Electrophoretic Deposition of Graphene Oxide and Reduced Graphene Oxide on the Rutile Phase of TiO$_2$ Nanowires for Rapid Reduction of Cr (VI) under Simulated Sunlight Irradiation

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1. Introduction

Chromates are used in many industrial processes, including metal fabrication, leather tanning, pulp and paper production, and electroplating [1]. Chronic acid, for example, has been used for electroplating chromium onto metal components to improve their corrosion resistance and increase their abrasive wear. In a typical electroplating process, a metal to be plated is immersed in a sodium cyanide or caustic soda solution as a pretreatment, followed by cleaning and rinsing before being transferred to a chrome bath for chromium plating. After this process, the metal parts are rinsed again. All of these processes result in a large volume of wastewater containing released cyanide and acidic Cr(VI). Cr(VI) is carcinogenic, highly corrosive, and very toxic [2,3]—considerably more toxic than Cr(III)—and hence must be removed from the wastewater. Chemical reduction of Cr(VI) to Cr(III) is commonly carried out to remove Cr(VI) from wastewater, for example, by using sulfur dioxide gas or sodium bisulfite and sulfuric acid. That treatment lowers the Cr(VI) concentration from the effluent, but not to zero, and it generally involves subsequent adjustment of the solution to precipitate the Cr(III) ions. Chemical reduction utilizes hazardous chemicals and can generate dangerous by-products and, potentially, the evolution of toxic gases.
Therefore, an alternative process that results in zero Cr(VI) effluent without the use or release of toxic chemicals or gases is sought. Among the strategies for total Cr(VI) removal using a more benign process, photocatalytic reduction is considered a promising approach [3]. In photocatalytic reduction, the Cr(VI) reduction occurs with free electrons that are generated when a semiconductor photocatalyst is illuminated with light with an appropriate amount of energy [4]. Titanium dioxide (TiO$_2$) is a well-known and efficient semiconductor photocatalyst that is also non-toxic, biologically and chemically inert, stable, and inexpensive [5].

TiO$_2$ can be synthesized in the form of one-dimensional (1D) nanostructures, which is beneficial because 1D nanomaterials have a large surface-to-volume ratio. This translates to a high-reactivity catalyst, thus leading to an enhanced photocatalytic performance [6]. There are many ways to synthesize 1-D TiO$_2$ nanostructures containing different morphologies, such as nanotubes, nanowires, and nanorods [7–11].

In this work, thermal oxidation of titanium was conducted in the presence of 1M potassium hydroxide (KOH) mist to produce rutile TiO$_2$ nanowires (TNWs). Oxidation is a simple process that can produce highly crystalline TNWs in a short processing time. Nevertheless, rutile TiO$_2$ is a wide-band-gap semiconductor (3.2 eV) and, hence, can only produce free electrons under ultraviolet (UV) light illumination (wavelength range <400 nm) [12,13]. Rutile TiO$_2$ is thus not very photoactive under sunlight. In efforts to produce a semiconductor photocatalyst that can be activated under sunlight, TiO$_2$ is often doped or coupled with organic materials such as graphene. The coupling has been shown to increase the visible light activity of TiO$_2$ by creating a new energy level within the energy band gap [14–16]. However, the defect levels can also act as recombination centers for the photogenerated electron-hole pairs [17]. In addition, graphene, which is known for various applications, such as electromagnetic interference shielding [18], supercapacitors [19–21], and other energy storage applications [22,23], when coupled with TiO$_2$, does not create defect states although electron transfer is expected [24]. This will create more electrons in the semiconductor. As a semi-metal with a very small band gap, graphene can also extend light absorption of TiO$_2$ to the visible light spectrum [25,26], and, hence, sunlight activation can be achieved.

Methods to combine TiO$_2$ with graphene or reduced graphene oxide (rGO) may vary depending on the thickness of the layers desired, the way the rGO is produced, and the features and geometry of the substrate. In this work, graphene oxide (GO) was used in an electrophoretic deposition (EPD) method to fabricate GO/TNWs. Another set of experiments was carried out by reducing GO to form reduced GO (rGO), and EPD was used to produce rGO/TNWs. EPD is a well-known technique whereby suspended particles are impelled from the suspension medium to a substrate using an electric field, and it has been shown to be a successful method for GO and rGO deposition [27]. Herein, GO and rGO in liquid suspension were used with deposition done on titanium foil comprising the TNWs. Nanocatalysts in dispersed particles have been reported to possess good catalytic performance due to a large, accessible surface area for a reaction to occur. However, they tend to form superfine particles in water, making it difficult to separate them from the treated water; thus, they become secondary pollutants in the water system.

A supported photocatalyst is proposed to address this problem: rGO/TiO$_2$ has several significant advantages, including good photoelectron injection from one material to another and simple post-separation and recycling of the system from the effluent after treatment. Moreover, to date, little work has explored the effect of EPD time and, therefore, the effect of the thickness of the GO or rGO on the photocatalytic reduction of Cr(VI) to Cr(III). It is anticipated that a thicker deposit will mean more electron transfer can occur, which may improve the reduction process of Cr(VI). In addition, the study on Cr(VI) reduction using supported rGO/TNWs is also rather limited.
2. Results and Discussion

Figure 1 shows a typical low-magnification FESEM image of the TNWs synthesized at 750 °C. As can be seen, the pristine sample comprises TNWs that uniformly cover the titanium foil. The length of the TNWs is ca. 500 nm, and the diameter ranges from 10 to 50 nm. The growth mechanism of the TNWs may be due to preferential oxide growth in the presence of the KOH mist. Accumulating a K-rich compound, such as K$_2$Ti$_6$O$_{13}$, at the sides of the growing TNWs, impedes radial growth and allows for c-axis growth [6].

![Figure 1](image_url)

**Figure 1.** Surface morphology of pristine TNWs before GO/rGO nanosheet deposition.

Surface FESEM morphologies of GO and rGO deposited on the TNWs using EPD at several deposition times are shown in Figures 2 and 3, respectively. Images on the left are low-magnification (100 µm), whereas higher magnification (1 µm) surface morphologies can be seen in the right column. From the low-magnification images, it can be observed that the amount of GO nanosheets and rGO nanosheets deposited on the surface of the TNWs increased as EPD time increased, as shown in Figures 2 and 3a–d-i. Higher magnification images, in Figures 2 and 3a–d-ii, were taken at the edge of the GO and rGO. In these images, the clear presence of TNWs with GO and rGO can be seen.

The XRD pattern of the TNWs, shown in Figure 4a, exhibited the presence of a rutile phase TiO$_2$ structure (ICSD No. 98-001-7802), with dominant diffraction peaks present at 2θ = 27.5°, 36.1°, and 54.3°. These diffraction peaks correspond to (110), (011), and (121) rutile-TiO$_2$, respectively. The appearance of two diffraction peaks at 11.4° and 29.8° can be ascribed to the K$_2$Ti$_6$O$_{13}$ phase (ICSD No. 98-001-1919), and the presence of KOH during the oxidation process may have resulted in this phase, which inhibited radial growth and induced the formation of 1D TNW structure. The XRD patterns of the GO/TNW and rGO/TNW samples show a similarity to the TNW sample, which indicates that the presence of GO or rGO does not affect the crystal planes of the underlying TNWs. No typical diffraction peaks of carbon species were observed in either sample, which may be due to the low quantity and relatively low diffraction intensity of GO or rGO [28].
Figure 2. FESEM images of GO deposited on TNWs using EPD with different deposition times: (a) 10 s; (b) 30 s; (c) 1 min; and (d) 5 min. Low-magnification images: left side (a-i to d-i) and high-magnification images: right side (a-ii to d-ii).
Figure 3. FESEM images of rGO deposited on TNWs using EPD with different deposition times: (a) 10 s; (b) 30 s; (c) 1 min; and (d) 5 min. Low-magnification images: left side ((a-i) to (d-i)) and high-magnification images: right side ((a-ii) to (d-ii)).
Raman spectra (see Figure 4b,c) further indicate the existence of rutile TiO$_2$ peaks ($B_{1g} = 142 \text{ cm}^{-1}$; $E_g = 449 \text{ cm}^{-1}$; $A_{1g} = 613 \text{ cm}^{-1}$) [29,30], and a $K_2Ti_6O_{13}$ peak (at approximately 240 cm$^{-1}$) [31] for all samples studied. The broad Raman peaks present at 1358 cm$^{-1}$ and 1605 cm$^{-1}$ correspond to D- and G-bands, respectively, and result from the presence of graphene derivatives as GO/rGO nanosheets in the GO/TNW and rGO/TNW samples but not in the pristine TNW sample. These Raman peaks belong to D-band and G-band carbon atoms from GO or rGO that are on the surface of the samples [19,22,32–35]. The stronger intensity of D over G peaks ($I_D/I_G$) may indicate a reduction of oxygen-functional groups in GO [36]. All Raman spectra for rGO/TNW samples show a higher intensity of D over G, thus indicating effective reduction from GO to rGO using chemical reduction with ascorbic acid.

Figure 4. (a) XRD patterns of TNWs, GO/TNWs, and rGO/TNWs samples; (b) Raman spectra of TNWs and GO/TNWs samples with different deposition times; and (c) Raman spectra of TNWs and rGO/TNWs samples with different deposition times.

Possible interactions between GO or rGO with TiO$_2$, as well as the chemical state of all the elements, can be studied with a high-resolution XPS. The high-resolution XPS images of C 1s core spectra are shown in Figure 5a for both GO/TNWs and rGO/TNWs. A peak at 285.1 eV, assigned to C-C from the sp$^3$ hybridized graphitic carbon atoms, can be detected for both samples. Deconvolution of the peak reveals several other peaks, such as for C=C bonds at 284.4 eV or C-C from sp$^3$ hybridized graphitic carbon atoms [37,38]. Oxygen-bound species can be seen at around 286–287 eV, possibly from C=O, carboxyl or carboxyl C=O, and C-O-C. It can only be detected for the GO/TNWs sample because GO contains more of such oxygen-functionalized species compared with rGO. Chemical reduction using ascorbic acid, therefore, significantly reduces the number of oxygen-bound...
species and successfully reduces GO to rGO [37]. The XPS results of O1s core level spectra are displayed in Figure 5b. The XPS peaks at 529.8 eV in rGO/TNWs and 530.6 eV in GO/TNWs correspond to the Ti-O bond of TiO$_2$ [37,39]. A small peak at ca. 531.8 eV is likely to come from OH absorbed on the surface of the oxide [39]. The oxygen-bound species C-O is detected at 532.7 eV in GO/TNWs but not in rGO/TNWs, further confirming the reduction from GO to rGO.

The photocatalytic performance of TNW, GO/TNW, and rGO/TNW samples in reducing Cr(VI) ions under visible light is illustrated in Figure 6. As can be seen, the reduction on the TNWs was negligible until GO or rGO was deposited onto them. For the GO/TNWs, the reduction performance improved as the deposition of GO was extended. The thicker the GO, the faster the removal of Cr(VI) that was observed. The maximum reduction of Cr(VI) was achieved for GO/TNWs with a 5-min deposition of GO on the TNWs. However, the reduction performance for rGO/TNWs is seen to be even better than GO/TNWs (Figure 6b). On rGO/TNWs, total removal of Cr(VI) can be observed after 60 min of illumination. In contrast to the previous set of samples, regarding rGO/TNWs, the reduction is faster for thinner rGO samples. For example, a 10-s deposited sample showed total removal of Cr(VI) after 30 min. The thickness of the rGO is obviously dependent on the time of rGO deposition. Typically, based on FESEM cross-section images, the rGO deposited has thicknesses of 50–90 nm after >30-s of deposition. For shorter deposition times, the thickness can be estimated to be ~ 10–40 nm. Several samples were then used for reusability tests; nevertheless, it appears that the adherence of the rGO weakened after being used more than once. This could be due to the very acidic nature of the Cr(VI) solution and the variation of thickness of the rGO on the surface of the TNWs.

The PL spectra of TNW, GO/TNW, and rGO/TNW samples are shown in Figure 7. The clear PL peak centered at 570 nm may be related to defects that are recombination centers of the photogenerated electron-hole pairs. Some examples are oxygen vacancies, the K$_2$Ti$_6$O$_{13}$ phase, and interstitial defects within the TiO$_2$ lattice [40–42]. Recombination is obvious for the TNW sample but not for the GO/TNWs and very much reduced for the rGO/TNW sample. This is possibly the result of the rapid transfer of electrons from GO or rGO suppressing recombination [43,44]. With more free electrons available and higher mobility of electrons in rGO, a more rapid reduction process leads to a fast and complete removal of Cr(VI) within 30 min of exposure to visible light. Furthermore, the improved photoreduction performance of the rGO/TNWs compared to TNWs is attributed to the great enhancement of electron transport through the rGO in the rGO/TNW sample and its consequent charge separation.
Photocatalytic reduction of Cr(VI) illuminated under visible light using different samples: (a) TNW and GO/TNW samples; and (b) TNW and rGO/TNW samples.

Photoluminescence spectra of TNW, GO/TNW, and rGO/TNW samples.
Table 1 compares this work with recent literature on the photoreduction of Cr(VI) [45–51]. It is evident that the photocatalytic reduction of rGO/TNWs formed in this work is comparable, if not superior, to the rGO/TiO$_2$ (nanoparticles) composite under visible light irradiation. Moreover, it is known that the addition of a scavenger can improve the efficiency of Cr(VI) photoreduction. There are several types of scavengers that can be used, and phenol is one of them. It can be seen from Table 1 that reduction in the presence of phenol (10 mM) is slower [46] than that of EDTA (this work), thus, concluding that EDTA is perhaps a better scavenger for this purpose.

Table 1. Comparison of obtained Cr(VI) reduction efficiency with recent studies under UV–Vis light irradiation (RGO = reduced graphene oxide; C = carbon).

| Photocatalysts           | Method       | Sample Amount/Size | Scavenger          | pH | Cr(VI) Conc. (ppm) | Source of Light | Removal Efficiency (%) | Time (min) | Ref.  |
|--------------------------|--------------|--------------------|--------------------|----|-------------------|----------------|------------------------|------------|-------|
| TNTs-Air                 | Anodization  | 1 cm$^2$           | –                  | 2  | 10                | Sunlight        | 10                     | 180        | [45]  |
| C-Modified n-TiO$_2$     | Sol–gel      | 1 g/L              | Phenol (10 mM)     | 5  | 5                 | Sunlight        | 100                    | 120        | [46]  |
| TiO$_2$–5%rGO           | Hydrothermal | –                  | –                  | 2  | 10                | Solar           | 98                     | 180        | [47]  |
| TiO$_2$–rGO             | Sol–gel      | –                  | –                  | 2.6| 12                | Mercury lamp    | 86.5                   | 240        | [38]  |
| Mn-TiO$_2$–/rGO         | Hydrothermal | 1 g/L              | –                  | –  | 20                | Sunlight        | 99.02                  | 60         | [48]  |
| CoS$_2$–/g-C$_3$N$_4$-rGO| Solvothermal | 10 mg              | Citric acid (100 ppm) | -  | 100               | 500 W Au halide lamp | 100                    | 80         | [50]  |
| TiO$_2$–rGO/CuO         | Hydrothermal | 50 mg              | Citric acid (100 ppm) | -  | 100               | 300 W Xe lamp   | 97                     | 240        | [51]  |
| TiO$_2$–g-C$_3$N$_4$-Microspheres/rGO | Hydrothermal | 50 mg              | -                  | 3  | 100               | 300 W Xe lamp   | 97                     | 240        | [51]  |
| TiO$_2$ NW-RGO          | Thermal Oxidation | 4 cm$^2$ | EDTA (1 mM) | 1  | 10                | Xenon lamp      | 100                    | 30         | This work |
3.2. Synthesis of rGO Nanosheets

10 mg/L GO nanosheet solution (Tokyo Chemical Industry Ltd., Tokyo, Japan) was diluted with deionized water to obtain a 0.1 mg/L GO nanosheet solution. Then, 50 mL of the solution was ultrasonically dispersed for 15 min in an ultrasonic bath; 1 mg of ascorbic acid (C₆H₈O₆) was then added to the solution, and the solution was heated to 95 °C. Prior to the addition of ascorbic acid, the pH of the solution was adjusted to 10 using NaOH.

3.3. GO/rGO Deposition on TNWs Sample Using EPD

EPD was conducted in 0.1 mg/L GO or rGO solution as the electrolyte with TNWs connected to the positive terminal of a DC power supply (GWS Instek GPS 3303, Transfer Multisort Elektronik Ltd., Łódź, Poland) and a Pt rod connected to the negative terminal. EPD in both electrolytes was performed at various deposition times (10 s, 30 s, 1 min, and 5 min) at 20 V. After the EPD process, the sample was dried in an oven at 100 °C for 15 min.

3.4. Characterizations

The surface structural morphologies of the GO/TNWs and rGO/TNWs were observed using a field-emission-scanning electron microscope (FESEM; Zeiss Supra 35, Germany). Phase identification and crystal-structure analysis were based on data obtained from an X-ray diffractometer [XRD; Bruker Advanced X-ray Solution D8 with Cu-Kα radiation (λ = 0.154 nm), United States] and a Raman spectrometer (Renishaw inVia Raman microscope, Gloucestershire, UK). Raman spectra were used to identify the presence of GO and rGO in the sample. Identification of chemical bonds in the sample was conducted by analyzing data from an X-ray photoelectron spectrometer [XPS; Kratos Axis Ultra with Al-Kα radiation (Eₚhotons = 1486.7 eV), Shimadzu Co., Ltd., Kyoto, Japan]. Photoluminescence studies were performed to identify impurities or defects that could be recombination centers of electron-hole pairs in the sample, using a monochromatic beam generated from a He-Cd laser (wavelength of 325 nm) and recorded using a monochromator (Nikon G250, Japan).

3.5. Cr (VI) Photoreduction Experiment

50 mL of the Cr(VI) (10 mg/L) solution was prepared by dissolving potassium dichromate salt (K₂Cr₂O₇) in distilled water. The pH value of the solution was adjusted to 2 by adding HCl solution. Then, 0.015 g of ethylene diamine tetra acetic acid was added to the solution and stirred for 5 min. GO/TNW or rGO/TNW samples were then immersed in the solution. The solution was then kept in the dark for 1 h prior to irradiation with visible light to achieve adsorption–desorption equilibrium. This was done using a solar simulator AM 1.5 (Xenon lamp, 1410 W/m² of intensity, LSPX150, Zolix Instruments Co. Ltd., Beijing, China). 3 mL aliquot samples were taken every 15 min during irradiation, and 1.5–diphenylcarbazide (DPC) was used to color the aliquot solution before subjecting it to measurement using a UV/Vis spectrometer (Varian Cary 50, Mulgrave, Australia).

4. Conclusions

GO or rGO deposition using the EPD method was carried out on TNWs. The TNWs were produced by thermal oxidation in the presence of KOH mist. rGO was obtained by the chemical reduction of commercially available GO using ascorbic acid. The fabricated TNW, GO/TNW, and rGO/TNW samples were used to reduce Cr(VI) in a photocatalysis experiment under simulated sunlight irradiation. It was found that a GO/TNW sample with 5 min of deposition was able to reduce 32.84% of the Cr(VI) ions after 1 h of irradiation, but rGO/TNWs with 10 s of deposition displayed a 100% reduction after 30 min of exposure to visible light. This could be due to the amount of transferred photogenerated electrons from GO or rGO to the TNWs.
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References
1. Cheng, H.; Zhou, T.; Li, Q.; Lu, L.; Lin, C. Anthropogenic chromium emissions in China from 1990 to 2009. PLoS ONE 2014, 9, e87753. [CrossRef]
2. IARC (International Agency for Research on Cancer). List of Classifications, Volumes 1–132. 2022. Available online: http://monographs.iarc.fr/ENG/Classification/latest_classif.php (accessed on 31 August 2022).
3. Alias, N.; Hussain, Z.; Tan, W.K.; Kawamura, G.; Muto, H.; Matsuda, A.; Lockman, Z. Nanoporous anodic Nb2O5 with pore-in-pore structure formation and its application for the photoreduction of Cr(VI). Chemosphere 2021, 283, 131231. [CrossRef]
4. Goyer, G.; Golub, M.; Choudhury, H.; Hughes, M.; Kenyon, E.; Stiefelman, M. Issue Paper on The Human Health Effects of Metals; U.S. Environmental Protection Agency: Washington, DC, USA, 2004.
5. Chen, X.; Mao, S.S. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. Chem. Rev. 2007, 107, 2891–2959. [CrossRef] [PubMed]
6. Rahmat, S.T.; Tan, W.K.; Kawamura, G.; Matsuda, A.; Lockman, Z. Synthesis of rutile TiO2 nanowires by thermal oxidation of titanium in the presence of KOH and their ability to photoreduce Cr(VI) ions. J. Alloys Compd. 2020, 812, 152094. [CrossRef]
7. Du, J.; Gu, X.; Guo, H.; Liu, J.; Wu, Q.; Zou, J. Self-induced preparation of TiO2 nanowires by chemical vapor deposition. J. Cryst. Growth 2015, 427, 54–59. [CrossRef]
8. Yun, G.; Song, G.Y.; Ahn, B.-E.; Lee, S.-K.; Heo, J.; Ahn, K.-S.; Kang, S.H. Beneficial surface passivation of hydrothermally grown TiO2 nanowires for solar water oxidation. Appl. Surf. Sci. 2016, 366, 561–566. [CrossRef]
9. Attar, A.S.; Hassani, Z. Fabrication and growth mechanism of single-crystalline rutile TiO2 nanowires by liquid-phase deposition process in a porous alumina template. J. Mater. Sci. Technol. 2015, 31, 828–833. [CrossRef]
10. Ge, M.; Li, Q.; Cao, C.; Huang, J.; Li, S.; Zhang, S.; Chen, Z.; Zhang, K.; Al-Deyab, S.S.; Lai, Y. One-dimensional TiO2 nanotube photocatalysts for solar water splitting. Adv. Sci. 2017, 4, 1600152. [CrossRef]
11. Hejazi, S.; Pour-Ali, S.; Killian, M.S.; Mohajerinia, S. One-dimensional suboxide TiO2 nanotubes for electronics applications. Electrochem. Commun. 2012, 13, 107246. [CrossRef]
12. Mangham, A.N.; Govind, N.; Bowden, M.E.; Shutthananand, V.; Joly, A.G.; Henderson, M.A.; Chambers, S.A. Photochemical properties, composition, and structure in molecular beam epitaxy grown Fe “doped” and (Fe,N) codoped rutile TiO2(110). J. Phys. Chem. C 2011, 115, 15416–15424. [CrossRef]
13. Xu, M.; Shao, S.; Gao, B.; Lv, J.; Li, Q.; Wang, Y.; Wang, H.; Zhang, L.; Ma, Y. Anatase (101)-like structural model revealed for metastable rutile TiO2(011) surface. ACS Appl. Mater. Interfaces 2017, 9, 7891–7896. [CrossRef]
14. Asahi, R.; Morikawa, T.; Irie, H.; Ohwaki, T. Nitrogen-doped titanium dioxide as visible-light-sensitive photocatalyst: Designs, developments, and prospects. Chem. Rev. 2014, 114, 9824–9852. [CrossRef]
15. Pan, J.; Li, C.; Zhao, Y.; Liu, R.; Gong, Y.; Niu, L.; Liu, X.; Chi, B. Electronic properties of TiO2 doped with Sc, Y, La, Zr, Hf, V, Nb and Ta. Chem. Phys. Lett. 2015, 628, 43–48. [CrossRef]
16. Xiao, L.; Li, Y.; Chen, F.; Xu, P.; Li, M. Facile synthesis of mesoporous titanium dioxide doped by Ag-coated graphene with enhanced visible-light photocatalytic performance for methylene blue degradation. RSC Adv. 2017, 7, 25314–25324. [CrossRef]
17. Khairy, M.; Zakaria, W. Effect of metal-doping of TiO2 nanoparticles on their photocatalytic activities toward removal of organic dyes. Egypt. J. Pet. 2014, 23, 419–426. [CrossRef]
18. Kumar, R.; Sahoo, S.; Joanni, E.; Singh, R.K.; Tan, W.K.; Kar, K.K.; Matsuda, A. Recent progress on carbon-based composite materials for microwave electromagnetic interference shielding. Carbon 2021, 177, 304–331. [CrossRef]
19. Kumar, R.; Sahoo, S.; Tan, W.K.; Kawamura, G.; Matsuda, A.; Kar, K.K. Microwave-assisted reduced graphene oxide-cobalt oxide nanocomposites as hybrids for electrode materials in supercapacitors. *Energy Storage 2021*, 40, 102724. [CrossRef]

20. Youssry, S.M.; El-Hallag, I.S.; Kumar, R.; Kawamura, G.; Matsuda, A.; El-Nahass, M.N. Synthesis of mesoporous Co(OH)₂ nanostructure film via electrochemical deposition using hydrotropic liquid crystal template as improved electrode materials for supercapacitors application. *Electrochim. Acta. 2020*, 57, 113728. [CrossRef]

21. Kumar, R.; Sahoo, S.; Joanni, E.; Singh, R.K.; Yadav, R.M.; Verma, R.K.; Singh, D.P.; Tan, W.K.; Pérez del Pino, A.; Moshkalev, S.A.; et al. A review on synthesis of graphene, b-NH₂ and MoS₂ for energy storage applications: Recent progress and perspectives. *Nanoscale Res. 2019*, 12, 2655–2694. [CrossRef]

22. Tan, W.K.; Asami, K.; Maegawa, K.; Kumar, R.; Kawamura, G.; Muto, H.; Matsuda, A. Fe₃O₄-embedded rGO composites as anode for rechargeable FeOₓ-air batteries. *Mater. Today Commun. 2020*, 30, 651007. [CrossRef]

23. Kumar, R.; Sahoo, S.; Joanni, E.; Singh, R.K.; Tan, W.K.; Kar, K.K.; Matsuda, A. Recent progress in the synthesis of graphene and derived materials for next generation electrodes of high performance lithium ion batteries. *Prog. Energy Combust. Sci. 2019*, 75, 100786. [CrossRef]

24. Zhang, L.W.; Fu, H.B.; Zhu, Y. Efficient TiO₂ photocatalysts from surface hybridization of TiO₂ particles with graphite-like carbon. *Adv. Funct. Mater. 2008*, 18, 2180–2189. [CrossRef]

25. Neto, A.C.; Guinea, F.; Peres, N.M.; Novoselov, K.S.; Geim, A.K. The electronic properties of graphene. *Rev. Mod. Phys. 2009*, 81, 109. [CrossRef]

26. Tayebi, M.; Kolaei, M.; Tayyebi, A.; Masoumi, Z.; Belbasi, Z.; Lee, B.K. Reduced graphene oxide (RGO) on TiO₂ for an improved photoelectrochemical (PEC) and photocatalytic activity. *Sol. Energy 2019*, 190, 185–194. [CrossRef]

27. An, S.J.; Zhu, Y.; Lee, S.H.; Stoller, M.D.; Emilsson, T.; Park, S.; Velamakanni, A.; An, J.; Ruoff, R.S. Thin film fabrication and simultaneous anodic reduction of graphene oxide platelets by electrophoretic deposition. *J. Phys. Chem. Lett. 2010*, 1, 1259–1263. [CrossRef]

28. Liu, X.; Pan, L.; Lv, T.; Zhu, G.; Lu, T.; Sun, Z.; Sun, C. Microwave-assisted synthesis of TiO₂-reduced graphene oxide composites for the photocatalytic reduction of Cr(VI). *RSC Adv. 2011*, 1, 1245–1249. [CrossRef]

29. Iliev, A.G.; Scarisoreanu, M.; Morjan, I.; Dutu, E.; Badiceanu, M.; Mihaielscul, I. Principal component analysis of Raman spectra for TiO₂ nanoparticle characterization. *Appl. Surf. Sci. 2017*, 417, 93–103. [CrossRef]

30. He, A.; Chen, G.; Chen, J.; Peng, J.; Srinivasakannan, C.; Ruan, R. A novel method of synthesis and investigation on transformation of synthetic rutile powders from Panzhihua sulphate titanium slag using microwave heating. *Powder Technol. 2018*, 323, 115–119. [CrossRef]

31. Meng, X.; Wang, D.; Liu, J.; Lin, B.; Fu, Z. Effects of titania different phases on the microstructure and properties of K₂Ti₆O₁₃ nanowires. *Solid State Commun. 2006*, 137, 146–149. [CrossRef]

32. Wang, M.; Duong, L.D.; Oh, J.-S.; Mai, N.T.; Kim, S.; Hong, S.; Hwang, T.; Lee, Y.; Nam, J.-D. Large-area, conductive and flexible reduced graphene oxide (RGO) membrane fabricated by electrophoretic deposition (EPD). *ACS Appl. Mater. Interfaces 2014*, 6, 1747–1753. [CrossRef]

33. Kumar, R.; Youssry, S.M.; Abdel-Galeil, M.M.; Matsuda, A. One-pot synthesis of reduced graphene oxide nanosheets anchored ZnO nanoparticles via microwave approach for electrochemical performance as supercapacitor electrode. *J. Mater. Sci. Mater. Electron. 2020*, 31, 15456–15465. [CrossRef]

34. Kumar, R.; da Silva, E.T.S.G.; Singh, R.K.; Savu, R.; Alaferdov, A.V.; Fonseca, L.C.; Carossi, L.C.; Singh, A.; Handika, S.; Kar, K.K.; et al. Microwave-assisted synthesis of palladium nanoparticles intercalated nitrogen doped reduced graphene oxide and their electrocatalytic activity for direct-electrol fuel cells. *J. Colloid Interface Sci. 2018*, 515, 160–171. [CrossRef]

35. Kumar, R.; Singh, R.K.; Vaz, A.R.; Savu, R.; Moshkalev, S.A. Self-assembled and one-step synthesis of interconnected 3D network of Fe₃O₄-reduced graphene oxide nanosheets hybrid for high-performance supercapacitor electrode. *ACS Appl. Mater. Interfaces 2017*, 9, 8880–8890. [CrossRef]

36. Stankovich, S.; Dikin, D.A.; Piner, R.D.; Kohlhaas, K.A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S.T.; Ruoff, R.S. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon 2007*, 45, 1558–1565. [CrossRef]

37. Žerjav, G.; Arshad, M.S.; Djunović, P.; Junkar, I.; Kovač, J.; Zavaznič, J.; Pintar, A. Improved electron–hole separation and migration in anatase TiO₂ nanorod/reduced graphene oxide composites and their influence on photocatalytic performance. *Nanoscale 2017*, 9, 4578–4592. [CrossRef]

38. Zhao, Y.; Zhao, D.; Chen, C.; Wang, X. Enhanced photo-reduction and removal of Cr(VI) on reduced graphene oxide decorated with TiO₂ nanoparticles. *J. Colloid Interface Sci. 2013*, 405, 211–217. [CrossRef] [PubMed]

39. Taib, M.A.A.; Razak, K.A.; Jaafar, M.; Lockman, Z. Initial growth study of TiO₂ nanotube arrays anodised in KOH/fluoride/ethylene glycol electrolyte. *Mater. Des. 2017*, 128, 195–205. [CrossRef]

40. Wu, J.-M.; Shih, H.C.; Wu, W.-T. Formation and photoluminescence of single-crystalline rutile TiO₂ nanowires synthesized by thermal evaporation. *Nanotechnology 2005*, 17, 105. [CrossRef]

41. Shi, J.; Chen, J.; Feng, Z.; Chen, T.; Liao, Y.; Wang, X.; Li, C. Photoluminescence characteristics of TiO₂ and their relationship to the photoassisted reaction of water/methanol mixture. *J. Phys. Chem. C 2007*, 111, 693–699. [CrossRef]

42. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO₂ photocatalysis: Mechanisms and materials. *Chem. Rev. 2014*, 114, 9919–9986. [CrossRef] [PubMed]
43. Yang, N.; Zhai, J.; Wang, D.; Chen, Y.; Jiang, L. Two-dimensional graphene bridges enhanced photoinduced charge transport in dye-sensitized solar cells. ACS Nano 2010, 4, 887–894. [CrossRef]
44. Fernández-Merino, M.J.; Guardia, L.; Paredes, J.; Villar-Rodil, S.; Solís-Fernández, P.; Martínez-Alonso, A.; Tascon, J. Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions. J. Phys. Chem. C 2010, 114, 6426–6432. [CrossRef]
45. Bashirom, N.; Tan, W.K.; Kawamura, G.; Matsuda, A.; Lockman, Z. Comparison of ZrO2, TiO2, and α-Fe2O3 nanotube arrays on Cr(VI) photoreduction fabricated by anodization of Zr, Ti, and Fe foils. Mater. Res. Express 2020, 7, 055013. [CrossRef]
46. Shaban, Y.A. Effective photocatalytic reduction of Cr(VI) by carbon modified (CM)-n-TiO2 nanoparticles under solar irradiation. World J. Nano Sci. Eng. 2013, 3, 154–160. [CrossRef]
47. Liu, L.; Luo, C.; Xiong, J.; Yang, Z.; Zhang, Y.; Cai, Y.; Gu, H. Reduced graphene oxide (rGO) decorated TiO2 microspheres for visible-light photocatalytic reduction of Cr(VI). J. Alloys Compd. 2017, 690, 771–776. [CrossRef]
48. Chen, Z.; Li, Y.; Guo, M.; Xu, F.; Wang, P.; Du, Y.; Na, P. One-pot synthesis of Mn-doped TiO2 grown on graphene and the mechanism for removal of Cr(VI) and Cr(III). J Hazard Mater. 2016, 310, 188–198. [CrossRef]
49. Wang, Y.; Bao, S.; Liu, Y.; Yang, W.; Yu, Y.; Feng, M.; Li, K. Efficient photocatalytic reduction of Cr(VI) in aqueous solution over CoS2/g-C3N4-rGO nanocomposites under visible light. Appl. Surf. Sci. 2020, 510, 145495. [CrossRef]
50. Wang, N.; Zhang, F.; Mei, Q.; Wu, R.; Wang, W. Photocatalytic TiO2/rGO/CuO Composite for Wastewater Treatment of Cr(VI) Under Visible Light. Water Air Soil Pollut. 2020, 231, 223. [CrossRef]
51. Li, G.; Wu, Y.; Zhang, M.; Chu, B.; Huang, W.; Fan, M.; Dong, L.; Li, B. Enhanced Removal of Toxic Cr(VI) in Wastewater by Synthetic TiO2/g-C3N4 Microspheres/rGO Photocatalyst under Irradiation of Visible Light. Ind. Eng. Chem. Res. 2019, 58, 8979–8989. [CrossRef]