Simple and Fast Microwave-Assisted Synthesis Methods of Nanocrystalline TiO₂ and rGO Materials for Low-Cost Metal-Free DSSC Applications

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ABSTRACT: Nanocrystalline TiO₂ and reduced graphene oxide (rGO) materials have been synthesized by a simple and low-cost microwave-assisted hydrothermal method and applied in dye-sensitized solar cells (DSSCs) as photoactive and metal-free counter electrodes, respectively. Different TiO₂ nanocrystalline materials have been synthesized via the acid hydrolysis sol–gel method, followed by microwave hydrothermal treatment at 210 °C and 300 psi and at different microwave irradiation times (20, 30, 45, and 60 min) instead of the usual hydrothermal time of 12 h. The properties of the produced mesoporous nanocrystalline TiO₂ are investigated in terms of their morphology, crystal structure, optical properties, and surface area behavior using relevant characterization techniques. Maximum specific surface area values (S_BET) of 97.77 and 100.7 m² g⁻¹ are measured for TiO₂, with the average crystallite sizes of 18.6 and 17.5 nm, at microwave irradiation times of 30 and 45 min, respectively. Different rGO samples have been prepared by the modified Hummers method, followed by microwave-assisted reduction at a temperature of 200 °C and pressure of 300 psi at different microwave irradiation times (3, 17, and 25 min). The physicochemical properties of the different rGO samples in terms of morphology, crystallization, and optical properties are characterized by TEM, XRD, and Raman spectroscopic analysis. The current density J_sc of the fabricated DSSCs based on TiO₂ as the photoelectrode and rGO as the counter electrode compared with DSSCs based on Pt as the counter electrode is found to be 11.25 and 9.28 mA cm⁻², respectively. Although the overall power efficiency of the fabricated DSSCs based on rGO as the counter electrode is lower than that based on the Pt electrode, the former still exhibits promising prospects for replacing Pt with low-cost metal-free carbon-based DSSCs.

1. INTRODUCTION

TiO₂ nanostructure materials have been widely used in many applications because of their nontoxicity, biocompatibility, low preparation cost, as well as their worldwide abundance. Some of these applications include health care products and either a thin film or a thick film as a photoanode layer in dye-sensitized solar cells (DSSCs). The TiO₂ thin-film electrode is considered as one of the best choices to obtain high light-to-electric conversion performance in DSSC applications. This photoanode layer based on the nanosized TiO₂ with various architectures, like nanorods, nanowires, and nanotubes in ordered mesostructured materials,¹⁻³ has been widely studied. The well-known natural polymorphs of TiO₂ are the rutile, brookite, and anatase phases. Anatase itself has a relatively low electron–hole recombination rate and has a higher photoactivity property, which is considered to yield high energy conversion and photocatalysis performance. It behaves as an n-type semiconductor material with an indirect energy gap of 3.2 eV. The anatase TiO₂ particle size has a great effect on its

Received: March 10, 2022
Accepted: April 18, 2022
Published: May 6, 2022
properties and, consequently, performance either in DSSCs or photocatalytic activities.\textsuperscript{4–7}

To date, high-efficiency DSSCs use TiO\textsubscript{2} nanoparticles in their various forms due to their unique properties and advantages such as high porosity, absorption of the dye, electron transport, and charge transfer. The sensitizers must be containing functional groups for stable adsorption onto the nanocrystalline TiO\textsubscript{2} thin films.\textsuperscript{8–10} Several research attempts have been proposed for the preparation of TiO\textsubscript{2} thin-film electrodes for DSSCs such as chemical vapor deposition, microwave hydrothermal methods, doctor blade, and/or spin coating techniques.

Among these methods, the microwave process combined with hydrothermal synthesis needs much less power and time and makes the synthesis of the nanomaterials possible at lower temperatures than those required for usual furnace heating.\textsuperscript{11} TiO\textsubscript{2} nanotubes were synthesized using the microwave-assisted hydrothermal technique.\textsuperscript{12} The authors argued that the conventional hydrothermal process for nanomaterial synthesis requires a long reaction time associated with large energy consumption, while the microwave-assisted method offers more rapid heating, higher yield, and better reproducibility of the fabricated nanocrystals.\textsuperscript{13} Therefore, the application of microwave energy to carry out chemical reactions has significant attractions because it is considered as a facile, highly efficient, and environmentally friendly process.\textsuperscript{14}

In this work, different TiO\textsubscript{2} nanopowders are synthesized via a simple sol–gel method,\textsuperscript{15,16} followed by microwave hydrothermal treatment under different working conditions. Investigations at different microwave irradiation times (20, 30, 45, and 60 min) instead of the usual hydrothermal time of 12 h are carried out. Different RGO samples have been prepared by the modified Hummers method, followed by microwave-assisted reduction at 200 °C and a pressure of 300 psi at different microwave irradiation times (3, 17, and 25 min). Both the nanocrystalline TiO\textsubscript{2} and RGO materials synthesized via microwave-assisted methods are applied in the fabrication of low-cost DSSCs as working and counter electrodes, respectively.

2. EXPERIMENTAL SECTION

2.1. Materials. All the chemicals utilized are used as received. Tetraethyl titanate [\(\text{C}_4\text{H}_{10}\text{O}_4\text{Ti}\)] (97%), Sigma-Aldrich, U.S.; nitric acid [HNO\textsubscript{3} (67–69%), Fisher, U.S.], polyethylene glycol [PEG, 20,000 (C\textsubscript{2}H\textsubscript{4}O\textsubscript{n})], Sinopharm, China; and Triton X-100 [(C\textsubscript{14}H\textsubscript{22}O(C\textsubscript{2}H\textsubscript{4}O\textsubscript{n})\textsubscript{4}], laboratory grade, Sigma-Aldrich, U.S.] are used as the reagents for the fabrication process. Fluorine-doped SnO\textsubscript{2} (FTO) glass is used as the substrate for the active electrodes (with 1 × 2 cm\textsuperscript{2} area and resistivity of 18 Ω cm\textsuperscript{-1}). Acetonitrile, iodine, and potassium iodide (ACS reagent, purity 99.8%) are used. Sensitive dye N-719 [RuL\textsubscript{2}(NCS)\textsubscript{2}, L = 4,4-dicarboxylate-2,2'-bipyridine] was obtained from Solaronix SA.

2.2. Synthesis of TiO\textsubscript{2} Nanocrystalline Photoactive Electrodes. Nanoporous photoactive TiO\textsubscript{2} thin-film layers are prepared using a modified procedure from our previously reported studies.\textsuperscript{15,16} In our typical procedure, 20 mL of tetrabutyl titanate is rapidly added to 200 mL of distilled water. The resultant white precipitate is filtered 3 times and washed with distilled water. Then, HNO\textsubscript{3} with a concentration of 0.1 M in 200 mL of aqueous solution is added to the filtered precipitate with continuous stirring at a temperature of 80 °C till the appearance of a semitransparent liquid with a blue-white color. This transparent gel-like liquid is then transferred to a microwave Teflon vessel (Speed Wave XPERT, Berghof). The microwave parameters are adjusted as follows: temperature is 210 °C, pressure limit is 300 psi, and heating power is 200 W.\textsuperscript{17} Different nanopowders have been prepared at various hydrothermal times (20, 30, 45, and 60 min) in the microwave oven at the same power and temperature. In this work, tetrabutyl titanate is used as the precursor for the titanium source, and the reaction mechanism is represented in Figure S1, Supporting Information.

A colloid containing nano-sized TiO\textsubscript{2} particles is then obtained. The solution is concentrated until a paste of the desired consistency is obtained by the addition of appropriate amounts of PEG with a molecular weight of 20,000 (10 wt % slurry); then, a small amount of Triton X-100 is dropped to form a paste of titania nanoparticles.\textsuperscript{18} This titania paste is then painted on FTO using the doctor blade technique 3 times to form a TiO\textsubscript{2} thick film (with about 0.25 cm\textsuperscript{2} active area and 3–5 μm thickness). Then, the porous film is sintered by firing in air at 450 °C for half an hour. After cooling down to room temperature, the film is sunk in a 0.5 mM ethanolic solution from N719 dye and kept in the dark for 24 h. Upon dyeing, the electrodes are rinsed thoroughly in absolute ethanol to remove the excess unattached dye and then left to dry at room temperature.\textsuperscript{19–21}

2.3. Metal-Free rGO Counter Electrode Fabrication. Reduced graphene oxide (rGO) material is prepared as follows: first, GO nanosheets are fabricated from commercially available graphite powder by applying the modified Hummers technique,\textsuperscript{22} followed by microwave irradiation treatment at 300 psi and different hydrothermal times (3, 17, and 25 min). The produced solutions are then centrifuged at 6000 rpm, washed several times by applying 10% v/v, and finally dried at 70 °C for 24 h.\textsuperscript{23} The rGO counter electrode is then fabricated by dispersing an appropriate amount of rGO (5 mg L\textsuperscript{-1}) in a dimethylformamide (DMF) solvent and 10% Naion, which is then coated on a cleaned FTO glass by the spin coating technique, followed by further air annealing at a temperature of 450 °C for 30 min.\textsuperscript{24}

2.4. Fabrication of TiO\textsubscript{2} Dye-Sensitized Solar Cell Devices. Fluorine-doped tin oxide (FTO)-covered glass substrates are carefully multicleaned in an ultrasonic bath using deionized water, acetone, and ethanol for 15 min, respectively. Finally, the substrates are dried in an open atmosphere. These cleaned FTO/glasses are used as substrates for the fabrication of both photoactive and counter electrodes. A DSSC device is completed by the filling of a solution from the electrolyte of 0.5 M LiI/50 mM I\textsubscript{2} in the solvents of 3-methoxypropionitrile and 0.5 M 4-tert-butyl pyridine between the dye-sensitized TiO\textsubscript{2} electrode and the counter electrode. Two types of counter electrode materials are used: metal-free rGO synthesized by the microwave-assisted hydrothermal method and Pt counter electrodes fabricated by the DC sputtering technique. The photoactive and counter electrodes are clipped together after the inclusion of the electrolyte, and performance measurements are carried out.\textsuperscript{25}

2.5. Material Characterization and Measurements. The morphology of TiO\textsubscript{2} nanoparticles is examined by a JEOL JSM-6360LV scanning electron microscope and a JEM-2000 EX (JEOL, Tokyo, Japan) transmission electron microscope, respectively. The crystal structure and phase identification of the nanoparticles are determined by X-ray diffraction (XRD) (X’Pert Philips). The optical analysis of TiO\textsubscript{2} thin solid films
and the measurement of dye adsorption are performed using a UV−vis double-beam JASCO V-550 spectrophotometer (Japan) equipped with an integrating sphere accessory. The specific surface area and pore volume of the nanopowders are measured using a Brunauer−Emmett−Teller (BET) (Quantachrome Instruments, NOVA series, USA) instrument at a temperature of 77.35 K. A Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S, Japan) is used with the measurement range between 500 and 4000 cm−1. The current−voltage (I−V) characteristics of the devices are studied at room temperature under UV−vis irradiation of 100 mW cm−2 by using a solar simulator device (PET Photo Emission Tech., Inc., USA).

3. RESULTS AND DISCUSSION

3.1. TiO2. The X-ray diffraction patterns (XRD) of mesoporous TiO2, which are fabricated using the microwave-assisted hydrothermal technique at a temperature of 210 °C and pressure of 300 psi at different microwave irradiation times of 20, 30, 45, and 60 min, are shown in Figure 1. The XRD patterns show the peak intensities of the prepared samples, which indicate the degree of crystallinity as well as the crystallite sizes of the nanocrystals. The peaks at 2θ = 25.25°, 37.7°, 47.98°, 53.88°, and 55.07° matched well with the anatase phase of nanocrystalline TiO2 for the planes (101), (004), (200), (105), and (211), respectively (JCPDS 00-021-1272).22 However, a peak at 27.47° has been observed for all samples in the XRD patterns, which is assigned to the (110) lattice plane of the rutile phase (according to JCPDS 21-1276).23

The anatase phase is formed as a result of rapid crystallization due to the generation of localized high temperatures in the presence of microwaves.24 The crystalline phase composition of the product depends on the concentration of the HNO3 solution. The calculated crystallite sizes of the anatase structure are determined from the Scherrer equation (eq 1)18 and are found to be 21.6, 18.6, 17.5, and 36.0 nm at the microwave irradiation times of 20, 30, 45, and 60 min, respectively (Table 1)

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Table 1. Average Band Gap Energy Values and Crystallite Sizes of Different TiO2 Nanocrystals Prepared at Different Microwave Irradiation Times

| sample          | calculated crystallite size (nm) | $E_g$ (eV) |
|-----------------|----------------------------------|------------|
| 20 min microwave| 21.6                             | 3.357      |
| 30 min microwave| 18.6                             | 3.343      |
| 45 min microwave| 17.5                             | 3.329      |
| 60 min microwave| 36.0                             | 3.306      |

where $k$ is a constant value ($0 < k < 1$), $\lambda$ is the X-ray beam wavelength (for Cu tube, $K_{\alpha} = 1.54 Å$), $\beta$ is determined as the full width at half-maximum (FWHM) of the peak, and $\theta$ is mentioned as the diffraction angle in radians.

From the XRD results in Table 1, it can be well recognized that the average crystallite size slightly decreases by an increase in the microwave irradiation time up to 45 min and then increases by a further increase in the microwave irradiation time up to 60 min. This is probably due to the small nanoparticles tending to be agglomerated into bigger ones with the increasing microwave irradiation time.26

The heating time of the fabricated mesoporous TiO2 nanocrystals is considerably decreased as compared with the hydrothermal methods (normally from 6 to 18 h). The FTIR results that confirm the purity of the obtained TiO2 nanocrystals are shown in Figure S2, Supporting Information. This short time period of the fabricated mesoporous TiO2 may be considered as economically suitable for both DSSCs and other applications.25

The UV−vis absorption spectra of the different TiO2 samples prepared at various microwave irradiation times (20, 30, 45, and 60 min) are recorded and shown in Figure 2a. It can be well recognized that a red shift toward longer wavelengths is observed by increasing the microwave irradiation time. These results well matched with the obtained by Kondalkar et al.27 The band gap energy ($E_g$) values for the prepared TiO2 nanopowders are computed from the direct transition allowed between the valence and conduction bands using Tauc’s law.28

$$\alpha = A(h\nu - E_g)$$

where $A$ is considered as a constant, $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy in eV, and $E_g$ is the direct band gap value. $E_g$ is determined through plotting $\alpha(h\nu)^2$ versus $h\nu$, and the linear portion extrapolated to the horizontal axis is the energy gap value, as shown in Figure 2b. The calculated band gap energies are listed in Table 1. From these results, it is found that the band gap energy is decreased by increasing the microwave irradiation time. This could be attributed to the increase in the crystallite size by increasing the microwave irradiation time from 20 to 60 min.29

The SEM images of the as-prepared TiO2 films fabricated at different microwave irradiation times are shown in Figure 3. Figure 3a–d exhibits the TiO2 films and shows the high quality of the compact and continuous films. This confirms the porosity and homogeneity of the crack-free thin films, which imply that the prepared thin films are suitable for DSSC applications.30

The typical TEM images of the TiO2 nanoparticles prepared by the microwave-assisted hydrothermal method at different irradiation times are shown in Figure 4. The morphology of all the TiO2 samples is clearly smooth and with adequate dispersion. A distinct polydispersity of spherical TiO2 nanoparticles is formed, with sizes ranging from 16 to 34.
nm, at microwave times of 20, 30, 45, and 60 min, as shown in Figure 4A−D, which is in accordance with the data obtained from XRD measurements. Figure 4E,H shows the HRTEM images of the TiO$_2$ sample treated by microwave irradiation at a time of 45 min. Distinguished anatase nanoparticles with sizes of 20 nm and d-spacing of 3.458 Å of the (101) plane are clearly detected (Figure 4G,I), while the rutile phase nanoparticles of 10 nm size are detected with a d-spacing of 3.505 Å of the (110) plane (Figure 4F,H). Elemental mapping shows a regular distribution of O K$\alpha$ and Ti K$\alpha$ elements, with a higher density of titanium. Figure 4J shows the SAED patterns, where the (101), (110), (004), (200), (105), and (211) planes of anatase and rutile phases are observed. The low margin between the TiO$_2$ nanocrystal sizes may be explained by the fast nucleation process during the transformation from the amorphous phase to the crystalline one (anatase and rutile), with the application of the microwave-assisted hydrothermal technique.

N$_2$ adsorption−desorption isotherms for the as-prepared TiO$_2$ nanopowders are given in Figure 5. The adsorption−desorption isotherms of all samples show isotherms of type 4 with a typical H3 hysteresis loop, referred to the classification of BDDT,$^{31}$ indicating the presence of mesopores (6−12 nm).
in the samples prepared at 30, 45, and 60 min. However, the TiO2 nanoparticles prepared at the microwave irradiation time of 20 min show a larger pore size distribution ranging from 15 to 20 nm. Thus, it can be concluded that as the microwave irradiation time increases, the average pore volume decreases (from 20 to 45 min) and begins to increase again at 60 min of irradiation. However, in the literature, there is no clear explanation or evidence on the effect of microwave irradiation time on the porosity of the solid samples. Our results are compatible with the previous work of Hong et al.32

The pore size distribution is plotted in Figure 6, which is set by applying the methodology of Barrett−Joyner−Halenda (BJH). The calculated specific surface area, porosity ($P$), total pore volume ($V_p$), and maximum pore volume ($P_{\text{max}}$) for all the samples are given in Table 2.

| Sample  | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $P_{\text{max}}$ (nm) | $V_p$ (cm$^3$ g$^{-1}$) | Porosity ($P$) |
|---------|-------------------------------|-----------------------|----------------------|-------------|
| 20 min MW | 77.55 | 17.15 | 0.4869 | 0.654523 |
| 30 min MW | 97.77 | 8.37 | 0.2394 | 0.48272 |
| 45 min MW | 100.27 | 7.79 | 0.2295 | 0.471737 |
| 60 min MW | 84.86 | 9.66 | 0.2246 | 0.466362 |

*Porosity ($P$) = $V_p/\rho_{-1} + V_p$, where $V_p$ is the specific pore volume in (cm$^3$/g) and $\rho_{-1}$ is the anatase TiO$_2$ inverse density ($\rho_{-1} = 0.257$ cm$^3$/g). $P_{\text{max}}$ is the pore size at the maximum frequency.*

Increasing the microwave irradiation time (XRD analysis results are provided in Table 2). The results are not significantly changed by increasing the microwave irradiation time from 30 to 45 min, as the specific surface area increased only slightly to 100.27 m$^2$ g$^{-1}$. However, increasing the microwave irradiation time up to 1 h leads to a significant decrease in the specific surface area, that is, it decreased to 84.86 m$^2$ g$^{-1}$. This presumably is due to the enhancement in the crystallite size at high microwaving times.33 Similar behavior has been observed from the results of the average interparticle pore sizes, calculated based on the BJH model.

Finally, we conclude that the prepared TiO2 nanopowders, using the microwave-assisted hydrothermal technique, are mesoporous with relatively high specific surface area values.30

3.2. rGO. The XRD patterns of GO and rGO synthesized at different microwave irradiation times (3, 17, and 25 min) have been displayed in Figure 7. It can be clearly seen that the characteristic peak of GO is detected at 2$\theta$ (10°−12°), which is assigned to the (001) reflection of GO.34 After treatment with microwave irradiation at 200 °C for 3 min, the intensity of the (001) peak begins to decrease, and a new small peak begins to appear at 2$\theta$ = 23.4° corresponding to the (002) plane of rGO.35 However, by a further increase of the microwave irradiation time up to 17 and 25 min, a complete conversion of GO into rGO has been achieved. This has been confirmed from the XRD patterns in Figure 7a−d, where the two characteristic peaks of rGO are well recognized at 2$\theta$ = 23.4° and 43° corresponding to the (002) and (101) diffraction peaks.
planes. The interlayer or layer-by-layer stacking distance (d) for the GO and rGO samples was calculated by using Bragg’s law.

The interplanar distances of the peak (d_{002}) are found to be 3.79 and 3.9 Å for rGO at 17 and 25 min, respectively, showing a higher quality ordering of the rGO nanosheets, whereas the theoretical value of d_{002} for graphite is about 3.3354 Å. The crystallographic parameters for the prepared rGO samples are given in Table 3. The average height of the crystallite parameter (Lc) represents the stacking height of the graphitic structure. This parameter is obtained from the Scherrer equation (eq 1).

### Table 3. Calculated and Measured Parameters of FLG Synthesized by the Microwave Hydrothermal Method

| sample description | 2θ degrees | FWHM (rad.) | d_{002} (Å) | Lc (Å) | number of layers |
|--------------------|------------|-------------|-------------|--------|-----------------|
| rGO 17 min         | 23.434     | 0.043       | 3.79        | 32.43  | 8               |
| rGO 25 min         | 23.434     | 0.0446      | 3.79        | 31.34  | 8               |

The calculated values of Lc are found to be 32.34 and 31.34 Å for the rGO samples at 17 and 25 min, respectively. The link between Lc and d_{002} may give the estimation that the fabricated rGO samples have about eight layers, which means that the prepared samples are few-layer graphene (FLG). Table 3 shows the values of FWHM of the peaks detected at 2θ = 23.434° (plane (002) of graphene), the interlayer distance (d_{002}), the average height of the crystallite (Lc), and the number of layers calculated from the ratio Lc/d_{002} for the prepared FLG.

Figure 8 depicts the TEM images of GO and rGO prepared at 210 °C and 300 psi at the microwave irradiation times of 3, 17, and 25 min, respectively. Through TEM observations, independent GO nanosheets are observed (Figure 8a). It is noted that the GO nanomaterials have a good level of transparency, which indicates a higher degree of oxidation. Also, the GO nanosheets present some darker areas, which may be related to the stacking behavior of some GO layers.

However, the rGO nanosheets are single- or few-layer nanosheets with a large number of wrinkles, as shown in Figure 8b−d. The transparent regions demonstrate the monolayer isoforms of the fabricated rGO. The dark areas represent the wrinkled structures that form a thick monolithic structure of several layers of reduced graphene oxide. Corrugation and scrolling suggested the intrinsic nature of graphene. This kind of special microstructure of rGO could provide more advances in solar cell technology.

Further microstructure characterization for graphite in both GO and rGO is performed by Raman spectroscopy. Figure 9 shows that GO displays a peak for the G band at 1596.5 cm^{-1} and another D band at 1364 cm^{-1}, which correspond to the sp^{2} carbon atoms and the proposed defects in GO, respectively. The Raman shifts of both the D and G bands from 1350 and 1602 cm^{-1} for GO to the lower values of 1349 and 1589 cm^{-1} for rGO samples assure successful in situ chemical reduction for graphene oxide. Also, the I_{D}/I_{G} value is gradually increased from 0.99 for GO to 1.74 for rGO, confirming the formation of smaller sp^{2} graphite bands upon GO reduction.

Finally, the 2D band value at 2677 cm^{-1} is observed in reduced rGO, which confirms the FLG synthesis.

#### 3.3. DSSC Efficiency

Figure 10 shows the J−V characteristics of DSSCs based on active TiO_{2} film electrodes fabricated from the TiO_{2} nanoparticle paste that has been prepared by
the microwave-assisted hydrothermal method at the microwave irradiation times of 20, 30, 45, and 60 min. The TiO₂ film photoanode is illuminated by Solar Simulator light with an intensity of 100 mW cm⁻², and electron–hole pairs are generated on the surface of TiO₂ electrodes, which resulted in the photocurrent flow. It has been observed that with the increase of the irradiation time in the microwave furnace from 20 to 30 min, the power conversion efficiency (PCE) is increased from 1.47 to 2.57%, respectively. However, further increase in the irradiation time of the microwave up to 60 min leads to a decrease in the PCE to 2.2%. These results are very consistent with the results of the amount of the dye loaded on the TiO₂ film electrodes (Table 4). The J–V characteristics of the fabricated DSSCs are summarized in Table 4. The electrolyte ion diffusion is more preferred in the porous TiO₂ films owing to the interfacial chemical reaction which may speed up due to the higher values of the surface area. This is in addition to the microwave irradiation time that increases the crystallinity of the nanopowders, which is more favored to minimize the interfacial charge recombination. The results are not changed significantly by increasing the microwave irradiation time from 30 to 45 min. However, by increasing the microwave irradiation time up to 60 min, a remarkable decrease in the PCE has been observed. This presumably is due to the enhancement in the crystallite size and consequently the reduction of the specific surface area values at high microwaving times.

In order to measure the dye (N719) amount loaded on various TiO₂ film electrodes, it was desorbed by an ethanolic solution of 0.5 M NaOH. The UV–visible absorption spectra of the dye solutions are then measured and given in Figure 11. The amount of the dye adsorbed per unit area for the different TiO₂ film electrodes is calculated and given in Table 4. It can be well recognized that the amount of dye adsorbed per unit area was increased by increasing the microwave irradiation time from 20 to 30 min, but by increasing the microwave irradiation time up to 60 min, the amount of dye adsorbed was decreased, which is consistent with the results of the specific surface areas reported in Table 4.

The photovoltaic performance is tested in comparison with a reference DSSC based on the Pt counter electrode. The curves J_{sc}–V for the DSSCs based on rGO and Pt thin-film counter electrodes are shown in Figure 12. The estimated performance parameters are summarized in Figure 12, where the photovoltaic parameters for the DSSCs are shown, including the open-circuit voltage, V_{oc}; short-circuit photocurrent density, J_{sc}; fill factor (FF); and the cell’s overall energy conversion efficiency (η). The PCE of an rGO-based solar cell is 2.82% while that of a Pt-based solar cell is 4.97%. However, the J_{sc} value of the rGO-based solar cell is much higher than that of the Pt-based cell, while the fill factor is low. This resulted in lowering the efficiency of the fabricated devices compared with the reference one. This could be attributed to the compact and relatively low uniform layer of rGO.

### Table 4. J–V Characteristics of DSSCs Based on TiO₂ Film Nanoparticle Electrodes Prepared by the Microwave Hydrothermal Method at Different Microwave Irradiation Times

| Sample | J_{sc} (mA/cm²) | V_{oc} (V) | dye adsorbed [M] × 10⁻³ | FF | Efficiency (η) |
|--------|-----------------|-----------|-------------------------|----|----------------|
| 20 min | 3.389 | 0.609 | 2.28 | 71.12% | 1.47% |
| 30 min | 4.9 | 0.6584 | 3.25 | 79.57% | 2.57% |
| 45 min | 7.42 | 0.6124 | 2.96 | 56.35% | 2.56% |
| 60 min | 4.692 | 0.6392 | 2.60 | 73.32% | 2.20% |

Figure 11. UV–visible absorption spectra per unit area of the different N719/TiO₂ thin-film electrodes.

Figure 12. J–V characteristics of rGO-based DSSCs, compared with a Pt-based solar cell as a reference device.

4. CONCLUSIONS

We successfully replaced the conventional longtime hydrothermal method by a fast and low-cost microwave-assisted method to synthesize nanocrystalline TiO₂ and metal-free rGO materials for DSSC applications. The physicochemical properties of the nanocrystalline TiO₂ materials prove a mesoporous structure with the highest specific surface area at a microwave irradiation time of 45 min (100.27 m² g⁻¹). This results in a higher amount of (N719) dye loading and hence gives the highest PCE when applied as a photoactive electrode in DSSCs. Compared with the Pt-based DSSC, the application of metal-free rGO counter electrode leads to a higher photo-efficiency.
current density \( J_{sc} \) from 9.25 to 11.25 mA cm\(^{-2}\). Despite the fact that the overall power efficiency of the fabricated DSSCs based on rGO as the counter electrode is lower than that based on Pt electrode, the former still exhibits promising prospects for replacing Pt with low-cost metal-free carbon-based DSSCs. Different TiO\(_2\) nanoparticles with different crystallite sizes from 21 to 36 nm have been synthesized via the microwave-assisted hydrothermal method at different microwave irradiation times (32, 30, 45, and 60 min).

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01455.

Reaction mechanism of tetrabutyl titanate for TiO\(_2\) production and FTIR of TiO\(_2\) nanoparticles prepared using the microwave irradiation times of 20 and 60 min (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors wish to express their thanks to the Department of Electronic Materials, Institute of Advanced Technology and New Materials, SRTA City, Egypt, and the Nanophos chemistry and its environmental applications lab. Nanotech. Dept., Environmental Studies and Research Institute, University of Sadat City, for the accomplishment of this research. Also, a part of this work was funded by the Academy of Scientific Research, Egypt, through a scholarship with grant no. ASRT/SNG/E/2014-32 for Hossam Hassan. The authors declare that they have no conflict of interest.

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