Research Article

Improved Synthesis of Reduced Graphene Oxide-Titanium Dioxide Composite with Highly Exposed {001} Facets and Its Photoelectrochemical Response

Gregory S. H. Thien,¹ Fatin Saiha Omar,¹ Nur Ily Syuhada Ahmad Blya,¹ Wee Siong Chiu,¹ Hong Ngee Lim,² Ramin Yousefi,³ Farid-Jamali Sheini,⁴ and Nay Ming Huang¹

¹ Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

² Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM, Serdang, Selangor (Darul Ehsan), Malaysia

³ Department of Physics, Masjed-Soleiman Branch, Islamic Azad University (I.A.U.), Masjed-Soleiman 64914, Iran

⁴ Department of Physics, Ahwaz Branch, Islamic Azad University, Ahwaz 63461, Iran

Correspondence should be addressed to Nay Ming Huang; huangnayming@gmail.com

Received 12 December 2013; Revised 19 March 2014; Accepted 26 March 2014; Published 14 April 2014

Academic Editor: Wonyong Choi

Copyright © 2014 Gregory S. H. Thien et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Crystal facet engineering has attracted worldwide attention, particularly in facet manipulation of titanium dioxide (TiO_2) surface properties. An improved synthesis by solvothermal route has been employed for the formation of TiO_2 with highly exposed {001} facets decorated on reduced graphene oxide (RGO) sheets. The RGO- TiO_2 composite could be produced with high yield by following a stringently methodical yet simple approach. Field emission scanning electron microscope and high resolution transmission electron microscope imaging reveal that the structure consists of TiO_2 nanoparticles covered with TiO_2 nanosheets of exposed {001} facets on a RGO sheet. The photocurrent response of the RGO- TiO_2 composite was discovered to outperform that of pure TiO_2 , as a ~ 10 -fold increase in photocurrent density was observed for the RGO- TiO_2 electrodes. This may be attributed to rapid electron transport and the delayed recombination of electron-hole pairs due to improved ionic interaction between titanium and carbon.

1. Introduction

Titanium dioxide (TiO_2) has been widely studied owing to its nontoxic, chemically inert, photostable characteristics, and cheap production cost, which make it a promising candidate for energy and environmental applications [1–3]. Over the past decade, significant progress has been made in crystal facet engineering of TiO_2 crystals, to enhance performance for applications, such as photocatalysis, lithium storage, dye sensitised solar cells, and gas sensors [4–7]. Generally, TiO_2 crystals can be described in terms of three main structures: anatase, rutile, and brookite. In recent years, focus has been directed toward anatase TiO_2 due to its higher activity, especially as a heterogeneous photocatalyst. The anatase phase of TiO_2 has a truncated tetragonal bipyramid structure

with two {001} facets and eight {101} facets [8]. According to the Wulff construction method for determining equilibrium crystal shapes [9], anatase TiO_2 crystals are usually dominated by {101} facets (more than 90% of the total number of facets), which have a lower surface energy (0.44 J m^{-2}) compared to the reactive {001} facets (0.96 J m^{-2}). Under equilibrium conditions, the lower surface energy plane is favourable during crystal growth to minimise the total surface energy, causing reactive {001} facets to diminish quickly, while encouraging the dominance of the thermodynamically stable {101} facets [10]. Hence, the percentage of exposed reactive {001} facets is greatly reduced, resulting in loss of performance in value-added applications [11]. This field was started by Yang and coworkers, who produced crystals consisting of approximately 50% reactive {001} facets by using

hydrofluoric acid (HF) as a capping agent [12]. Consequently, more effort is being directed toward improving the synthesis of TiO_2 structures with a high percentage of exposed {001} facets, including control of the concentration of precursor [13], selective use of solvents [14, 15], and use of fluorine-sourced chemicals (HF, NH_4F), in which fluorine species were discovered to have the potential to stabilise {001} facet growth [16, 17].

The performance efficiency of TiO_2 crystals can also be enhanced by doping with metal ions or nonmetal ions, noble metal loading, or attaching the crystals onto large surface area materials such as graphene sheets [18–20]. Recently, graphene, a two-dimensional sheet of sp^2 bonded carbon atoms densely packed in a honeycomb crystal lattice structure, has attracted much attention due to its exceptional electronic, biological, mechanical, and thermal properties [21–24]. The efficiency of graphene-based semiconductor photocatalysts is vastly increased compared to that of pure TiO_2 , which was evident in terms of extended light adsorption range, enhanced charge separation, and high dye adsorption [25]. These beneficial characteristics of the composite materials would have great potential in enhancing photoelectrochemical performance applications. In addition, the role of the increased exposed {001} facets of TiO_2 on graphene could be demonstrated in its photoelectrochemical performance properties.

In this work, a fluorine-free solvothermal route is reported to produce highly exposed {001} facets in anatase TiO_2 nanosheets patterned on reduced graphene oxide (RGO) sheets. Photoelectrochemical behaviour was investigated based on the materials photocurrent response for various electrodes sintered at different temperatures.

2. Experimental Methods

2.1. Materials. Graphite flakes (3061, Asbury Graphite Mills Inc.), potassium permanganate (KMnO_4 , 98%), tetraisopropyl orthotitanate (TIPT) (98%), and diethylenetriamine (DETA) (98%) were supplied from Merck, USA. Sulphuric acid (H_2SO_4 , 98%), phosphoric acid (H_3PO_4 , 98%), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2 , 30%), potassium chloride (KCl), and isopropyl alcohol were purchased from Systerm (Malaysia). Absolute ethanol and ethanol (95%) were purchased from HmbG Chemical, Malaysia, and potassium hexa-cyanoferrate(III) was purchased from Sigma-Aldrich. Deionised water was used throughout sample preparation. All chemicals were used as received without further purification.

2.2. Preparation of Graphene Oxide (GO). GO aqueous suspension was synthesized using a simplified Hummers method [26]. Graphite flakes (3 g) were slowly added into a H_2SO_4 and H_3PO_4 (9:1) solution. Following this, 18 g of KMnO_4 powder was gradually added into the mixture and stirred for 3 days to allow oxidation to occur. The obtained solution was transferred into a beaker containing ice, and 27 mL of 30% H_2O_2 was added. A yellowish-brown

solution was observed and washed with 1 M HCl solution and deionised water.

2.3. Preparation of RGO- TiO_2 Composite. The RGO- TiO_2 composite was synthesized using a solvothermal route. GO aqueous suspension was freeze-dried for 24 h using a freeze dryer (Martin Christ, ALPHA 1-2/LD plus). Then, 40 mg of freeze-dried GO was dispersed in a solution containing 40 mL of isopropyl alcohol and gently sonicated for 1 hour. Following this, 0.824 mL of TIPT was added drop-wise into the GO solution (14:1), and then 30 μL of DETA was added and stirred for a few minutes. This step is crucial as it ensures the formation of the desired morphology. The solution was then transferred into a Teflon-lined autoclave and heated at 200°C for 24 h. The resulting black precipitate was washed with ethanol and left to dry in an oven at 60°C overnight. Finally, the obtained black powder was calcined at 400°C in air, with a heating rate of 1°C min⁻¹ for 2 h. Pure TiO_2 and RGO were synthesized for comparison purposes.

2.4. Fabrication of RGO- TiO_2 Electrodes. The samples were ground and mixed with absolute ethanol to obtain a slurry paste. The paste was painted onto taped-down clean indium tin oxide (ITO) glass and then spread over using a glass rod. To study the effect of the sintering temperature on the photocurrent response, the ITO glass was sintered in a furnace under purified N_2 gas flow at different temperatures: 300, 400, and 500°C. The fabricated electrodes were labeled as G- TiO_2 300, G- TiO_2 400, and G- TiO_2 500, and a TiO_2 500 electrode was fabricated for comparison purposes.

2.5. Characterisation. The crystallographic phases of the samples were analysed using X-ray diffraction (XRD, D5000, Siemens), with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a scan rate of 0.02° s⁻¹. The morphology and structural properties were investigated using a field emission scanning electron microscope (FESEM, JEOL JSM-7600F) and a high resolution transmission electron microscope (HRTEM, JEOL JEM-2100F). X-ray photoelectron spectroscopy (XPS) measurements were performed using synchrotron radiation from beamline number 3.2 at the Siam Photon Laboratory in the Synchrotron Light Research Institute, Thailand. Raman and photoluminescence (PL) spectra were obtained using 514 nm and 325 nm laser beams, using a Renishaw inVia Raman microscope system. Electrochemical impedance spectra (EIS) measurements were carried out using a VersaSTAT 3 potentiostat (Princeton Applied Research) in a 0.1 M KCl solution containing 1 mM $\text{K}_4[\text{Fe}(\text{CN})_6]$.

2.6. Photocurrent Response Measurements. Photocurrent response measurements were carried out using a VersaSTAT 3 potentiostat and recorded in VersaStudio v2.2 data acquisition software. In a three-electrode cell configuration, the fabricated electrodes were employed as the working electrode a saturated calomel electrode was used as the reference electrode, and a Pt wire was used as the counter electrode. A 150 W Xenon lamp was used as a light source and all electrodes were dipped in 0.5 M KCl electrolyte. All

FIGURE 1: Schematic illustration of the preparation of RGO-TiO₂ composite in sequence, producing, after centrifugation, (a) three different layers (RGO, TiO₂ and RGO-TiO₂), and (b) a single homogeneous layer of the RGO-TiO₂ composite.

FIGURE 2: XRD patterns of graphite, GO, RGO, TiO₂, and the RGO-TiO₂ composite.

the photoelectrochemical experiments were carried out in the presence of N₂ atmosphere. The CA measurements were carried out at applied potential of 0.8 V under light “on-off” condition using Newport solar simulator with manual shutter.

3. Results and Discussion

The RGO-TiO₂ composite was synthesized by mixing GO, TIPT, and DETA in a solution. Figure 1 illustrates two

preparation routes to obtain RGO-TiO₂ composites, using different mixing sequences. The mixing sequence of TIPT and DETA was found to influence the final product of synthesis. Figure 1(a) shows an initial synthesis route similar to Chen et al. [27], first mixing GO with DETA, and then adding TIPT. However, the stirred solution was found to be nonhomogeneously dispersed and yielded irreversible agglomerations, as mixing GO with DETA causes flocculation of the GO sheets. Thus, after centrifugation, three different distinct layers were formed that can be attributed to TiO₂, RGO-TiO₂, and RGO. By altering the mixing sequence, using TIPT first instead of DETA, as shown in Figure 1(b), a homogeneously dispersed solution was observed, in which a single homogenous layer of RGO-TiO₂ composite, without any evidence of pure TiO₂ or RGO, was easily obtained. The distinguishable end-products of Figures 1(a) and 1(b) were clearly influenced by the sequence in which the chemicals were mixed. In Figure 1(a), GO could plausibly be reduced by the amine groups of DETA, not unlike the reduction of GO with NaOH. This gives rise to certain degree of aggregation caused by the π - π restacking interaction of RGO. When TIPT was added into the coagulate, only the exposed active sites of GO, which had not formed complexes with DETA, interacted with TIPT to form TiO₂ on RGO during the solvothermal reaction. On the contrary, the order of addition of chemicals in Figure 1(b) allows complete reaction between GO and TIPT. After TIPT was introduced to GO, the network of TIPT molecules expanded, forming a cage-like continuous network structure that enabled maximum electrostatic interaction with GO. The addition of DETA stabilised the complex scaffold, leading to 100% formation of RGO-TiO₂. Throughout this paper,

FIGURE 3: FESEM images of ((a), (b)) TiO_2 and ((c), (d)) RGO-TiO_2 composite.

the characterisation results are given for samples obtained using Figure 1(b) mixing sequence.

Figure 2 depicts the XRD patterns of graphite, GO, RGO, TiO_2 , and the RGO-TiO_2 composite. The peak position at $2\theta = 26^\circ$ of the (002) graphite plane corresponds to a d-spacing value of 3.4 Å. It was observed that the graphite peak completely disappeared for GO, and a new peak position emerged at 9.7° with an increase of the d-spacing to 9.1 Å, which was thought to be due to exfoliation and oxidation of graphite to GO. On the other hand, a similar peak position to graphite was shown for RGO, but with a much broader peak, indicating the successful dispersion of GO sheets after the solvothermal reaction [28]. Clearly, RGO was successfully synthesized through this route, by reduction and removal of the oxide functional groups from GO to RGO. Both TiO_2 and RGO-TiO_2 characteristic peaks at 25.2° , 37.8° , 48.1° , 53.9° , and 55.1° corresponded well to the (101), (004), (200), (105), and (211) crystal planes of anatase TiO_2 , with lattice constants of $a = b = 3.7852 \text{ Å}$ and $c = 9.5139 \text{ Å}$ (JCPDS 21-1272) [29]. Therefore, no other TiO_2 phases were detected. Additionally, the absence of RGO peak at 25.2° in the RGO-TiO_2 composite

was probably due to the relatively low diffraction intensity of RGO that was shielded by the (101) crystal peak of TiO_2 [30].

Morphological features of the as-prepared samples were obtained using FESEM imaging. Pure TiO_2 nanoparticles can be observed in Figure 3(a), agglomerating together, with a surface that appears rough. Increased magnification (Figure 3(b)) of the surface reveals the presence of randomly assembled TiO_2 nanosheets, which will be discussed in the HRTEM section. Similar features were observed for the RGO-TiO_2 composite (Figure 3(c)), as the agglomeration of TiO_2 nanosheets was greatly reduced limiting them to the surface of RGO, indicating the successful anchoring of TiO_2 nanosheets onto RGO sheets. With higher magnification, Figure 3(d) reveals that the surface of RGO-TiO_2 is composed of two different types of TiO_2 features: TiO_2 nanoparticles and TiO_2 nanosheets (white worm-like features due to folding of the TiO_2 nanosheet) that cover the entire surface of the RGO.

HRTEM characterisation was employed to further determine the structure and planes of the samples. In Figure 4(a), the morphological similarities of agglomerated TiO_2 crystals

FIGURE 4: ((a), (b)) Low magnification TEM images of TiO_2 and (c) high magnification TEM image of the edge of a TiO_2 nanosheet. ((d), (e)) Low magnification TEM image of the RGO- TiO_2 composite and (f) high magnification TEM image of the surface of the composite.

were consistent with the FESEM results; such a structure formed to minimise the surface energy [31]. A magnified view, shown in Figure 4(b), reveals that the outer region was populated with thin layers of TiO_2 that resemble sheet-like features. However, the entire inner sphere was populated with densely packed TiO_2 nanoparticles. The output of these two different types of TiO_2 nanostructures could be attributed to the Oswald ripening process and the use of DETA as the morphology controlling agent [32]. At high magnification, the image of a TiO_2 nanosheet edge (Figure 4(c)) reveals a lattice with fringe spacing of 0.19 nm that corresponds to either the (020) or (200) planes of anatase TiO_2 . According to Chen et al. [27], the TiO_2 spheres formed have almost 100% of their {001} planes exposed. It was noted that DETA played a key role, as the growth along the (001) direction was retarded, stabilising the growth of the exposed {001} facets and eventually leading to a higher amount of exposed {001} facets. Similarly, the RGO- TiO_2 composite (Figure 4(d)) reveals the same structure. Two different structures of TiO_2 nanoparticles and nanosheets were wrapped around the RGO sheet (Figure 4(e)). Therefore, this exhibits two different fringe spacings, 0.19 nm and 0.351 nm in Figure 4(f), which correspond to the {001} planes of TiO_2 nanosheets and the thermodynamically stable {101} planes of TiO_2 nanoparticles [17, 33].

To investigate the chemical state of the as-prepared samples, XPS measurements were carried out; the results are shown in Figure 5. In Figure 5(a), a considerable degree of oxidation for the peaks at binding energies of 284.5 eV, 286.2 eV, 287.8 eV, and 289 eV in the C 1s of GO could be attributed to C-C, C-O, C=O, and O=C-O bonds [34, 35]. However, in comparison with RGO- TiO_2 , the oxide functional groups' peak intensities were greatly reduced, which confirms that reduction from GO to RGO was successful. In addition, the small peak at 282.4 eV could be attributed to the Ti-C bond, which reflects the chemical bonding between titanium and carbon. For the Ti 2p peaks in Figure 5(b), two peaks centred at 453.5 eV and 459.2 eV were observed for TiO_2 , which correspond to the Ti 2p_{3/2} and Ti 2p_{1/2} spin-orbital splitting photoelectrons in the Ti^{4+} state [36]. These peaks redshift to 453.8 eV and 459.6 eV for RGO- TiO_2 due to the interaction between Ti and the oxygen groups of RGO. Since oxygen is much more electronegative than carbon, the TiO_2 electron density is attracted more strongly, which then increases the binding energy of Ti in the composite [37]. In addition, the calculated spin orbit splitting between Ti 2p_{3/2} and Ti 2p_{1/2} was 5.7 eV in both samples, which indicates the presence of normal states of Ti^{4+} [38].

Raman spectroscopy was employed for molecular morphology characterisation of carbonaceous materials. As

FIGURE 5: XPS spectra of (a) C 1s of GO and RGO-TiO₂ composite and (b) Ti 2p of TiO₂ and RGO-TiO₂ composite.

FIGURE 6: Raman spectra of G-TiO₂ electrodes sintered at various temperatures. The inset shows the typical peak positions for anatase TiO₂.

shown in Figure 6, two peaks were located at 1353 cm⁻¹ and 1597 cm⁻¹ for the fabricated electrodes. These peaks correspond well to the documented D band, which is attributed

to sp³ defects, and to the G band, which is due to in-plane vibrations of sp² carbon atoms and a doubly-degenerated phonon mode (E_{2g} symmetry) at the Brillouin zone centre [39]. In addition, shifts at 142, 395, 514, and 637 cm⁻¹ can be attributed to the E_g, B_{1g}, A_{1g}, and E_g modes of anatase TiO₂ (inset) and are consistent with the XRD results [19]. This also suggests that the fabricated G-TiO₂ electrodes' TiO₂ anatase phase was retained, even with increased sintering temperature.

PL spectra of various samples were recorded, which reveal the surface structure and excited state of the semiconductor [40]. In Figure 7, the PL intensity was greatly affected by the recombination rate of electron-hole pairs. A lower PL intensity indicates an enhanced charge separation of electron-hole pairs. A low PL emission intensity was depicted for the RGO-TiO₂ composite, which was attributed to RGO sheets acting as an electron shuttle for TiO₂ to hinder electron-hole recombination. Thus, the recombination rate was greatly suppressed. The inset of Figure 7 shows the PL spectra of the fabricated electrodes sintered at various temperatures. As shown, TiO₂ 500 has the highest emission intensity, greater than G-TiO₂ 500 or any of the composite electrodes, which is consistent with the previous explanation. The PL intensity decreases with increasing sintering temperatures, with G-TiO₂ 500 being the lowest. Wang et al. reported that thermal

FIGURE 7: PL spectra of the as-prepared TiO_2 and RGO- TiO_2 composite. The inset shows the PL spectra of fabricated TiO_2 and various G- TiO_2 electrodes.

FIGURE 8: EIS measurement of TiO_2 and RGO- TiO_2 composite electrodes in the presence of 0.1 M KCl containing 1 mM $\text{K}_4[\text{Fe}(\text{CN})_6]$.

annealing of photocatalysts under N_2 gas reduces the density of surface defects [41]. Hence, the decrease of recombination points for the electron-hole pairs enhances charge separation efficiency.

In order to confirm the charge recombination kinetics of the TiO_2 and RGO- TiO_2 composite electrodes, EIS measurements were applied to understand the interfacial charge transfer process. The Nyquist plots of TiO_2 and RGO- TiO_2 composite electrodes were plotted in Figure 8 as the arc shape reveals information of the charge transport and recombination properties and a depressed semicircle was observed for RGO- TiO_2 composite compared to TiO_2 . The charge transfer resistance (R_{CT}) was determined by the diameters of the

FIGURE 9: Photocurrent response of TiO_2 and G- TiO_2 electrodes to ON-OFF cycles of UV illumination.

semicircles and RGO- TiO_2 composite (48.244Ω) has a lower R_{CT} value than TiO_2 (83.192Ω) indicating increase charge transport and reduced recombination rate that is in good agreement with the PL results [42, 43].

Photocurrent response measurements of the photo-generated electron-hole interaction of the fabricated electrodes were carried out under repeated ON-OFF cycles, and the results are shown in Figure 9. In this case, the photocurrent density is greatly affected by two significant factors: the time taken for the photo-induced electrons to withdraw from the TiO_2 to the ITO substrate and the rate of electron-hole recombination within the film and the film/electrolyte interface [44]. In the results shown, the photocurrent density under dark conditions is relatively small and negligible. A rapid current rise and decay was observed when the light was switched on and off. The effect of the sintering temperature of the RGO- TiO_2 films on the photocurrent response was investigated. The output of the photocurrent density was observed to increase with higher sintering temperatures. The highest recorded photocurrent response was that of the G- TiO_2 500 electrode ($104.4 \mu\text{A cm}^{-2}$) which is around ten times higher than that of the G- TiO_2 300 electrode ($9.6 \mu\text{A cm}^{-2}$). The dramatic increase could be attributed to a delayed recombination rate and longer electron lifetime, as shown in the PL spectra [45, 46]. When comparing both the TiO_2 500 and G- TiO_2 500 electrodes, the photocurrent response of the G- TiO_2 was observed to be better than that of the TiO_2 500 electrode. This suggests that the presence of RGO sheets increases the photocurrent response due to their extensive two-dimensional π - π conjugation structure. Hence, photo-induced electrons from TiO_2 can be accepted by RGO and transferred to the external circuit more quickly [47, 48]. Moreover, the charge separation efficiency increases due to the electronic interaction between TiO_2 and RGO in the composite [49]. The highly exposed {001} facets of the TiO_2 nanosheets in a hierarchical structure contribute to

the photocurrent response by favouring electron transport, which minimises the grain interface effect and improves the light harvesting efficiency [50, 51].

4. Conclusions

RGO-TiO₂ composite composed of highly exposed {001} TiO₂ facets was successfully synthesized through a solvothermal route with 100% yield of composite material. The advantage of this method harnesses the benefits of both the highly exposed {001} facets for higher reactivity and RGO as an excellent platform with a large surface area, by using DETA instead of the commonly-used HF, which is hazardous and toxic to the environment. The role of the sintering temperature on the characteristics of the fabricated electrodes was remarkably interesting, as the highest photocurrent density, 104.4 $\mu\text{A cm}^{-2}$, was observed for a sintering temperature of 500°C, which is attributed to the reduced recombination of electron-hole pairs and improved light harvesting efficiency. We anticipate that this study of the RGO-TiO₂ composite with highly exposed {001} facet features would aid in further improving photoelectrochemical performance applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The author would like to express his gratitude to the staff at photoemission spectroscopy (PES) synchrotron beamline 3.2a at the Synchrotron Light Research Institute, Thailand, for their assistance. This work was financially supported by the High Impact Research Grant of Ministry of Higher Education of Malaysia (UM.C/625/1/HIR/MOHE/05) and Postgraduate Research Grant (PPP) (PG107-2012B) of the University of Malaya.

References

- [1] A. Fujishima, X. Zhang, and D. A. Tryk, "TiO₂ photocatalysis and related surface phenomena," *Surface Science Reports*, vol. 63, no. 12, pp. 515–582, 2008.
- [2] T.-D. Nguyen-Phan and E. W. Shin, "Morphological effect of TiO₂ catalysts on photocatalytic degradation of methylene blue," *Journal of Industrial and Engineering Chemistry*, vol. 17, no. 3, pp. 397–400, 2011.
- [3] S. K. Deb, "Dye-sensitized TiO₂ thin-film solar cell research at the national renewable energy laboratory (NREL)," *Solar Energy Materials and Solar Cells*, vol. 88, no. 1, pp. 1–10, 2005.
- [4] M.-H. Jung, M.-J. Chu, and M. G. Kang, "TiO₂ nanotube fabrication with highly exposed (001) facets for enhanced conversion efficiency of solar cells," *Chemical Communications*, vol. 48, no. 41, pp. 5016–5018, 2012.
- [5] Z. Ni, Y. Wang, T. Yu, and Z. Shen, "Raman spectroscopy and imaging of graphene," *Nano Research*, vol. 1, no. 4, pp. 273–291, 2010.
- [6] Y. Zhang, L. Wang, B. Liu et al., "Synthesis of Zn-doped TiO₂ microspheres with enhanced photovoltaic performance and application for dye-sensitized solar cells," *Electrochimica Acta*, vol. 56, no. 18, pp. 6517–6523, 2011.
- [7] L. Kavan, M. Kalbáč, M. Zúkalová et al., "Lithium storage in nanostructured TiO₂ made by hydrothermal growth," *Chemistry of Materials*, vol. 16, no. 3, pp. 477–485, 2004.
- [8] J. H. Pan, G. Han, R. Zhou, and X. S. Zhao, "Hierarchical N-doped TiO₂ hollow microspheres consisting of nanorods with exposed anatase {001} facets," *Chemical Communications*, vol. 47, no. 24, pp. 6942–6944, 2011.
- [9] M. Lazzeri, A. Vittadini, and A. Selloni, "Structure and energetics of stoichiometric TiO₂ anatase surfaces," *Physical Review B*, vol. 63, no. 15, Article ID 155409, 2001.
- [10] G. Liu, J. C. Yu, G. Q. Lu, and H.-M. Cheng, "Crystal facet engineering of semiconductor photocatalysts: motivations, advances and unique properties," *Chemical Communications*, vol. 47, no. 24, pp. 6763–6783, 2011.
- [11] X. H. Yang, Z. Li, C. Sun, H. G. Yang, and C. Li, "Hydrothermal stability of 001 faceted anatase TiO₂," *Chemistry of Materials*, vol. 23, no. 15, pp. 3486–3494, 2011.
- [12] H. G. Yang, C. H. Sun, S. Z. Qiao et al., "Anatase TiO₂ single crystals with a large percentage of reactive facets," *Nature*, vol. 453, no. 7195, pp. 638–641, 2008.
- [13] G. Liu, C. Sun, H. G. Yang et al., "Nanosized anatase TiO₂ single crystals for enhanced photocatalytic activity," *Chemical Communications*, vol. 46, no. 5, pp. 755–757, 2010.
- [14] H. G. Yang, G. Liu, S. Z. Qiao et al., "Solvothermal synthesis and photoreactivity of anatase TiO₂ nanosheets with dominant 001 facets," *Journal of the American Chemical Society*, vol. 131, no. 11, pp. 4078–4083, 2009.
- [15] J. Zhu, S. Wang, Z. Bian et al., "Solvothermally controllable synthesis of anatase TiO₂ nanocrystals with dominant {001} facets and enhanced photocatalytic activity," *CrystEngComm*, vol. 12, no. 7, pp. 2219–2224, 2010.
- [16] L. Pan, J.-J. Zou, S. Wang, X.-Y. Liu, X. Zhang, and L. Wang, "Morphology evolution of TiO₂ facets and vital influences on photocatalytic activity," *ACS Applied Materials and Interfaces*, vol. 4, no. 3, pp. 1650–1655, 2012.
- [17] W. Wang, C. Lu, Y. Ni, and Z. Xu, "Crystal facet growth behavior and thermal stability of 001 faceted anatase TiO₂: mechanistic role of gaseous HF and visible-light photocatalytic activity," *CrystEngComm*, vol. 15, no. 13, pp. 2537–2543, 2013.
- [18] A. Zaleska, "Doped-TiO₂: a review," *Recent Patents on Engineering*, vol. 2, no. 3, pp. 157–164, 2008.
- [19] K. Zhou, Y. Zhu, X. Yang, X. Jiang, and C. Li, "Preparation of graphene-TiO₂ composites with enhanced photocatalytic activity," *New Journal of Chemistry*, vol. 35, no. 2, pp. 353–359, 2011.
- [20] M. Ni, M. K. H. Leung, D. Y. C. Leung, and K. Sumathy, "A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production," *Renewable and Sustainable Energy Reviews*, vol. 11, no. 3, pp. 401–425, 2007.
- [21] W. Choi, I. Lahiri, R. Seelaboyina, and Y. S. Kang, "Synthesis of graphene and its applications: a review," *Critical Reviews in Solid State and Materials Sciences*, vol. 35, no. 1, pp. 52–71, 2010.
- [22] M. I. Katsnelson, "Graphene: carbon in two dimensions," *Materials Today*, vol. 10, no. 1-2, pp. 20–27, 2007.
- [23] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials*, vol. 6, no. 3, pp. 183–191, 2007.

- [24] A. K. Geim, "Graphene: status and prospects," *Science*, vol. 324, no. 5934, pp. 1530–1534, 2009.
- [25] Q. Xiang, J. Yu, and M. Jaroniec, "Graphene-based semiconductor photocatalysts," *Chemical Society Reviews*, vol. 41, no. 2, pp. 782–796, 2012.
- [26] D. C. Marcano, D. V. Kosynkin, J. M. Berlin et al., "Improved synthesis of graphene oxide," *ACS Nano*, vol. 4, no. 8, pp. 4806–4814, 2010.
- [27] J. S. Chen, Y. L. Tan, C. M. Li et al., "Constructing hierarchical spheres from large ultrathin anatase TiO₂ nanosheets with nearly 100% exposed (001) facets for fast reversible lithium storage," *Journal of the American Chemical Society*, vol. 132, no. 17, pp. 6124–6130, 2010.
- [28] S. Ding, J. S. Chen, D. Luan, F. Y. C. Boey, S. Madhavi, and X. W. Lou, "Graphene-supported anatase TiO₂ nanosheets for fast lithium storage," *Chemical Communications*, vol. 47, no. 20, pp. 5780–5782, 2011.
- [29] M. S. A. Shah S, R. Park, K. Zhang, J. H. Park, and P. J. Yoo, "Green synthesis of biphasic TiO₂-reduced graphene oxide nanocomposites with highly enhanced photocatalytic activity," *ACS Applied Materials & Interfaces*, vol. 4, pp. 3893–3901, 2012.
- [30] B. Y. S. Chang, N. M. Huang, M. N. An'amt et al., "Facile hydrothermal preparation of titanium dioxide decorated reduced graphene oxide nanocomposite," *International Journal of Nanomedicine*, vol. 7, pp. 3379–3387, 2012.
- [31] H. Wang, M. Liu, C. Yan, and J. Bell, "Reduced electron recombination of dye-sensitized solar cells based on TiO₂ spheres consisting of ultrathin nanosheets with [001] facet exposed," *Beilstein Journal of Nanotechnology*, vol. 3, pp. 378–387, 2012.
- [32] C. H. Sun, X. H. Yang, J. S. Chen et al., "Higher charge/discharge rates of lithium-ions across engineered TiO₂ surfaces leads to enhanced battery performance," *Chemical Communications*, vol. 46, no. 33, pp. 6129–6131, 2010.
- [33] L. Zhu, K. Liu, H. Li, Y. Sun, and M. Qiu, "Solvothermal synthesis of mesoporous TiO₂ microspheres and their excellent photocatalytic performance under simulated sunlight irradiation," *Solid State Sciences*, vol. 20, pp. 8–14, 2013.
- [34] D. R. Dreyer, S. Park, C. W. Bielawski, and R. S. Ruoff, "The chemistry of graphene oxide," *Chemical Society reviews*, vol. 39, no. 1, pp. 228–240, 2010.
- [35] S. Pei, J. Zhao, J. Du, W. Ren, and H.-M. Cheng, "Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids," *Carbon*, vol. 48, no. 15, pp. 4466–4474, 2010.
- [36] N. Dwivedi, S. Kumar, and H. K. Malik, "Nanostructured titanium/diamond-like carbon multilayer films: deposition, characterization, and applications," *ACS Applied Materials and Interfaces*, vol. 3, no. 11, pp. 4268–4278, 2011.
- [37] F. Dong, S. Guo, H. Wang, X. Li, and Z. Wu, "Enhancement of the visible light photocatalytic activity of C-doped TiO₂ nanomaterials prepared by a green synthetic approach," *Journal of Physical Chemistry C*, vol. 115, no. 27, pp. 13285–13292, 2011.
- [38] N. K. Allam, F. Alamgir, and M. A. El-Sayed, "Enhanced photoassisted water electrolysis using vertically oriented anodically fabricated Ti-Nb-Zr-O mixed oxide nanotube arrays," *ACS Nano*, vol. 4, no. 10, pp. 5819–5826, 2010.
- [39] D. Naumenko, V. Snitka, B. Snopok, S. Arpiainen, and H. Lipsanen, "Graphene-enhanced Raman imaging of TiO₂ nanoparticles," *Nanotechnology*, vol. 23, Article ID 465703, 2012.
- [40] S. K. Choi, S. Kim, S. K. Lim, and H. Park, "Photocatalytic comparison of TiO₂ nanoparticles and electrospun TiO₂ nanofibers: effects of mesoporosity and interparticle charge transfer," *Journal of Physical Chemistry C*, vol. 114, no. 39, pp. 16475–16480, 2010.
- [41] X. Wang, K. Maeda, Y. Lee, and K. Domen, "Enhancement of photocatalytic activity of (Zn^{1+x}Ge)(N₂O_x) for visible-light-driven overall water splitting by calcination under nitrogen," *Chemical Physics Letters*, vol. 457, no. 1–3, pp. 134–136, 2008.
- [42] H. Kim, S. Kim, J. Kang -K, and W. Choi, "Graphene oxide embedded into TiO₂ nanofiber: effective hybrid photocatalyst for solar conversion," *Journal of Catalysis*, vol. 309, pp. 49–57, 2014.
- [43] K. Ghowsi, H. R. Ebrahimi, F. Kazempour-baravati, and H. Bagheri, "Synthesize of ZnO/NPs and investigation of its effect in reduction of electrochemical charge transfer resistance; application of it for photodecomposition of calcon (C.I.15705) dye in various media," *International Journal of Electrochemical Science*, vol. 9, no. 4, pp. 1738–1746, 2014.
- [44] N. J. Bell, Y. H. Ng, A. Du, H. Coster, S. C. Smith, and R. Amal, "Understanding the enhancement in photoelectrochemical properties of photocatalytically prepared TiO₂-reduced graphene oxide composite," *Journal of Physical Chemistry C*, vol. 115, no. 13, pp. 6004–6009, 2011.
- [45] N.-G. Park, G. Schlichthörl, J. Van De Lagemaat, H. M. Cheong, A. Mascarenhas, and A. J. Frank, "Dye-sensitized TiO₂ solar cells: structural and photoelectrochemical characterization of nanocrystalline electrodes formed from the hydrolysis of TiCl₄," *Journal of Physical Chemistry B*, vol. 103, no. 17, pp. 3308–3314, 1999.
- [46] K.-M. Lee, V. Suryanarayanan, and K.-C. Ho, "A study on the electron transport properties of TiO₂ electrodes in dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 91, no. 15–16, pp. 1416–1420, 2007.
- [47] P. Wang, Y. Ao, C. Wang, J. Hou, and J. Qian, "Enhanced photoelectrocatalytic activity for dye degradation by graphene-titania composite film electrodes," *Journal of Hazardous Materials*, vol. 223–224, pp. 79–83, 2012.
- [48] Y. Min, K. Zhang, W. Zhao, F. Zheng, Y. Chen, and Y. Zhang, "Enhanced chemical interaction between TiO₂ and graphene oxide for photocatalytic decolorization of methylene blue," *Chemical Engineering Journal*, vol. 193–194, pp. 203–210, 2012.
- [49] J. S. Lee, K. H. You, and C. B. Park, "Highly photoactive, low bandgap TiO₂ nanoparticles wrapped by graphene," *Advanced Materials*, vol. 24, no. 8, pp. 1084–1088, 2012.
- [50] Y. Wang, W. Yang, and W. Shi, "Preparation and characterization of anatase TiO₂ nanosheets-based microspheres for dye-sensitized solar cells," *Industrial and Engineering Chemistry Research*, vol. 50, no. 21, pp. 11982–11987, 2011.
- [51] W. Q. Fang, X.-Q. Gong, and H. G. Yang, "On the unusual properties of anatase TiO₂ exposed by highly reactive facets," *Journal of Physical Chemistry Letters*, vol. 2, no. 7, pp. 725–734, 2011.