Langmuir-Blodgett assembly of visible light responsive TiO₂ nanotube arrays/graphene oxide heterostructure

*Ying Chen, Hongyan Gao, Danming Wei, Xinju Dong, Yan Cao**

(* Dr. Yan Cao is the corresponding author, Tel: +1-270-779-0202, Email: yan.cao@wku.edu)

Institute for Combustion Science and Environmental Technology, Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101, USA

ABSTRACT The hybrid nanocomposites of titanium dioxide (TiO₂) with graphene oxide (GO) have recently garnered much attention as electronic devices, energy conversion devices, photocatalysts and other applications. In this study, Langmuir-Blodgett (LB) assembly method was firstly reported to prepare a TiO₂ nanotube arrays (TNA)-GO heterostructure. The as-prepared TNA-GO sample was characterized by X-ray diffraction, Raman spectra, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The promising characteristics of this TNA-GO material, the inexpensive, nontoxic and highly visible-light responsiveness, may raise the potential uses in many, various photocatalytic applications.

1. Introduction

Titanium dioxide (TiO₂), as a nontoxic, stable, less costly, and highly efficient photocatalyst, has wide applications in photovoltaics¹, dye-sensitized solar cell (DSSC)², hydrogen generation³, solar fuel

producing⁴, pollution photo-digestion and other photocatalytic reactions. Due to its superb properties and abundant applications, various ways have been practiced to synthesize photocatalytic TiO₂, i.e. sol-gel method⁵, hydrothermal method⁶, chemical vapor deposition (CVD)⁷, liquid phase deposition (LPD)⁸, etc. For the first time in 1999, Zwillling et al. reported the anodic oxidation method to fabricate highly ordered TiO₂ nanostructured arrays (TNA) on titanium foil in a HF electrolyte⁹, which has been followed by considerable research works since then. Compared to the aforementioned preparation methods, anodic oxidation of anodization TNA is not only an easy and convenient way, but also offers a strong mechanical strength directly on titanium substrates which can reduce the recombination of intrinsic electron-hole pairs to some degree.¹⁰ Moreover, a relatively large surface to volume ratio of TNA brings different bonding characteristics on the surface, and eventually different properties from the thin film or bulk TiO₂.¹¹

However, TiO₂ materials also have their own limitations as photocatalysts. Their band gap is 3.2 eV, leading it responsive only to UV light which is only about 3–5% of the total solar energy. Moreover, its intrinsic electron-hole pair recombination is relatively high. To overcome this disadvantage, a series of TiO₂ based nanocomposites have been co-synthesized with Ag¹², Au¹³, ZnO¹⁴ and other materials. Graphene with a two dimensional structure has been widely studied in materials science recently for its excellent properties, such as large surface to mass ratio, high mechanical strength (second- and third-order elastic stiffness of 340 Nm⁻¹ and -690 Nm⁻¹, breaking strength of 42 Nm⁻¹)¹⁵, great charge-carrier mobility (105 cm²/Vs at an ambient temperature and 106 cm²/Vs at low temperatures¹⁶), excellent thermal conductivity (up to ~5000 W/mK for the suspended single-layer graphene at room temperature¹⁶) and ease of functionalization¹⁷. Graphene oxide (GO), with graphene domains, defects, and oxygen-containing groups on the surface of graphene sheets, is also popular. It can offer many reactive handles for surface-modification reactions to form functionalized GO-based, or reduced graphene-based materials. Very recently, different types of TiO₂/graphene, or TiO₂/GO composites

have been reported¹⁸, in which TiO₂ received light to excite photo-electrons, and the graphene can capture electrons and transport them out of circuit. These improved TiO₂ composite can be readily applied in efficient photocatalytic utilizations.

Various methods have been used to prepare TiO₂/graphene and TiO₂/GO composites, i.e. sol-gel method¹⁹, hydrothermal method^{18h}, UV-assisted photoreduction method^{18j}, microwave-assisted synthesis, etc²⁰. Compared to the mentioned preparation methods, Langmuir–Blodgett (LB) assembly and deposition is a convenient and inexpensive method that can fabricate nano-films on solid substrate in a continuous manner over a large area. However, to our knowledge, no publications have been found up to this point using the LB assembly to prepare the co-photocatalysts. This study reports an easy and convenient way, using LB trough, to spread GO monolayers on TiO₂ nanotube arrays (TNA) substrates and finally obtain a hybrid TNA-GO composite. Sufficient characterization methods have been applied for assisting in presenting an elaborate discussion.

2. Experimental Section

2.1. Chemicals.

All chemicals in this study were of analytical grade and used without any further purification. Among them, sodium nitrate (NaNO₃, extra pure), and ammonium fluoride (NH₄F; 98+%, extra pure) were purchased from Acros Organics Corporation. Sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂; 30%), graphite powder, potassium permanganate (KMnO₄), sodium hydroxide (NaOH), methanol, ethanol, acetone and ethylene glycol were all purchased from Fisher Scientific Corporation. Titanium foil (Ti; ca. 99.7%) was purchased from STREM Chemicals. Throughout this study, deionized water (DI water) was always used.

2.2. Synthesis of GO.

GO was synthesized from graphite using a modified Hummers method.²¹ First, 1g of graphite powder and 1g of NaNO₃ were put into 45mL of concentrated H₂SO₄. Then, 6g of KMnO₄ was gradually added into the solution with vigorous stirring in an ice bath to keep the temperature of the mixture below 30 °C. After 10 minutes, the ice bath was switched to a water bath, in which the mixture was stirred at 35 °C for 4h. After the color of the mixture turned to dark brown, 200mL of deionized water was slowly dipped into the mixture. After continuously stirring for 1 hour, the water bath was switched to oil bath and the mixture was then stirred at 98°C for 2 more hours. Then, 30mL of 30% H₂O₂ was slowly added to the mixture. When the color of the mixture turned fully to brown, the mixture was transferred to a large beaker and washed to remove other ions using DI water.

2.3. Synthesis of TNA.

The highly ordered TiO₂ arrays was synthesized by an anodization approach. Prior to the anodization, the 3cm×1cm titanium foils were respectively pretreated in acetone, ethanol, and deionized water using ultrasonic cleaning, and then air dried at 60 °C. Then, the anodic oxidization was performed in a two-electrode system with the pre-washed titanium foil as anode, a platinum (Pt) sheet as cathode and ethylene glycol solution containing 0.5 wt% NH₄F and 2 vol% DI water as electrolyte at room temperature. The applied potential was held at a constant 60 V for 2h. After the anodization, the TNA sample was cleaned with deionized water and ethanol successively, and then air dried. After that, the prepared TNA sample was annealed in air at 500 °C for 2 h after a heating rate of 5 °C/min.

2.4. Assembly of TNA-GO.

GO films were assembled on TNA using the published Langmuir–Blodgett (LB) method.²² To be specific, a DI water/methanol mixture with an optimal ratio of 1:5 was chosen as a solvent to spread

GO monolayers rapidly onto the water surface in LB trough (Kibron Inc., MicroTroughXS). Using an accurate glass syringe, 5 mL of the GO dispersion was slowly dropped on the DI water surface at a speed of 100 $\mu\text{L}/\text{min}$. When all GO dispersion was made on the surface, the pretreated TNA foil was raised by the vertical micromotor of the LB trough at a speed of 10 mm/min, while two barriers were moving from both sides to the center at the same speed. The surface pressure was monitored by a sensor to record any movement. After the deposition, the substrate was dried in air overnight for 12 hours to stabilize the adhesion of GO layer to TNA. The GO deposition was repeated for 5 times to get the final TNA-GO composite.

Figure 1 Flow chart for the fabrication of TNA-GO.

2.5. Characterization.

For each sample, X-ray diffraction (XRD; ARL™ X'TRA Powder Diffractometer, Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$) was recorded at room temperature with a scan step of 0.02, a scanning speed of 0.2 s/step. Scanning electron microscopy (SEM; Model JSM-6510LV, JEOL Ltd., Tokyo, Japan) and high resolution transmission electron microscopy (HRTEM; Model JEM-1400Plus, JOEL Ltd., Tokyo, Japan) were used to characterize the morphologies and size of the synthesized samples. Their chemical composition were investigated by the energy dispersive X-ray spectroscopy (EDX). Raman spectra of samples were collected using a DXR Raman microscope (Thermo DXR), including a 780 nm

excitation laser and a confocal microscope. The Fourier transform infrared spectra were recorded by FT-IR Spectrometer (PerkinElmer, Spectrum Two) from 4000 to 500 cm^{-1} . The X-ray photoelectron spectroscopy (XPS) measurements were performed with a multi-functional photoelectron spectrometer (Axis Ultra DLD, Kratos) using Al Ka radiation. UV-vis diffuse-reflectance spectroscopy (DRS) spectra were recorded with a UV-vis spectrophotometer (Cary, 100 Bio) at wavelengths in the range of 200-800 nm, with a baseline corrected by barium sulfate (BaSO_4) powder.

2.6. Electrochemical Measurement.

For the electrochemical impedance spectroscopy (EIS) measurement, the as-prepared TNA and TNA-GO were served as the working electrodes, with a platinum foil as the counter electrode and a SCE (saturated calomel electrode) as the reference electrode. All EIS measurements were carried out in 0.5 M Na_2SO_4 solution by using a three-electrode system on Zennium electrochemical workstation (Zahner, INC. Germany). The impedance spectra were recorded under an AC perturbation signal of 5 mV over the frequency range of 0.01 Hz to 100,000 Hz at the initial potentials of working electrode materials. To further study the charge transfer behaviors of TNA and TNA-GO, EIS measurements under LED irradiation (TLS02, Zahner, INC. Germany) with a power 100 mW/cm^2 were also performed.

2.7. Photocurrent Measurement.

Photocurrent studies of TNA and TNA-GO on both the 1st day, and 61st day were performed in a photoelectrochemical quartz cell containing 0.5 M Na_2SO_4 solution on the Zennium electrochemical workstation CIMPS system. In the three-electrode configuration, the TNA and TNA-GO sheets were working electrodes and, a Pt foil and a SCE were the counter electrode and reference electrode respectively. A LED lamp with a power 100 mW/cm^2 served as simulated visible light irradiation source. Between the photocurrent measurements on the 1st day and 61st day, both TNA and TNA-GO

were stored at the ambient condition. As reference, the dark currents of TNA and TNA-GO were also measured.

Unlike the conventional optical filter approach to cut-off the UV light of the applied light source, we directly used a commercial LED lamp set together with Zennium electrochemical workstation as our experimental setup. The applied Zahner CIMPS system can accurately provide the visible light source in several certain wavelengths, and mixed white light (specification of instrument). In our photocurrent measurement tests, the mixed white light was applied, which does not emit UV light. Thus, all photocurrent measurements can be limited to light with a wavelength larger than 400 nm.

3. Results and discussion

3.1. Material Characterizations

The surface morphology, structure, and consistence of TNA and TNA-GO samples were investigated using SEM, TEM and EDX (Figure 1). From Figure 2a, which shows the SEM image of TNA from top view, highly ordered TNA grown on a Ti substrate were observed. The nanotubes formed in TNA were uniformly distributed and similar in size, with approximate wide tube diameter of 120 nm. The surface of TNA was relatively smooth. Meanwhile, the SEM images of TNA from side view were shown in Figure 2c and 2d. From the side-view images the length of nanotubes in TNA can determined as about 20 μm (medium tubes⁹). More detailed information regarding structural features were displayed in TEM images of TNA (Figure 2e and 2f). TEM images further confirmed that the diameter of the nanotubes in TNA was about 120 nm with wall thickness of about 20 nm.

Compared to the top-view SEM image of TNA in Figure 2a, Figure 2b showed the SEM image of a confirmed formation of TNA-GO. It can be seen from Figure 2b that, after the LB assembly, TNA has been successfully covered by GO nanosheets. The chemical composition of the TNA and TNA-GO

were both determined by EDX experiments (Figure 2g and 2h), which demonstrated that the as-prepared TNA samples contained elements Ti and O while TNA-GO containing Ti, O and C. These EDX results also confirmed the GO assembly on TNA surface.

Figure 2 50,000 times magnification SEM images from top view of **(a)** TNA and **(b)** TNA-GO. **(c)** 5,000 and **(d)** 10,000 times magnification SEM images of TNA from side view. **(e)** 10,000 and **(f)** 100,000 times magnification TEM images of TNA. EDX analysis of **(g)** TNA and **(h)** TNA-GO.

The phase structures of TNA and TNA-GO were analyzed by powder XRD patterns (Figure 3a). Facets (101), (004), (200), (105), (211), (204), (116), (220), (215) and (303) of the anatase TiO_2 were found in both TNA and TNA-GO samples (JCPDS No. 99-101-0957) at 25.33° , 37.83° , 48.08° , 53.93° , 55.11° , 62.74° , 68.82° , 70.35° , 75.12° and 82.76° , respectively. The peak at 2θ values of 40.2° , circled in Figure 3a, matched the (101) crystal plane of Ti metal phase (JCPDS No. 99-101-0388), which were brought in by Ti substrate. Compared with TNA pattern, one more broad peak at around $2\theta = 11.5^\circ$ showed up in TNA-GO pattern. This peak should be corresponding to a (002) facet diffraction of GO, which verified the existence of GO in the TNA-GO composite.

The consistence of TNA and TNA-GO composite were further investigated by Raman spectra (Figure 3b). In Figure 3b, four peaks were observed in TNA curve at around 144 cm^{-1} , 395 cm^{-1} , 512 cm^{-1} and 639 cm^{-1} , matching four modes of TiO_2 as $\text{Eg}(1)$, $\text{B1g}(1)$, $\text{A1g}+\text{B1g}(2)$ and $\text{Eg}(2)$ respectively, while the peaks at 144 cm^{-1} being the highest. These four peaks can also be seen in the Raman curve of TNA-GO composite, but the intensity of the peaks were largely reduced. This decreased intensity was likely associated with a shielding effect of GO nanosheets on TNA, because the Raman test could only reflect the surface information of tested materials based on its surface-enhanced scattering mechanism²³. Meanwhile, the typical peaks at around 1345 cm^{-1} and 1580 cm^{-1} of GO were found in TNA-GO, commonly corresponding to the D band of the sp^3 defects and the G band of sp^2 plane vibrations. Generally, the intensity ratio of D band and G band (ID/IG) represents defects in graphene. With an ID/IG value of 2.1, the GO on TNA-GO's surface was found to be well oxidized from graphite.

Figure 3 (a) XRD patterns and **(b)** Raman spectra of TNA and TNA-GO.

XPS characterizations were further carried out to investigate TNA and TNA-GO composite (Figure 4). The entire XPS survey of TNA and TNA-GO was shown as Figure 4a, while the high-resolution spectra of C 1s and O 1s as Figure 4b and 4c. In Figure 4a, C 1s, Ti 2p and O 1s peaks at around their corresponding binding energies, as 284.5 eV, 458 eV and 531 eV were exhibited. It can be easily determined from the curves that the intensity of Ti 2p and O 1s peaks in TNA and TNA-GO composite were about the same, while the C 1s peak intensity of TNA being markedly smaller than the TNA-GO composite. Technically, no C 1s peak should show up in TNA XPS survey. This small C 1s peak of TNA was most likely due to the residual ethylene glycol on its surface which may not have been totally washed out after the anodization synthesis. To have a closer look on the C 1s core level analysis of TNA and TNA-GO composite (Figure 3b), three peaks as C=C, C-O and C=O with corresponding banding energies at around 284.8 eV, 286.3 eV and 288.2 eV²⁴ were observed in TNA-GO composite, while only two peaks as C-C (284.6 eV)²⁵ and C-OH (286.9 eV)²⁶ showing up in TNA. In the O 1s core level spectrum, two peaks around 530.5 eV and 532.7 eV, corresponding to bulk oxygen (O²⁻) in Ti-O and in H-O/C-O covalent bond respectively, could be found in TNA-GO composite²⁴, while only one peak of Ti-O at around 529.8 eV showed up in TNA. The reason why the energy of Ti-O drifted

increased a little in TNA-GO was likely due to the fact that GO made the lattice of TNA more compacted. Thus, the core level analyses of C 1s and O 1s further confirmed the GO in TNA-GO composite. Moreover, the increasing binding energy of the internal electron (1s orbital electron) of O would reversely lead a relax of O neutron to hold its external valance electrons, and thus the excitation of electron in TNA/GO composite became easier and response to a longer-wavelength energy was likely. Therefore, what we found was the shift of the binding energy in O^{1s} to a larger value in TNA/GO composite likely revealed the change of its band gap to be smaller.

Figure 4 (a) XPS whole survey spectrum of TNA and TNA-GO. The high-resolution (b) C 1s and (c) O 1s XPS spectra of TNA and TNA-GO.

3.2. Performance of TNA-GO

3.2.1. Visible Light Absorption

It is well known that TiO₂, as a photosensitized semiconductor, has a large band gap and good response to UV light. However, the UV spectra only accounts for about 3-5% of the total solar energy. Thus, to

make a better use of solar energy, it is necessary to expand the photo-responsive spectra of TiO₂ materials from the UV light to the visible light. This is also the major goal of our current studies.

The UV-vis diffuse reflectance spectra (DRS) and the corresponding relationship between $(A\text{h}\nu)^{1/2}$ and $h\nu$ were performed to examine the photocatalytic activities of TNA and TNA-GO composite. As shown in the Figure 5a, both TNA and TNA-GO composite responded predominantly to UV light. With direct band gap, the band gap of TNA and TNA-GO composite can be determined by the Kubelka-Munk equation as the intercepts in Figure 5b. Respectively, the band gap of TNA and TNA-GO composite were about 3.0 eV (corresponding to wavelength of ~ 400 nm, UV light range) and 2.8 eV (corresponding to wavelength of ~ 450 nm, visible light range). Thus, the band gap of TNA-GO was narrowed down 0.2 eV compared to TNA itself. Similar results were also found by other groups.^{18j, 18k, 18n, 18o} By having narrower band gap, the photo-response range of TNA can then change from UV to visible light, which also enlarges the utilization range of natural sun light.

Here, an up-conversion photoluminescence (UCPL) effect of GO may provide a synergic explanation to this improvement of light absorption. According to published studies, UCPL is a phenomenon that the photon energy of emission is higher than that of excitation, which has been widely reported with solid-state materials doped with rare-earth elements, semiconductors with heterostructures, quantum dots, etc.²⁷ Recently, normal PL as well as UCPL features of carbon quantum dots, graphene quantum dots and graphene oxide quantum dots have been well characterized.^{18m, 28 29} By mentioning RG quantum dots, it does not only refer to the actual dots with size smaller than 10 nm, but also the graphene sheets with graphene oxide quantum islands on it, both being in a nano-thickness.³⁰ In this study, the GO on TNA can be seen as a quantum graphene structure material. Normally, the visible light with wavelength larger than 420 nm is not be able to be used by TiO₂ materials alone (The absorbable light wavelength limitation of the rutile TiO₂ is 414 nm, while the absorbable light wavelength limitation of the anatase TiO₂ is 388 nm^{28b}). However, the visible light within this range

can excite GO and transfer to the light with shorter wavelength, which is then able to be utilized by TiO_2 . Thus, the absorbable light wavelength limitation is accordingly changed.

3.2.2. Charge Carriers' Migration

The charge carriers' migration behaviors of TNA and TNA-GO composite were also explored by measuring EIS. As shown in the $-Z''$ -Nyquist plots (Figure 5c), the radii of the quadrants at high frequencies range (closer to the origin) can reflect charge transfer resistance, and the material with larger radius is supposed to have relatively larger resistance. From Figure 5c it can be determined that the radius of TNA's quadrant was marginally larger than the radius of TNA-GO's, which should be according to the existence of GO on the surface of TNA decreasing the charge transfer resistance across the solid-liquid junction. To further study the charge transfer behaviors of TNA and TNA-GO composite, we also performed similar EIS measurements under LED irradiation (Figure 5d). As shown in Figure 5d, when TNA and TNA-GO composite were under irradiation (100 mW/cm^2), both charge transfer resistances decreased, and the one of TNA-GO composite decreased more than the one of TNA. The reason of this falling is likely the influence of the photocurrent produced by TNA and TNA-GO composite under irradiation conditions.

3.2.3. Photocurrent Measurements

To test the visible light photoresponsive activities of TNA and TNA-GO composite, the transient photocurrent responses measurements with 50 s visible light on-off cycles were also performed of both samples (Figure 5e and 5f). As shown in 5e, while no significant photocurrent was observed in the dark, both TNA and TNA-GO electrodes had both fairly stable photocurrent response under subsequent repetitive visible light irradiation (LED light source, $\lambda > 400 \text{ nm}$). To compare these two samples, the TNA-GO electrode showed a much better photocurrent response with the photocurrent density of $32 \mu\text{Acm}^{-2}$, which is more than two times higher than bare TNA electrode (approximately $12 \mu\text{Acm}^{-2}$). The

result can be also noticed that both TNA and TNA-GO electrodes suffered a gradually increase of photocurrent density during photocurrent testing, which should be due to the fact that a certain heat created by light irradiation can help speeding up electron movement in the system and then increasing the photocurrent as a result. To test the stability of as-prepared TNA and TNA-GO sample, the same transient photocurrent responses measurements were tested again after 2-month (Figure 5f). In this subsequent test, the photosensitivity of both TNA and TNA-GO was retained at about the same value ($\sim 31 \mu\text{Acm}^{-2}$) as 60 days ago. Moreover, compared to the 1st day sample, the photosensitivity of after-2-month day TNA-GO sample showed more consistent, unvarying, response steadiness. Dark currents of both TNA and TNA-GO were also performed as contrasted reference (Figure 5g). The dark currents of TNA and TNA-GO resulted in being both relatively small and steady (TNA $\sim 1 \mu\text{Acm}^{-2}$, TNA-GO $\sim 2 \mu\text{Acm}^{-2}$).

The mechanism of the TNA-GO enhanced photoresponse, compared to TNA, can be schemed as: 1) The band gap of TNA-GO is narrower than TNA, which gives TNA-GO a better response to visible light compared to TNA. 2) When TNA was excited by light irradiation, the electrons in the valence band of TiO_2 can jump into its conduct band and the photogenerated electron-hole pairs are then formed. Since GO has a relatively smaller band gap and a larger work function, a Schottky junction will be formed between TNA and GO. Owing to the Schottky junction, electrons in the conduct band of TNA can be transferred to GO and the holes stay in the valence band of TNA, which will certainly lead to efficient charges' separation.³¹ Thus, by having Schottky junction, the rate of recombination of the photogenerated electron-hole pairs decreases significantly, which then consequently enhances the photocurrent.

3.2.4. Hydrophilic Ability

The hydrophilic ability of TNA and TNA-GO were also tested by our self-made goniometer camera (Figure 6). Compared to TNA (Figure 5h), the contact angle of water on TNA-GO composite (Figure 5i) was greatly reduced. This difference should be attributed to the fact that the participation of GO brought some hydroxyl groups on TNA' surfaces, and these aqueous-favoring hydroxyl groups made TNA-GO sample more hydrophilic.

Figure 5 (a) UV-vis DRS and (b) relationship between $(Ahv)^{1/2}$ and $h\nu$. -Nyquist plots of the TNA and TNA-GO samples (c) without light exposure and (d) with light exposure. Transient photocurrent responses of TNA and TNA-GO with 50 s visible light on-off cycles ($\lambda > 400$ nm) tested on the (e) 1st day and (f) 61st day. (g) Dark current of TNA and TNA-GO. Photograph depicting the hydrophilic surface of (h) TNA and (i) TNA-GO.

4. Conclusion

From all the results above, highly ordered TNA sample was synthesized by utilizing anodic oxidation method. After LB assembly, GO nanosheets have been successfully fabricated on the TNA's surface. This nanostructure is uniform and is able to be formed on large-scale substrates. Though the TNA-GO layer is very thin compared to its titanium substrate, the absorption range of light has had a red-shift of 0.2 eV, which means more sunlight with longer wavelength can be used by applying this composite to photocatalyst. Meanwhile, compared to TNA, the resistance of TNA-GO composite decreased marginally, especially under an irradiation condition. The hydrophilicity of TNA-GO was greatly improved as compared to TNA. More thorough photocatalytic properties tests and characterizations of this LB assembled TNA-GO composite will be performed in further study.

Acknowledgment

This study was supported by the 2014-2015 NSF RSP EPSCoR program and 2015-2017 NSF REG & RSP EPSCoR program (the National Science Foundation under Cooperative Agreement No. 1355438), and the support from the NSF-CHE-MRI under the Award ID of 1338072. Authors also extend our acknowledgement to partial support by the U.S. Department of Agriculture (5040-12630-004-00D). Additionally, the authors also very much appreciate the help from Dr. Sanju Gupta (sanju.gupta@wku.edu) - Raman tests, Dr. John Andersland (john.andersland@wku.edu) - electron microscope training, Dr. Hanjing Tian (htian@mail.wvu.edu) - XPS tests, and Mr. Craig Clark (william.clark927@topper.wku.edu) - proofreading.

References

1. Kim, Y.-G.; Walker, J.; Samuelson, L. A.; Kumar, J., Efficient light harvesting polymers for nanocrystalline TiO₂ photovoltaic cells. *Nano Letters* **2003**, 3 (4), 523-525.
2. Tributsch, H., Reaction of excited chlorophyll molecules at electrodes and in photosynthesis*. *Photochemistry and Photobiology* **1972**, 16 (4), 261-269.
3. Fujishima, A.; Honda, K., TiO₂ photoelectrochemistry and photocatalysis. *Nature* **1972**, 238 (5358), 37-38.
4. Yamashita, H.; Nishiguchi, H.; Kamada, N.; Anpo, M.; Teraoka, Y.; Hatano, H.; Ehara, S.; Kikui, K.; Palmisano, L.; Sclafani, A., Photocatalytic reduction of CO₂ with H₂O on TiO₂ and Cu/TiO₂ catalysts. *Research on Chemical Intermediates* **1994**, 20 (8), 815-823.
5. Miao, Z.; Xu, D.; Ouyang, J.; Guo, G.; Zhao, X.; Tang, Y., Electrochemically induced sol-gel preparation of single-crystalline TiO₂ nanowires. *Nano Letters* **2002**, 2 (7), 717-720.
6. Testino, A.; Bellobono, I. R.; Buscaglia, V.; Canevali, C.; D'Arienzo, M.; Polizzi, S.; Scotti, R.; Morazzoni, F., Optimizing the photocatalytic properties of hydrothermal TiO₂ by the control of phase composition and particle morphology. A systematic approach. *Journal of the American Chemical Society* **2007**, 129 (12), 3564-3575.
7. Baik, J. M.; Kim, M. H.; Larson, C.; Chen, X.; Guo, S.; Wodtke, A. M.; Moskovits, M., High-yield TiO₂ nanowire synthesis and single nanowire field-effect transistor fabrication. *Applied Physics Letters* **2008**, 92 (24), 242111.
8. Yu, J.-G.; Yu, H.-G.; Cheng, B.; Zhao, X.-J.; Yu, J. C.; Ho, W.-K., The effect of calcination temperature on the surface microstructure and photocatalytic activity of TiO₂ thin films prepared by liquid phase deposition. *The Journal of Physical Chemistry B* **2003**, 107 (50), 13871-13879.
9. Zwilling, V.; Darque - Ceretti, E.; Boutry - Forveille, A.; David, D.; Perrin, M.-Y.; Aucouturier, M., Structure and physicochemistry of anodic oxide films on titanium and TA6V alloy. *Surface and Interface Analysis* **1999**, 27 (7), 629-637.
10. (a) Park, J. H.; Kim, S.; Bard, A. J., Novel carbon-doped TiO₂ nanotube arrays with high aspect ratios for efficient solar water splitting. *Nano letters* **2006**, 6 (1), 24-28; (b) Wang, M. Z.; Liang, F. X.; Nie, B.; Zeng, L. H.; Zheng, L. X.; Lv, P.; Yu, Y. Q.; Xie, C.; Li, Y. Y.; Luo, L. B., TiO₂ nanotube array/monolayer graphene film Schottky junction ultraviolet light photodetectors. *Particle & Particle Systems Characterization* **2013**, 30 (7), 630-636.
11. Richter, C.; Schmuttenmaer, C. A., Exciton-like trap states limit electron mobility in TiO₂ nanotubes. *Nature Nanotechnology* **2010**, 5 (11), 769-772.
12. Cozzoli, P. D.; Fanizza, E.; Comparelli, R.; Curri, M. L.; Agostiano, A.; Laub, D., Role of metal nanoparticles in TiO₂/Ag nanocomposite-based microheterogeneous photocatalysis. *The Journal of Physical Chemistry B* **2004**, 108 (28), 9623-9630.
13. Subramanian, V.; Wolf, E. E.; Kamat, P. V., Influence of metal/metal ion concentration on the photocatalytic activity of TiO₂-Au composite nanoparticles. *Langmuir* **2003**, 19 (2), 469-474.
14. Liao, D.; Badour, C.; Liao, B., Preparation of nanosized TiO₂/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange. *Journal of Photochemistry and Photobiology A: Chemistry* **2008**, 194 (1), 11-19.
15. Lee, C.; Wei, X.; Kysar, J. W.; Hone, J., Measurement of the elastic properties and intrinsic strength of monolayer graphene. *science* **2008**, 321 (5887), 385-388.
16. Sun, Z.; Chang, H., Graphene and graphene-like two-dimensional materials in photodetection: mechanisms and methodology. *ACS nano* **2014**, 8 (5), 4133-4156.
17. Park, S.; Ruoff, R. S., Chemical methods for the production of graphenes. *Nature nanotechnology* **2009**, 4 (4), 217-224.
18. (a) Pan, X.; Zhao, Y.; Liu, S.; Korzeniewski, C. L.; Wang, S.; Fan, Z., Comparing graphene-TiO₂ nanowire and graphene-TiO₂ nanoparticle composite photocatalysts. *ACS applied materials & interfaces* **2012**, 4 (8), 3944-3950; (b) Wang, P.; Wang, J.; Ming, T.; Wang, X.; Yu, H.; Yu, J.; Wang, Y.; Lei, M., Dye-sensitization-induced visible-light reduction of graphene oxide for the enhanced TiO₂

photocatalytic performance. *ACS applied materials & interfaces* **2013**, 5 (8), 2924-2929; (c) Pan, D.; Jiao, J.; Li, Z.; Guo, Y.; Feng, C.; Liu, Y.; Wang, L.; Wu, M., Efficient Separation of Electron-hole Pairs in Graphene Quantum Dots by TiO₂ Heterojunctions for Dye Degradation. *ACS Sustainable Chemistry & Engineering* **2015**; (d) Huang, Q.; Tian, S.; Zeng, D.; Wang, X.; Song, W.; Li, Y.; Xiao, W.; Xie, C., Enhanced photocatalytic activity of chemically bonded TiO₂/graphene composites based on the effective interfacial charge transfer through the C–Ti bond. *ACS Catalysis* **2013**, 3 (7), 1477-1485; (e) Jiang, Y.; Wang, W.-N.; Biswas, P.; Fortner, J. D., Facile aerosol synthesis and characterization of ternary crumpled graphene–TiO₂–magnetite nanocomposites for advanced water treatment. *ACS applied materials & interfaces* **2014**, 6 (14), 11766-11774; (f) Zhang, H.; Xu, P.; Du, G.; Chen, Z.; Oh, K.; Pan, D.; Jiao, Z., A facile one-step synthesis of TiO₂/graphene composites for photodegradation of methyl orange. *Nano Research* **2011**, 4 (3), 274-283; (g) Sher Shah, M. S. A.; Park, A. R.; Zhang, K.; Park, J. H.; Yoo, P. J., Green synthesis of biphasic TiO₂–reduced graphene oxide nanocomposites with highly enhanced photocatalytic activity. *ACS applied materials & interfaces* **2012**, 4 (8), 3893-3901; (h) Perera, S. D.; Mariano, R. G.; Vu, K.; Nour, N.; Seitz, O.; Chabal, Y.; Balkus Jr, K. J., Hydrothermal synthesis of graphene-TiO₂ nanotube composites with enhanced photocatalytic activity. *Acs Catalysis* **2012**, 2 (6), 949-956; (i) Ramadoss, A.; Kim, S. J., Improved activity of a graphene–TiO₂ hybrid electrode in an electrochemical supercapacitor. *Carbon* **2013**, 63, 434-445; (j) Fan, W.; Lai, Q.; Zhang, Q.; Wang, Y., Nanocomposites of TiO₂ and reduced graphene oxide as efficient photocatalysts for hydrogen evolution. *The Journal of Physical Chemistry C* **2011**, 115 (21), 10694-10701; (k) Long, M.; Qin, Y.; Chen, C.; Guo, X.; Tan, B.; Cai, W., Origin of visible light photoactivity of reduced graphene oxide/TiO₂ by in situ hydrothermal growth of undergrown TiO₂ with graphene oxide. *The Journal of Physical Chemistry C* **2013**, 117 (32), 16734-16741; (l) Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J., P25-graphene composite as a high performance photocatalyst. *ACS nano* **2009**, 4 (1), 380-386; (m) Zhu, S.; Song, Y.; Zhao, X.; Shao, J.; Zhang, J.; Yang, B., The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective. *Nano Research* **2015**, 8 (2), 355-381; (n) Ong, W.-J.; Tan, L.-L.; Chai, S.-P.; Yong, S.-T.; Mohamed, A. R., Self-assembly of nitrogen-doped TiO₂ with exposed {001} facets on a graphene scaffold as photo-active hybrid nanostructures for reduction of carbon dioxide to methane. *Nano Research* **2014**, 7 (10), 1528-1547; (o) Zhang, Y.; Tang, Z.-R.; Fu, X.; Xu, Y.-J., TiO₂– graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: is TiO₂– graphene truly different from other TiO₂– carbon composite materials? *ACS nano* **2010**, 4 (12), 7303-7314; (p) Qian, W.; Greaney, P. A.; Fowler, S.; Chiu, S.-K.; Goforth, A. M.; Jiao, J., Low-temperature nitrogen doping in ammonia solution for production of N-doped TiO₂-hybridized graphene as a highly efficient photocatalyst for water treatment. *ACS Sustainable Chemistry & Engineering* **2014**, 2 (7), 1802-1810.

19. Jiang, G.; Lin, Z.; Chen, C.; Zhu, L.; Chang, Q.; Wang, N.; Wei, W.; Tang, H., TiO₂ nanoparticles assembled on graphene oxide nanosheets with high photocatalytic activity for removal of pollutants. *Carbon* **2011**, 49 (8), 2693-2701.

20. Yang, Y.; Liu, E.; Fan, J.; Hu, X.; Hou, W.; Wu, F.; Ma, Y., Green and facile microwave-assisted synthesis of TiO₂/graphene nanocomposite and their photocatalytic activity for methylene blue degradation. *Russian Journal of Physical Chemistry A* **2014**, 88 (3), 478-483.

21. Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M., Improved synthesis of graphene oxide. *ACS nano* **2010**, 4 (8), 4806-4814.

22. (a) Cote, L. J.; Kim, F.; Huang, J., Langmuir– Blodgett assembly of graphite oxide single layers. *Journal of the American Chemical Society* **2008**, 131 (3), 1043-1049; (b) Zheng, Q.; Ip, W. H.; Lin, X.; Yousefi, N.; Yeung, K. K.; Li, Z.; Kim, J.-K., Transparent conductive films consisting of ultralarge graphene sheets produced by Langmuir–Blodgett assembly. *Acs Nano* **2011**, 5 (7), 6039-6051.

23. Campion, A.; Ivanecky III, J.; Child, C.; Foster, M., On the mechanism of chemical enhancement in surface-enhanced Raman scattering. *Journal of the American Chemical Society* **1995**, *117* (47), 11807-11808.
24. Yang, S.; Lin, Y.; Song, X.; Zhang, P.; Gao, L., Covalently Coupled Ultrafine H-TiO₂ Nanocrystals/Nitrogen-Doped Graphene Hybrid Materials for High-Performance Supercapacitor. *ACS applied materials & interfaces* **2015**, *7* (32), 17884-17892.
25. (a) Akhavan, O.; Abdollahad, M.; Esfandiar, A.; Mohatashamifar, M., Photodegradation of graphene oxide sheets by TiO₂ nanoparticles after a photocatalytic reduction. *The Journal of Physical Chemistry C* **2010**, *114* (30), 12955-12959; (b) Bell, N. J.; Ng, Y. H.; Du, A.; Coster, H.; Smith, S. C.; Amal, R., Understanding the enhancement in photoelectrochemical properties of photocatalytically prepared TiO₂-reduced graphene oxide composite. *The Journal of Physical Chemistry C* **2011**, *115* (13), 6004-6009; (c) Xiao, F.-X., Construction of highly ordered ZnO-TiO₂ nanotube arrays (ZnO/TNTs) heterostructure for photocatalytic application. *ACS applied materials & interfaces* **2012**, *4* (12), 7055-7063.
26. Hsu, H.-C.; Shown, I.; Wei, H.-Y.; Chang, Y.-C.; Du, H.-Y.; Lin, Y.-G.; Tseng, C.-A.; Wang, C.-H.; Chen, L.-C.; Lin, Y.-C., Graphene oxide as a promising photocatalyst for CO₂ to methanol conversion. *Nanoscale* **2013**, *5* (1), 262-268.
27. Ha, H. D.; Jang, M.-H.; Liu, F.; Cho, Y.-H.; Seo, T. S., Upconversion photoluminescent metal ion sensors via two photon absorption in graphene oxide quantum dots. *Carbon* **2015**, *81*, 367-375.
28. (a) Liu, F.; Jang, M. H.; Ha, H. D.; Kim, J. H.; Cho, Y. H.; Seo, T. S., Facile synthetic method for pristine graphene quantum dots and graphene oxide quantum dots: origin of blue and green luminescence. *Advanced Materials* **2013**, *25* (27), 3657-3662; (b) Zhuo, S.; Shao, M.; Lee, S.-T., Upconversion and downconversion fluorescent graphene quantum dots: ultrasonic preparation and photocatalysis. *ACS nano* **2012**, *6* (2), 1059-1064; (c) Hu, Y.; Yang, J.; Tian, J.; Jia, L.; Yu, J.-S., Oxygen-driven, high-efficiency production of nitrogen-doped carbon dots from alkanolamines and their application for two-photon cellular imaging. *RSC Advances* **2015**, *5* (20), 15366-15373; (d) Gan, Z.; Wu, X.; Zhou, G.; Shen, J.; Chu, P. K., Is There Real Upconversion Photoluminescence from Graphene Quantum Dots? *Advanced Optical Materials* **2013**, *1* (8), 554-558.
29. (a) Zhu, S.; Zhang, J.; Liu, X.; Li, B.; Wang, X.; Tang, S.; Meng, Q.; Li, Y.; Shi, C.; Hu, R., Graphene quantum dots with controllable surface oxidation, tunable fluorescence and up-conversion emission. *Rsc Advances* **2012**, *2* (7), 2717-2720; (b) Zheng, X. T.; Ananthanarayanan, A.; Luo, K. Q.; Chen, P., Glowing graphene quantum dots and carbon dots: properties, syntheses, and biological applications. *Small* **2015**, *11* (14), 1620-1636.
30. (a) Loh, K. P.; Bao, Q.; Eda, G.; Chhowalla, M., Graphene oxide as a chemically tunable platform for optical applications. *Nature chemistry* **2010**, *2* (12), 1015-1024; (b) Gómez-Navarro, C.; Weitz, R. T.; Bittner, A. M.; Scolari, M.; Mews, A.; Burghard, M.; Kern, K., Electronic transport properties of individual chemically reduced graphene oxide sheets. *Nano letters* **2007**, *7* (11), 3499-3503; (c) Kaiser, A. B.; Gómez-Navarro, C.; Sundaram, R. S.; Burghard, M.; Kern, K., Electrical conduction mechanism in chemically derived graphene monolayers. *Nano letters* **2009**, *9* (5), 1787-1792.
31. Ma, Y.; Wang, X.; Jia, Y.; Chen, X.; Han, H.; Li, C., Titanium dioxide-based nanomaterials for photocatalytic fuel generations. *Chemical reviews* **2014**, *114* (19), 9987-10043.