three decades, (Gong et al., 2017; Grätzel, 2003; Hardin et al., 2012; Mathew et al., 2014) with a record efficiency of $\approx 13\%$ (Mathew et al., 2014), few challenges that still plague the community are the long-term stability for commercialization & overall cell performance (Fakharuddin et al., 2014; Shahimin et al., 2015), use of expensive platinum-based counter electrodes (CE) (Iqbal and Khan, 2018; Mozaffari et al., 2017; Ye et al., 2015) and use of various organic solvent-based liquid electrolytes (Yu et al., 2011). Particularly, the use of liquid electrolytes come with various drawbacks such as high vapor pressure, toxic and sometimes explosive resulting in sever environmental impact. To further this issue, iodide based liquid electrolyte to be corrosive and damage the platinum electrodes in a long run (Shahimin et al., 2015). Moreover, a long-standing and critical issue still unresolved in the DSSC community is the contamination of standard aprotic DSSC systems by means of moisture/water. To counter the issues of corroding liquid electrolyte and instability in moisture environment, lot of efforts are directed towards the development of aqueous dye-sensitized solar cells (Bella et al., 2015; Law et al., 2010; Risbridger, 2013). Novel sensitizers were developed towards aqueous DSSC fabrication (Li et al., 2017). Considering naturally occurring dyes and pigments, most of which are soluble in water, offer cost-effective alternatives, the use of natural dyes and pigments as effective sensitizers are yet to fructify its potential (Hao et al., 2006; Iqbal et al., 2019; Richhariya et al., 2017; Sanjay et al., 2018; Shalini et al., 2015; Zhou et al., 2011). In view of being cost-effective and stable in the aqueous environment, an ideal DSSC should consist of inexpensive sensitizer, water-based non-toxic electrolytes, and platinum-free counter electrode, giving it the true definition of eco-friendly 'green' photovoltaic device.

In this report, we present our results on a 'green' DSSC making use of an inexpensive magenta dye, New Fuchsin, for the first time as a photosensitizer, employing a water based Fe^{3+}/Fe^{2+} electrolyte with CoS deposited on C-fabric as the counter electrode. New Fuchsin [C₂₂H₂₄N₃Cl,4-

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Scheme 1. Schematic illustration of the preparation of the photoanode, counter electrode and DSSC.

((4-amino-3-methylphenyl)(4-imino-3-methyl-2,5-cyclohexadien-1-ylidene) methyl)-2-methylphenyl-amine-monohydrochloride)] is a triphenylmethane derivative exhibiting intense magenta colour in both solutions and thin films with applications demonstrated in dye staining, antibacterial stain, drugs for photodynamic therapy (Churukian and Schenk, 1983; Cooksey and Dronsfield, 2015; Montes de Oca et al., 2010; 2013) and sporadic reports of its utility in organic electronics (Chen and Fa, 2003; Güllü et al., 2010; 2008). Considering that this dye has never been used so far as a photosensitizer for DSSC, comprehensive theoretical and experimental investigations, that includes, DFT calculations, steady-state photo-physical characterization and excited state studies using femtosecond transient absorption spectroscopy & time-resolved photoluminescence spectroscopy were carried out. The fabricated DSSC is then systematically characterized using electrochemical impedance spectroscopy (EIS), Mott-Schottky, cyclic voltammetry techniques. The best device showed photoconversion efficiency of 2.9%. Further, the transistor characteristics of New Fucshin based OFETs demonstrated poor performance suggesting their limited applications in organic electronic devices. A most important aspect of this work is the choice of component materials making this extremely inexpensive device.

2. Experimental section

2.1. Chemicals

New Fuchsin (NF), LiI, Iodine (I₂), tert-butylpyridine, guanidine thiocyanate (GuSCN), acetonitrile, was purchased from Sigma Aldrich. Potassium chloride (KCl), potassium hexacyanoferrate (III) (K₃[Fe (CN)₆]), potassium hexacyanoferrate (II) trihydrate (K₄[Fe (CN)₆].3H₂O), Cobalt (II) acetate tetrahydrate (Co(CH₃COO)₂·4H₂O), Sodium sulfide (Na₂S), 3-propyl-1-methylimidazolium iodine, methanol was purchased from Merck. Carbon fabric (C-fabric) purchased from Alibaba Pvt Ltd. Fluorine-doped Tin oxide (FTO) glass with sheet resistance of $12 \Omega \text{ cm}^{-2}$ (Pilkington) and were cleaned in a soap solution, 30% HCl solution, twice distilled water and acetone, in that sequence, prior to use. TiO₂ paste (DSL 18NR-T) was purchased from Dyesol.

2.2. Preparation of electrodes and cells

A layer of Dyesol TiO₂ paste applied over washed FTO by using the doctor blade method. The deposited TiO₂ films were annealed at 80 °C for 30 min. followed by the annealing at 500 °C for 30 min. (temperature increase at the rate of 5 °C min⁻¹). One more layer of TiO₂ paste was applied and sequential annealing at 80 and 500 °C for 30 min. each. The above TiO₂ plates were dipped in an aqueous solution of 0.4 M TiCl₄ at 70 °C for 20 min., and the coated substrates were rinsed in ultrapure water to remove unabsorbed excess TiO₂ and annealed at 500 °C (temperature increase at the rate of 5 °C min⁻¹). The obtained

TiO₂ plates were dipped in the 0.1 mM New Fuchsin dissolved in ethanol for 3 hr for adsorption on the TiO₂ electrodes. CoS was deposited on C-fabric by successive ionic layer adsorption and reaction (SILAR) process, the C-fabric was dipped in a solution of 0.1 M (Co (CH₃COO)₂·4H₂O) in methanol at 25 °C for 1 min, rinsed in methanol and dried at 50 °C for 2 min. The resulting electrode was dipped in 0.1 M Na₂S in methanol at 25 °C for 1 min, rinsed in methanol and dried at 50 °C for 2 min and a CoS layer was obtained. The dipping of the C-fabric in two different (Co²⁺ and S²) solutions constitutes one SILAR cycle.

DSSCs were constructed by affixing a double-sided tape spacer of 120 μ m thickness along the periphery of the active photoanode area, such that a cavity is created with the exposed photoanode. A clear aqueous solution of (0.001) M Fe³⁺/(0.02 M) Fe²⁺ and 0.1 M KCl electrolyte was prepared and was injected into the cavity. For supporting the CE, the CoS/C-fabric electrode was glued to a glass slide, and it was placed on top of the FTO/photoanode/electrolyte assembly. The whole assembly was held together with binder clips, and the edges were sealed with an epoxy and the cells were ready to use. A schematic illustration of the preparation of the photoanode, CE and DSSC is shown in Scheme 1.

2.3. Characterization techniques

Mesoporous TiO₂, New Fuchsin (NF), and NF coated TiO₂ were deposited on micro-slide glass plates and used for all characterizations. PG Instruments Ltd. X-ray diffraction (XRD) patterns of samples were recorded on a PANalytical, X'PertPRO instrument with Cu-Ka $(\lambda = 1.5406 \text{ Å})$ radiation. The optical absorption spectra were measured on a T90 + UV-Vis spectrometer. Photoluminescence (PL) spectra of films were recorded by fixing the sample/substrate configuration in a solid sample holder and on a Horiba Flouromax-4 fluorescence spectrometer. A nano LED diode emitting pulses at 370 nm with 1 MHz repetition rate and a pulse duration of 1.3 ns was used for timeresolved PL measurements using Time-correlated single photon counting (TCSPC) method. The obtained PL kinetics was analysed and decay time constants were deduced using the Horiba Jobin Yvon DAS6 fluorescence decay analysis after considering the instrument response. The excited state absorption dynamics were measured for (a) thin film coated on a glass slide and (b) NF deposited on mesoporous TiO₂ thin film. Femtosecond transient absorption spectrometer (HELIOS, Ultrafast Systems) pumped by a 70 fs laser (LIBRA, M/S Coherent) pulses at 1 kHz repetition rate equipped with an optical parametric amplifier (TOPAS) was used to perform the TA experiments with photoexcitation at 550 nm. The measurements recorded were analyzed as the differential transmission ($\Delta T/T$) data. Surface morphology analysis of NF and TiO₂/NF electrode were performed using a field emission scanning electron microscope (FE-SEM, Carl Zeiss AG Supra 40).

A LOT-Oriel solar simulator encompassing a 150 W Xe lamp, an AM 1.5 filter, and capable of delivering an collimated output beam of 25 mm diameter, was coupled with a Metrohm Autolab PSTAT302N and was used for measuring the current versus potential (I-V) data of DSSCs, under 1 sun (100 mW cm⁻²) illumination. The spatial uniformity of irradiance was confirmed by calibrating with a $2 \text{ cm} \times 2 \text{ cm}$ Si reference cell and re-confirmed with an ILT1400 radiometer/photometer. External quantum efficiency (EQE) plots were recorded using a Quantum Efficiency Measurement System, Oriel IQE-200™ capable of measurements compliant to ASTM E1021-06. The light source was a 250 W quartz tungsten halogen lamp; the monochromator path length was 1/8M spot and the size was $1 \text{ mm} \times 2.5 \text{ mm}$ rectangular at the focus. Cyclic voltammograms (CVs) of TiO₂ and NF films deposited over FTO substrates and also for CEs: C-fabric and CoS/C-fabric were recorded in a three-electrode cell, with the above-described electrodes as working electrodes (WEs), a Pt rod as the counter electrode and an Ag/ AgCl/KCl as the reference electrode (RE) in an aqueous 0.1 M KCl electrolyte solution. The linear sweep voltammogram (LSV) of the $S^{2-}/$ poly(HEMA) gel was recorded by a two-probe method, by sandwiching the gel between two stainless steel (SS) electrodes, 1 cm apart at a scan rate of 10 mV s⁻¹. Mott-Schottky (M-S) plots were recorded at two different frequencies, under an ac amplitude of 20 mV in dark NF/FTO (as WEs) in a 0.1 M KCl solution, with Pt as CE, and Ag/AgCl/KCl as RE. Electrochemical impedance spectra (EIS) spectra were recorded in two electrode configurations over a frequency range of 1 MHz to 0.1 Hz under a V_{ac} of 20 mV for: (a) DSSCs under dark and at $V_{dc} = 0$ and (b) symmetric cells of CEs. EIS, CVs, MS and LSV experiments were all performed on the same electrochemical workstation (Autolab PSTAT302N, with a frequency response analyzer). The electrical characteristics of the OFETs were performed in vacuum using a semiconductor characterization system (Keithley 4200-SCS).

2.4. DFT studies

The ground state geometry of the molecule is fully optimized in ethanol solvent without any symmetric considerations by DFT method. The minimal energy search for the molecule was carried out using BLYP functional (Becky's hybrid function with Lee-Yang-Parr correlation functions) with 6-311 + + G (d, p) basis set. The calculated vibrational spectrum in the optimized structure has no imaginary frequencies, which indicates that the optimized structure is located at the minimum point of the potential surface. Electronic absorption properties were carried out using the TD-DFT methodologies for the optimized geometry and frontier molecular orbitals responsible for the excitations leading to the absorption maximum were pictorially visualized from the population analysis. All the calculations were performed using the Gaussian 16 software (Frisch et al., 2016).

3. Results and discussion

The absorption spectra of NF is shown in Fig. 1a. The absorption in the visible region due to $\pi - \pi^*$ transitions can be observed in the 450–650 nm region. The measured absorption extinction coefficient (ε) of NF from the solution data is $1.12 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at its absorption peak. The absorption peaks (λ_{max}) for the NF in solution, thin film deposited on glass, and ND deposited on mesoporous TiO₂ were observed at 554 nm, 523 nm and 492 nm, respectively. The observed spectra exhibited a distinct hypsochromic shift of ≈ 30 nm for solution to thin film and $\approx 60 \text{ nm}$ for solution to NF on TiO₂, typical of H-aggregation. The spectra in the visible region is much broader for the NF in thin film on both glass substrate as well as on TiO₂ form compared to that in its the solution form. The broadened spectral coverage of NF deposited on TiO₂, thereby enhancing the light-harvesting and DSSC performance. Fig. 1b shows the chemical structure of pristine NF dye. Similar aggregation and a hypsochromic shift of their absorption bands upon deposition on TiO2 were exhibited by few ionic dyes such as acid

orange 7, crystal violet, and methylene blue (Strataki et al., 2007). There has been recent reports providing the evidence of efficient electron injection into the conduction band (CB) of TiO₂ by H-aggregates of pyrogallol red molecules (Sirimanne, 2008) and chalcogenorhodamine molecules (Mulhern et al., 2012).

To gain an insight into the absorption spectrum of NF, TD-DFT calculations has been carried out at BLYP method with 6-311 + + G (d, p) basis set in an ethanol solvent. The calculated absorption maxima for NF is at 533 nm with the oscillator strength 0.571 (Table 1) and the major transition is from HOMO to LUMO (Fig. 2). Evidently, the electron cloud distribution is delocalized over the entire molecule in the case of LUMO. Along with major transition, the minor transition also observed from HOMO-1 to LUMO. The calculated absorption values are in good agreement with the experiment.

Cyclic voltammograms of pristine- TiO₂ and NF films (as working electrodes), recorded in an aqueous 0.1 M KCl solution, with a Pt rod as the CE and an Ag/AgCl/KCl as the RE are shown in Fig. 3. For pristine TiO₂ (Fig. 3a), a reduction peak was observed in the cathodic sweep at -80.67 V versus Ag/AgCl/KCl, and this Ered can be equated to the conduction band (CB) or LUMO (lowest unoccupied molecular orbital) position of TiO₂. The electrode potential of the reference is +0.197 V. So, E_{red} NHE (normal hydrogen (versus electrode)) of $TiO_2 = -0.67 V + 0.197 V = -0.473 V$. The value of -0.473 V (versus NHE) in eV is given by: $-4.5 \text{ eV} (\cong 0 \text{ V versus NHE}) - (-0.473 \text{ V}) =$ $-4.027 \simeq -4.03 \,\text{eV}$. The position of the valence band (VB) or HOMO (highest occupied molecular orbital) of TiO2 is determined by addition of the pre-determined optical band gap energy value to the CB energy, i.e., $-4.03 \text{ eV} + (-3.2 \text{ eV}) = -87.227 \cong -7.23 \text{ eV}$. For NF electrode (Fig. 3b), a reduction peak was observed in the cathodic sweep at -1.32 V versus Ag/AgCl/KCl, and this $E_{\rm red}$ can be equated to the CB or LUMO position of NF. So, E_{red} (versus NHE) of NF = -1.32 V +0.197 V = -1.123 V. The value of -1.123 V (versus NHE) in eV is given by: $-4.5 \text{ eV} - (-1.123 \text{ V}) = -3.37 \cong 3.4 \text{ eV}$. By adding the optical E_{σ} of NF to the CB energy level (-3.4 eV + (-2.1 eV)), the VB energy level is calculated to be at -5.5 eV. DFT calculated HOMO and LUMO of the NF molecule is -5.23 and -3.46 eV respectively. The corresponding HOMO-LUMO gap is 1.77 eV, which is in good agreement with the experiment. DFT calculated HOMO, LUMO and HOMO-LUMO gap for NF is also tabulated in Table 1. An oxidation peak was witnessed for CoS/C-fabric in the anodic sweep at 0.54 V versus Ag/AgCl/KCl, and this Eoxd can be linked to the VB or HOMO position of CoS/C-fabric (Fig. 3c). Hence, Eoxd (versus NHE) of CoS/C-fabric = 0.54 V + 0.197 V = 0.737 V. The value of +0.737 V (*versus* NHE) in eV is given by: -4.5 eV $(0.737 \text{ V}) = -5.237 \cong -5.4 \text{ eV}$. Fig. 3d shows the cyclic voltammogram shows the oxidation and reduction positions of an electrolyte.

Fig. 4a shows a broad photoluminescence (PL) peak in the spectral region from 400 to 800 nm, with a λ_{max} at 430 nm for NF deposited on a glass substrate (black curve) and NF adsorbed on mesoporous TiO₂ (blue curve). A comparison of area under the entire PL spectral curve for NF/glass and NF/TiO₂ shows the PL from photo-excitation of NF was quenched by 85% in the presence of TiO₂. This significant decrease in the PL peak intensity of TiO2/NF can be attributed to the electron transfer from the excited NF to TiO2. To confirm the various deactivation modes, time-resolved emission decay plots were recorded for the same samples at an excitation wavelength of 370 nm and at the emission wavelength of 430 nm were shown in the Fig. 4b and the parameters were tabulated in Table 2. The PL decay profiles for was fitted after accounting for the instrument response. The best fit obtained for the PL decya for glass/NF and glass/TiO2/NF exhibited a single exponential and a bi-exponential functions respectively. The decay lifetime was expectedly longer for glass/NF with 6.4 ns, in comparison to the average lifetime for glass/TiO2/NF estimated to be 2.5 ns. The biexponential fit for PL decay data of glass/TiO2/NF had a fast decay component of 1.7 ns, which we conjecture to be due to electron injection from an excited NF to the CB of TiO2. The slow decay component of 4.1 ns can be explained as the natural de-excitation mechanism of the



Fig. 1. Absorption spectra of (a) NF solution, NF and TiO₂/NF on glass films and (b) chemical structure of NF.

Table 1

DFT calculated Absorption energies (λ_{max} in nm), Oscillator strength (f), Major transitions (MT), weight in % (%Ci), HOMO (in eV), LUMO (in eV) and HOMO-LUMO gap (HLG in eV).

	λ_{max} (nm)	f	MT	%Ci	НОМО	LUMO	HLG
NF	533	0.571	$\mathrm{H} \rightarrow \mathrm{L}$	97.0	-5.23	-3.46	1.77



Fig. 2. Transitions from HOMO-1 to LUMO and HOMO to LUMO for NF molecule.

tail states of excited NF.

Femtosecond transient absorption measurements were performed to obtain a direct proof of efficient electron injection from at the dye/TiO₂ interface (Brown et al., 2011; Caranzi et al., 2014; Kumar et al., 2013). Fig. 5 shows the TA spectra till the first 10 ps of 0.05 mM NF solution in ethanol, NF thin film and NF-TiO2 with photo-excitation at 550 nm corresponding to the peak of NF absorption in the visible region. For ease of understanding the entire spectra is divided into three spectral regions, positive $\Delta T/T$ signal seen in the 450–600 nm corresponding to the absorption of NF as ground state photobleach (GSB) band, positive $\Delta T/T$ signal corresponding to the emission region seeing between 600 and 750 nm region as stimulated emission (SE) band and the negative $\Delta T/T$ signal observed in the lower wavelength region of < 450 nm corresponding to excited state absorption region denoted as PA band. The comparative kinetics data for probe wavelength of 500 nm and 430 nm that representative of GSB and PA regions respectively for NF solution and the thin film is shown in Fig. 6. Notably, in solution, NF exhibited very short excited lifetime with all the three bands (GSB, SE,

and PA) decaying within the first 20 ps. Considering the natural excited state lifetime of NF is 6.4 ns, the fast relaxation of the excited state manifold in the TA measurements indicates domination of various nonradiative decay channels among which the internal conversion IC_{1-0} to the hot ground state could be one the main contributor. Another conjecture is that in solution state there is a molecular conformational relaxation of from the initially excited Franck-Condon (FC) region via energetically allowed conical intersection (CI) in its excited state potential energy landscape (Bhongale et al., 2005; Shi et al., 2017). On the other hand, the TA spectra recorded for NF thin film showed a long GSB lifetime > 500 ps as is evident from the kinetics data. Another important observation is the strong SE band exhibited in the thin film data compared to that of solution data. The most viable explanation for this could be that that the vibrational coordinate, along which the conical intersection is reached in case of the dye in solution, is blocked in the solid state. Thus, the long-lived excited states make the NF in thin film form favorable for electron transfer as is evident from the transient PL measurements. NF is a symmetric dye with three branches and there is an equal chance that any one or two branches get adsorbed on the mesoporous TiO₂. The DFT computations showed the electron cloud is localized on two arms of the molecule in the HOMO while the electron cloud is delocalization throughout the molecule in LUMO. Thus it can be conjectured that this delocalization on the electron upon photoexcitation enabled favorable condition for electron injection into the TiO₂

Since the electron transfer rate is in direct competition with the natural lifetime of the excited state, the SE band is expected to decay concomitantly with the electron injection. This particular feature is evident while the SE band is compared for the NF thin film and NF-TiO₂. Evidently, from Fig. 5, the distinct positive SE band observed for NF-thin film becomes negative within the first 1 ps for the NF-TiO₂ indicating ultrafast quenching. Figs. 6 and 7 shows the kinetics data of NF-thin film and NF-TiO₂ at the probe wavelength of 500 nm and 620 nm that are representatives of GSB and SE bands. It is evident from the kinetics data at 620 nm that there is a signature of ultrafast electron injection as the only way the loss of population from the excited state of NF is via electron transfer to the available acceptor component, TiO₂. There have been earlier reports where the presence of Li⁺ ions has hastened the electron injection process (Abrusci et al., 2011; Grancini et al., 2012). Similar treatment may be used in this system as well to increase the electron transfer rate. The samples under study were not treated with any additives for spectroscopy measurements.

After establishing the favorable and efficient electron transfer between NF to TiO_2 using both transient fluorescence and absorption studies, solar cells were fabricated and optimized. The dye-sensitized



Fig. 3. Cyclic voltammograms of (a) TiO₂, (b) NF, and (c) CoS/C-fabric serving as working electrodes. All CV plots were recorded in a 0.1 M KCl solution as electrolyte, with a Pt sheet as the counter electrode and an Ag/AgCl/KCl as the reference electrode, at a scan rate of 10 mV s^{-1} . (d) CV of (0.001) M $Fe^{3+}/(0.02 M) Fe^{2+}$ and 0.1 M KCl electrolyte with two Pt electrodes as working and counter electrode, Ag/AgCl/KCl as the reference electrode at a scan rate of $10 \,\mathrm{mV \, s^{-1}}$.

Fig. 4. (a) Photoluminescnce spectra of NF and TiO2-NF recorded at $\lambda_{ex}=370$ nm. Time resolved PL decay traces of (b) NF and TiO_2-NF recorded at

solar cells were constructed with the TiO₂/NF photoanode. Carbon fabric (C-fabric) and CoS deposited C-fabric was used as a counter electrode and three different hole transport layers I⁻/I₃⁻, 0.1 M Na₂S and a clear aqueous solution of (0.001) M $\mathrm{Fe}^{3\,+}/(0.02\,\mathrm{M})~\mathrm{Fe}^{2\,+}$ and

 $\lambda_{ex} = 370$ nm, and at $\lambda_{em} = 430$ nm wavelengths.

Table 2								
Kinetic	parameters	of PL	decay	analysis	of	photosensitizers	deduced	from
louble/	single evpor	ential	fits: the	-λ was	fiv	ed at 370 nm for	all sample	ec a

2

1

Fe³⁺/Fe²

Fe²

Sample	B ₁	τ_1 (ns)	B ₂	τ_2 (ns)	$< \tau >$ (ns)	Σ^2
NF	100	6.4	-	-	6.4	1.01
TiO ₂ /NF	79.8	1.7	20.3	4.1	2.5	1.02

^a B is the relative amplitude of each lifetime, τ_1 and τ_2 are the components of PL lifetime and χ^2 denotes the fit quality.



Fig. 5. Difference Transmission ($\Delta T/T$) Spectra for NF solution, film on glass substrate and on mesoporous TiO_2 coated glass substrate with $\lambda_{ex}=550\,\text{nm}.$

0.1 M KCl were explored as electrolytes. J-V characterization was performed under an irradiance of 100 mW cm $^{-2}$ (AM 1.5 G spectra) and are presented in Fig. 8. The devices were fabricated in a sandwich architecture with back illumination.



Fig. 6. Comparison of kinetics of the for NF solution and NF film for the $\lambda_{probe} = 430$ nm as a representative of PA band and 500 nm as a representative of GSB band.



Fig. 7. Comparison of kinetics of the for NF film and NF-TiO₂ film for the $\lambda_{\rm probe}=500\,\rm nm$ as a representative of GSB band and 620 nm as a representative of SE band.

To optimize the concentration of NF on to the TiO₂ electrode, the TiO₂ electrode was dipped in 0.05 mM and 0.1 mM NF in ethanol for 3 hr, the obtained electrode was rinsed with ethanol to remove the unabsorbed dye, 0.5 M LiI, 0.05 M I₂, 0.5 M 4-tertt-butylpyridine, 0.6 M 3-propyl-1-methylimidazolium iodide, 0.1 M GuSCN in acetonitrile-valerenitrile (1:1) ratio, and C-fabric as a counter electrode achieved a photo conversion efficiency of 0.0082 and 0.02% respectively. JV plots were shown in Fig. 8a and the parameters were tabulated in Table 3. There is an increase in PCE by 144%. The low efficiency of the cell is due to the dissolution of NF dye from the TiO₂ electrode in the I⁻/I₃⁻ electrolyte.

The same electrode stated above with 0.01 mM NF was measured by changing the electrolyte from I^-/I_3^- to 0.1 M Na₂S as a hole transport layer and 0.1 M KCl as supporting electrolyte and C-fabric as counter electrode shown in the Fig. 8b and the parameters were tabulated in Table 3. The maximuim PCE achieved with this configuration was 0.22%, with an open-circuit voltage (V_{OC}) of 518 mV and short-circuit current density (J_{SC}) of 0.686 mA cm⁻² which are better than the values obitained for devices with the I^-/I_3^- electrolyte. However, the overall efficiency is still very low and furthermore in this electrolyte environment the NF-sensitized TiO₂ layer degraded within few minutes of measurements. Therefore in order to achieve better stabiliity of the dye on the TiO₂ electrode an the aqueous, neutral and saturated

electrolyte (0.001) M $\mathrm{Fe}^{3+}/(0.02 \mathrm{M}) \mathrm{Fe}^{2+}$ and 0.1 M KCl was used, in which $Fe^{3+/2+}$ acts a hole transport layer and KCl was used to stabilize the NF dye attached strongly to the TiO₂ electrode by saturating the electrolyte. For the same TiO_2/NF photoanode electrode, $Fe^{3+/2+}$ as electrolyte and C-fabric as CE, achieved a PCE of 1.84%, with a short circuit current density (J_{SC}) of 10.6 mAcm⁻², open circuit voltage (V_{OC}) of 589 mV and fill factor (FF) of 29.5%. the increase in the PCE from the change in the electrolyte from Na_2S to $Fe^{3+/2+}$ is 736%, which is a great achievement in an increase in PCE and as well as the stabilizing the photoanode to a great extent. For the same photoanode, electrolyte $(Fe^{3+/2+})$ and one-layer CoS/C-fabric as CE, the PCE achieved was 2.9%, with a V_{OC} of 689 mV, J_{SC} of 12.16 mA cm⁻² and FF of 34.4%. The increase in the PCE was 56%, due to the more electroactivity and the conductance of CoS/C-fabric CE. Here CoS makes the more facile to give back the electron from the external circuit to the electrolyte. For, the same photoanode, JV characterization was done under the dark condition for the same cell, shows the PCE of 0.0126% with a V_{OC} of 370 mV and J_{SC} of 0.036 mA cm⁻². Ogale and co-workers fabricated a DSSC by using a natural dye Isobutrin extracted from Butea monosperma flower as photosensitizer achieved a PCE of 1.8% with a V_{OC} of 0.58 V for an optimized architecture of the photoanode and I^{-}/I^{3-} electrolyte (Agarkar et al., 2011). Seigo et al. fabricated a DSSC by with and without a light-scattering layer of TiO₂ and N719 as a sensitizer, I^-/I^{3-} as electrolyte and Pt as a counter electrode achieved an efficiency of 10.1 and 9.12% respectively. There is an increase in PCE of 10% in the presence of the light-scattering layer. The light-scattering layer of TiO₂ helps in the photo-trapping system and active in a photovoltaic generation by itself (Ito et al., 2008). Furukawa and coworkers achieved an efficiency of 0.41% with curcumin dye as a photosensitizer, I^{-}/I^{3-} as electrolyte and Pt as a counter electrode (Furukawa et al., 2009).

Stability tests were performed for the champion cell exhibiting 2.9% PCE with CoS/C-fabric as a CE and Fe^{3+/2+} electrolyte shown in Fig. 8c and the parameters were tabulated in Table 3. Each time before measuring the JV, the electrolyte was injected into the cell. After 1 h continuous irradiance under the sunlight 2.61%, with V_{oc} of 687 mV, J_{SC} of 11.05 mA cm⁻² and FF of 34.38%. Again the cell was exposed to the sunlight for one more hour and achieved a PCE of 2.3%, with a V_{oc} of 653 mV, J_{SC} of 12.01 mA cm⁻² and FF of 29.3%. After continuous exposure to the sunlight for 3, 4 and 5 h the PCE obtained to be 1.82, 1.03 and 0.6% respectively. These results are quite interesting about the good stability and efficiency without the loss of deposited NF.

Fig. 8d shows the variation of EQE responses as a function of wavelength for the TiO_2/NF photoanode and having two different CEs: CoS/C-fabric and C-fabric. For the TiO_2/NF photoanode and C-fabric CE, the maximum EQE is about 60% in the wavelength range of 300–350 nm, which contributes from the TiO_2 and NF. Then, EQE decreases from 60% to 20% in the range of 350–450 nm, as the contribution of NF is less, which will be confirmed from absorbance spectra. EQE varies from 20 to 27% in the region of 450 to 580 nm. For the same cell with C-fabric as a counter electrode, it follows the same trend with the 28–30% decrease in the EQE when compared with to the cell with CoS/C-fabric as the counter electrode.

The *I*–*V* characteristics of the two electrodes measured over a voltage range of -0.1 to +0.1 V are shown in Fig. 9a. The plots show an Ohmic behavior over a narrow voltage range of approximately -0.1 to +0.1 V. The slopes of the straight line fits, in the Ohmic regimes, correspond to the conductance's of the CE materials, as per the relation $[I/V = 1/R = G(\Omega^{-1})]$. The conductance's of C-fabric and CoS/C-fabric are 0.06 and $0.15 \Omega^{-1}$ respectively. The conductance was increased upon the deposition of CoS onto the C-fabric. These conductance values are sufficient for directing the electrons from the external circuit to the oxidized electrolyte species in DSSCs when these materials are employed therein as CEs.

To demonstrate the charge transfer and transport capability of the CoS/C-fabric in the comparison to the C-fabric as a CE, symmetric cells



Fig. 8. *J-V* characteristics of DSSCs under 1 sun (100 mW cm⁻²) illumination (AM 1.5G) with TiO₂/NF as photoanode: (a) with 0.5 and 1 nM concentration of NF, I^-/I^{3-} as electrolyte, C-fabric as counter electrode. (b) with I^-/I^{3-} , 0.1 M Na₂S and (0.001) M Fe³⁺/(0.02 M) Fe²⁺ and 0.1 M KCl as electrolyte, C-fabric as CE and (c) (0.001) M Fe³⁺/(0.02 M) Fe²⁺ and 0.1 M KCl as electrolyte, CoS/C-fabric as CE and at studied after different time. (d) EQE spectra of DSSCs with TiO₂/NF as photoanodes, (0.001) M Fe³⁺/(0.02 M) Fe²⁺ and 0.1 M KCl as electrolyte, CoS/C-fabric as CE.

constructed with $Fe^{3+/2+}$ and KCl as an electrolyte and the EIS were recorded under the dark conditions, at an ac amplitude of 20 mV. The Nyquist plots and the bode plots were performed at short-circuit (Vdc = 0 V) condition and over a frequency range of 1 MHz-0.1 Hz(Fig. 9b). The plots were fitted into a Randles circuit, which is shown in the insert of Fig. 9b, fitted parameters were tabulated in Table 4. In this technique, the same electrode (CoS/C-fabric or C-fabric) serves as a working and counter electrode. R_b is the bulk resistance offered by the electrolyte, obtained from the starting point at high frequency. R_{ct} is the charge transfer resistance of electroactive electrode at the electrode/ electrolyte interface and is obtained from the radius of the first semicircle. $R_{\rm b}$ for the C-fabric is 23.7 Ω cm², which is high when compared to that of the CoS/C-fabric (15.6 Ω cm²). R_{ct} for the CoS/C-fabric is 1.5 Ω cm², which is low when compared to that of C-fabric of 3.6 Ω cm². The low R_{ct} for the CoS/C-fabric indicates the high electrocatalytic activity and good charge transfer rate. Moreover, R_{ct} also measures the reaction barrier in the catalytic reduction of the electrolyte by CE materials and its value is inversely proportional to the redox couple electrolyte regeneration rate (Du et al., 2016). Cdl represents the double layer capacitance at the electrode/electrolyte interface due to the accumulation of ions at the electrode surface. The higher the C_{dl} value for an electrode greater the electrocatalytic activity. The CoS/C-fabric electrode shows a high C_{dl} of 88.6 mF cm² and that of for C-fabric electrode is 39.4 mF cm². The corresponding bode plots were plotted in Fig. 9c and the parameters are tabulated in Table 4. Bode plots give information about the time for charge diffusion across the cross-section

of the electrode. The diffusional time for C-fabric and CoS/C-fabric are 0.6 and 0.26 s respectively, confirms the faster electron diffusion for CoS/C-fabric when compared to that of C-fabric. The SEM images of pristine C-fabric (Fig. 9d, e), show that the fabric is consists of solid cylindrical like carbon fibers with a smooth texture, approximately $5 \,\mu$ m thickness, and their length extends to several millimeters. These interweave and endow the fabric with a mat like an appearance, shown in Scheme 1. Upon SILAR deposition of CoS NPs onto the C-fabric, a CoS/C-fabric CE is formed, and the corresponding SEM image (Fig. 9f, g) shows that the QDs coat on the carbon fibers of the fabric homogeneously and no uncovered portions are visible, implying an intimate contact between the fibers and the dye, which is more favorable for fast electron from the C-fabric to the Fermi level of CoS NPs during DSSC operation.

The morphologies of NF, and TiO_2/NF film are shown in Fig. 10. The FE-SEM images of NF (Fig. 10a) illustrates aggregated particles, with no specific shapes and the sizes of the particles. The porosity in the electrode at different regions is evident from the images marked with yellow circles/eclipses, which allows the easy diffusion of the electrolyte in the electrode (Fig. 10b). The average size of NF particles are in the range of 40–60 nm. The cross-sectional image of the TiO_2/NF photoanode is shown in Fig. 10c. It is observed that the thickness of the film is 5.6 µm, and the deposition of NF is uniform and homogenous. The energy band diagram for a TiO_2/NF assembly is shown in Fig. 11. The positions of VBs and CBs of the different components used in the diagram were determined from CV and absorption studies. Upon

Table 3

Solar cell parameters of cells with different stated electrolyte, exposed cell area: 0.13 to 0.15 cm^2 , under 1 sun illumination (100 mW cm⁻²) with a TiO₂/NF photoanode and C-fabric and CoS/C-fabric as the CE.

Photoanode	Electrolyte	Counter Electrode	V _{OC} (mV)	J_{SC} (mA cm ⁻²)	FF	η (%)
TiO ₂ /NF(0.05 M)	I ⁻ /I ₃ ⁻	C-fabric	389	0.034	62	0.0082
TiO ₂ /NF(0.1 M)	I^{-}/I_{3}^{-}	C-fabric	333	0.103	53	0.018
	0.1 M Na ₂ S	C-fabric	518	0.686	62	0.22
	Fe ³⁺ /Fe ²⁺	C-fabric	589	10.6	29.5	1.84
	Fe ³⁺ /Fe ²⁺	CoS/C-fabric	689	12.16	34.4	2.88
TiO ₂ /NF(1hr sun)	Fe ³⁺ /Fe ²⁺	CoS/C-fabric	687	11.05	34.4	2.61
TiO ₂ /NF(2hr sun)	Fe ³⁺ /Fe ²⁺	CoS/C-fabric	653	12.01	29.3	2.3
TiO ₂ /NF(3hr sun)	Fe ³⁺ /Fe ²⁺	CoS/C-fabric	543	11.98	28	1.82





Table 4

Fitting parameters for EIS spectra of symmetric cells of CEs: C fabric and CoS/C fabric.

CE	$R_b(\Omega)$	R_{ct} (Ω)	C _{dl} (F)	Y _o (S s ^{1/2})	τ (s)
C-fabric CoS/C-fabric	23.7 15.6	3.6 1.5	$\begin{array}{c} 39.4 \times 10^{-6} \\ 88.6 \times 10^{-6} \end{array}$	$\begin{array}{c} 96.3 \times 10^{-3} \\ 175 \times 10^{-3} \end{array}$	0.6 0.26



Fig. 10. SEM images of (a) NF/glass, (b) NF/TiO₂. Cross-sectional image of (c) TiO_2/NF electrode. The yellow colored ellipses in (b) enclose the pores in the films. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 11. Energy band diagram of the complete device.

illumination, the energy level offsets allow excited electrons to be injected from the CB of NF to the CB of TiO_2 . From TiO_2 , the intrinsically produced and injected charge carriers are transferred from the CB of TiO_2 to the current collector (FTO).

Electrochemical impedance spectroscopy of DSSCs with TiO₂/NF as a photoanode, Fe^{3+}/Fe^{2+} with KCl as an electrolyte and with two different CEs; C-fabric and CoS/C-fabric were recorded under the dark conditions, at an ac amplitude of 20 mV. The Nyquist plots are performed at short-circuit ($V_{dc} = 0 V$) condition and over a frequency range of 1 MHz-0.1 Hz are shown in the Fig. 12a and the plots were fitted into a Randles circuit, which is shown as the inset. The fitted parameters were tabulated in Table 5. The point of commencement of the arc (at $Z'' = 0 \Omega$) is attributed to the charge transfer resistance (R_{ct}) at counter electrode/electrolyte, and it is nearly the same for the two different CEs. R_{ct} for both the cells with C-fabric and CoS/C-fabric as CE shows ~ 2.36 and $2.12\,\Omega\,\text{cm}^2.$ The R_{rec} represents the electron recombination resistance offered by the TiO₂/NF and electrolyte interface. The $R_{\rm rec}$ for the C-fabric and CoS/C-fabric as a CE was obtained to be 113 and $84 \,\Omega \,\text{cm}^2$. The respective double layer capacitance C_{dl} represents the accumulation of Fe³⁺/Fe²⁺ species and electrons from the external circuit at CE/electrolyte interface. The C_{dl} values for the cell when the CE C-fabric and CoS/C-fabric was found to be 230 and 197 μ F cm². The greater value of C_{dl} for CoS/C-fabric, suggests the good performance of CE in the solar cell. Yo is a component of the Warburg impedance, and it is directly proportional to the measure of the ease of diffusion of oxidized or reduced (Fe^{3+} or Fe^{2+}) species in the cell. The



Fig. 12. (a) Nyquist and (b) Bode plots of DSSCs with TiO_2/NF photoanode, and C-fabric and CoS/C-fabric as the CE, and recorded under the dark condition and at DC potentials of 0 V. Inset of (a) shows an equivalent Randles circuit.

Table 5

EIS parameters of solar cells with (0.001) M $Fe^{3\,+}/(0.02$ M) $Fe^{2\,+}$ and 0.1 M KCl electrolyte under dark at $V_{dc}=0$ V.

CE	R_{ct} (Ω cm ²)	R_{et} (Ω cm ²)	C_{dl} (µF cm ²)	$Y_{o} (S s^{1/2})$	τ (ms)
C-fabric	2.36	113	230	$\begin{array}{c} 2.14 \times 10^{-3} \\ 8.71 \times 10^{-3} \end{array}$	3.8
CoS/C-fabric	2.12	83.7	197		2.8

 Y_o value was high for the cell when CE as CoS/C-fabric when compared to that of C-fabric. The corresponding bode phase plots are plotted in Fig. 12b and the parameters were summarized in Table 5. The electron transits time (τ_d), is the time taken by the photo-excited electron to reach the current collector through the CB of TiO_2. τ_d can be calculated by the expression $\tau_d = 1/(2\pi f)$, where f is the frequency of the maximum imaginary component. τd for the cell with CoS/C-fabric is 2.8 ms, which is fast when compared to that of the C-fabric (3.8 ms).

To affirm the electron conductivity capability of the New Fuchsin dye, a Mott-Schottky plot is performed in 0.1 M KCl electrolyte with NF deposited on FTO electrode as working electrode, Pt as a counter electrode and Ag/AgCl/KCl as a reference electrode. The Mott–Schottky plots $(1/C^2 \text{ versus } E)$, where C is the capacitance and E is the applied bias varied from -1 to +1 V, are obtained for the NF at two different frequencies of 1 Hz and 10 Hz are shown in Fig. 13. Positive slopes observed for the plots indicating n-type semiconducting with electrons as majority charge carriers.

Finally, to augment the existing literature on the application of NF in organic electronics (Güllü et al., 2010; 2008) thin film transistors were fabricated and tested. Bottom-gate top-contacts OFETs were fabricated using the NF dye as a semiconductor layer. Before the device fabrication process, the glass substrates were cleaned obeying the following steps: (i) an ultrasonic bath with KOH solution and after with deionized water, (ii) boiling acetone bath for 10 min, and (iii) isopropanol bath for 10 min. After that, the gold gate electrode with a thickness of 70 nm was thermally evaporated using a shadow mask. Poly(methyl methacrylate) (PMMA, Sigma Aldrich, MW = 120 kD) was used as the dielectric layer. PMMA (70 mg/mL) was dissolved in



Fig. 13. Mott-Schottky plots of a FTO/NF film, recorded in 0.1 M KCl in dark, with an Ag/AgCl/KCl as a reference electrode, and a Pt rod as the counter electrode.

methyl-ethyl-ketone (MEK) and the solution was deposited by spincoating at 800 rpm for 30 s on top of the gate electrode. The PMMA films were annealed in vacuum at 80 °C for 15 min. The NF dye was dissolved in ethanol (3 mg/mL) and then deposited by spin-coating at 5000 rpm for 1 min on top of the dielectric layer. The device structure was completed by the deposition of the source and drain contacts by thermal evaporation of aluminum (30 nm). The current–voltage characteristics (output and transfer curves) of the New Fuchsin based OFET are presented in Fig. 14. The linear and the saturation regime of the transistor can be observed in the output curves. The device showed poor performance, with low drain current (in the order of 10^{-9} A, so that gate leakage currents were non-negligible) and with the transfer curve showing relatively low changes of the drain current (I_d) as a function of the gate voltage (V_g). Furthermore, the threshold voltage (minimum in the transfer curve) shifted significantly with drain



Fig. 14. (a) Output and (b) transfer curves of the New Fuchsin based OFET.

voltage, indicating the presence of charge traps in the film (Wang et al., 2006). This low drain current can be attributed to the insufficient charge carrier supply from the source to the channel and poor carrier mobility in the film. Thus, NF in its present form seems to be a bad material for the transistor application.

4. Conclusions

In this work, New Fuschin (NF) dye, which is a triphenylmethane derivative, was explored as a photosensitizer in aqueous dye-sensitized solar cell (DSSC) for the first time to the best of our knowledge. A comprehensive study was carried out to understand its molecular and photophysical properties of NF by combining DFT calculations, steadystate absorption and photoluminescence, femtosecond transient absorption (TA) and nanosecond time-resolved fluorescence (TrPL) measurements. The cyclic voltammetry measurements established LUMO level of -3.4 eV, which is higher than the conduction band of TiO2 (-4.2 eV) making the electron injection from the photo-excited NF to the oxide at the NF/TiO2 interface. Both TA and TrPL measurements on NF-adsorbed on mesoporous TiO₂ confirmed ultrafast electron injection at the dye/TiO2 interface. DSSC based on liquid electrolyte was fabricated using carbon fabric as the counter electrode. Interestingly, DSSC fabricated using the most common redox iodide based liquid electrolyte showed extremely poor device performance. Devices used Na₂S based electrolyte showed improved performance compared to iodide electrolyte. However, the best performing device was fabricated using Fe^{3+}/Fe^{2+} in water-based electrolyte with an efficiency 2.9% using CoS/C-fabric counter electrode. Electrochemical impedance spectroscopy studies reveal that the CoS/C-fabric have low R_{ct} and better conductivity and electrocatalytic activity than that of the C-fabric CE. Mott-Schottky shows that the NF dye behaves as an n-type semiconductor. Considering the search for eco-friendly and inexpensive photosensitizers for aqueous DSSC is still in nascent stage. NF is an inexpensive dye available off-shelf in most of the supermarkets in India for price of \approx \$2/gm from reputed chemical supplier Sigma Aldrich while a more efficient DSSC, N719 costs \approx \$ 439/gm. In terms of price comparison of counter electrode the cost of carbon fabric is \$0.1/cm², while Pt-coated CE costs \approx \$10/cm². Finally, the KCL solution with Fe²⁺/Fe³⁺ is very inexpensive and non-toxic, conversely, the Iodide Redox electrolyte is known to be corrosive and expensive. The optimization procedure of the device presented in the manuscript suggests that NF based DSSC is functional in aqueous medium and it doesn't perform well when one employs the standard components of ubiquitous N719 based DSSC. It is possible that NF-based DSSC solar cell performance could be significantly improved with further optimisation by functionalization of end groups with anchoring groups. Thus, by the choice of cell components during the fabrication, a low cost 'green' dyesensitized solar cells based on NF dye with aqueous electrolyte and platinum-free counter electrodes is achieved.

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