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# Efficiency enhancement in dye-sensitized solar cells through neodymium-doped graphene quantum dot-modified TiO<sub>2</sub> photoanodes

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#### ABSTRACT

This study explored the effects of Neodymium-doped graphene quantum dots (NdGQDs) on improving the performance efficiency of  $TiO_2$  based dye-sensitized solar cells (DSSCs). By employing in-situ physical assisted mixing, DSSCs with optimized NdGQDs in  $TiO_2$  photoanodes showed a power conversion efficiency of 8.76 %, a significant improvement compared to the 6.01 % efficiency of pristine  $TiO_2$ -based DSSCs under 100 mW cm<sup>-2</sup> illumination (AM 1.5). Notably, the short-circuit current density increased by 74 %. HRTEM analysis revealed that the NdGQDs have a size range of approximately 7–9 nm. UV–visible spectroscopy and Mott-Schottky analysis revealed a positive shift in the Fermi level, promoting better electron transfer and increased photo-current density at the expenses of the open circuit voltage. Electrochemical impedance spectroscopy characterization of DSSCs incorporating NdGQD-modified photoanodes revealed a reduction in electron transfer resistance at the photoanode|dye|electrolyte interface, accompanied by an increase in recombination resistance within the device suppressing the electron recombination rate.

#### 1. Introduction

Nanotechnology has revolutionized material science, leading to the discovery of advanced carbon-based materials with nanoscale dimensions and exceptional properties. This journey began with the identification of buckminsterfullerene (C60) in 1985, followed by carbon nanotubes in 1991, and graphene in 2004 [1]. Graphene, a two-dimensional, single-atom-thick carbon sheet, has drawn significant attention due to its large surface area, mechanical strength, high carrier mobility, and remarkable flexibility. Its extraordinary electronic properties, particularly its high carrier mobility, position it as a potential alternative to silicon in nanoscale electronic circuits [1–3]. The confinement of electronic states within graphene's honeycomb lattice has given rise to scientific interest of graphene quantum dots (GQDs) in

recent years. These are graphene-based structures with lateral dimensions of a few nanometers, combining the properties of graphene and traditional quantum dots. GQDs offer tunable electronic properties via quantum confinement effects, enabling bandgap engineering for diverse applications, such as third-generation solar cells [4–8]. The doping of GQDs introduces additional functionality, such as luminescence, spin, and electron transport, making them promising candidates for energy conversion and photonic devices. However, challenges persist in synthesizing GQDs with high quantum yield, uniform size, and reproducibility [9–11]. Recent studies have shown that both the doped and un-doped GQDs can effectively be used in Dye-sensitized solar cells (DSSCs) [12–14]. DSSCs a third-generation photovoltaic technology, leverage nanostructured photoanodes to enhance light harvesting and electron transport. DSSCs are attractive due to their cost-effectiveness,

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simple fabrication, and superior performance under diffuse light conditions compared to silicon-based solar cells, which suffer efficiency losses under low-light or angled illumination [15-19]. A typical DSSC comprises three primary components: a TiO2-based photoanode coated with a sensitizing dye, an electrolyte, and a counter electrode. The efficiency of DSSCs heavily depends on the design of the photoanode, with advancements focusing on incorporating nanostructured TiO<sub>2</sub> materials, such as nanoparticles, nanotubes, and mesoporous structures, to increase the surface area for dye adsorption and improve light absorption [20,21]. Surface modifications, such as doping TiO<sub>2</sub> with elements like nitrogen or carbon, further enhance the photoanode's electronic properties, reducing recombination losses and improving electron mobility [22,23]. Recent innovations, such as embedding plasmonic nanoparticles like Ag or Au and developing composite structures (e.g., AgNW@TiO2 or Ag/AgBr/TiO2), have demonstrated significant efficiency enhancements in DSSCs [24-27]. There are limited studies on the doping of TiO<sub>2</sub> with rare-earth elements, including lanthanum (La) [28], cerium (Ce) [29], and neodymium (Nd) [30,31]. Doping with La and Ce has been shown to enhance the short-circuit current density  $(J_{SC})$  by increasing dye loading [32] and improving the electron injection rate [32,33]. Among these, neodymium is considered an excellent dopant for enhancing the electrocatalytic activity of TiO<sub>2</sub>, as the incorporation of  $Nd^{3+}$  ions into the TiO<sub>2</sub> lattice effectively narrows its band gap [30,31, 34,35]. Tadge et al. utilizes the doping of rare earth elements to harvest NIR-visible range light to enhance the photovoltaic performance for their material Y<sub>2</sub>O<sub>3</sub>:Ho<sup>3+/</sup>Yb<sup>3+</sup> into TiO<sub>2</sub> [36]. Moreover, niobium is extensively utilized across various fields, primarily due to its exceptional corrosion resistance and high electrical conductivity, underscoring its critical role in ensuring durability and optimal performance [37].

Apart from that, recent studies have also shown that both the doped and un-doped GQDs can effectively be used in DSSCs [12-14]. The incorporation of carbon-based materials, particularly graphene quantum dots (GQDs), has significantly enhanced the power conversion efficiency (PCE) of DSSCs. Pioneering studies by Lee et al., in 2014 demonstrated that incorporating GQDs into TiO2 based DSSCs improved the PCE from 7.28 % to 7.95 %, reflecting a 9.2 % efficiency enhancement [38]. Similarly, Fang et al., in 2014 achieved a 6 % increase in efficiency, reaching 6.10 % with GQDs-modified TiO2 photoanodes [39]. Salaman et al. documented a notable 29.31 % improvement, attaining an efficiency of 6.22 % using GQDs-decorated electrospun TiO<sub>2</sub> nanofibers [40]. These advancements are attributed to enhanced electron transport, reduced charge recombination, improved dve adsorption, and superior visible light absorption. Further advancements include Riaza et al.'s work on nitrogen-doped carbon quantum dots (N-GQDs), which increased DSSC efficiency by  $\sim$ 15 %, achieving 8.2 % while improving device stability [41]. Kundu et al. reported a 43 % enhancement, achieving an efficiency of 11.7 % through N, F, and S co-doped GQDs [42]. Jahantigh et al. demonstrated a 35 % increase in efficiency, reaching 8.92 %, attributed to reduced charge recombination and improved charge collection efficiency [43]. Other studies explored alternative photoanode materials, such as ZnO with boron-doped GQDs, achieving 3.72 % efficiency [44]. GQDs have also been employed in counter electrode modifications. Chang et al. achieved a PCE of 9.59 % integrating GQDs with graphene foam, leveraging the bv electro-catalytic properties of GQDs for improved photovoltaic performance [45]. Apart from that, rare-earth metal ions doped GQDs have been also used for Near-IR In Vitro/In Vivo/Ex Vivo imaging applications [46]. Although extensive research has been conducted on GQDs and doping of Nd separately in various applications, the incorporation of NdGQDs in DSSCs remains unexplored. Therefore, we have decided to use a Nd as a dopant in the GQDs which shows the absorption in the range of visible to NIR and to integrate NdGQDS with mesoporous TiO<sub>2</sub> films and to investigate the optical, electrical, and its application in DSSCs towards the efficiency enhancement.

#### 2. Experimental details

#### 2.1. Preparation of Nd-doped graphene quantum dots (Nd-GQDs)

The materials utilized are extensively described in S 2.1 (Supporting Information). Neodymium (III) nitrate hexahydrate (8, 32, 128, and 256 mM) aqueous solution and glucosamine hydrochloride (0.04 M) aqueous solution were prepared separately, combined, and stirred for 30 min to synthesize NdGQDs at various concentrations. The mixture was transferred in 5 mL vials to the monowave 200 (microwave reactor) for 45 min at 180 °C and 12 bars of pressure to facilitate the hydro-thermal process with the help of microwave heating. After that, the synthesized quantum dots were removed and cleaned several times in an ultracentrifuge at 20,000 rpm for 20 min.

#### 2.2. Photo-anode preparation

Two-layer TiO<sub>2</sub> photo-anodes on FTO substrates were fabricated according to the previously reported procedure [24]. Initially, for the compact  $TiO_2$  layer, 0.25 g of P90  $TiO_2$  powder was mixed with 1 ml of 0.1 M HNO<sub>3</sub> and ground for 20 min using an agate mortar. The resulting paste was spin-coated for 60 s at 3000 rpm onto an FTO glass substrate that had been cleaned, and then it was sintered for 45 min at 450 °C. After cooling to room temperature, a mesoporous TiO<sub>2</sub> layer was formed using P25 TiO<sub>2</sub> powder. In particular, 0.02 g of Triton X-100 and 0.05 g of PEG 2000 were added as binders to 0.25 g of P25 TiO<sub>2</sub> powder that had been crushed with 1 ml of 0.1 M HNO<sub>3</sub>, resulting in a creamy paste. Using the doctor-blading process, this paste was spread across a 0.25  $cm^2$  area to the previously sintered P90 TiO<sub>2</sub> layer. The substrate with both layers was then sintered again at 450 °C for 45 min, resulting in a photo-anode with a porous TiO2 surface layer. Finally, the photo-anodes were soaked in an ethanolic solution containing 0.3 mM N719 dye at room temperature for 24 h. To assess the impact of incorporating Nd-GQDs into TiO2 on DSSCs performance, various amounts of pre-prepared Nd-doped GQDs solutions at different molar concentrations were physically mixed with P25 TiO2. For the synthesis of TiO<sub>2</sub>-GQDs nanocomposites, physical mixing is the most straightforward technique. Numerous studies have reported synthesizing TiO2-GQDs nanocomposites using this approach, including Sun et al. [47] and Qu et al. [48]. In Sun et al.'s work, a P25 TiO2 (Degussa TiO2) nanomaterial is dissolved into an aqueous GQDs solution and stirred for a whole day. Here, it should be noted that, the weighed amount of 0.25 g of TiO<sub>2</sub> P25 powder sample, was first mixed with doping amounts of NdGQDs solution and was grounded using a mortar and a pestle until it becomes a thick paste then the rest of the P25 layer preparation steps used in reference system starting from adding 0.1 M HNO<sub>3</sub>, 0.6 ml solution were carried out. Table 1 shows the quantities of NdGQDs used in fabricating various TiO<sub>2</sub> photoanodes and their sample codes used.

#### 2.3. Fabrication of DSSCs

Preparation of liquid electrolyte is given in the S 2.2 (Supporting Information). TiO<sub>2</sub> photo-anodes with and without NdGQDs and Pt counter electrodes were sandwiched with the electrolyte ensuring that the active sides of both electrodes were facing each other. These electrodes were held together with steel clips as shown in Fig. 1. Further characterization of the photoanode and the DSSCs device is detailed in the S 2.3 (Supporting Information).

#### 3. Results and discussion

#### 3.1. HRTEM studies of Nd-GQDs

Fig. 2 (a) shows the HRTEM of the NdGQDs. The estimated particle size of these NdGQDs was approximately  $\sim$ 7 ± 2 nm in size and they exhibit high crystallinity as can be seen by the fringes. Fig. 2(b) shows

#### Table 1

The quantities of NdGQDs used in fabricating various  ${\rm TiO}_2$  photoanodes and their sample codes.

Seed Solution	Doping amount	Sample description	Sample code
NdGQDs 8 mM Solution	75 µl	NdGQDs 08 mM(75µl)/ TiO <sub>2</sub>	8M1
	100 µl	NdGQDs 08 mM(100µl)/ TiO <sub>2</sub>	8M2
	150 µl	NdGQDs 08 mM(150µl)/ TiO <sub>2</sub>	8M3
	200 µl	NdGQDs 08 mM(200µl)/ TiO <sub>2</sub>	8M4
NdGQDs 32 mM Solution	75 µl	NdGQDs 32 mM(50µl)/ TiO <sub>2</sub>	32M1
Solution	100 µl	NdGQDs 32 mM(750µl)/ TiO <sub>2</sub>	32M2
	150 µl	NdGQDs 32 mM(100µl)/ TiO2	32M3
	200ul	NdGQDs 32 mM(150µl)/	32M4
NdGQDs 128 mM	75ul	NdGQDs 128 mM(75µl)/	128M1
30101011	100 µl	NdGQDs 128 mM	128M2
	150 µl	(100µ1)/1102 NdGQDs 128 mM (150µ1)/TiO	128M3
NdGQDs 256 mM	75 µl	NdGQDs 256 mM(75µl)/	256M1
Solution	100 µl	NdGQDs 256 mM	256M2
	150 µl	(100µ1)/11O <sub>2</sub> NdGQDs 256 mM	256M3
TiO <sub>2</sub> reference	0	(150µl)/TiO <sub>2</sub> Without Nd-QDs	0M



Fig. 1. Configuration of DSSCs with NdGRQD incorporated  $TiO_2$  photo anode and Pt counter electrode sandwiched with the electrolyte (Not in a scale).

the HRTEM of TiO<sub>2</sub> nano particles obtained from the photoanode and the average crystallite size appears to be in the range of  $\sim$ 15–20 nm.

#### 3.2. SEM studies on photoanodes

Fig. 3 illustrates SEM micrographs of photoanodes prepared with pristine (a)  $TiO_2$  and (b) with the optimized amount of NdGQDs doped  $TiO_2$ . The optimal concentration of NDGQDs was determined through the fabrication and testing of a large number of DSSCs, as detailed in subsequent sections. The SEM images indicate that incorporating NdGQDs does not significantly alter the morphology of the  $TiO_2$  nanoparticles. The estimated average diameter of the  $TiO_2$  nanocrystallites is approximately 15–19 nm, which is consistent with the HRTEM results of  $TiO_2$ .

The cross sectional SEM micrographs of the  $TiO_2$  photoanodes with and without NdGQDs are shown in Fig. 4. The estimated film thickness



Fig. 2. HRTEM image of (a) NdGQDs and (b) P25 TiO<sub>2</sub>.

of TiO<sub>2</sub> photoanodes with and without NdGQDs is approximately  ${\sim}14.06~\mu m$  and  ${\sim}14.08~\mu m$  respectively. These results indicate that the incorporation of NdGQDs does not result in a significant change in the thickness of the photoanode.

Fig. 5 presents the XRD profiles of pristine TiO<sub>2</sub> and NdGQDs integrated TiO<sub>2</sub> samples that were sintered at 450 °C. The diffraction peaks corresponding to the anatase phase (JCPDS No.: 01-084-1285) are evident from the crystal planes (101), (004), (200), (105), (211), and (204). These peaks appear at 20 values of 25.30°, 37.80°, 48.03°, 53.89°, 55.06°, and 62.69°, respectively. The collection of lines with 20 values of 27.39°, 36.08°, 41.23°, and 54.27° is ascribed to the rutile phase (JCPDS No.: 01-089-0552) which corresponds to the crystal planes (110), (101), (111), and (211) respectively. Since the anatase to rutile phase ratio of the P25 TiO<sub>2</sub> is 70:30 the dominance of pure anatase phase can be seen. It suggests that the addition of NdGQDs does not cause a phase shift.

In comparison to pure TiO<sub>2</sub> nanocrystallites, the crystallite size of NdGQDs decorated TiO<sub>2</sub> films rose from 15.38 nm to 19.27 nm, as determined by Scherrer's equation (equation (1)). This is because, during grinding and calcination, some NdGQDs were able to enter the pores of TiO<sub>2</sub> nanocrystalites.

$$\mathbf{D} = \mathbf{K}\lambda/\beta\cos\theta \tag{1}$$

Where K = 0.89 (Schere's constant,  $\lambda = 1.54$  Å and  $\beta =$  FWHM (in radians) and  $\theta =$  Bragg's diffraction angle (in radians) [47–50].

Prominent peaks indicating GQDs in the NdGQDs-TiO<sub>2</sub> mixture are



Fig. 3. Surface view SEM image of (a) Pristine  $\rm TiO_2$  (b) Nd-GQDs/TiO\_2 - photoanode.

also missing from Fig. 5 due to the high surface coverage of TiO<sub>2</sub> and the lower fraction of NdGQDs (100 µl). Moreover, the main peak of graphene ( $2\theta = 24^{\circ}$ ) is obscured by the dominant peak of anatase TiO<sub>2</sub> at ( $2\theta = 25.1^{\circ}$ ). In the same way, Nd-related peaks in the patterns of the nanocomposite samples are also lowered. Since XRD analysis of NdGQDs with TiO<sub>2</sub>, is not available in the literature, a comparison of our data can be somewhat linked and correlated with the results obtained by Ramachandran et al. [51] in the studies of NGQDs/TiO<sub>2</sub> nanocomposites and the results published by Rawal et al. in the composites of N, S-GQDs anchored TiO<sub>2</sub> nanocomposites [52].

Similar to the XRD data reported by previous researchers, the diffraction peak associated with GQDs is typically absent in the diffraction patterns of TiO<sub>2</sub>GQDs nanocomposites. However, when a significant amount of GQDs are incorporated with TiO<sub>2</sub>, the GQDs peak becomes discernible in the diffraction pattern. For instance, Rajender et al. [53] synthesized a TiO<sub>2</sub>-GQDs composite using equal weights of TiO<sub>2</sub> and GQDs. Their observations showed that the strongest peak at  $2\theta = 25^{\circ}$  is associated with the (101) plane of the anatase phase of TiO<sub>2</sub>. Additionally, another prominent peak at  $2\theta = 26.3^{\circ}$  was attributed to the (002) plane of hexagonal sp2-hybridized carbon GQDs. This (002) peak is particularly intense due to the equal weight ratio of TiO<sub>2</sub> and GQDs used in the hybrid sample preparation. Consequently, our results confirm the successful synthesis of a TiO<sub>2</sub>-NdGQDs hybrid with distinct



Fig. 4. Cross-sectional SEM image of (a) pristine TiO<sub>2</sub> (b) NdGQDs/TiO<sub>2</sub>.



Fig. 5. XRD profiles of (a) pristine TiO<sub>2</sub> and (b) TiO<sub>2</sub> with NdGQDs.

crystalline phases [54]. The structural and optical properties of both pristine  $TiO_2$  and NdGQDs-doped  $TiO_2$  are summarized in Table 2. The lattice constants were calculated using the following equation (equation (2)):

#### Table 2

The estimated structural and optical specifications for both pristine TiO<sub>2</sub> (0M) and optimized Nd-GQDs in cooperated TiO<sub>2</sub> (8M2) (Where  $\lambda$  is the X-ray wavelength (1.54178 Å),  $\beta$  is the FWHM of the diffraction peak,  $\theta$  is the angle of diffraction, and D is the average crystallite size).

Sample code	2 <i>θ</i> °	$\beta$ (FWHM) (Deg.)	$D = \frac{k\lambda}{\beta\cos\theta} (\mathrm{nm})$	$a = \left(\frac{\lambda^2}{4(\sin\theta)^2(h^2 + k^2 + l^2)^2}\right)^{1/2}$ (nm)	$c=rac{\lambda}{\sin heta}$ nm	Energy Band gap (eV)
0M	25.410	0.389	22.820	0.377	0.948	3.200
8M2	25.336	0.529	16.780	0.378	0.949	3.080

#### Table 3

Photovoltaic properties of DSSCs fabricated with different photoanodes incooprating NdGQDs under 100 mW cm<sup>-2</sup> (AM 1.5) illumination.

Sample code	$V_{ m OC}$ (mV) $\pm$ 0.04	$J_{ m SC}$ (mA/cm <sup>2</sup> ) $\pm$ 0.03	FF (%) ± 0.04	η (%) ± 0.05
8M1	723.20	16.20	57.27	6.71
8M2	709.05	21.20	58.25	8.76
8M3	724.70	17.10	58.14	7.21
8M4	710.00	16.30	59.54	6.90
32M1	732.80	15.50	58.91	6.69
32M2	752.20	15.50	59.88	7.03
32M3	720.00	16.90	60.43	7.35
32M4	732.70	15.00	59.65	6.62
128M1	723.20	15.30	58.78	6.50
128M2	709.50	17.00	59.04	7.12
128M3	719.70	16.4	58.71	6.90
256M1	745.50	14.40	59.98	6.43
256M2	740.4	17.00	58.02	7.29
256M3	739.70	16.20	58.32	6.99
0M	747.80	12.20	65.80	6.01

#### Table 4

Photovoltaic characteristics of DSSCs fabricated with two different photoanodes (Pristine  $TiO_2$  and  $TiO_2$  with optimized amount of NdGQD).

Sample	Sample code	Voc (mV)	Jsc (mA/ cm <sup>2</sup> )	FF (%)	η (%)
TiO <sub>2</sub> (Reference)	0M	$\begin{array}{c} 747.80 \\ \pm 0.50 \end{array}$	12.20 ±0.25	$\begin{array}{c} 65.80 \\ \pm 0.05 \end{array}$	6.01 ±0.24
TiO <sub>2</sub> with optimized NdGQDs	8M2	$\begin{array}{c} 709.05 \\ \pm 0.60 \end{array}$	$\begin{array}{c} 21.20 \\ \pm 0.04 \end{array}$	$\begin{array}{c} 58.25 \\ \pm 0.04 \end{array}$	$\begin{array}{c} 8.76 \\ \pm 0.25 \end{array}$

#### Table 5

Estimated interfacial resistance in DSSCs with pristine  $\rm TiO_2$  and  $\rm TiO_2$  with optimized amount of NdGQDs photoanodes.

Electrode S	Sample code	<i>Rs</i> (Ω)	$R_{\mathrm{CT1}}\left(\Omega\right)$	$R_{\mathrm{CT2}}\left(\Omega\right)$
TiO <sub>2</sub> ( NdGQD.TiO <sub>2</sub> 8	0M 8M2	$\begin{array}{c} 11.35 \pm 0.35 \\ 09.48 \pm 0.25 \end{array}$	$\begin{array}{c} 5.41 \pm 0.55 \\ 5.88 \pm 0.15 \end{array}$	$\begin{array}{c} 10.80 \pm 0.26 \\ 33.23 \pm 0.34 \end{array}$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} + \frac{l^2}{c^2}$$
(2)

Where d is the inter-planar distance and the Miller indices are (h,k,l). The parameters "a" and "c" are the lattice parameters of the tetragonal structure.

The table reveals a slight decrease in the average crystallite size (D) of  $TiO_2$  upon the addition of Nd-GQDs, as calculated using Scherer's equation. This decrease can be attributed to the confinement effect of graphene, which influences the size of the sp<sup>2</sup> domains, as noted by Ramachandran et al. [51]. Similar observations have also been documented by Gao et al. [54] and Zhang et al. [55]. The Rietveld refinement of the XRD patterns for both samples provided valuable data. As shown in Table S1 (Supporting Information), the lattice parameters "a" and "c" for both TiO<sub>2</sub> nanoparticles (NPs) and the NdGQDs/TiO<sub>2</sub> composite were calculated from the XRD patterns. We observed differences in the lattice parameters for both the anatase and rutile phases of TiO<sub>2</sub>, which

indicates that the incorporation of NdGQDs affects the lattice structure of TiO<sub>2</sub>.

However, despite scanning the  $2\theta$  range of  $20-25^{\circ}$  (where GQDs typically show characteristic peaks), no significant XRD peaks corresponding to GQDs were observed in the composite. We employed a finer scan rate in this region, but still found no discernible peak shifts or intensity changes between the TiO<sub>2</sub> and TiO<sub>2</sub>/NdGQDs composites. This suggests that, while NdGQDs appear to influence the lattice parameters of TiO<sub>2</sub>, their presence is not directly detectable in the XRD patterns within the scanned range.

Fig. 6(A) presents the UV–visible absorption spectra of TiO<sub>2</sub> with and without the incorporation of the optimal amount (100  $\mu$ L) of 0.8 mM) NdGQD. Additionally, Fig. 6(B) illustrates the UV–visible absorbance of both pristine and modified TiO<sub>2</sub> in the presence of the dye. Consistent with the SEM analysis, the absorbance comparison was conducted using the optimized NdGQD concentration in the photoanode, which corresponds to the highest  $J_{SC}$  in the DSSCs.

The intrinsic properties of graphene quantum dots (GQDs)including shape, size, and edge structures-play a crucial role in determining the positioning of absorption peaks in UV-Vis spectra. These properties are further influenced by factors such as functional groups, solvent interactions, and temperature variations. Curve (b) in Fig. 6 (A) shows that pristine  $TiO_2$  exhibits low absorption in the 390-800 nm range, with a characteristic cut-off wavelength at approximately 384 nm, primarily due to electron transitions from the valence band to the conduction band in titania, which has a wide band gap energy of 3.2 eV. This wide band gap restricts TiO<sub>2</sub> to predominantly UV light absorption. In addition to that, the NdGQDs/TiO2 composite displays similar absorption characteristics in the visible and near-IR regions. However, the absorption intensity of the NdGQDs/TiO2 composite is higher than that of pristine TiO<sub>2</sub> as can be seen from the curve (a) in Fig. 6(A). As it is evident from Fig. 6 (B) the NdGQDsincorporated TiO<sub>2</sub>/Dye sample exhibits a significant red shift in the absorption peak, moving from 530 nm to 533 nm, following the deposition of NdGQDs onto TiO<sub>2</sub>. This red shift enhances the photoresponse into the visible and near-infrared (NIR) regions, largely due to the wide absorption range of NdGQDs, which extends up to around 700 nm, as observed by Yu et al. [57]. Furthermore, the spectral intensity of the NdGQDs-incorporated sample is higher than that of the pristine TiO<sub>2</sub> sample. This indicates that the incorporation of NdGQDs enhances the visible light absorption of  $TiO_2$ , resulting in increased sensitivity of the semiconductor to visible light [56–58].

The calculated optical bandgap curves of TiO<sub>2</sub> nanoparticles (NPs) and NdGQDs/TiO<sub>2</sub> are illustrated in Fig. 7 as in the supplementary information. These band gaps were derived using the Kubelka-Munk method by plotting  $(kh\nu)'_2$  against photon energy  $(h\nu)$ . The findings reveal that the incorporation of NdGQDs into TiO<sub>2</sub> reduces the energy band gap to 3.08 eV, contrasting with the pristine TiO<sub>2</sub> band gap of 3.19 eV.

As demonstrated by Lim et al. [58] and Bokare et al. [59], this notable blue-shift in the bandgap energy of NdGQDs/TiO<sub>2</sub> is linked to the formation of Ti-O-C bonds between NdGQDs and TiO<sub>2</sub> [60]. This interaction facilitates an efficient interfacial charge transfer between TiO<sub>2</sub> and NdGQDs, resulting in an extended lifetime of the excited states due to enhanced charge separation within the nanocomposites. As a result, the integration of NdGQDs onto the surface of TiO<sub>2</sub> modifies the



Fig. 6. UV–Visible absorption spectra of (A): (a) Pristine TiO<sub>2</sub> and (b) NdGQDs/TiO<sub>2</sub> photoanodes and (B): (a) Pristine TiO<sub>2</sub>/Dye and (b) NdGQDs/TiO<sub>2</sub>/Dye. (With the optimum NdGQD amount 100 µl of 08 mm NdGDQ).

optical bandgap, enabling the nanocomposite to generate electron-hole pairs under irradiation with longer-wavelength of light. Incorporating NdGDQ into TiO<sub>2</sub> reduces the band gap and causes a corresponding shift in the quasi-Fermi level  $(E_{Fn})$  or flat-band potential, leading to change in energy level differences between the redox potential and  $E_{\rm Fn}$  [61,62]. In order to see this effect, Mott-Schottky measurements were employed to estimate the flat-band potentials of pure TiO2 and NdGQDs/TiO2 photo anodes, as shown in Fig. 7(a) and (b). The  $E_{\rm Fn}$  was derived from the x-axis intercept of the Mott-Schottky plots. A positive shift is observed in the  $E_{\rm Fn}$  from -0.457 V to -0.317 V upon NdGDQ incorporation indicating a lower  $E_{\rm Fn}$  for NdGQD/TiO<sub>2</sub> compared to that of TiO<sub>2</sub>. Since the open-circuit photovoltage (Voc) of a DSSC depends on the energy difference between the  $E_{\rm Fn}$  and the redox potential of  $I_3^-/I^-$  [63–65], this shift results in a slight decrease in Voc, as illustrated schematically in Fig. 8. However, despite this reduction in Voc, the energy gap between the LUMO level of the dye and *E*<sub>Fn</sub> increases, enhancing the driving force for electron injection. This improvement boosts electron transfer efficiency from the LUMO of the dye to  $E_{\rm Fn}$  of TiO<sub>2</sub>, reducing recombination between injected electrons and dye cations or triiodide ions. Consequently, the short circuit current density  $(J_{SC})$  is enhanced. Similar effects have been reported by others when modifying TiO<sub>2</sub> as well as SnO<sub>2</sub> with various materials [62,64,65].

#### 3.3. Cyclic voltammetry analysis of photoandes

The  $V_{OC}$  value of DSSCs is determined by the relationship between the quasi Femi level of electrons ( $E_{Fn}$ ) and the redox potential ( $E_{redox}$ ) of



Fig. 7. Mott-Schottky analysis and the calculated flat band potential values of (a) TiO\_2 and (b) NdGQDs/TiO\_2.

the electrolyte. Assuming  $E_{\text{redox}}$  remains constant,  $V_{\text{OC}}$  is primarily governed by  $E_{\text{F,n}}$  of TiO<sub>2</sub>. The  $E_{\text{Fn}}$  is expressed as follows [66]:

$$E_{\rm F,n} = E_{\rm CB} + k_B T \ln\left(\frac{n}{N_{\rm CB}}\right) \tag{3}$$

Where,  $E_{CB}$  is the conduction band edge of TiO<sub>2</sub>, *T* is the absolute temperature,  $k_B$  is the Boltzmann constant,  $N_{CB}$  represents the effective density of states in the conduction band and *n* is the electron concentration in TiO<sub>2</sub>. The electron concentration *n* is influenced by the carrier transfer processes such as electron injection and recombination [67].

According to equation (2)  $E_{\rm Fn}$  can be increased either by shifting  $E_{\rm CB}$  closer to the vacuums level or by increasing electron concentration *n* in TiO<sub>2</sub>. These changes lead to an enhancement in  $V_{\rm OC}$  [67]. To examine the alterations in trap states induced by the incorporation of Nd-GQDs and their impact on  $V_{\rm OC}$ , cyclic voltammetry (CV) measurements were conducted. These studies were performed on TiO<sub>2</sub> electrodes sensitized with N719 dye alone (curve a, Fig. 9 A) and in combination with Nd-GQDs (curve b, Fig. 9(A)) with a scan rate of 50 mV/s and the AgCl/Ag reference electrode.

CV studies can be employed to determine the energy distribution of acceptor states on the  $TiO_2$  electrode surface. The measured current, I (V), is proportional to the differential capacitance (C) under linear potential sweeps with a constant scan rate (dV/dt = v). The injected charge, Q, can be expressed as:

$$dQ = \frac{1}{\nu} I(V) dV \tag{4}$$

By dividing the derivative dQ/dV by the elementary charge (e), the density of occupied states (DOS) is obtained [68,69] The total injected charge (Q) can be calculated by integrating the above expression, and the resulting values are plotted as a function of electrode potential in Fig. 9(B)

As illustrated in the figure, the onset potential for the TiO<sub>2</sub> electrode sensitized with N719 alone (Fig. 9 (B)) was approximately -0.62 V. In contrast, the TiO<sub>2</sub> electrode incorporated with Nd-GQDs exhibited an onset potential around -0.43 V. This shift suggests a slight lowering of the conduction band edge of TiO<sub>2</sub>, as well as the Fermi level (*E*) and eventually decrease in the  $V_{OC}$  [70,71].

As described in the experimental section,  $TiO_2$  photoanodes were prepared with varying amounts of NdGQDs, derived from four different seed solutions containing Nd concentrations of 8 mM, 32 mM, 128 mM, and 256 mM. In each of these solutions, the amount of Nd is varied. From each seed solution, four different amounts of NdGQDs were used in the fabrication of photoanodes. Table 2 presents the doping concentrations of Nd-GQDs used in the fabrication of  $TiO_2$  photoanodes and their



Fig. 8. Schematic diagram showing the effect of incorporation of NdGQDs in  $TiO_2$  shifting of conduction band and the Fermi level of  $TiO_2$  towards the redox potential.



Fig. 9. (A) Cyclic voltammograms of pristine and NdGQD incorporated TiO<sub>2</sub> photoanodes and (B) Energy levels at the TiO<sub>2</sub>/electrolyte interface.

corresponding photovoltaic properties under 100 mW cm<sup>-2</sup> (AM 1.5) illumination. As can be seen from the table, the incorporation of NdGQDs into the TiO<sub>2</sub> increased the photovoltaic properties of DSSCs. Eight DSSCs were tested in each composition to ensure that all of these devices could be repeated; the table shows any differences in efficiency ratings. As is observed from the table, the incorporation of NdGQDs from 100 µl of 8 mM seed solution gave the highest efficiency in DSSCs. The optimal amount of neodymium NdGQDs for achieving the highest efficiency in DSSCs is determined to be within the 100 µL of 8 mM seed solution. The highest photo-conversion efficiency ( $\eta$ %) is observed in DSSC with NdGQDs 08 mM (100 µl)/TiO<sub>2</sub> which is 8.761 % with short circuit current density ( $J_{SC}$ ) of 21.2 mA cm<sup>-2</sup>, Open circuit voltage ( $V_{OC}$ ) of 709.05 mV and 58.25 % fill factor (FF).

Fig. 10 presents the J-V characteristics of DSSCs fabricated using TiO<sub>2</sub> photoanodes, with and without the incorporation of optimized NdGQDs. The estimated photovoltaic parameters are tabulated in Table 4. The DSSCs fabricated with NdGQDs CEs showed a remarkably high  $J_{SC}$  at the expenses of the  $V_{OC}$  with more than a 45 % overall efficiency enhancement. This phenomenon is correlated with the positive shift of the flat potential of TiO<sub>2</sub> as observed in the Mott-Schottky analysis and the UV–Vis absorption of the photoanode with NdGQDs. The  $J_{SC}$  and  $V_{OC}$  of the DSSCs fabricated with NdGQDs/TiO<sub>2</sub>/Dye photoanode are 20.03 mA/cm<sup>2</sup> and 0.73V, respectively, which show improvements compared to cells with bare TiO<sub>2</sub>/dye. As a result, the DSSCs employing NdGQDs/TiO<sub>2</sub>/Dye demonstrated an enhanced power conversion efficiency (PCE) of 8.76 %, whereas the DSSCs utilizing bare TiO<sub>2</sub> achieved a PCE of 6.01 %. A significant enhancement in the  $J_{SC}$ , approximately 74 %, is observed for the NdGQDs/TiO<sub>2</sub>/Dye cell in



Fig. 10. Current density vs voltage (*J-V*) curves of the DSSCs fabricated with different photoanodes (a)  $TiO_2$  and (b)  $TiO_2$  with optimized NdGQDs.

comparison to the TiO<sub>2</sub>/Dye cell. Consequently, the  $\eta$  of the NdGQDs/TiO<sub>2</sub>/Dye cell exhibits an increase of approximately 46 %, attributed to the elevated Jsc (see Table 5).

Fig. 11 illustrates the incident photon-to-electron conversion efficiency (IPCE) spectra for DSSCs throughout a wavelength range of 300–800 nm. The DSSCs with optimized NdGQDs incorporated  $TiO_2$  photoanode exhibited an approximately 10 % improvement in IPCE, achieving a peak value of 49 %, compared to the pristine  $TiO_2$  photoanode, which had a IPCE peak of 44 %. The IPCE spectrum data for the DSSCs utilizing NdGQD -incorporated  $TiO_2$  photoanode exhibit strong correspondence with their absorption spectra (Fig. 6) and the *J*sc values derived from *J*–V measurements, as summarized in Table 3. Further, the *J*sc values determined from both the *J*-V characteristics (21.20 mA cm<sup>-2</sup>) and the integration of the IPCE curve (20.85 mA cm<sup>-2</sup>) exhibit a close agreement.

The improved efficiency of these DSSCs can be attributed to two primary mechanisms. Firstly, the incorporation of NdGQDs enhances the porosity and surface roughness of TiO<sub>2</sub> crystallites, facilitating the adsorption of more dye molecules. This results in a higher generation of photoelectrons, as confirmed by IPCE studies, thereby increasing *Jsc.* Secondly, as revealed by UV–Visible absorption and Mott-Schottky analysis, NdGQDs induce a positive shift in the  $E_{\rm Fn}$  and CB of TiO<sub>2</sub>. This shift enhances the electron transfer rate from the excited dye molecules to the conduction band, as illustrated in Fig. 8. Consequently, this accelerated electron transfer reduces recombination with the oxidized electrolyte, aligning with findings from previous studies on various dopants in TiO<sub>2</sub> [28–30].

An electrochemical impedance study (EIS) might be used to discuss the interfacial charge transfer mechanism. Usually, EIS spectra or Nyquist plots consist of two semicircles: one in the high-frequency region and the other half semi-circle in the low-frequency range. The redox reaction of I  $^{-}/I_{3}^{-}$  at the Pt/electrolyte interface is represented by the first semicircle in the high-frequency area, while the electron transfer at the photoanode/electrolyte interface (Rct) is shown by the second semicircle in the low-frequency zone [72].

Fig. 12 shows the corresponding Nyquist plots of the DSSCs fabricated either with pristine  $TiO_2$  or NdGDQ/ $TiO_2$  photoanode. Impedance data obtained were analyzed using equivalent electrical circuit model (insert in Fig. 12(c)) and NOVA software, allowing estimation of EIS parameters. The following is a description of the fitting components.  $R_{CT1}$  is the charge transfer resistance of the Pt/electrolyte interface, while  $R_S$  is mostly made up of the device's series resistance.  $R_{CT2}$ , sometimes referred to as the recombination resistance, is the charge transfer resistance at the photoanode/electrolyte interface. The components in constant phase are CPE<sub>1</sub> and CPE<sub>2</sub>. W is the element of finite



Fig. 11. The IPCE spectra of DSSCs with (a) pristine  $\rm TiO_2$  and (b) NdGQDs/  $\rm TiO_2$  photoanodes.

Warburg impedance associated with the diffusion process. The resistances  $R_{\rm S}(\Omega)$ ,  $R_{\rm CT1}(\Omega)$ , and  $R_{\rm CT2}(\Omega)$  were calculated from the fitting data and listed in Table 4.

As shown in Table 4, the  $R_{\rm S}$  values and the  $R_{\rm CT1}$  values are nearly the same in both cases, regardless of whether NdGQDs is incorporated or not. The slight variations and reduction in R<sub>S</sub> and R<sub>CT1</sub> observed in the NdGQD-incorporated cells can be attributed to modifications at the FTO/TiO<sub>2</sub> interface caused by the presence of NdGQDs. The incorporation of NdGQDs likely enhances the electron-conducting pathways, as evidenced by the increased short-circuit current density (Table 3), thereby contributing to an overall improvement in device efficiency. In contrast, DSSCs containing NdGQDs incorporated TiO<sub>2</sub> photoanode exhibited much higher R<sub>CT2</sub> value than that of the DSSCs fabricated with pristine TiO<sub>2</sub>. This suggests that the recombination of the photoelectrons at the photoanode/electrolyte interface is reduced and effective electron transfer from TiO<sub>2</sub> into the FTO layer is enhanced, resulting in the increase in the short circuit current density as well as the overall efficiency of the DSSCs. These values are correlated with the higher  $J_{SC}$  observed in the DSSCs with NdGQDs incorporated photoanode. The high charge transfers resistance (R<sub>CT2</sub>) is essential for suppressing dark current resulting from charge recombination thereby improving the shortcircuit current density in DSSCs [73-76].

## 3.4. Raman spectroscopy studies on photo anodes with and without Nd-GQDs

Raman spectroscopy is widely recognized as a versatile, non-invasive optical technique that enables high-throughput analysis of graphene, including the assessment of structural defects, layer count, and doping levels. In order to see the existence of the NdGDQ is in the photoanode Raman analysis have been carried out on the TiO<sub>2</sub> electrodes with and without incooperation of NdGQDs and spectra are shown in Fig. 13.

The Raman spectrum of anatase TiO<sub>2</sub> exhibits five prominent Ramanactive modes at 151 cm<sup>-1</sup>, 199 cm<sup>-1</sup>, 397 cm<sup>-1</sup>, 515 cm<sup>-1</sup>, and 639 cm<sup>-1</sup>, as illustrated in Fig. 13. These peaks confirm that the anatase phase is the sole TiO<sub>2</sub> structure present. The Raman spectrum of graphene is characterized by two key features: the G and D bands, each originating from distinct physical phenomena. The G band, observed at approximately 1580 cm<sup>-1</sup>, corresponds to the doubly degenerate E2g mode of graphite and arises from zone-center optical phonons, representing the in-plane vibration of sp<sup>2</sup>-bonded carbon atoms. The D band, located at around 1347 cm<sup>-1</sup>, is associated with structural defects and disorders. For exfoliated graphene, the intensity ratio of the D to G bands (I<sub>D</sub>/I<sub>G</sub> = 0.086) is remarkably low, indicating minimal defect density in the graphene [77]. Combined high-resolution transmission electron microscopy (HRTEM) and Raman analyses of Nd-GQDs and NdGQD/TiO<sub>2</sub> confirm the presence of NdGQDs within the photoanode.

#### 4. Conclusion

We have successfully explored that the incorporation of NdGQDs into the TiO<sub>2</sub> photoanode impressively enhances the photovoltaic properties of DSSCs. Nd-doped GQDs were synthesized with an average size below 10 nm with four different dopant amounts (8, 32,128, and 256 mM) of Nd. It was observed that the photoelectric conversion efficiency of DSSCS reached a maximum of 8.76 % when 100 µl of 8 mmol NdGQDs were incorporated with TiO<sub>2</sub> anodes in DSSCs. A remarkable enhancement in the short-circuit current density  $(J_{sc})$ , approximately 74 %, is observed for the DSSCs with NdGQDs/TiO2 photoanode positive shift in the Fermi level is revealed by the UV vis and Mott-Schotkey analysis. The improved light absorption of the dye-adsorbed photoanode and the enhanced injection efficiency of electrons from the lowest unoccupied molecular orbital (LUMO) of the dye to the conduction band of TiO2 could be the cause of the enhancement in the photovoltaic parameters of the DSSCs with NdGQDs incorporated photoanodes. EIS analysis of DSSCs with NdGQD-modified photoanodes demonstrated a



Fig. 12. Nyquist plots of fabricated DSSCs cells (a) with pristine TiO<sub>2</sub> (b) TiO<sub>2</sub> with optimized NdGQDS in DSSCS and (c) Equivalent circuit diagram used to estimate the interfacial resistances.



Fig. 13. Raman spectra of (a) pristein and (b) NdGQD/TiO<sub>2</sub> electrodes.

reduction in electron transfer resistance at the photoanode|dye|electrolyte interface, along with an increase in the recombination resistance of the device. These factors collectively contributed to enhanced cell efficiency and a reduced electron recombination rate.

#### CRediT authorship contribution statement

G.K.R. Senadeera: Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Conceptualization. W. M.S.K. Weerasekara: Investigation, Formal analysis, Data curation. T. Jaseetharan: Investigation, Formal analysis, Data curation. P.U. Sandunika: Investigation, Formal analysis, Data curation. J.M.K.W. Kumari: Investigation, Formal analysis, Data curation. M.A.K.L. Dissanayake: Supervision, Resources, Project administration, Funding acquisition. Mohammad Muhiuddin: Validation, Resources, Methodology, Conceptualization. Mohammad Rizwan Rahman: Writing – review & editing, Resources, Methodology, Investigation, Formal analysis, Conceptualization. Udaya Bhat K: Writing – review & editing, Funding acquisition, Conceptualization. Mohammad Waseem Akhtar: Writing – review & editing, Visualization, Validation, Resources. Udaya Kumar: Writing – review & editing, Validation, Resources, Project administration, Investigation. A.B. Siddique: Writing – review & editing, Visualization, Validation, Resources. Piyasiri Ekanayake: Writing – review & editing, Visualization, Resources, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:G. K.R. Senadeera reports a relationship with Open University of Sri Lanka that includes: employment and funding grants. M.A.K.L. Dissanayake reports a relationship with National Institute of Fundamental studies, Kandy, Sri Lanka that includes: employment. Piyasiri Ekanayake reports a relationship with University of Brunei Darussalam that includes: funding grants. No If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.physb.2024.416797.

#### Data availability

Data will be made available on request.

#### References

- Z. Zhang, J. Zhang, N. Chen, Liangti Qu, Graphene quantum dots: an emerging material for energy-related applications and beyond, Energy Environ. Sci. 5 (2012) 8869–8890, https://doi.org/10.1039/c2ee22982j.
- [2] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films,", Sci. Sci. 306 (2004) 666–668, https://doi.org/10.1126/science.1102896.
- [3] Z. Wang, H. Zeng, L. Sun, Graphene quantum dots: versatile photoluminescence for energy, biomedical, and environmental applications, J. Mater. Chem. C 3 (6) (2014) 1157–1165, https://doi.org/10.1039/C4TC02536A.
- [4] M. Bacon, S.J. Bradley, T. Nann, Graphene quantum dots, Particle and Particle system characterization 31 (2014) 4415–4428, https://doi.org/10.1002/ ppsc.201300252.
- [5] P. Tian, L. Tang, K.S. Teng, S.P. Lau, Graphene quantum dots from chemistry to applications, Mater. Today Chem. 10 (2018) 221–258, https://doi.org/10.1016/j. mtchem.2018.09.007.
- [6] X. Yan, X. Cui, L.S. Li, Synthesis of large, stable colloidal graphene quantum dots with tunable size, J. Am. Chem. Soc. 132 (17) (2010) 5944–5945, https://doi.org/ 10.1021/ja1009376.
- [7] Y. Yan, J. Chen, N. Li, J. Tian, K. Li, J. Jiang, J. Liu, Q. Tian, P. Chen, Systematic bandgap engineering of graphene quantum dots and applications for photocatalytic water splitting and CO<sub>2</sub> reduction, ACS Nano 12 (4) (2018) 3523–3532, https:// doi.org/10.1021/acsnano.8b00498.
- [8] Z. Jin, P. Owour, S. Lei, L. Ge, Graphene, graphene quantum dots and their applications in optoelectronics, Curr. Opin. Colloid Interface Sci. 20 (5–6) (2015) 439–453, https://doi.org/10.1016/j.cocis.2015.11.007.
- [9] S.M.M. Dubois, Z. Zanolli, X. Declerck, J.C. Charlier, Electronic properties and quantum transport in Graphene-based nanostructures, Eur. Phys. J. B 72 (1) (2019) 1–24, https://doi.org/10.1140/epjb/e2009-00327-8.
- [10] S.J. Lee, J. Theerthagiri, P. Nithyadharseni, P. Arunachalam, D. Balaji, A. M. Kumar, J. Madhavan, V. Mittal, M.Y. Choi, Heteroatom-doped graphene-based materials for sustainable energy applications: a review, Renew. Sustain. Energy Rev. 143 (2021), https://doi.org/10.1016/j.rser.2021.110849. June 110849.
- [11] M. Muhiuddin, N.A. Devi, N. Bharadishettar, S. Meti, A.B. Siddique, M. N. Satyanarayan, B.K. Udaya, W. Akhtar, M.R. Rahman, Facile and rapid method to synthesis sulfur and nitrogen co-doped graphene quantum dots as an electrode material with excellent specific capacitance for supercapacitors application, Diam. Relat. Mater. 146 (2024), https://doi.org/10.1016/j.diamond.2024.111232.
- [12] L. Kim, B. Lee, Y.J. Kim, S.W. Hwang, Enhancement of dye-sensitized solar cells efficiency using graphene quantum dots as, Photoanode Bull. Korean Chem. Soc. 40 (2019) 56–61, https://doi.org/10.1002/bkcs.11664, 2019.
- [13] T. Dey, A. Ghorai, S. Das, S.K. Ray, Solvent-engineered performance improvement of graphene quantum dot sensitized solar cells with nitrogen functionalized GQD photosensitizers, Sol. Energy 236 (1) (2022) 17–25, https://doi.org/10.1016/j. solener.2022.02.048.
- [14] M.V. Prabhagar, M.P. Kumar, C. Takahashi, S. Kundu, T.N. Narayanan, D. K. Pattanayak, Boron-doped graphene quantum dots: an efficient photoanode for a dye sensitized solar cell, New J. Chem. 43 (2019) 14313–14319, https://doi.org/10.1039/C9NJ00052F.
- [15] K. Sharma, V. Sharma, S.S. Sharma, Dye-sensitized solar cells: fundamentals and current status, Nanoscale Res. Lett. 13 (2019) 381, https://doi.org/10.1186/ s11671-018-2760-6.
- [16] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO<sub>2</sub> films, Nature 353 (1991) 737–740, https://doi.org/ 10.1038/353737a0.
- [17] E. Tylianakis, G. Psofogiannakis, G.E. Froudakis, Li-doped pillared graphene oxide: a graphene-based nanostructured material for hydrogen storage, J. Phys. Chem. Lett. 1 (16) (2010) 2459–2464, https://doi.org/10.1021/jz100733z.
- [18] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells, Chem. Rev. 110 (11) (2010) 6595–6663, https://doi.org/10.1021/cr900356p.
- [19] T.V. Arjunan, T.S. Senthil, Dye sensitized solar cells, Materials Technology Advanced Performance Materials 28 (1–2) (2013) 9–14, https://doi.org/10.1179/ 1753555712Y.0000000040.
- [20] H.A. Ribeiro, P.M. Sommeling, J.M. Kroon, A. Mendes, C.A.V. Costa, Dye-sensitized solar cells: novel concepts, materials, and state-of-the-art performances, Int. J. Green Energy 6 (3) (2009) 245–256, https://doi.org/10.1080/ 15435070902880901.
- [21] M.A.K.L. Dissanayake, S. Senthuran, G.K.R. Senadeera, Efficiency enhancement in dye-sensitized solar cells using hierarchical TiO<sub>2</sub> submicron size spheres as a light scattering layer, J. Solid State Electrochem. 24 (2020) 2261–2269, https://doi.org/ 10.1007/s10008-020-04727-7.
- [22] J. Zhang, Q. Sun, J. Zheng, X. Zhang, Y. Cui, P. Wang, W. Li, Y. Zhu, The characterization of nitrogen doped TiO<sub>2</sub> photoanodes and its application in the dye sensitized solar cells, J. Renewable Sustainable Energy 3 (2011) 033108, https:// doi.org/10.1063/1.3599840.
- [23] A. Colombo, C. Dragonetti, D. Roberto, R. Ugo, N. Manfredi, P. Manca, G. Brusatin, A carbon doped anatase TiO<sub>2</sub> as a promising semiconducting layer in Ru-dyes based dye-sensitized solar cells, Inorg. Chim. Acta. 19 (1) (2019) 263–268, https:// doi.org/10.1016/j.ica.2019.02.024, 489.

- [24] M.A.K.L. Dissanayake, J.M.K.W. Kumari, G.K.R. Senadeera, C.A. Thotawatthage, Efficiency enhancement in plasmonic dye-sensitized solar cells with TiO<sub>2</sub> photoanodes incorporating gold and silver nanoparticles, Appl Electrochem 46 (2019) 47–58, https://doi.org/10.1007/s10800-015-0886-0.
- [25] H.K.H. D, Kankanamge, J.M.K.W. Kumari, M.A.K.L. Dissanayake, G.K. R. Senadeera, B.S. Dassanayake, H.C.S. Perera, Highly efficient dye-sensitized solar cells with TiO<sub>2</sub>-coated silver nanowire-incorporated tri-layered photoanode, Bull. Mater. Sci. 46 (2023) 145, https://doi.org/10.1007/s12034-023-02977-5.
- [26] I.H.K. Madigasekara, H.C.S. Perera, J.M.K.W. Kumari, G.K.R. Senadeera, M.A.K. L. Dissanayake, Photoanode modification of dye-sensitized solar cells with Ag/ AgBr/TiO<sub>2</sub> nanocomposite for enhanced cell efficiency, Sol. Energy 230 (8) (2021) 59–72, https://doi.org/10.1016/j.solener.2021.10.015.
- [27] D.A.K. Ramadhani, N. Sholeha, N.N. Khusna, M. Diantoro, A.N. Afandi, Z. Osman, H. Pujiarti, Ag-doped TiO<sub>2</sub> as photoanode for high performance dye sensitized solar cells, Materials Science for Energy Technologies 7 (2024) 274–281, https://doi. org/10.1016/j.mset.2024.02.002.
- [28] J. Zhang, Z. Zhao, X. Wang, T. Yu, J. Guan, Z. Yu, Z. Li, Z. Zou, Increasing the oxygen vacancy density on the TiO<sub>2</sub> surface by La-doping for dye-sensitized solar cells, J. Phys. Chem. C (2010) 18396–18400, https://doi.org/10.1021/jp911663k.
- [29] M.I. Khan, A. Suleman, M.S. Hasan, S.S. Ali, I. Tahani Al-Muhimeed, A. Abeer, AlObaid, M. Iqbal, M.M. Almoneef, N. Alwadai, Effect of Ce doping on the structural, optical, and photovoltaic properties of TiO<sub>2</sub> based dye-sensitized solar cells, Mater. Chem. Phys. 274 (1) (2021) 125177, https://doi.org/10.1016/j. matchemphys.2021.125177.
- [30] A. Gopalraman, J. Anandha Raj, S. Karuppuchamy, S. Vijayaraghavan, Investigation on the effect of neodymium ion doping in TiO<sub>2</sub> on the photovoltaic performance of dye-sensitized solar cells, Mater. Chem. Phys. 292 (2022) 126785, https://doi.org/10.1016/j.matchemphys.2022.126785.
- [31] Q. Yao, J. Liu, Q. Peng, X. Wang, Y. Li, Nd-doped TiO<sub>2</sub> nanorods: preparation and Application in Dye-sensitized solar cells, Chem. Asian J. 1 (2006) 737–741, https://doi.org/10.1016/j.jpowsour.2011.02.031.
- [32] S. Yahav, S. Rühle, S. Greenwald, H.N. Barad, M. Shalom, A. Zaban, Strong efficiency enhancement of dye-sensitized solar cells using a La-modified TiCl<sub>4</sub> treatment of mesoporous TiO<sub>2</sub> electrodes, J. Phys. Chem. C 115 (2011) 21481–21486, https://doi.org/10.1021/jp2042679.
- [33] S.W. Chen, J.M. Lee, K.T. Lu, C.W. Pao, J.F. Lee, T.S. Chan, J.M. Chen, Band-gap narrowing of TiO2 doped with Ce probed with X-ray absorption spectroscopy, Appl. Phys. Lett. 97 (2010) 2–5, https://doi.org/10.1021/jp2042679.
- [34] Nettu, S. Singh, P. Srivastava, L. Bahadur, Hydrothermal synthesized Nd-doped TiO<sub>2</sub> with Anatase and Brookite phases as highly improved photoanode for dyesensitized solar cell, Sol. Energy 208 (15) (2020) 173–181, https://doi.org/ 10.1016/j.solener.2020.07.085.
- [35] E.H. Onah, N.L. Lethole, P. Mukumba, Luminescent materials for dye-sensitized solar cells: advances and directions: a review, Appl. Sci. 14 (2024) 9202, https:// doi.org/10.3390/app14209202.
- [36] P. Tadge, R.S. Yadav, P.K. Vishwakarma, S.B. Rai, T.M. Chen, S. Sapra, S. Ray, Enhanced photovoltaic performance of Y<sub>2</sub>O<sub>3</sub>:Ho<sup>3+</sup>/Yb<sup>3+</sup> upconversion nanophosphor based DSSC and investigation of color tunability in Ho<sup>3+</sup>/Tm<sup>3+</sup>/Yb<sup>3</sup> <sup>+</sup> tridoped Y<sub>2</sub>O<sub>3</sub>, J. Alloys Compd. 821 (2020), https://doi.org/10.1016/j. iallcom.2019.153230.
- [37] Y.R. Kim, Y.W. Yoo, D.Y. Hwang, T.Y. Shim, C.Y. Kang, H.J. Park, H.S. Kim, S. H. Lee, Effect of niobium doping to enhance electrochemical performances of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> cathode material, Solid State Ionics 389 (2023) 116108, https://doi.org/10.1016/j.ssi.2022.116108.
- [38] E. Lee, J. Ryu, J. Jang, Fabrication of graphene quantum dots via size-selective precipitation and their application in upconversion-based DSSCs, Chem. Commun. 50 (2014) 15616–15618, https://doi.org/10.1039/C4CC06567K.
- [39] X. Fang, M. Li, K. Guo, J. Li, M. Pan, L. Bai, M. Luoshan, X. Zhao, Graphene quantum dots optimization of dye-sensitized solar cells, Electrochim. Acta 137 (2014) 634–638, https://doi.org/10.1016/j.electacta.2014.06.075.
- [40] Z. Salam, E. Vijayakumar, A. Subramania, N. Sivasankar, S. Mallick, Graphene quantum dots decorated electrospun TiO<sub>2</sub> nanofibers as an effective photoanode for dye sensitized solar cells, Sol. Energy Mater. Sol. Cells 143 (2015) 250–259, https://doi.org/10.1016/j.solmat.2015.07.001.
- [41] R. Riaza, M. Ali, T. Maiyalaganc, A.S. Anjuma, S.L. Lee, S.H. Jeonga, Dye-sensitized solar cell (DSSC) coated with energy down shift layer of nitrogen-doped carbon quantum dots (N-CQDs) for enhanced current density and stability, Appl. Surf. Sci. 483 (2019) 425–431, https://doi.org/10.1016/j.apsusc.2019.03.236.
- [42] K. Kundu, P. Sarojinijeeva, R. Karthick, G. Anantharaj, G. Saritha, R. Berae, S. Anand, A. Patrae, P. Ragupathya, M. Selvaraja, D. Jeyakumara, K.V. Pillaia, Enhancing the efficiency of DSSCs by the modification of TiO<sub>2</sub> photoanodes using N, F and S, co-doped graphene quantum dots, Electrochim. Acta 242 (2017) 337–343, https://doi.org/10.1016/j.electacta.2017.05.02.
- [43] F. Jahantigh, M.B. Ghorashi, A. Bayat, F. Jahantigh, S.M.B. Ghorashi, A. Bayat, Hybrid dye sensitized solar cell based on single layer graphene quantum dots, Dyes and Pigments Dyes and Pigments 175 (6346) (2019) 108118, https://doi.org/ 10.1016/j.dyepig.2019.108118.
- [44] V. Prabhagar, M.M.P. Kumar, C. Takahashi, S.S. Kundu, T.N. Narayananc, D. K. Pattanayaka, Boron-doped graphene quantum dots: an efficient photoanode for dye sensitized solar cell, New J. Chem. 43 (2019) 14313–14319, https://doi.org/10.1039/C9NJ00052F.
- [45] Q. Chang, Z. Ma, J. Wang, P. Li, Y. Yan, W. Shi, Q. Chen, Y. Huang, L. Huang, Hybrid graphene quantum Dots@Graphene foam nanosheets for dye-sensitized solar cell electrodes, Energy Technol. 3 (2015) 1–8, https://doi.org/10.1002/ ente.201500194.

- [46] Md T.r Hasan, R.G. Rodriguez, C.W. Lin, E. Campbell, S. Vasireddy, U. Tsedev, A. M. Belcher, A.V. Naumov, Rare-earth metal ions doped graphene quantum dots for near-IR in vitro/in vivo/ex Vivo imaging applications, Adv. Optical Mater 8 (2020) 2000897, https://doi.org/10.1002/adom.202000897.
- [47] X. Sun, H.J. Li, N. Ou, B. Lyu, B. Gui, S. Tian, D. Qian, X. Wang, J. Yang, Visiblelight driven TiO<sub>2</sub> photocatalyst coated with graphene quantum dots of tunable nitrogen doping, Molecules 24 (2) (2019) 344, https://doi.org/10.3390/ molecules24020344.
- [48] D. Qu, Z. Sun, M. Zheng, J. Li, Y. Zhang, G. Zhang, H. Zhao, X. Liu, Z. Xie, Three colors emission from S,N Co-doped graphene quantum dots for visible light H 2 production and bioimaging, Adv. Opt. Mater. 3 (2015) 360–367, https://doi.org/ 10.1002/adom.201400549.
- [49] P. Sharma, C.R.M. Lal, Synthesis and photocatalytic potential of Nd-doped TiO<sub>2</sub> under UV and solar light irradiation using a sol-gel ultra sonication method, Results in Materials 15 (2022), https://doi.org/10.1016/j.rinma.2022.100308. September 100308.
- [50] M. Lal, P. Sharma, C. Ram, Synthesis and photocatalytic potential of Nd-doped TiO<sub>2</sub> under UV and solar light irradiation using a sol-gel ultrasonication method, Results in Materials 15 (2022) 100308, https://doi.org/10.1016/j. rinma.2022.100308.
- [51] P. Ramachandran, B.K. Khor, C.Y. Lee, R.A. Doong, C.E. Oon, N.T.K. Thanh, H. L. Lee, N-doped graphene quantum dots/titanium dioxide nanocomposites: a study of ROS-forming mechanisms, cytotoxicity and photodynamic therapy, Biomedicines 10 (2022) 421, https://doi.org/10.3390/biomedicines10020421.
- [52] J. Rawal, U. Kamran, M. Park, D. Pant, S.J. Park, Nitrogen and sulfur Co-doped graphene quantum dots anchored TiO<sub>2</sub> nanocomposites for enhanced photocatalytic activity, Catalysts 12 (2022) 548, https://doi.org/10.3390/ catal12050548.
- [53] G. Rajender, J. Kumar, P.K. Giri, Interfacial charge transfer in oxygen deficient TiO<sub>2</sub>-graphene quantum dot hybrid and its influence on the enhanced visible light photocatalysis, Appl. Catal., B 224 (2022) 960–972, https://doi.org/10.1016/j. apcatb.2017.11.042.
- [54] Y. Gao, X. Pu, D. Zhang, G. Ding, X. Shao, J. Ma, Combustion synthesis of graphene oxide-TiO<sub>2</sub> hybrid materials for photodegradation of methyl orange, Carbon N. Y. 50 (2012) 4093–4101, https://doi.org/10.1016/j.carbon.2012.04.057.
- [55] Q. Zhang, N. Bao, X. Wang, X. Hu, X. Miao, M. Chaker amd M. Dongling, Advanced Fabrication of chemically bonded graphene/TiO<sub>2</sub>, continuous fibers with enhanced broadband photocatalytic properties and involved mechanisms exploration, Sci. Rep. 1 (6) (2016) 38066, https://doi.org/10.1038/srep38066.
- [56] M. Lal, P. Sharma, C. Ram, Synthesis and photocatalytic potential of Nd-doped TiO<sub>2</sub> under UV and solar light irradiation using a sol-gel ultrasonication method, Results in Materials 15 (2022) 100308, https://doi.org/10.1016/j. rinma.2022.100308.
- [57] S. Yu, Y.Q. Zhong, B.Q. Yu, S.Y. Cai, L.Z. Wu, Y. Zhou, Graphene quantum dots to enhance the photocatalytic hydrogen evolution efficiency of anatase TiO<sub>2</sub> with exposed (001) facet, Phys. Chem. Chem. Phys. 18 (2016) 20338–20344, https:// doi.org/10.1039/C6CP02561G.
- [58] P.F. Lim, K.H. Leong, L.C. Sim, A.A. Aziz, P. Saravanan, Amalgamation of Ngraphene quantum dots with nanocubic like TiO<sub>2</sub>: an insight study of sunlight sensitive photocatalysis, Environ. Sci. Pollut. Control Ser. (2018), https://doi.org/ 10.1007/s11356-018-3821-1.
- [59] A. Bokare, S. Chinnusamy, F. Erogbogbo, TiO<sub>2</sub>-Graphene quantum dots nanocomposites for photocatalysis in energy and biomedical applications, Catalysts 11 (2021) 319, https://doi.org/10.3390/catal11030319.
- [60] D. Zhao, G. Sheng, C. Chen, X. Wang, Enhanced photocatalytic degradation of methylene blue under visible irradiation ongraphene@TiO<sub>2</sub> dye structure, Appl. Catal. B Environ. 111 (2012) 303–308, https://doi.org/10.1016/j. apeatb.2011.10.012.
- [61] A.M. Hussein, A.V. Iefanova, R.T. Koodali, B.A. Logue, R.V. Shende, Interconnected ZrO<sub>2</sub> doped ZnO/TiO<sub>2</sub> network photoanode for dye-sensitized solar cells, Energy Rep. 4 (2018) 56–64, https://doi.org/10.1016/j.egyr.2018.01.007.

- [62] A. Atilgan, A. Yildiz, Ni-doped TiO<sub>2</sub>/TiO<sub>2</sub> homojunction photoanodes for efficient dye-sensitized solar cells, Int. J. Energy Res. 46 (2022) 14558–14569, https://doi. org/10.1002/er.8175.
- [63] J.T. Abdallaa, Y.-W. Huanga, Q.-J. Yua, J.-Z. Wanga, J.-N. Wanga, C.-L. Yuc, S.-Y. Gaoa, S.-J. Jiaoa, D.-B. Wanga, A.M. Alarabia, TiCl<sub>4</sub> surface-treated SnO<sub>2</sub> photoanodes for self-powered UV photodetectors and dye-sensitized solar cells, Mater. Technol. 32 (7) (2017) 443–450, https://doi.org/10.1080/ 10667857.2016.1267935.
- [64] J. Yu, Y. Yang, R. Fan, L. Li, X. Li, Rapid electron injection in nitrogen- and fluorine-doped flower- like anatase TiO<sub>2</sub> with {001} dominated facets and dyesensitized solar cells with a 52% increase in photocurrent, J. Phys. Chem. C 118 (2014) 8795–8802, https://doi.org/10.1021/jp500870vCommunication.
- [65] S.G. Kim, M.J. Ju, I.T. Choi, W.S. Choi, H.K. Kim, Sol-Gel derived nitrogen-doped TiO<sub>2</sub> photoanodes for highly efficient dye-sensitized solar cells, Rapid Communication in Photoscience 3 (1) (2014) 20–24, https://doi.org/10.5857/ RCP.2014.3.1.20.
- [66] S.Y. Huang, G. Schlichthörl, A.J. Nozik, M. Grätzel, A.J. Frank, J. Phys. Chem. B 101 (1997) 2576–2582, https://doi.org/10.1021/jp962377q.
- [67] N. Kopidakis, N.R. Neale, A.J. Frank, J. Phys. Chem. B 110 (2006) 12485–12489, https://doi.org/10.1021/jp0607364.
- [68] Z. Zhang, S.M. Zakeeruddin, B.O. Regan, R. Humphry-Baker, M. Gratzel, Influence of guanidinobutyric acid as coadsorbent in reducing recombination in dyesensitized solar cells, J. Phys. Chem. B 24 (46) (2005) 21818–21824, https://doi. org/10.1021/jp054305h, 109.
- [69] Q. Wang, S.M. Zakeeruddin, J. Cremer, P. Bäuerle, R. Humphry-Baker M, M. Grätzel, Cross surface ambipolar charge percolation in molecular triads on mesoscopic oxide films, J. Am. Chem. Soc. 127 (15) (2005) 5706–5713, https:// doi.org/10.1021/ja0426701.
- [70] S.Y. Huang, G. Schlichtho A.J. Nozik, M. Gratzel, A.J. Frank, Charge recombination in dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells, J. Phys. Chem. B 101 (14) (1997) 2576–2582, https://doi.org/10.1021/jp962377q.
- [71] G. Anantharaj, N. Lakshminarasimhan, Interfacial modification of Photoanode Electrolyte interface using oleic acid enhancing the efficiency of dye- sensitized solar cells, ACS Omega 3 (12) (2018) 18285–18294, https://doi.org/10.1021/ acsomega.8b02648.
- [72] N.C.T. Martins, J. Ångelo, A.V. Girão, T. Trindade, L. Andrade, A. Mendes, N-doped carbon quantum dots/TiO<sub>2</sub> composite with improved photocatalytic activity, Appl. Catal. B Environ. 193 (2016) 67–74, https://doi.org/10.1016/j. apcatb.2016.04.016.
- [73] S. Kundu, P. Sarojinijeeva, R. Karthick, G. Anantharaj, G. Saritha, R. Bera, K. V. Pillai, Enhancing the efficiency of DSSCs by the modification of TiO<sub>2</sub> photoanodes using N, F and S, co-doped graphene quantum dots, Electrochim. Acta 242 (2017) 337–343, https://doi.org/10.1016/j.electacta.2017.05.024.
- [74] N.F.M. Sharifa, M.Z.A.A. Kadir, S. Shafiea, S.A. Rashid, W.Z.W. Hasana, S. Shaban, Charge transport and electron recombination suppression in dye-sensitized solar cells using graphene quantum dots, Results Phys. 13 (2019) 102171, https://doi. org/10.1016/j.rinp.2019.102171.
- [75] M. Adachi, M. Sakamoto, J. Jiu, Y. Ogata, S. Isoda, Determination of parameters of electron transport in dye-sensitized solar cells using electrochemical impedance spectroscopy, J. Phys. Chem. B 110 (28) (2006) 13872–13880, https://doi.org/ 10.1021/jp061693u.
- [76] M.A.K.L. Dissanayake, T. Jaseetharan, G.K.R. Senadeera, C.A. Thotawatthage, A novel, PbS:Hg quantum dot-sensitized, highly efficient solar cell structure with triple layered TiO<sub>2</sub> photoanode, Electrochim. Acta 269 (02.140) (2018) 172–179, https://doi.org/10.1016/j.electacta.2018.
- [77] W. Qian, P.A. Greaney, S. Fowler, S.-K. Chiu, A.M. Goforth, J. Jiao, Lowtemperature nitrogen doping in ammonia solution for production of N-doped TiO2hybridized graphene as a highly efficient photocatalyst for water treatment, ACS Sustainable Chem. Eng. 2 (2014) 1802–1810, https://doi.org/10.1021/sc5001176.