Reduced Graphene Oxide-Laminated One-Dimensional TiO₂−Bronze Nanowire Composite: An Efficient Photoanode Material for Dye-Sensitized Solar Cells

Pronay Makal and Debajyoti Das*

ABSTRACT: A facile one-step hydrothermal method was developed to prepare reduced graphene oxide-laminated TiO₂−bronze (TiO₂-B) nanowire composites (TNWG), which contain two-dimensional graphene oxide nanosheets and TiO₂-B nanowires. In the hydrothermal process, the functional groups of graphene oxide were reduced significantly. Dye-sensitized solar cells (DSSCs) were fabricated using TNWG as the photoanode material. The effects of different reduced graphene oxide contents in TNWG on the energy conversion efficiency of the dye-sensitized solar cells were investigated using J−V and incident photon-to-current conversion efficiency characteristics. DSSCs based on a TNWG hybrid photoanode with a reduced graphene oxide content of 8 wt % demonstrated an overall light-to-electricity conversion efficiency of 4.95%, accompanied by a short-circuit current density of 10.41 mA cm⁻², an open-circuit voltage of 0.71 V, and a fill factor of 67%, which were much higher than those of DSSC made with a pure TiO₂-B NW-based photoanode. The overall improvement in photovoltaic performance could be associated to the intense visible light absorption and enhanced dye adsorption because of the increased surface area of the composite, together with faster electron transport due to reduced carrier recombination.

INTRODUCTION

In view of the present-day global energy crisis, the development of renewable clean energy is of paramount importance. Dye-sensitized solar cells (DSSCs) have been proven extremely promising to address the issue.¹ DSSCs have drawn considerable interest in the photovoltaic sector by virtue of its low-cost manufacturing technology,²−⁴ although silicon solar cells are still the giant in today’s PV world.⁵−⁹ A typical DSSC device is normally composed of a photoanode in which a layer of semiconducting material sensitized with photoactive dye molecules is used on a TCO (transparent conducting oxide)-coated glass substrate, a counter electrode, and an electrolyte.¹⁰ Among various semiconductor materials such as ZnO, MoS₂, WO₃, etc., the TiO₂-based photoanode is extremely promising owing to its high photoactivity.¹¹−¹⁹ The fabricated DSSC devices are significantly sensitive to the morphology and structure of TiO₂ in photoanodes. TiO₂ in a one-dimensional (1D) nanostructured configuration, such as of nanorods, nanotubes, nanowires, etc., has drawn significant attention over nanoparticles in its use as a DSSC photoanode material.²⁰ The 1D TiO₂ structure offers a greater area to volume ratio, resulting in enhanced dye molecule accommodation and reduction of the photoexcited electron−hole recombination. Anatase, rutile, brookite, and TiO₂−bronze (TiO₂-B) are the four commonly observed phases of titanium dioxide.²¹ Among them, the TiO₂-B phase has drawn substantial consideration as the material of choice.²²,²³ The monoclinic TiO₂-B phase possesses an asymmetric structure with characteristic open channels within its network that provides a superior surface area to its other phases and results in efficient photovoltaic performance. For improvement in electron transport and minimization in charge carrier recombination to yield an effective DSSC performance, a combination of carbon-related materials, e.g., CNTs,²⁴ graphene,²⁵,²⁶ and graphene oxide (GO),²⁷ with different TiO₂ nanostructures have been employed in the past.

An efficacious approach to impede the charge carrier recombination is to synthesize a composite of 1D nanostructured TiO₂ with reduced graphene oxide (RGO).²⁸,²⁹ As a 2D single-molecular layered structure, graphene has drawn much attention due to its outstanding thermal, optical, and...
mechanical properties. In the graphene structure, each carbon atom forms three $\sigma$ bonds with other three adjacent carbon atoms lying in the same plane, leaving a free electron in its $p$ orbital. Therefore, the electrons can move freely without any restriction arising from the crystal lattice and behave as a massless relativistic particle. As a consequence, graphene shows outstanding electrical conductivity and high photoexcited-charge carrier mobility ($>2 \times 10^5$ cm$^2$ V$^{-1}$ s$^{-1}$). Again, 1D TiO$_2$ nanostructures can be easily bound to the graphene surface due to the presence of some intermolecular forces (physiosorption and electrostatic binding) or charge transfer interactions between them. Thus, a combination with graphene can accelerate the electron transport and minimize the charge pair recombination. Compared with graphene, reduced graphene oxide (RGO) contains lots of oxygenated functional groups, which facilitate intimate combining with TiO$_2$. Furthermore, RGO sheets offer superior surface areas, which could increase the dye loading on the photoanode. Accordingly, these unique characteristics of RGO make the TiO$_2$/RGO composites more compatible as a photoanode material in the DSSCs.

In this paper, synthesis of reduced graphene oxide-laminated TiO$_2$-B nanowire composites (TNWG) with varying GO weight fractions through a two-step wet-chemical approach and their use as photoanodes in DSSC fabrication have been explored. The photoanode based on 8 wt % GO-loaded TNW composites exhibited the highest photocurrent conversion efficiency of 4.95%, which is increased by 46% compared to the pure TiO$_2$-B nanowire photoanode. Thus, the incorporation of graphene oxide has been demonstrated to effectively promote electron transportation from TiO$_2$-B NWs to the electrolyte by impeding the backward charge combination of photoexcited electrons and improve the DSSC performance.

### EXPERIMENTAL SECTION

**Chemicals.** Commercial titanium dioxide anatase powder was bought from Sigma-Aldrich, U.S.A. Sodium nitrate, potassium permanganate, and graphite powder were obtained from Loba Chemie, India. Hydrochloric acid, sodium hydroxide pellets, and sulfuric acid were supplied from Merck Chemicals, India. Ruthenizer S35 dye (N3) and iodolyte AN-50 electrolyte were supplied by Solaronix. All the chemicals employed in this experiment were of analytical grade and utilized without additional purification.

**Synthesis of 1D TiO$_2$-B Nanowires.** The synthesis of titanium dioxide bronze phase (TiO$_2$-B) nanowires was carried out by adopting a facile hydrothermal method. In a standard synthesis process, 1 g of bulk anatase TiO$_2$ powder was poured into 80 mL of aqueous solution containing 32 g of sodium hydroxide and thoroughly mixed under constant magnetic stirring for 10 h to prepare a homogeneous suspension. The alkaline suspension was shifted carefully into a Teflon-lined stainless steel hydrothermal autoclave with a capacity of 100 mL. Then, the reaction system was transferred into a furnace and heated at 180 °C for 48 h. After the reaction was completed, the hydrothermal autoclave was brought to normal temperature. The resulting hydrothermal products were dipped into 0.1 N hydrochloric acid solution overnight. Then, the residue was filtered several times by centrifugation with deionized water and ethanol and dried at 100 °C for 24 h. Finally, the obtained sample was annealed under vacuum at 600 °C for 2 h, and it was designated as TNW.

**Synthesis of Graphene Oxide.** Graphene oxide was synthesized by oxidation of natural graphite powder adopting Hummer’s method. In a typical synthesis procedure, 1 g of graphite powder and 1 g of sodium nitrate were added by stirring into 50 mL of concentrated (12.1 M) sulfuric acid for 30 min within an ice bath maintained at 0 °C. Then, potassium permanganate (6 g) was slowly added in portion to the above solution and stirred for another 30 min, maintaining the temperature at 0 °C. The suspension was further heated at 40 °C for another one and half-hour under constant magnetic stirring. The mixture was subsequently diluted with 150 mL of deionized water to terminate the reaction. In the very next step, 10 mL of hydrogen peroxide (30%) was added to quench the vigorous oxidation reactions into the solution. Finally, the resulting suspension was washed with dilute HCl and DI water several times. The solid graphene oxide product was collected after drying at 80 °C for 24 h.

**Synthesis of TiO$_2$-B NW/RGO Composites (TNWG).** Reduced graphene oxide-laminated TiO$_2$-B nanowire (TNWG) hybrids were synthesized via a concerted hydrothermal method. Typically, at first, a certain amount of graphene oxide nanosheets were added into a 50 mL 1:1 (v/v) ethanol–water solution and ultrasonically exfoliated for 2 h. After that, calculated amounts of TiO$_2$-B NWs were added to the above suspension and magnetically stirred for another 30 min. The mixture was then placed into a Teflon-lined hydrothermal autoclave and heated at 120 °C for 4 h. After bringing to room temperature, the subsequent product was filtered by centrifugation with DI water and then vacuum-dried overnight. GO was partially converted into reduced graphene oxide during heat treatment due to the vigorous environment of the hydrothermal process. To study the influence of reduced graphene oxide content on the performance of DSSC, three different TNWG hybrids were prepared by varying the weight ratio (0%, 4%, 8%, and 12%) of GO with respect to TNWs, and the corresponding products were denoted as TNWG-0, TNWG-4, TNWG-8, and TNWG-12.

**Material Characterization Techniques.** Powder X-ray diffraction patterns of the prepared samples were recorded by Panalytical X’Pert Pro with Ni-filtered Cu Kα ($\lambda = 0.15406$ nm) to investigate the phase purity and degree of crystallinity. Raman spectra of the prepared samples were obtained using a Renishaw inVia Raman microscope with an Ar ion laser source with an excitation wavelength of 514.5 nm. The surface valence states and elemental composition of the prepared composite and pure graphene oxide were characterized by an X-ray photoelectron spectrometer (Omicron). Transmission electron microscopy (JEOL-JSM 2010 HR-TEM) was used to study the microstructural properties of the samples. In the sample preparation for TEM, the prepared composites were dispersed in ethanol and stirred manually and then a few drops of this suspension were drop-casted on a carbon-coated copper grid. The BET surface area of the composite samples was analyzed by taking their N$_2$ adsorption–desorption isotherms using a surface area analyzer (Quantachrome Autosorb I C1). The optical behavior of the composite products was achieved by taking absorption spectra in the diffuse reflectance mode using a UV–vis spectrophotometer (Varian Cary 5000 UV–vis spectrophotometer).

**Fabrication of DSSCs.** The fabrication of DSSCs was implemented as per previous reports. In brief, 1 g of the prepared TNW or TNWG composite was mixed with 5 mL of acetylacetone, 5 mL of ethanol, and 0.5 mL of triton X-100 (binder) to make a viscous paste, using which the photoanode
was prepared on pre-cleaned indium-doped tin oxide (ITO) glass, adopting a doctor blade method. Then, the prepared TiO2-based electrodes were heated at 400 °C for 30 min to eliminate the binder molecules. The calculated effective area of the photoanode was 0.25 cm^{-2} (0.5 cm × 0.5 cm), and the thickness of the active layers was about 18 μm, as measured by using surface profilometry (Alpha-Step IQ Surface Profiler). To sensitize with dye, the prepared thin-film photoanodes were dipped in ruthenizer 535 dye (N3) solution (0.5 mM, in the 1:1 volume mixture of acetonitrile and tert-butanol, Solaronix) overnight in dark conditions and subsequently washed with acetonitrile to remove the excess dye molecules. On the other hand, platinum was sputtered using an RF magnetron sputtering system operating at 6 × 10^{-3} Torr of Ar (30 sccm) under 130 W of power on a pre-drilled ITO-coated glass to use as a counter electrode. A sandwich-type cell was constructed by these two electrodes and sealed with a paraffin spacer. Through a tiny hole in the counter electrode, the electrolyte (Iodolyte AN-50, Solaronix) was injected into the cell and sealed carefully with glass with the help of a paraffin spacer.

Photocurrent Density versus Voltage (J–V) Measurements of DSSCs. A Keithley 2634B system was used to measure the photocurrent characteristics, e.g., short-circuit current (JSC), open-circuit voltage (VOC), fill factor (FF), and overall conversion efficiency, of the fabricated DSSCs under an illumination of 100 mW cm^{-2} (AM 1.5G) using a solar simulator. The photovoltaic performance of the device in terms of the fill factor (FF) and photovoltaic conversion efficiency (η) was determined based on the following fundamental equations:

\[
\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}}
\]

\[
FF = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}}
\]

where J_{max} and V_{max} represent the maximum current and voltage output of the device, respectively, and the incident power density is expressed by P_{in}.

To investigate the dye adsorption capacity of the individual photoanodes, a 10 mL N3 dye solution was freshly prepared separately for each case by adding 0.35 μmol of N3 dye into a 1:1 v/v mixture of tert-butanol and acetonitrile. At first, the photoanodes were subjected to adsorb N3 dye molecules by immersing it in the dye solution for 10 h. Then, to estimate the amount of adsorbed dye, the photoanode was dipped into a 10 mL 0.1 N NaOH ethanol/water solution (1:1 v/v mixture). Then, a 5 mL aliquot was taken out and subjected to UV−vis spectroscopy measurement. The interfacial characteristics in terms of electrical and electrochemical parameters of the solar cell were subjected to study by electrochemical impedance spectroscopy (EIS). A computer-controlled electrochemical workstation (CHI660C, CH Instruments) was used to perform this EIS measurement under similar illumination conditions by applying sinusoidal perturbation of a 5 mV amplitude over a frequency range of 10^5−10^1 Hz at a respective bias open-circuit potential (V_{OC}). Furthermore, the incident photon to current conversion efficiency (IPCE) of the fabricated devices was examined using the same electrochemical system connected with a 200 W xenon lamp under an illumination of 50 mW cm^{-2} power.

### RESULTS AND DISCUSSION

**Morphology and Compositional Characterization.**

Figure 1 represents the X-ray diffraction pattern of the hydrothermally synthesized TNWG nanocomposite with different graphene oxide loadings, pure TiO2-B NW, graphite powder, and graphene oxide to evaluate the phase purity and the structural composition of the samples. A sharp and prominent diffraction peak centered at 2θ = 11.2° in the case of the graphene oxide sample was associated to the (002) plane, whereas for graphite powder a strong diffraction peak appeared at 2θ = 26.3°, which fully disappeared after conversion of GO from graphite.37 It is considered that most of the GO moieties were reduced during the hydrothermal treatment at 120 °C for 4 h. The XRD diffractogram of pure TiO2 NWs demonstrates a number of peaks that are attributed to the monoclinic crystal structure of the TiO2−bronze phase (TiO2-B) with space group C2/m (JCPDS no. 74-1940). There is no contamination with the other phases of TiO2 in the prepared samples. The peaks located at 14.2°, 24.8°, 28.7°, 29.8°, 33.0°, 37.6°, 43.7°, 44.3°, 47.9°, 52.9°, 57.4°, 61.9°, 67.6°, and 76.3° are associated to (001), (110), (002), (111), (200), (202), (310), (401), (003), (601), (020), (113), (022), (403), (023), and (712) crystal planes of TiO2-B, respectively.23,38 The characteristic diffraction signals related to the TiO2-B phase were well preserved for all the synthesized composite materials, indicating that the incorporation of RGO did not affect the structural composition of the TiO2-B nanowire. However, the diffraction peaks corresponding to the graphene-related species were not observed because of the low content of reduced graphene oxide and the relatively weak diffraction signal of RGO located at about 24.6°, which was masked by the strong (110) TiO2-B diffraction at 24.8°.39 It was noticed that the intensity of the TiO2-B related peaks increased marginally in the case of the TNWG-4 sample. This might have influenced on the crystalline morphology of TiO2-B NW at a lower content of RGO.

Raman spectroscopy is an effective nondestructive technique to study the different nonpolar vibrational bonds present in the crystal structure of the prepared samples. The reduction of
oxygenated groups present in prepared samples. (b) Relative Raman intensity ratio of the D and G bands of the corresponding samples.

Figure 3. FTIR spectra of GO, RGO, and TNWG-8 samples.

The reduction of graphene oxide during the synthesis of the TNWG composite was investigated using FTIR characterization. The formation of RGO was carried out via a similar hydrothermal process in the absence of TiO2-B NWs. Figure 3 represented the FTIR spectra of GO, RGO, and TNWG-8 composite samples. The synthesized GO sheets exhibited a broad absorption band centered at 3410 cm\(^{-1}\), attributed to the hydroxyl group due to the presence of COOH and H\(_2\)O in the GO moiety.50 The other prominent bands attributed to the hydroxyl group due to the presence of COOH exhibited a broad absorption band centered at 3410 cm\(^{-1}\). In the case of the pure TiO2-B NW specimen, several typical Raman active modes located at 121, 145, 195, 247, 296, 364, 406, 434, 467, 510, 632, and 657 cm\(^{-1}\) are observed that correspond to the monoclinic structure of the TiO\(_2\)-brass phase and are also designated by corresponding Mulliken term symbols.45 For the composite samples, all the Raman active modes related to the TiO\(_2\)-B phase as well as GO were well retained. Compared to the characteristic D and G band positions of GO, minor redshifts were noticed in the composite material, which we assign to the successful formation of coupling between TiO2-B NWs and RGO via Ti–O–C bond formation.56 In addition, with the increase of GO content in the composites, the intensity ratio of the D and G bands (I\(_D\)/I\(_G\)) was also increased systematically from 0.92 (GO) to 1.07 (TNWG-12), conforming with the gradual reduction of the oxygenated functional groups on GO, as shown in Figure 2b. This result indicates a decrease in the average size of the graphene sheet and restoration of several sp\(^2\) domains, suggesting that the graphene oxide has been successfully reduced to graphene during the hydrothermal reaction.47 According to various published reports, the hydrothermal treatment of GO affords highly reduced products.48,49 Therefore, it is not surprising that GO was well reduced by the hydrothermal reaction in our study.

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The chemical states of graphene oxide and the TNWG-8 composite were further investigated by X-ray photoelectron spectroscopy (XPS). The high-resolution C 1s XPS spectra of the above two samples display a comparison between GO and TNWG-8 on reduction of the oxygenated group present in GO. The deconvoluted C 1s spectrum of GO in Figure 4a shows three components located at 284.5, 286.9, and 288.5 eV. Two main components centered at 284.5 and 286.9 eV usually originate from a graphitic sp\(^2\) (C=C) boned carbon atom57 and hydroxyl carbon (C–OH),58 respectively. Another relatively weak peak at 288.5 eV can be ascribed to carboxyl carbon (O= C–O).59 The existence of such oxygenated functional groups in GO can be responsible for the direct connection to the surface of TiO2-B nanowires, possibly by esterification of the –OH groups present in TiO2-B NWs with the C–COOH groups on the GO surface.60 Furthermore, the quantitative analysis of the integrated area of each deconvoluted peak of the C 1s spectrum of GO and TNWG-8 samples in Figure 4 shows that the peak...
intensity for the C−OH group decreased significantly in comparison with GO, whereas the contribution of the O−C=O group reduced drastically or almost disappeared, as shown by the corresponding data summarized in Table 1. This result implied that the oxygen-containing functional groups of graphene oxide were efficiently reduced during the hydrothermal treatment.

The Brunauer−Emmett−Teller (BET) analysis is a useful technique for precise measurement of the specific surface area and porosity of the prepared samples. Figure 5 shows N2 adsorption−desorption isotherms of the GO, TNWG-0, and other TNWG composites with different amounts of RGO loading carried out at 77 K. The pore volume distribution of the above samples was calculated by adopting the Barrett−Joyner−Halenda (BJH) adsorption method, shown in the inset of Figure 5. The obtained isotherms for all the samples display a type-IV pattern according to Brunauer, Deming, Deming, and Teller (BET) nomenclature, having a hysteresis loop profile at a relatively high pressure (P/P0) range of 0.7−1, suggesting the mesoporous nature of the samples. The capillary condensation of nitrogen molecules into the mesopores of the samples is solely responsible for generating this kind of hysteresis loop. The specific surface area (SBET) and total pore volume of TNWG-0 are 97.4 m² g⁻¹ and 0.199 cc g⁻¹, which increased significantly with the incorporation of RGO up to 8 wt % and attained a value of 152.8 m² g⁻¹ and 0.682 cc g⁻¹, respectively. The RGO nanosheets provide a smooth matrix to accelerate the dispersion of TiO2-B NWs grown at 600 °C, which can be assigned to the (110) and (001) planes of TiO2-B, respectively, as shown in Figure 6e. This result reveals that the TiO2-B NWs are distributed uniformly and tightly coupled with wrinkled two-dimensional RGO nanosheets owing to strong interactions between the hydrophilic functional groups (e.g., OH and COOH) of GO and the hydroxyl groups present on the TiO2 surface. This intimate interaction enables the photoexcited electrons to transfer more easily from the TiO2 NW to graphene oxide sheets and subsequently impedes the charge combination. In the higher-resolution TEM images of an isolated TiO2-B NW, there are two sets of lattice fringes with spacing values of 0.36 and 0.62 nm, which can be assigned to the (110) and (001) planes of TiO2-B, respectively, as shown in Figure 6e. This result reveals that the nanowire sample has a higher degree of crystallinity and grown particularly along the [110] direction.

**Table 2. Optical Band Gap, Surface Area, and Pore Volume of the Prepared Samples**

| sample name | band gap (eV) | specific surface area (m² g⁻¹) | pore size (nm) | total pore volume (cc g⁻¹) |
|-------------|--------------|-------------------------------|---------------|---------------------------|
| GO          | 3.23         | 64.2                          | 107.6         | 0.199                     |
| TNWG-0      | 2.95         | 97.4                          | 9             | 0.682                     |
| TNWG-4      | 2.89         | 138.3                         | 8             | 0.531                     |
| TNWG-8      | 2.85         | 152.8                         | 9             | 0.682                     |
| TNWG-12     | 2.72         | 127.6                         | 9             | 0.427                     |

**Optical Characterization.** UV−vis diffusive reflectance spectroscopy (DRS) is a powerful tool to investigate the light absorption phenomenon arising due to strong interactions between TiO2-B and RGO nanosheets, as shown in Figure 7a. An absorption edge was identified at ~380 nm (UV region) for commercialized anatase TiO2 nanoparticles, which resulted from band-to-band transition of photoexcited electrons. In the pure TiO2-B NW sample, the absorption edge was shifted

Figure 4. High resolution C 1s XPS spectra of (a) GO and (b) the TNWG-8 composite.

Figure 5. N2 adsorption−desorption isotherms and the subsequent pore volume distribution curves (inset) of TNWG-0 and various TNWG composites.

**Table 1. C 1s XPS Results of Pure GO and the TNWG-8 Composite**

| sample name | peak 1: C=−C bond | peak 2: C−O bond | peak 3: O−C=O bond | \[(C=\text{C})/[(C−\text{O})+(O−C=\text{O})]\] intensity ratio |
|-------------|--------------------|------------------|---------------------|----------------------------------------------------------|
| GO          | 284.5 eV           | 286.9 eV         | 288.5 eV            | 1.33                                                     |
| TNWG-8      | 284.4 eV           | 286.1 eV         | 288.7 eV            | 1.89                                                     |
to ~420 nm, making it suitable for absorbing an extended portion of visible light compared to TiO$_2$ nanoparticles. Furthermore, for the TNWG composite samples, the absorption edge gradually redshifted with the introduction of RGO content.

Figure 6. SEM image of (a) TNWG-0 and (b) TNWG-8. TEM image of (c) TNWG-0 and (d) TNWG-8 with its (e) magnified view.
in an ascending order. The obtained results indicate that a strong interaction is established between TiO$_2$-B and RGO in the TNWG composite materials, which could facilitate improved visible light absorption and certainly boost the light harvesting performance when used in DSSCs. The optical band gap energy ($E_g$) of the examined samples was calculated by adopting the Kubelka–Munk function$^{68,69}$ from a plot of $(F(R)\times h\nu)^{\frac{1}{2}}$ as a function of photon energy ($h\nu$), as shown in Figure 7b. The value of $n$ is taken as 1/2 since TiO$_2$ is an indirect band-gap material. The band-gap values of the samples were derived by extrapolation of the tangent to the X axis and are summarized in Table 2. The optical indirect band gap of the TiO$_2$-B NW sample reduced significantly to ~2.95 eV from ~3.23 eV in TiO$_2$ anatase powder. Again, the gradual increment in the RGO content in the composite narrowed the energy of the band-gap value successively, as shown in Table 2, suggesting that the interaction between TiO$_2$-B NWs and RGO nanosheets enhanced with the increase of RGO content. It is also reported that the bond formation between TiO$_2$ and RGO via a Ti–O–C or O–Ti–C linkage is highly responsible for reduction of band-gap energy.$^{70}$ This result also confirms the successful formation of TNWG composites via a hydrothermal process.

**Performance of Dye-Sensitized Solar Cells (DSSCs).**

The as-prepared photoanodes based on different TNWG composites and TNWG-0 were assembled to investigate their photovoltaic performance under a stimulated solar light illumination of 100 mW cm$^{-2}$ (AM 1.5G). Figure 8 depicts the photocurrent density–voltage ($J−V$) characteristic curves of the prepared DSSCs, and the analogous photovoltaic parameters are summarized in Table 3. The DSSCs fabricated with 8 and 4 wt % RGO-incorporated TiO$_2$-B NW composites showed enhanced photocurrent conversion efficiency (η) and short-circuit current density ($J_{sc}$) compared to that based on TNWG-0 material (Table 3). The TNWG-8 composite exhibited the highest conversion efficiency of 4.95% with a short-circuit photocurrent density ($J_{sc}$) of 10.41 mA cm$^{-2}$, open-circuit voltage ($V_{oc}$) of 0.71 V, and fill factor (FF) of 67%, whereas a significantly lower conversion efficiency of 2.65% was recorded from the DSSC based on a TNWG-0 photoanode having a short-circuit photocurrent density ($J_{sc}$) of 6.21 mA cm$^{-2}$, open-circuit voltage ($V_{oc}$) of 0.70 V, and fill factor (FF) of 61%. It is also observed that the addition of RGO in amounts higher than 8 wt % in the TNWG resulted in a decline in the photocurrent conversion efficiency. The results suggest that the recombination rate of electron–hole charge carriers can be effectively inhibited by RGO in the composite and an optimum amount of RGO content in the composite is necessary to increase the rate of electron transfer in the DSSC operation. The presence of a high amount of RGO may increase the electrode resistance and reduce the anodic reaction rate of the dye on the TNWG matrix, which obstructs the electron transportation process during solar light irradiation.$^{71}$ The photovoltaic performance depends on various factors, e.g., dye adsorption capacity, light-harvesting efficiency, charge transfer resistance, etc.$^{72}$ The following experiments are performed in order to identify some of the issues related to the enhancement of the DSSC performances based on TNWG composites.

**Enhanced Dye Adsorption.**

The increased dye loading capacity of the photoanode was a crucial factor for improving the solar light absorption property. The amounts of dye adsorbed on the photoanodes were estimated by extracting the dye from the dye-sensitized films in 10 mL of 0.1 N NaOH ethanol/water solution (1:1 v/v mixture). Figure 9 exhibits the UV–visible absorption spectra of N3 dye extracted from the individual dye-adsorbed photoanodes, and the results are summarized in Table 3. The dye adsorption capacity reached its maximum (0.26 μmol cm$^{-2}$) in the case of TNWG-8 (8 wt % RGO-incorporated

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**Table 3. DSSC Parameters of the Fabricated Devices**

| sample | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (mV) | FF (%) | η (%) | IPCE (%) | N3 dye loading (μmol cm$^{-2}$) |
|--------|----------------*******|--------------|--------|-------|----------|----------------|
| TNWG-0 | 6.21            | 702          | 61     | 2.65  | 30       | 0.18          |
| TNWG-4 | 8.34            | 698          | 64     | 3.71  | 39       | 0.22          |
| TNWG-8 | 10.41           | 714          | 67     | 4.95  | 51       | 0.26          |
| TNWG-12| 5.36            | 691          | 58     | 2.04  | 25       | 0.13          |
| TiO$_2$ np | 1.56        | 558          | 37.3   | 0.32  | 0.05     |               |
TNWG composite), which could be correlated to its enhanced specific surface area (Table 2). At a further increased RGO content of above 8 wt %, the reduced specific surface area is responsible for the degraded dye adsorption capacity. The increased dye loading on the TNWG-8 composite-based photoanode could facilitate the production of an increased number of electrons under solar light illumination and thereby increase the short-circuit photocurrent density as well as conversion efficiency of the DSSC.73

**Improved Light-Harvesting Ability.** To understand the light-harvesting phenomena, the incident photon-to-current conversion efficiency (IPCE) spectra were taken with the fabricated DSSC devices. The result in Figure 10 shows a broad IPCE spectrum ranging from 300 to 800 nm and centered at ~510 nm for each of the prepared DSSC devices. The result in Figure 10 shows a broad IPCE spectrum ranging from 300 to 800 nm and centered at ~510 nm for each of the prepared DSSC devices. The current conversion efficiency gradually increased with the increase of RGO content in the composite and attained a maximum value of 51% for the photoanode based on 8 wt % RGO loading. Further increment in the RGO amount on TiO2-B NWs significantly reduced the IPCE value. All the obtained data from the ICPE spectra are summarized in Table 3. The enhanced IPCE value for the TNWG-8 composite is attributed to the highest specific surface area providing significantly greater dye adsorption and the ability to convert more incident photons into electrons. Moreover, the increased short circuit density and photocurrent conversion efficiency suggest an improvement in electron transport ability within the DSSC.74 A lower specific surface area and subsequent inferior dye adsorption led to reduced charge collection efficiency at the TiO2/ITO substrate for both the DSSC devices with photoanodes based on TiO2-B NWs without graphene (TNWG-0) and the excess-graphene composite (TNWG-12), as evident from the diminished IPCE response in Figure 10.75

**Efficient Electron Separation and Transportation.** To understand the charge transfer and their recombination resistance in the fabricated DSSC devices with different photoanodes, the electrical impedance spectroscopy (EIS) was studied. Figure 11 displays the Nyquist plots of the cells for EIS analysis in the range of 10^5−10^8 Hz by applying a forward applied bias of VOC. In the obtained Nyquist plots, two semicircles appeared with an ohmic series resistance (Rh) on the ITO glass substrate where the small semicircle located at the high-frequency region represents the charge transfer resistance (R1) at the platinum counter electrode and the larger semicircle at the moderate-frequency region denotes the electron charge transfer resistance (R2) at the photoanode/dye/electrolyte interface.76 The magnitudes of all the experimental parameters (Rh, R1, and R2) were calculated and are summarized in Table 4 after analyzing each plot by eisalyzer software, adopting an equivalent circuit comprising resistance (R) and a constant phase element (CPE), shown in the inset of Figure 11. A reduction in the magnitude of R2 signifies a lower charge recombination rate at the photoanode/dye/electrolyte interface. The result reveals that the incorporation of up to 8 wt % RGO on TiO2-B NW successfully increases the electron lifetime that impedes the recombination of photexcited charge carriers and accelerates the electron transport. The composite having more than 8 wt % RGO loading shows an increased interfacial resistance against charge transport. It might be caused by the agglomeration of RGO on the surface of the nanowires. The agglomerates might have served as trapping centers at the photoanode and minimized the carrier lifetime. The fabricated DSSC based on the TNWG-8 composite exhibits the highest charge separation and transportation and displays the highest open-circuit voltage as well as superior photovoltaic efficiency.
Comparison on the DSSC Performance of Various TiO2-B and RGO/TiO2 Composite-Based Photoanodes. In order to understand the improved photovoltaic performance, a comparison has been made among the data obtained from the present study with TiO2-B NWs and different RGO-loaded TiO2 composites. The photoanode material and their various DSSC parameters are listed in Table 5. Considering the diversity in test parameters, e.g., thickness of the photoanode, surface area and nature of the dye, and the subsequent results on the short-circuit photocurrent, open-circuit voltage, efficiency, the RGO-laminated TiO2-B nanowire composites displayed lower interfacial resistance against charge transport that significantly improved the performance of the solar cell. The fabricated DSSC based on a photoanode containing 8 wt % RGO (TNWG-8) exhibited a much superior photocurrent conversion efficiency of 4.95% with a $J_{SC}$ of 10.41 mA cm$^{-2}$, $V_{OC}$ of 0.71 V, and FF of 67%, demonstrating a significant improvement in performance compared with that of DSSCs based on a pure TiO2-B NW photoanode, which had a conversion efficiency of 0.87% with a $J_{SC}$ of 7.10 mA cm$^{-2}$, $V_{OC}$ of 0.70 V, and FF of 61%. Hence, the RGO-laminated TiO2-B composite emerges as a strategic material for its efficient use as a photoanode for applications in dye-sensitized solar cells.

### Mechanism of Enhanced Photovoltaic Performance.
A possible mechanism was proposed based on the above study to justify the substantial improvement in the photovoltaic performance of the TNWG composite-based electrode and is schematically represented in Figure 12. The increased photovoltaic performance of the fabricated DSSCs based on TNWG photoanodes was primarily due to the increased transportation of electrons on the ITO substrate. The relative energy band position of each constituent of the fabricated DSSC was essential for efficient electron conduction. The work function of RGO is −4.5 eV, which is fairly lower than the conduction band of TiO2-B (−4.33 eV in the vacuum scale) as calculated considering Mulliken electronegativity theory (band gap of TNW: 2.95 eV) and somewhat higher than that of the ITO substrate (−4.70 eV in vacuum scale). Therefore, the extremely conductive RGO could perform as a good charge transfer medium between the ITO substrate and TiO2-B NW, which favored the transportation of photoexcited electrons from TiO2 to ITO without any energy barriers. Now, it was reported that the lowest unoccupied molecular orbital (LUMO) energy of N3 dye was at −2.79 eV. Thus, the position of LUMO also facilitated the collection of photoexcited electrons from the dye molecule to the conduction band of TiO2, wherefrom those were subsequently transported to the external circuit without resistance.

### CONCLUSIONS
A two-step hydrothermal process was adopted to synthesize reduced graphene oxide-laminated TiO2-B nanowire composites for DSSC application. During the growth process, various oxygenated functional groups present on the GO moiety were drastically reduced, leading to a more graphene-like structure. The combination of RGO with TiO2-B nanowires significantly enhanced the specific surface area and visible light absorption capacity of the prepared composites. The increased surface area of the composite furthermore facilitated greater adsorption of photoactive dye molecules and light scattering capabilities. Compared to the pure TiO2-B nanowire analogue, TNWG composites displayed lower interfacial resistance against charge transport that significantly improved the performance of the solar cell. The fabricated DSSC based on a photoanode containing 8 wt % RGO (TNWG-8) exhibited a much superior photocurrent conversion efficiency of 4.95% with a $J_{SC}$ of 10.41 mA cm$^{-2}$, $V_{OC}$ of 0.71 V, and FF of 67%, demonstrating a significant improvement in performance compared with that of DSSCs based on a pure TiO2-B NW photoanode, which had a conversion efficiency of 2.65% with a $J_{SC}$ of 6.21 mA cm$^{-2}$, $V_{OC}$ of 0.70 V, and FF of 61%. Hence, the RGO-laminated TiO2-B composite emerges as a strategic material for its efficient use as a photoanode for applications in dye-sensitized solar cells.

### AUTHOR INFORMATION

**Corresponding Author**
Debajoti Das — Energy Research Unit, School of Materials Sciences, Indian Association for the Cultivation of Science, Kolkata 700 032, India; orcid.org/0000-0002-3096-7023; Email: erdd@iacs.res.in, profdebajotidas@gmail.com

**Author**
Pronay Makal — Energy Research Unit, School of Materials Sciences, Indian Association for the Cultivation of Science, Kolkata 700 032, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05707

**Author Contributions**
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