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Article

One-step fabrication of TiO₂/graphene hybrid mesoporous film with enhanced photocatalytic activity and photovoltaic performance

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ABSTRACT

We synthesized a mesoporous film based on TiO₂-reduced graphene oxide (RGO) hybrids using a one-step vapor-thermal method without the need for an additional annealing process. The vapor-thermally prepared TiO₂-graphene hybrid (VTH) features unique structures with an ultra-large specific surface area of ~260 m² g⁻¹ and low aggregation, giving rise to enhanced light harvesting and increased charge generation and separation efficiency. It was observed that a mesoporous film with uniform pore distribution is simultaneously obtained during the VTH growth process. When a 5.0 wt% RGO VTH film was used as the active layer in photocatalysis, the highest photocatalytic activity for degradation of methyl orange was achieved. For another, when a 0.75 wt% RGO VTH film was used as the photoanode in a dye-sensitized solar cell, the power conversion efficiency reached 7.58%, which represents an increase of 73.1% compared to a solar cell using an a photoanode of pure TiO₂ synthesized by a traditional solvothermal method. It is expected that this facile method for the synthesis of TiO₂/graphene hybrid mesoporous films will be useful in practical applications for preparing other metal oxide/graphene hybrids with ultra-high photocatalytic activity and photovoltaic performance.

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1. Introduction

Nanostructured TiO₂ is widely used in photocatalysis and solar energy conversion due to its merits of low cost, facile fabrication, chemical stability, and high photo-responsivity [1–3]. Typically, the utilization of TiO₂ nanoparticles for the fabrication

of mesoporous films helps in achieving a large surface area for absorbing pollutants or sensitizers, separating the photo-induced electron pairs, and transporting the excited electrons [4,5]. However, the efficiency of the reaction or conversion of photo-generated electrons is heavily limited by the high rate of electron-hole recombination, determined by the inter-

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face resistance in the mesoporous films, resulting in a low catalytic activity or power conversion efficiency [6].

Recently, many methods have been developed to modify nanostructured TiO_2 for the inhibition of its intrinsically fast electron-hole recombination, such as chemical doping [7–9], introducing semiconductors [10,11], and hybridization with carbon materials [12]. In particular, the integration of graphene sheets and TiO_2 nanoparticles has attracted a growing interest for enhancing the catalytic and photoelectric performance of TiO_2 -based devices [13–20]. For the enhancement of TiO_2 -graphene hybrid-based devices, an ultra-large surface area is of great importance as it allows the anchoring of pollutant and sensitizer molecules. Secondly, the intrinsic bandgap of the formed TiO_2 -graphene composites can be easily tuned, thus enhancing the photo-responsivity in a broad range of wavelengths. Thirdly, the introduction of graphene sheets to TiO_2 and tuning the bandgap offers a fast route for transporting photoelectrons, which prevents the recombination of photo-induced charges. Lin and co-workers [21] reported TiO_2 -graphene nanocomposites that exhibited significantly higher photocatalytic activity, which was strongly affected by the amount of graphene in the hybrids, for degradation of pharmaceuticals as compared to pure TiO_2 . Bonaccorso et al. [22] suggested that the TiO_2 -graphene hybrids can serve as transparent conductive electrodes, which could obviously improve the power conversion efficiency in photovoltaic modules.

Despite the above-mentioned promising results, TiO_2 -graphene hybrids have some disadvantages, as the TiO_2 nanoparticles tend to agglomerate and have high interfacial resistance with the graphene surface because of the nanoparticles' disordered distribution [23]. In addition, according to most reports, fabricating mesoporous films based on TiO_2 -graphene hybrids requires annealing at high temperature, thus worsening the disorder and agglomeration of TiO_2 nanoparticles, resulting in low photocatalytic activity and poor photovoltaic performance [24,25]. Therefore, a uniform structure without agglomeration is essential for enhancing the photo-to-electron conversion activities of TiO_2 -graphene hybrid-based films. In previous work, we fabricated mesoporous TiO_2 films by a one-step vapor-thermal process using the titanium precursor directly [26]. Compared with the traditional annealing methods, the prepared vapor-thermal mesoporous TiO_2 films had lower interfacial resistance, possessed a more homogeneous pore distribution, and exhibited reduced nanoparticle agglomeration [27]. These results potentially provide a new approach to prepare TiO_2 -graphene hybrid mesoporous films for improving catalytic and photovoltaic performance.

Herein, we report a facile route for the growth of TiO_2 nanoparticles on reduced graphene oxide (RGO) sheets via vapor-thermal synthesis. Interestingly, while TiO_2 nanoparticles were grown on the graphene oxide (GO) surface, a simultaneous deoxygenation of GO to RGO was observed. More importantly, a mesoporous film with a uniform pore distribution and low agglomeration was obtained during the synthesis of TiO_2 -graphene hybrids. The reduced graphene oxide/ TiO_2 nanoparticle hybrid-based films exhibited excellent catalytic activity for the degradation of methyl orange and ultra-high pho-

tovoltaic performance in the visible region. The enhancement of the photocatalytic and photovoltaic performance could be attributed to the fabricated high-quality hybrid films with uniform pore distribution and low agglomeration via a vapor-thermal method, which greatly lowers the interfacial resistance and promotes the intrinsic charge transfer of graphene.

2. Experimental

2.1. Materials and sample preparation

An aqueous colloidal suspension of GO without surfactants was bought from Tanfeng, Suzhou, China. Titanium tetraisopropoxide (TTIP), acetic acid, acetone, ethanol, methyl orange, urea, and poly(ethylene glycol) (PEG-2000) were purchased from Aladdin, Shanghai, China. Chloroplatinic acid paste, electrolyte solution, N719 dye, and FTO (SnO_2/F , $8 \Omega \text{ cm}^{-2}$) glass were obtained from DHS, Dalian, China.

The details of the solvothermal synthesis of graphene- TiO_2 composites have been described earlier [28]. In brief, different amounts of dispersed GO were added into the TTIP solution diluted with acetic acid and the total volume was fixed by adding ethanol under vigorous stirring conditions to form a homogeneous solution. Then, the solution was transferred to a polyphenyl (PPL)-lined autoclave for thermal treatment at 180°C for 12 h to produce a TiO_2 -graphene hybrid. The details of the synthesis process are described in Fig. 1(a). After this, the solvothermally prepared TiO_2 -graphene hybrid (STH) was washed with acetone, ethanol, and deionized (DI) water and dried in vacuum.

The obtained STH powder, PEG-2000, and DI water were

Fig. 1. The schematic process. (a) solvothermal method combined with annealing process for synthesis pure TiO_2 (ST) and TiO_2 -graphene hybrid (STH) based porous films; (b) One-step vapor-thermal method for synthesis pure TiO_2 (VT) and TiO_2 -graphene hybrid (VTH) based porous films. The inset is the vapor-thermal configuration for fabrication of TiO_2 -graphene mesoporous film.

added to ethanol to form a paste by a balling technique. The paste was transferred to the FTO glass with a mask to fabricate a film using a doctor-blade method. Then, the paste film was dried at 120 °C for 30 min and a mesoporous structure was produced via annealing at 450 °C for 30 min. The details of the fabrication of STH-based mesoporous films are described in Fig. S1.

The details of the vapor-thermally fabricated TiO₂-graphene hybrid (VTH) mesoporous films are shown in Fig. 1(b). The homogeneous titanium precursor was stirred to form a hydro-sol via the addition of urea. The sol was applied to the FTO glass with a mask to form a film by spin coating. The obtained film hovered on the hollow glass tubes, which were then placed in PPL-lined autoclave with 60% volume of ethanol in advance, and then treated at 180 °C for 12 h. It is interesting to note that a nanostructured porous film was achieved simultaneously during the formation of the TiO₂-graphene hybrid by a vapor-thermal process, which removes the need for a second thermal process, unlike the fabrication of STH-based porous films (Fig. 1(a)).

2.2. Characterization and measurements

Scanning electron microscope (SEM) images were obtained using a JEOL JSM-7500F SEM at 15 kV (JEOL Co. Ltd.). Transmission electron microscope (TEM) images were obtained using a Tecnai G2 F20 S-TWIN TEM at 200 kV (FEI Co. Ltd.). Atomic force microscope (AFM) images were acquired using a Veeco D3100 AFM (Bruker Co. Ltd.). Specific surface area and pore size distribution plots were collected using a Gemini Micromeritics ASAP-2010 analyzer using the Brunauer-Emmett-Teller (BET) method at 77 K. X-ray diffraction (XRD) patterns were recorded using a Shimadzu XRD-7000 diffractometer (Cu K_α radiation). Raman spectroscopy was conducted using a Renishaw inVia reflex spectrophotometer at 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed using an Escalab 250Xi system (Thermo Fisher Scientific Co. Ltd.). UV-vis spectroscopy measurements were recorded using an Agilent Cary5000 spectrophotometer.

The photocatalytic activities of the fabricated mesoporous films were evaluated by monitoring the degradation of a methyl orange solution in DI water (15 mg L⁻¹). Firstly, the porous films were immersed in 100 mL of the dye solution in a 250-mL quartz flask and then placed in a dark box combined with a 500-W mercury lamp. After the film absorbed the dye in the dark for 1 h, the film was irradiated with the light produced by the mercury lamp for 90 min. Meanwhile, 5-mL aliquots were removed at 10-min intervals and then the absorbance was measured by UV-vis spectroscopy.

Before measuring the photovoltaic performances, the films were assembled into solar cells using our previous method. In brief, the films were immersed in a 0.5 mM N719 dye solution with ethanol to form dye-sensitized photoanodes [26]. After washing and drying, the photoanodes were assembled with Pt-covered counter electrodes, encapsulated with a heat-sealing film, and then injected with I₃⁻/I⁻ electrolyte to fabricate solar cells. The external quantum efficiency (EQE) was

measured using a PV Measurements QEX10-PP quantum efficiency system. Photovoltaic performance and electrochemical impedance spectroscopy (EIS) measurements were performed using a BOS-500X-Z solar simulator providing an irradiation of 960 W m⁻² associated with a CHI 660C electrochemical workstation.

3. Results and discussion

3.1. Morphology of pure TiO₂ and TiO₂-graphene hybrids

In a typical synthesis of TiO₂-graphene hybrids with TiO₂ loading on 0.75 wt% RGO sheets, TTIP (3.6 mL) was mixed with 12 mL of a 0.6 mg mL⁻¹ GO dispersion in the titanium precursor. If the GO concentration was changed, for example, by using 12 mL of a 4 mg mL⁻¹ GO dispersion, we could easily obtain TiO₂-graphene hybrids with 5.0 wt% RGO. For comparison, we also synthesized pure TiO₂ porous films using our one-step vapor-thermal method (VT) and a conventional solvothermal process (ST), which were used as control samples. Fig. 2 documents the morphological characteristics of the fabricated mesoporous films produced using the different routes shown in Fig. 1. As shown in Fig. 2(a)–(j), the SEM images indicate that the VT films and VTH films were formed without the aggregation of TiO₂ particles and possessed a well-defined pore distribution, compared with ST films and STH films. In general, the monolayer RGO sheets tend to aggregate to the graphite structure due to the van der Waals interactions [29]. Functionalizing RGO sheets with metal oxide nanoparticles, e.g. TiO₂, is a useful method to weaken the strong interactions between individual RGO sheets [30]. That is, when TiO₂ nanoparticles are

Fig. 2. Morphology characterizations of as-prepared pure TiO₂ and TiO₂-graphene hybrids. SEM images of ST film after annealing at 450 °C (a), VT film (b), STH film (c) after annealing at 450 °C and VTH film (d). High-resolution SEM images of TiO₂ nanoparticles grown on the surface of RGO sheets in STH (e) and VTH (f) films. Cross-section SEM images of ST (g), VT (h), STH (i), and VTH films (j). (k) SEM image of TiO₂-graphene composite prepared by vapor-thermal method. AFM images of TiO₂-graphene hybrid (l) and TiO₂ nanoparticles grown on the RGO sheets (m) synthesized using vapor-thermal process.

Fig. 3. Morphology characterizations of as-prepared materials. TEM (a) and HRTEM (b) images of synthesized STH. Specific surface area (c) and pore size distribution (d) plots of fabricated films.

grown on the surface of RGO via a vapor-thermal process, the hybrids tend to maintain a two-dimensional shape, which is illustrated in Fig. 2(k). The AFM images further prove that the introduction of TiO₂ in VTH effectively reduces the π - π stacking interactions among the RGO sheets, and that the hybrids still maintain a two-dimensional morphology (Fig. 2(l) and (m)). It shows that the radial size of VTH reaches up to several micrometers, while the height of VTH is only on the order of nanometers.

The TEM image shown in Fig. 3(a) shows that the bare RGO

has a flake-like structure with wrinkles and a very small thickness, like silk. Moreover, the high-resolution TEM (HRTEM) image in Fig. 3(b) displays lattice fringes with an interplanar spacing of 0.342 nm, which is perfectly equal to the lattice constant of the (101) crystal planes of the anatase phase of TiO₂. It is also observed that the unique structure of VTH features an ultra-large specific surface area of ~ 260 m² g⁻¹, compared with the ~ 150 m² g⁻¹ of pure TiO₂, as shown in Fig. 3(c). The BET results further confirm that the VTH-based films have a better pore distribution compared with the STH-based films. As shown in Fig. 3(d), the pore sizes of VT and VTH are centered at ~ 11 , ~ 10 , and ~ 300 nm, respectively, but those of ST and STH are disordered. The low level of aggregation, ultra-large specific area, and well-defined pore distribution of the synthesized VTH film are expected to enhance its photocatalytic activity and photovoltaic performance in practical applications.

3.2. Structures of TiO₂-graphene hybrids

Similar to the formation process of TiO₂-graphene using a solvothermal method, GO was successfully reduced to RGO sheets during the crystallization of TiO₂ particles during the vapor-thermal treatment. The evidence is presented in Fig. 4. Firstly, before the thermal treatment, the GO sheets absorb most Ti⁴⁺ ions and other organic groups via electrostatic forces and chemisorption with abundant oxygen groups (Fig. 4(b)). When the titanium precursor formed a homogeneous hydrosol, the Ti⁴⁺ cations gave rise to nucleation sites for the crystallization of TiO₂ [31]. The amount of C=O bonds of GO after forming a titanium-GO hydrogel (Fig. 4(a), 0 h) remained near-constant,

Fig. 4. XPS spectra of C 1s (a), Ti 2p (b) and O 1s (c) region of TiO₂-graphene hybrids with different vapor-thermal reaction time of 0, 3, 6, 12, 18 and 24 h. Raman spectra (d) and XRD patterns (e) of fabricated films, ST, VT, STH and VTH films.

compared with that of the pristine GO dispersion (Fig. S2). This trend may be connected with the fact that Ti^{4+} ions are free of oxidation from that lower valence state, which is distinctly different from Zhu and co-workers' report [32]. Next, during the vapor-thermal process, the GO sheets are obviously reduced (Fig. 4(a)) and form a two-dimensional wrinkling hybrid (Fig. 2(k)). The self-assembly route of TiO_2 grown on the RGO sheets is suggested to start when most of the oxygen groups are removed from the surface of the GO sheets (Fig. 4(a), 6 h). Finally, TiO_2 -loaded RGO hybrids are obtained after vapor-thermal treatment for 12 h. The end of the synthesis process could be monitored by XPS inspection, which suggests that the intensity of the as-formed Ti–O bonds is much higher than that of the C–O bonds (Fig. 4(c)), and there is no further decrease of oxygen-containing groups (Fig. 4(a), 12, 18 and 24 h).

Raman spectroscopy is a powerful tool to study the structural properties of nanoparticles. Fig. 4(d) shows the Raman spectra of the pure TiO_2 and TiO_2 -graphene hybrid-based films prepared by different methods. The Raman bands at 142 (E_g), 478 (B_{1g}), 519 ($A_{1g}B_{1g}$), and 635 cm^{-1} (E_g) for the composites are well matched with the anatase phase of TiO_2 . It is worth mentioning that the E_g bands of the hybrids were both shifted and broadened, compared with that of pure TiO_2 particles. The shifting and broadening of the Raman band could be attributed to the weakened crystallization of the nanoparticles induced by the surface pressure or phonon confinement effects [33]. Compared with the pure TiO_2 particles, the E_g band for the hybrids was shifted from 167 to 146 cm^{-1} (Fig. S3). It is suggested that a strong phonon confinement effect in the RGO sheets or a nanoscale size effect in the TiO_2 particles could play a key role in the asymmetric broadening [33]. XRD patterns were further employed to confirm that the size effect [34], that is, the diffractive angle, is larger for hybrids than for pure TiO_2 (Fig. S4). In addition, the XRD patterns clearly prove that the TiO_2 nanoparticles loaded on the RGO sheets are in the anatase phase (Fig. 4(e)). As previously reported for TiO_2 /carbon nanotube (CNT) and TiO_2 nanotube/RGO composites, this blue-shift of the E_g band in the Raman spectrum clearly indicates that the vapor-thermally prepared TiO_2 -graphene hybrids exhibited a strong chemical interaction between the TiO_2 nanoparticles and RGO sheets [31]. This strong chemisorption interaction may provide a new efficient route for electron transfer, which is expected to enhance the photocatalytic ability and improve the efficiency for photon-to-electron conversion.

Raman spectroscopy is also widely used to investigate the electronic properties of layered materials. The peaks at 1343 and 1602 cm^{-1} (Fig. 4(d), inset) correspond to the D band and G band of RGO, respectively. In general, the D band and G band provide information about sp^3 defects in carbon and in-plane vibrations of sp^2 -bonded carbons in graphene [35]. The intensity ratio of the D band to the G band (I_D/I_G) is usually used to index the order of defects in graphene [36]. Firstly, the calculated I_D/I_G of RGO sheets (0.91) is lower than that of GO (1.02), indicating a lower level of defects appearing in RGO (Fig. S5). Secondly, the calculated I_D/I_G values of STH and VTH are 1.07 and 0.98, respectively (Fig. 4(d), inset). The increases in the calculated I_D/I_G values for TiO_2 -graphene synthesized via va-

por-thermal and solvothermal processes are induced by the fragmentation of sp^2 domains [37]. On the other hand, the decreased I_D/I_G of VTH suggests that the vapor-thermal method we used results in a more homogeneous particle size distribution, and also allows for the retention of more initial sp^2 domains due to the lack of a second thermal process, compared to the traditionally annealed STH films. The lower I_D/I_G ratio signifies a better defect repair mechanism and a faster photoelectron transfer route [37].

3.3. Photocatalytic activity

As shown in the illustration inserted in Fig. 5, the photocatalytic mechanism of both pure TiO_2 and TiO_2 -graphene hybrids involves three steps: (I) absorption of pollutant, (II) absorption of incident light by the catalyst support to excite an electronic transition, and (III) charge separation and transfer to form free radicals for decomposing the pollutant [31]. The as-prepared TiO_2 -graphene hybrids offer an ultra-large specific surface area of $\sim 260 \text{ m}^2 \text{ g}^{-1}$ (Fig. 3(a)), much larger than that of pure TiO_2 , to absorb pollutants on the surface of the photocatalyst (Fig. 5 inset, step I). Furthermore, the introduction of RGO sheets provides a route to creating π - π stacking interactions with the aromatic groups in the dyes and related pollutants like industrial wastes. The above-mentioned two processes could obviously increase the concentration of pollutants near the porous catalytic film, which is a key factor to obtain improved photocatalytic materials with high degradation rates. The measurement of total organic carbon (TOC) was applied during the methyl orange photodegradation to explore whether methyl orange had been mineralized. As shown in Fig. 5(a)–(c), the TOC removal efficiency of VTH reached around 90% after reacting for 90 min. This demonstrates that the obtained photocatalysts can degrade methyl orange into inorganic carbon. A

Fig. 5. Photocatalytic activity ($1-c/c_0$, %) plots of ST and VT films (a), STH and VTH films (b) versus time for the degradation of methyl orange. The inset images show a schematic of proposed model of pure TiO_2 (a) and TiO_2 -graphene hybrids (b) for photocatalytic reaction in application of degradation of methyl orange; (c) Total organic carbon (TOC) concentration under irradiation; (d) Photodegradation kinetics over the as-prepared samples. The gray lines correspond to the fitted results.

potential mechanism is suggested in the inset of Fig. 5, following the previously reported models [38,39].

In addition, we also estimated the photocatalytic decomposition rate using the relationship $\ln(c/c_0) = -kt$, where k , t , c , and c_0 are degradation rate constant, reaction time, residual concentration, and initial concentration, respectively [23]. The recorded catalytic activity ($1-c/c_0$, %) results and calculated decomposition rates of VT, ST, VTH, and STH films are presented in Fig. 5(a) and (b). Apparently, the capacities of TiO₂-hybrids for TOC removal (Fig. 5(b)) were enhanced compared with bare TiO₂ (Fig. 5(a)). As shown in Fig. 5(d) and Table 1, the calculated rate constant for the VTH film was 0.062 min⁻¹ in the first 40-min interval, which is almost three times greater than that of the conventional pure TiO₂ film (ST, 0.023 min⁻¹). From the above-mentioned results, the VTH-based film had a significantly higher catalytic activity compared with other graphene hybrid catalysts [18,38,39].

Furthermore, these results show that the photocatalytic activities of porous films prepared by our vapor-thermal method (VT, VTH) were higher than those of traditionally annealed (ST, STH) films, as shown in Fig. 5. The enhanced photocatalytic activity of vapor-thermally synthesized films may be connected with the lower recombination rates and more homogeneous pore size distributions. It is well-known that the photo-generated electron-hole pairs (Fig. 5 inset, Step II) have a short intrinsic recombination time of $\sim 10^{-9}$ s, while the excitation reaction time (Fig. 5 inset, Step III) is long as $10^{-8} \sim 10^{-3}$ s, resulting in a high level of photoelectron emission and a low catalytic activity [40]. It is therefore important to optimize the catalytic activity by controlling the equilibrium between step II and step III in the catalytic mechanism. According to previous reports, the conduction band position of TiO₂ and the work function of graphene are ~ 4.2 and ~ 4.5 eV, respectively. Thus, TiO₂ loaded on the RGO sheets allows the photo-generated electrons to be directly injected into the graphene, due to the narrow bandgap of ~ 0.26 eV (Fig. 5(b) inset), which is much faster than the route of carrier transport in TiO₂ networks (Fig. 5(a) inset) [41].

The charge recombination performances of pure TiO₂ and TiO₂-graphene hybrid films were further investigated using EIS analysis. As shown in Fig. S6, the Nyquist plots consist of two semicircles: (I) R_s is the diffusion resistance in the electrolyte and (II) R_{ct} is the charge transfer resistance at the electrolyte/catalyst interface [42]. In general, the resistance of the system is determined by R_{ct} because the same electrolyte and counter electrodes are used. It can clearly be seen that the order of charge transfer resistance of the fabricated films is $R_{ct}(\text{VTH}) < R_{ct}(\text{STH}) < R_{ct}(\text{VT}) < R_{ct}(\text{ST})$, as shown in Fig. S6. A low interface resistance means that the catalyst has a low

probability of carrier recombination and a high catalytic activity [43]. This evidence could directly prove that the introduction of RGO sheets into hybrids via a vapor-thermal process is an effective method to improve the photocatalytic activity of pure TiO₂.

We further evaluated the stability and reusability of the VTH photocatalysts using cycling experiments for the photocatalytic degradation of methyl orange over the VTH, shown in Fig. S7. Obviously, a non-distinct activity decay was observed after five recycling runs, indicating that the VTH photocatalysts are relatively stable during the photo-degradation process.

3.4. Photovoltaic performance

Photon-to-electron conversion is another important application of TiO₂ and related hybrid-based materials. In this work, the as-prepared porous films were sensitized by an N719 dye solution to form photoanodes and were then assembled into solar cells using Grätzel's method [44]. As shown in Fig. 6(a), (b) insets, the mechanism of photoelectron transfer during device operation mainly involves two steps: (I) absorption of incident wavelengths for the excitation of electron transitions from the LUMO to HOMO of dye molecules and (II) photo-induced electron-hole pair separation and transfer to electrodes via different routes [45]. Fig. 6(a) and (b) show the current density-voltage (J - V) characteristics of cells based on pure TiO₂ and TiO₂-graphene films prepared with a solvothermal process and a hydrothermal method. Under simulated illumination of 960 W m⁻², the solar cell based on vapor-thermally synthesized TiO₂-graphene (VTH) films gave a short-circuit current (J_{sc}) of 15.06 mA cm⁻², and an open-circuit voltage (V_{oc}) of 0.715 V, yielding a power conversion efficiency (PCE, η) of 7.58%. For the control cells based on STH, VT, and ST films, the J_{sc} values were 13.63, 10.48, 8.73 mA cm⁻², the V_{oc} values were 0.719, 0.791, 0.792 V, and the PCE values were 7.05%, 5.25%, 4.38%, respectively. The details of the photovoltaic performances for the assembled cells are described in Table 2.

When comparing the photovoltaic performances of the assembled cells, it is clear that, while the V_{oc} has slight variations, there was a significant improvement in J_{sc} , leading to a 73.1% increase in PCE. It is well-known that the V_{oc} is predominately controlled by the potential difference between the Fermi level of the illuminated mesoporous semiconductor and the Nernst potential of the redox couple in the liquid electrolyte [46]. That is, a lower V_{oc} of the TiO₂-graphene hybrid-based devices means a lower Fermi level in the mesoporous hybrid films compared with that of pure TiO₂ films. Therefore, the enhanced overall photovoltaic performances are mainly due to the increase in J_{sc} . According to previous reports, the enhanced performance of the VTH-based cell should be attributed to (1) the ultra-large surface area for absorbing more dye molecules to generate photoelectrons (Fig. 6(b) inset, Step I), resulting in a higher light-harvesting capability; and (2) the lower charge transfer resistance at the interfaces during cell operation, facilitating the separation and injection of electrons and decreasing the probability of recombination (Fig. 6(b) inset, Step II) [47].

IPCE measurements were employed to investigate the effect

Table 1
Photocatalytic activity of prepared porous films.

Code	k (min ⁻¹)	R^2
ST	0.023	0.99
VT	0.029	0.98
STH	0.041	0.98
VTH	0.062	0.97

Fig. 6. *J-V* curves of assembled solar cells based on pure TiO_2 (a) and TiO_2 -graphene hybrids (b) under irradiation of 960 W m^{-2} . The inset images show a schematic of proposed model of pure TiO_2 (a) and TiO_2 -graphene hybrids (b) for photoelectron generation and transport at the interfaces in the fabricated porous films. Absorptions (c) and IPCE (d) plots of photoanodes sensitized by 0.5 mM dye N719. (e) EIS characteristics for fabricated solar cells under illumination of 960 W m^{-2} .

of the incorporation of RGO sheets produced via a vapor-thermal method on the light-harvesting ability. As shown in Fig. 6(c), the measured IPCE intensities follow the order $\text{VST} > \text{STH} > \text{VT} > \text{ST}$. This trend is identical to that of the J_{sc} , indicating that the introduction of RGO to porous TiO_2 films via a vapor-thermal process maximizes the light-harvesting capability. The enhanced light-harvesting ability is further proved by UV-vis absorption spectra. As shown in Fig. 6(d), all the photoanodes exhibited strong absorption in the wavelength range of 300–600 nm. Apparently, the TiO_2 -graphene hybrid-based photoanodes showed higher absorption intensity compared with the pure TiO_2 -based photoanodes. The enhanced light absorption ability could be attributed to the incorporation of the ultra-large surface area of the RGO sheets [46].

It is noted that the photovoltaic performances of the cells based on films prepared by the vapor-thermal method (VTH, VT) are superior to those of the cells based on the traditionally annealed films (STH, ST). Besides the improved light-harvesting ability, the enhanced photovoltaic properties of the VTH-based cell may be mainly attributed to the fast charge transfer rate and low carrier recombination. This hypothesis is validated by the EIS analysis and dark *J-V* curves, as shown in Fig. 6(e) and Fig. S8. The R_2 located in the middle of the Nyquist plot (Fig. 6(e)) represents the charge transfer resistance at the interfaces between the photoanode and the dye/electrolyte [48]. The calculated R_2 values of the photoanodes follow the order $R_2(\text{VTH}) < R_2(\text{STH}) < R_2(\text{VT}) < R_2(\text{ST})$, indicating that the photoanode based on VTH exhibited improved carrier transfer efficiency. Moreover, compared with

other devices, a lower dark current density at the same potential was generated in the VTH-based device (Fig. S8), and the dark current represents the recombination of photo-induced electrons with I_3^- ions in the electrolyte [49]. Therefore, these observations prove that the incorporation of RGO sheets via a vapor-thermal process could give rise to strong light-harvesting ability, high charge transfer efficiency, and low carrier recombination, and thus substantially enhance the solar cell performance.

4. Conclusions

In summary, we synthesized TiO_2 nanoparticles on reduced graphene sheets by a one-step vapor-thermal process, and their photocatalytic activity and photovoltaic performance were investigated. The method we developed has two interesting advantages in preparing TiO_2 -graphene hybrids for applications such as photocatalysts and solar cells. Firstly, the grown TiO_2 -graphene hybrids possess an ultra-large specific surface area ($\sim 260 \text{ m}^2 \text{ g}^{-1}$), facilitating the absorption of pollutants or sensitizers. Secondly, mesoporous films with a uniform pore distribution and low agglomeration were obtained during the synthesis of TiO_2 -graphene hybrids. Benefiting from their unique structure, the as-prepared mesoporous films showed an enhanced photocatalytic activity and photovoltaic performance when serving as active anodes. The photocatalytic results show that a TiO_2 -5.0 wt% RGO VTH film possessed the highest photocatalytic activity for degrading methyl orange. Furthermore, when a TiO_2 -0.75 wt% RGO VTH film was used as a pho-

Table 2
Photovoltaic performances of assembled solar cells.

Code	J_{sc} (mA)	V_{oc} (V)	P_{max} (mW/cm ²)	PCE (%)	FF	PCE enhancement (%)
ST	8.73	0.792	4.20	4.38	0.61	
VT	10.48	0.791	5.04	5.25	0.61	19.86
STH	13.63	0.719	6.77	7.05	0.69	61.01
VTH	15.06	0.715	7.28	7.58	0.68	73.14

toanode, the highest PCE obtained was 7.58%, which represents an enhancement of 73.1% compared with a pure TiO₂ photoanode synthesized by a traditional solvothermal method. Therefore, we have demonstrated that high-quality TiO₂-graphene hybrid films can be easily prepared by a one-step vapor-thermal method, and that a mesoporous film with uniform nanostructures can be simultaneously formed without an additional annealing process, with the TiO₂ grown on the RGO sheets. This novel strategy could be used for the fabrication of other metal oxide/carbon nanoporous films for various applications.

Conflicts of interest

There are no conflicts of interest to declare.

Appendix A. Supplementary material

Supplementary data to this article can be found online.

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Graphical Abstract

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One-step fabrication of TiO₂/graphene hybrid mesoporous film with enhanced photocatalytic activity and photovoltaic performance

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A mesoporous film based on TiO₂-reduced graphene oxide hybrids was fabricated using a one-step vapor-thermal method, which exhibits an ultra-high photocatalytic activity and enhanced photovoltaic performance.

TiO₂/RGO hybrid via vapor-thermal process

Photocatalytic activity and mechanism
Photovoltaic performance and mechanism

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一步法制备TiO₂/石墨烯复合多孔薄膜应用于增强光催化活性及光伏性能

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摘要: 纳米二氧化钛具有制备简单、成本低、化学稳定性好及光响应度高等诸多优势, 因而广泛应用于光催化及太阳能转化等诸多领域中。然而, 传统TiO₂纳米材料受限于较高光电子空穴复合率, 导致其光催化活性及光电转化效率较低。为解决这一问题, 研究者采用多种方法用以改善纳米TiO₂的结构, 包括化学掺杂、半导体材料插层、碳材料杂化等; 另一方面则关注材料结构的设计, 例如将合成的纳米材料进一步加工为多孔薄膜, 以增大材料比表面积及器件稳定性, 以增强其器件性能。其中, 将石墨烯引入纳米TiO₂中, 形成复合纳米材料, 以提升材料本身的光电子传输效率, 降低光生载流子复合率, 为制备高性能光催化剂及光伏器件开辟了一条可行之路。然而, 目前制备的纳米TiO₂/石墨烯复合材料的性能仍不理想, 其中常见的问题为合成的材料团聚严重, 导致光生载流子在界面传输阻力及复合率都十分高, 限制其实际应用。此外, 当前大多数关于纳米TiO₂/石墨烯的制备方法仍为溶胶凝胶法、水热法等, 所得材料需要进一步进行微纳加工方能形成介孔结构; 这些加工方式往往需要二次退火处理, 这会进一步加重纳米材料的团聚现象, 导致孔隙率分布混乱、材料界面缺陷增多等不良结果。

因此, 本文采用一步法-蒸汽热法成功制备了TiO₂/石墨烯复合多孔薄膜, 无需二次热处理。实验结果表明, 所制TiO₂/石墨烯复合物(VTH)的形貌为二维结构, 其比表面积高达260 m² g⁻¹, 获得的多孔薄膜无明显团聚且孔隙分布集中。当复合物中还原氧化石墨烯含量为5.0 wt%时, 其光催化活性最高, 高于单一的TiO₂薄膜近3倍; 将还原氧化石墨烯含量为0.75 wt%的复合物用于染料敏化太阳能电池的光阳极时, 光电转化效率达到7.58%, 明显高于传统方法制备的单一TiO₂的(4.38%)。

关键词: TiO₂-石墨烯复合物; 光催化活性; 光阳极; 蒸汽热法; 介孔薄膜

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