

Research Article

Photoelectrochemical Activity of Graphene Supported Titanium Dioxide

Rodrigo A. Segura,¹ Fernanda Olivares,¹ Jeronimo Maze,²
Patricio Häberle,³ and Ricardo Henríquez³

¹Instituto de Química y Bioquímica, Facultad de Ciencias, Universidad de Valparaíso, Av. Gran Bretaña 1111, Valparaíso, Chile

²Instituto de Física, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Macul, Santiago, Chile

³Departamento de Física, Universidad Técnica Federico Santa María, Avenida España 1680, Valparaíso, Chile

Correspondence should be addressed to Rodrigo A. Segura; rodrigo.segura@uv.cl

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Thin TiO₂ layers grown over few-layers graphene were prepared in order to evaluate the photoinduced chemical response of this composite. Graphene was grown over copper foils by decomposition of acetylene in a standard chemical vapor deposition apparatus. Graphene was subsequently transferred to a silicon substrate, on which the titanium dioxide was grown to form a TiO₂/FLG/SiO₂/Si composite. The formation of each layered material was verified by Raman spectroscopy and the morphology was characterized by scanning electron microscopy. The photoelectrochemical evaluation of the resulting composite, using it as a photoanode, was accomplished with a potentiostat, a solar simulator, and a three-electrode configuration. The electrochemical response indicates that the new composite preserves the average photoactive properties of the base material and at the same time shows a singular transient response where explicit benefits seem to be derived from the FLG/TiO₂ combination.

1. Introduction

The basis of photocatalytic systems, supported mainly by semiconductor materials, is that they can promote certain chemical reactions in the presence of light without being consumed in the process [1]. Probably the most noteworthy example in this field is the generation of molecular hydrogen (H₂) from the dissociation of water molecules. Some studies indicate [2] that this mechanism could be the best solution to the problems arising from the use of fossil fuels as energy sources. Although it is now possible to obtain H₂ through electrolysis [3], this process is highly energy consuming and hence costly to produce. An alternative and very attractive method is to obtain H₂ by the photocatalytic splitting of water using solar radiation to reduce the energy requirements. H₂ obtained through this process may then be used as a clean and efficient source of energy for a variety of applications.

Water splitting, using electromagnetic radiation and semiconductors as catalysts, has been studied for at least four decades [4, 5]. Among the many well-known semiconductors

used in this field, titanium dioxide (TiO₂) is one of the most promising catalysts for the production of H₂ from the water photoelectrolysis due to its high chemical stability, low toxicity, and relatively low production cost. It does however exhibit a rapid recombination of photogenerated charge carriers, which decreases substantially the quantum efficiency of photoinduced processes. Some strategies used to improve the photocatalytic performance consist of doping TiO₂ with transition metal elements such as silver (Ag) [6] or nonmetallic elements like carbon (C), nitrogen (N), and also sulfur (S) [7]. Another option to improve the efficiency of the photocatalytic process or even diminish production costs has recently been proposed and consists of locating TiO₂ nanoparticles in close contact with carbon nanostructured materials to form a hybrid nanostructure, in which the photocatalytic properties of TiO₂ are combined with complementary properties of the host nanostructure [8–10].

Graphene is an allotrope of carbon, whose unusual transport properties make it a very attractive material for the development of new technologies, particularly when the large

carrier mobilities represent a benefit. Graphene has indeed high electron mobility at room temperature, high elasticity, and resistance, among other singular physical properties [11]. With the purpose of examining new materials to be used in the photoelectrolysis of water, in this paper, we examine the preparation method of a TiO_2 /graphene composite and evaluate its photoelectrochemical activity considering graphene as the conducting material and TiO_2 as the photoactive component.

2. Materials and Methods

2.1. Synthesis and Transfer of Graphene. Graphene was synthesized by atmospheric pressure chemical vapor deposition (CVD) at 1000°C using acetylene as carbon source [12]. High purity copper foils were used as substrates ($1.5 \times 1.5 \text{ cm}^2$, $25 \mu\text{m}$, purity > 99.99% MTI). In the CVD furnace, the Cu substrates were heated at a rate of $20^\circ\text{C}/\text{min}$ in a flow of an argon/hydrogen mixture (100 sccm each) up to 1000°C . This temperature was maintained for 20 min in order to remove any residual oxide and improve the nucleation density [13]. After this process, the flow of argon and hydrogen was set to 500 and 5 sccm, respectively, and acetylene was admitted into the reactor at a rate of 2 sccm during 1 min. Subsequently, the furnace was cooled down to room temperature at a rate of $20^\circ\text{C}/\text{min}$ in an Ar/H_2 atmosphere.

Graphene was then transferred onto silicon substrates following Suk's recipe [14]. A poly-methyl methacrylate (PMMA) layer was deposited over the graphene/Cu substrate by spin-coating; $100 \mu\text{L}$ of a PMMA/chlorobenzene (20 mg/mL) dissolution was spread over the substrate (10 s/500 rpm + 50 s/1500 rpm). The PMMA layer was cured at 120°C for 5 minutes. The PMMA/graphene/Cu material was then floated on a 1.0 M $\text{Fe}(\text{NO}_3)_3$ /water dissolution in order to dissolve the copper layer. The remaining PMMA/graphene stamp was thoroughly washed in deionized water and carefully placed onto clean silicon chips for the photoelectrode fabrication and SEM characterization [Si(100), n-type, P-doped] or $\text{SiO}_2/\text{Si}(100)$ for Raman characterization ($\sim 100 \text{ nm}$ thermal oxide grown by Si dry oxidation at 1100°C for 36 min). The PMMA/graphene/substrate was then dried in vacuum and subsequently heated up to 180°C for 30 min to improve the graphene adhesion. PMMA was later dissolved and washed away with acetone and 2-propanol, respectively, to obtain a graphene/Si chip.

2.2. Synthesis of TiO_2 . TiO_2 layers were deposited on bare Si and on graphene covered Si substrates. Titanium (IV) tetraisopropoxide (TTIP) was used as a precursor, which was evaporated in a two-zone CVD tube furnace [15]. The TTIP introduced to the first zone of the furnace was evaporated at a temperature of 130°C in a low pressure environment ($\sim 3.5 \text{ torr}$). The collecting substrates were located in the second heating zone at 500°C . The characteristic time of synthesis was 15 min. As expected, the availability of TiO_2 obtained through decomposition of TTIP is inhomogeneous along the reactor, since the density of material is gradually rarified by

collection on the furnace walls along the second zone. Hence, the amount of material deposited on the substrates depends on the relative position of the substrates with respect to the separation of the two heating zones. We have used a fixed distance (6 cm) to prepare the photoelectrode materials.

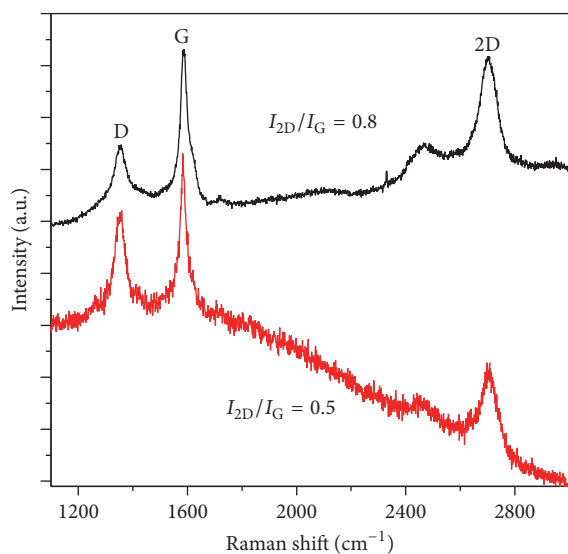
2.3. Characterization. The morphological and structural characterization was made by using several techniques. Samples and substrates characterization through Raman spectroscopy was performed using a Renishaw in-Via, with a 532 nm laser. Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) characterization was performed in a Thermo-Nicolet ISI0 apparatus. Scanning electron microscopy (SEM) characterization was done using a Carl-Zeiss, EVO MA10.

The photoelectrochemical response was evaluated by measuring linear sweep voltammetry and chronoamperometry. A 3-electrode arrangement and a potentiostat (Gamry Interface 1000) were used to register the response of samples when they were illuminated with a 300 W solar simulator (Sciencetech SF300A with an AM1.5 filter). Standard Ag/AgCl electrodes and a platinum wire counter electrode were used to characterize the photoanodes (working electrode), with the samples prepared as described in Section 2.2. The measurements were done using KCl 0.1 M as electrolyte.

3. Results and Discussion

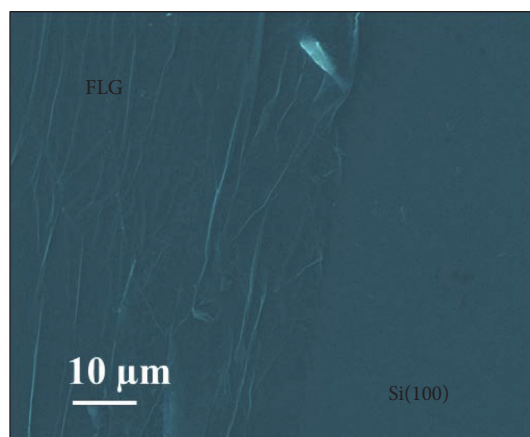
Figure 1(a) shows a typical Raman spectrum of a sample prepared by the decomposition of acetylene on copper, as previously described. The red curve in Figure 1 (lower trace) corresponds to the sample attached to the copper substrate, while the black curve corresponds to the same sample after being transferred onto a thermal silicon dioxide substrate. The characteristic ratio of intensities I_{2D}/I_G (after transfer) was ~ 0.8 indicating that the synthesized material corresponds to few-layers graphene (FLG). In agreement with the criteria presented by Song et al. [16] and Hao et al. [17], our material corresponds to 2 to 3 layers of graphene. Figure 1(b) shows a SEM image of a sample transferred onto a monocrystalline silicon substrate. The image shows the wrinkled FLG in the left side and the flat surface of silicon in the right side.

The TiO_2 layer was deposited on graphene transferred onto silicon to form a $\text{TiO}_2/\text{FLG}/\text{Si}$ composite. For comparative purposes TiO_2 was also deposited over bare silicon to form a binary TiO_2/Si composite. As mentioned in the experimental section, the deposition rate of TiO_2 depends on the position inside the furnace. We have chosen distances between 5 and 6 cm from the furnace zone boundary, where evident accumulation of material was observed and the samples have a uniform optical appearance. In order to verify the presence of TiO_2 we have performed ATR-FTIR and Raman spectroscopy. Figure 2(a) shows the formation of TiO_2 that was identified by the infrared absorption band close to 850 cm^{-1} . This frequency corresponds to a characteristic vibrational mode, related to the bending of the Ti-O-Ti bond [18]. Figure 2(b) shows the Raman spectra of TiO_2/Si and



— FLG/SiO₂
— FLG/Cu

(a)

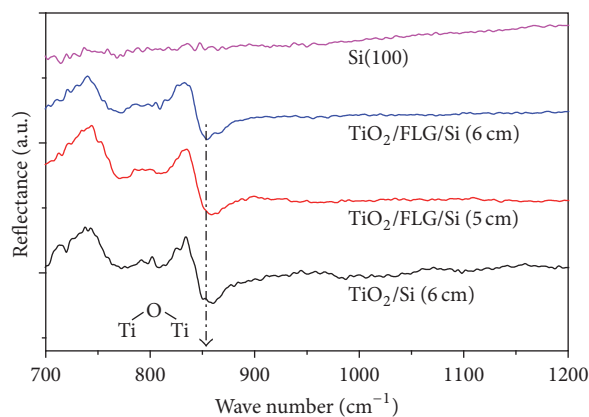


(b)

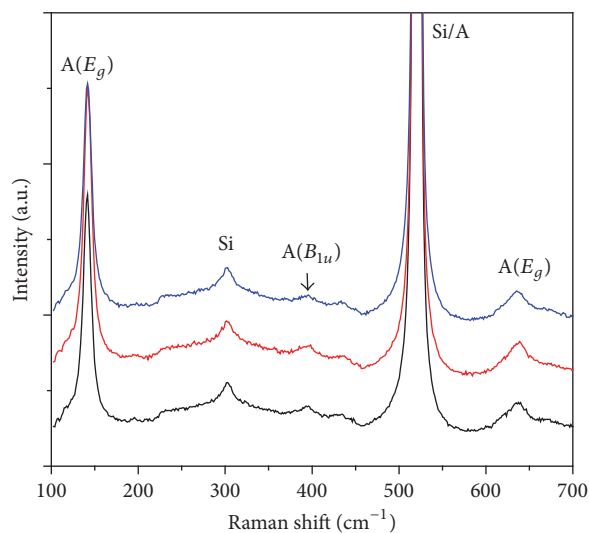
FIGURE 1: (a) Raman spectra of graphene on copper (FLG/Cu) and graphene transferred to silicon dioxide (FLG/SiO₂) and (b) SEM image of graphene transferred to Si(100).

TiO₂/FLG/Si samples in the low frequency range. The Raman signals revealed that the TiO₂ is mainly in the anatase (A) phase as indicated by the characteristic peaks at 145 cm⁻¹, 396 cm⁻¹, and 636 cm⁻¹ associated with *E_g*, *B_{1u}*, and *E_g* active modes, respectively [19]. In the TiO₂/FLG/Si samples it is possible to observe the Raman signals corresponding to graphene with a similar *I_{2D}/I_G* ratio but with a higher *D* band intensity; this is due probably to the introduction of edge defects in the FLG during the TiO₂ growth process.

Figures 3(b) and 3(c) show SEM images of the surface of TiO₂/Si and TiO₂/FLG/Si, respectively, prepared under identical growth conditions. The TiO₂ grown over bare silicon showed a granulated surface, whereas those on FLG/Si exhibited a similar morphology but with larger grain sizes.



(a)



— TiO₂/Si, 6 cm
— TiO₂/FLG/Si, 5 cm
— TiO₂/FLG/Si, 6 cm

(b)

FIGURE 2: ATR-FTIR (a) and Raman (b) spectra for TiO₂ samples synthesized on Si and FLG/Si substrates. In both figures the TiO₂ features are more intense in the sample closer to the precursor source.

This difference could be explained by the stronger interaction of TiO₂ with silicon compared to FLG, thus resulting in a higher surface density of nucleation sites and as a consequence a larger density of TiO₂ grains. Both samples exhibited a golden color (Figure 3(a)) due to the TiO₂ film, thus indicating a similar thickness. This color corresponds to a TiO₂ layer with a thickness in the range of 20–25 nm [20].

Photoelectrochemical measurements were performed to evaluate the response of the individual materials and the hybrid system. The linear sweep voltammetry of TiO₂ (6 cm)/Si sample showed the behavior expected for a semiconductor [21] (figure not shown here). The current density increased almost linearly as the voltage is raised, only under illumination, reaching a value close to 80 μA/cm², for

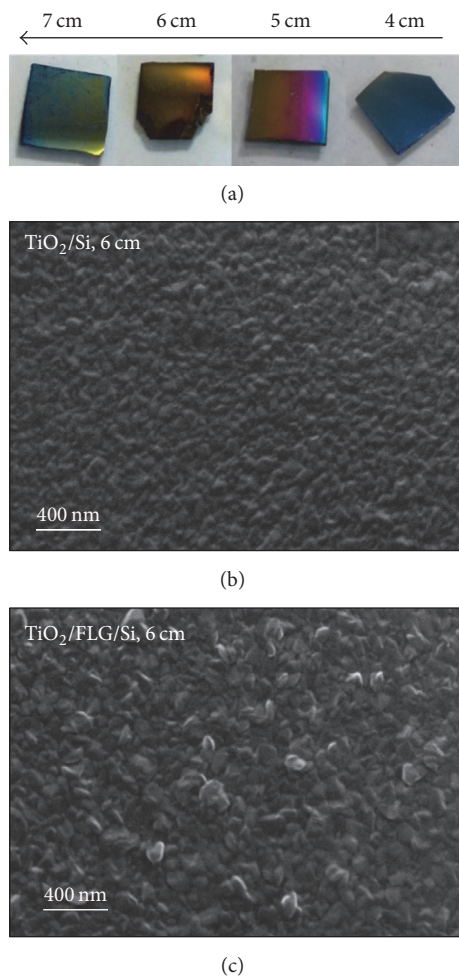


FIGURE 3: (a) Optical image of typical TiO_2 samples placed at different distances from the separation between the two heating zones in the furnace. For the study we considered just the samples between 5 and 6 cm, with a golden appearance. (b) and (c) SEM image for TiO_2/Si and $\text{TiO}_2/\text{FLG}/\text{Si}$, respectively, both synthesized 6 cm away from the middle of the furnace.

a potential difference of 1.0 V, while in darkness it showed no significant response. On the other hand, FLG supported on silicon presented a much higher current response, which also increased almost linearly, reaching a value close to $3 \text{ mA}/\text{cm}^2$ for an applied voltage of 1.0 V. No significant differences were observed for the FLG/Si materials, between light and dark conditions, in either the general behavior or the magnitude of the current in the linear sweep voltammograms.

Figure 4(a) shows a linear sweep voltammetry for the $\text{TiO}_2/\text{FLG}/\text{Si}$ composite. The current was measured under both dark and illumination conditions. The optical response is roughly similar to that of FLG/Si. In order to observe the contribution of TiO_2 in the composed material, we performed chronoamperometric measurements, alternating dark and light cycles for different constant voltages. Figure 4(b) shows the photocurrent density for TiO_2/Si for different voltages. The current density follows the cyclic nature of the light intensity, with almost no response in the

dark and a current density that scales with the applied voltage under illumination. Figure 4(c) shows the current response of the $\text{TiO}_2/\text{FLG}/\text{Si}$ composite for different voltages. In order to compare with the TiO_2/Si sample we have subtracted the FLG background contribution and normalized it to the electrode area. Figure 4(d) shows the photocurrent for the $\text{TiO}_2/\text{FLG}/\text{Si}$, after subtracting the graphene background contribution. The average value displayed during illumination is quite similar in magnitude to that observed in TiO_2/Si . Nevertheless spike-like features were present at the photocurrent rise, upon switching on the light, followed by a rapid exponential decay. At the end of the cycle a cathodic current overshoot occurred when the light was switched off.

This latter phenomenon has been reported for TiO_2 by several authors as a typical fingerprint of intense surface charge recombination processes [22–24]. Its occurrence requires the existence of electronic surface states, above the valence band edge, which allows the production of extra photoinduced charge carriers during irradiation, even with wavelengths larger than that of the TiO_2 band gap. These electronic states can also act as recombination centers, inducing a rapid photocurrent decay. When the light is switched off, the unoccupied states remain active as recombination centers, inducing a characteristic cathodic overshoot of current as displayed in our data in Figure 4. What is the exact origin of this effect in the $\text{TiO}_2/\text{FLG}/\text{Si}$ system remains to be explored: if it is really a surface effect at the TiO_2/FLG interface or a bulk characteristic of the complete TiO_2 film grown on FLG. If for a certain application a transient operation mode is a requirement and the “on” cycle is kept short with respect to the time constant for current decay, the use of the $\text{TiO}_2/\text{FLG}/\text{Si}$ composite is indeed more efficient than the TiO_2/Si . In this case the use of the new composite becomes an advantageous option.

The results presented here indicate that the photoelectrochemical behavior is similar to the combined effect of both materials, with no synergistic effects in terms of the average photocurrent. This property opens the possibility of using the layered composite without a conducting substrate, for example, a low cost support, such as glass, with an electrode design that removes the charge directly from the graphene. On the other hand, this new layered material presents an interesting transient photoresponse where explicit benefits seem to be derived from the FLG/ TiO_2 combination.

4. Conclusions

The experimental evidence shows that TiO_2 films grown on FLG/Si present similar morphological characteristics as those grown directly on Si. FTIR and Raman spectroscopy, together with SEM and optical images, show no significant changes between both systems. The average photoelectrochemical response of $\text{TiO}_2/\text{FLG}/\text{Si}$ to a sun simulator showed the expected behavior based on the combination of the base materials, which is an advantage for pursuing further uses of this particular composite. A singular effect is nonetheless detected in the transient response of this composite, in which the interaction TiO_2/FLG seems to play a significant role.

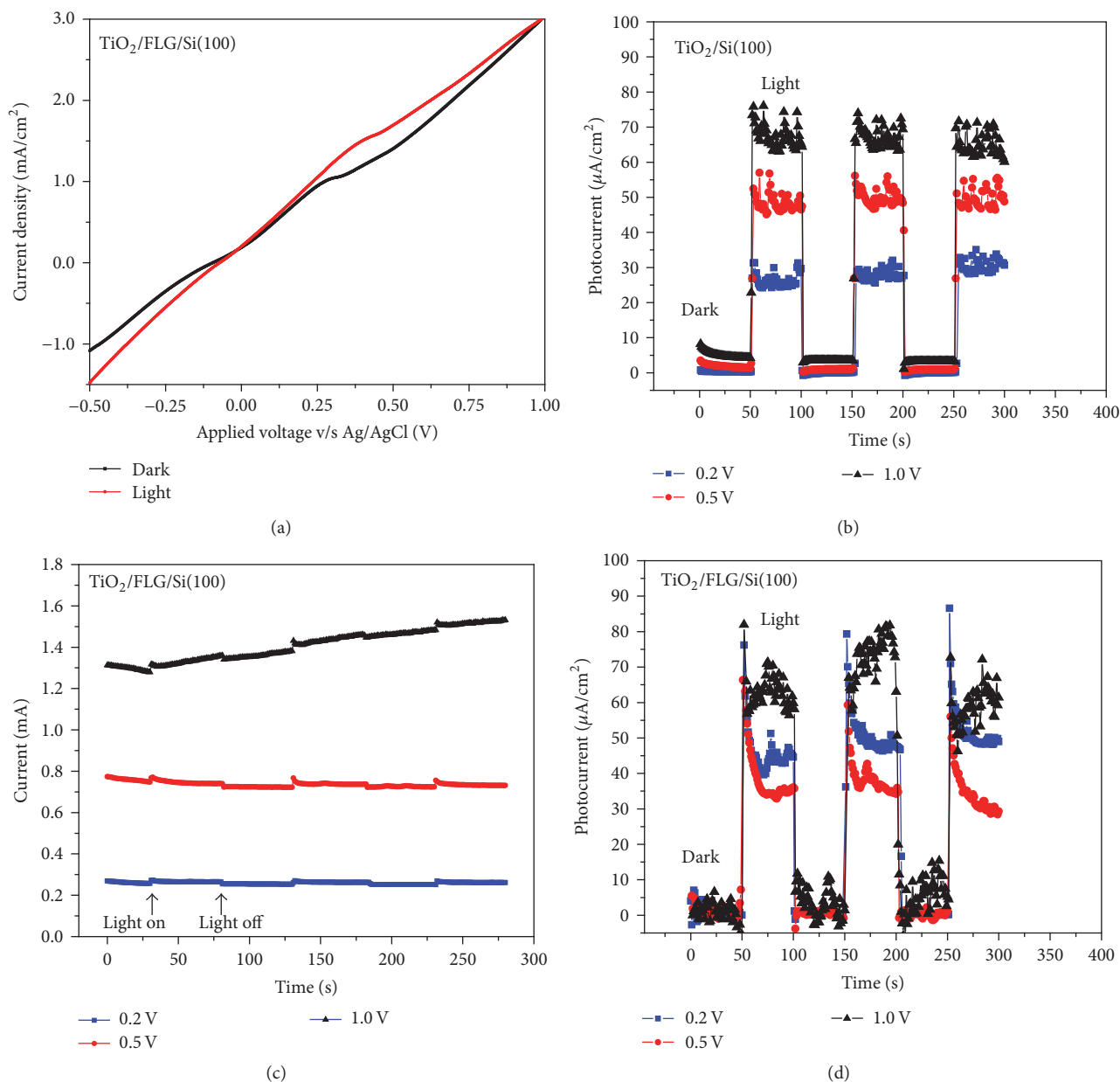


FIGURE 4: (a) Linear sweep voltammetry for $\text{TiO}_2/\text{FLG}/\text{Si}$ system, (b) photocurrent density plots versus time, at different potentials, and alternating cycles of light and darkness for TiO_2/Si , (c) chronoamperometry for the $\text{TiO}_2/\text{FLG}/\text{Si}$ system at different voltages, and (d) photocurrent density plots for $\text{TiO}_2/\text{FLG}/\text{Si}$ sample.

Future research is needed to optimize this system such as the direct contact of graphene with the external circuit for measuring their efficiency for H_2 generation.

Competing Interests

The authors declare that there are no competing interests related to this paper.

Acknowledgments

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References

- [1] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [2] T. Kawai and T. Sakata, "Hydrogen evolution from water using solid carbon and light energy," *Nature*, vol. 282, no. 5736, pp. 283–284, 1979.
- [3] P. Millet and S. Grigoriev, "Water electrolysis technologies," in *Renewable Hydrogen Technologies*, L. M. Gandia, G. Arzamendi, and P. M. Dieguez, Eds., pp. 19–41, Renewable Hydrogen Technologies, Amsterdam, The Netherlands, 2013.

- [4] A. Fujishima, X. Zhang, and D. A. Tryk, "Heterogeneous photocatalysis: from water photolysis to applications in environmental cleanup," *International Journal of Hydrogen Energy*, vol. 32, no. 14, pp. 2664–2672, 2007.
- [5] A. A. Ismail and D. W. Bahnemann, "Photochemical splitting of water for hydrogen production by photocatalysis: a review," *Solar Energy Materials and Solar Cells*, vol. 128, pp. 85–101, 2014.
- [6] Y. Yang, E. Liu, H. Dai et al., "Photocatalytic activity of Ag-TiO₂-graphene ternary nanocomposites and application in hydrogen evolution by water splitting," *International Journal of Hydrogen Energy*, vol. 39, no. 15, pp. 7664–7671, 2014.
- [7] B. Zhou, M. Schulz, H. Y. Lin, S. I. Shah, J. Qu, and C. P. Huang, "Photoelectrochemical generation of hydrogen over carbon-doped TiO₂ photoanode," *Applied Catalysis B: Environmental*, vol. 92, no. 1-2, pp. 41–49, 2009.
- [8] E. Lee, J.-Y. Hong, H. Kang, and J. Jang, "Synthesis of TiO₂ nanorod-decorated graphene sheets and their highly efficient photocatalytic activities under visible-light irradiation," *Journal of Hazardous Materials*, vol. 219–220, pp. 13–18, 2012.
- [9] J. Liu, Y. Niu, X. He, J. Qi, and X. Li, "Photocatalytic Reduction of CO₂ Using TiO₂-Graphene Nanocomposites," *Journal of Nanomaterials*, vol. 2016, Article ID 6012896, 5 pages, 2016.
- [10] Y. Yu, J. C. Yu, J.-G. Yu et al., "Enhancement of photocatalytic activity of mesoporous TiO₂ by using carbon nanotubes," *Applied Catalysis A: General*, vol. 289, no. 2, pp. 186–196, 2005.
- [11] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, "A roadmap for graphene," *Nature*, vol. 490, no. 7419, pp. 192–200, 2012.
- [12] M. Qi, Z. Ren, Y. Jiao et al., "Hydrogen kinetics on scalable graphene growth by atmospheric pressure chemical vapor deposition with acetylene," *The Journal of Physical Chemistry C*, vol. 117, no. 27, pp. 14348–14353, 2013.
- [13] Y. Hao, M. S. Bharathi, L. Wang et al., "The role of surface oxygen in the growth of large single-crystal graphene on copper," *Science*, vol. 342, no. 6159, pp. 720–723, 2013.
- [14] J. W. Suk, A. Kitt, C. W. Magnuson et al., "Transfer of CVD-grown monolayer graphene onto arbitrary substrates," *ACS Nano*, vol. 5, no. 9, pp. 6916–6924, 2011.
- [15] S. Hevia, P. Homm, A. Cortes et al., "Selective growth of palladium and titanium dioxide nanostructures inside carbon nanotube membranes," *Nanoscale Research Letters*, vol. 7, no. 1, pp. 342–349, 2014.
- [16] W. Song, C. Jeon, S. Y. Kim et al., "Two selective growth modes for graphene on a Cu substrate using thermal chemical vapor deposition," *Carbon*, vol. 68, pp. 87–94, 2014.
- [17] Y. Hao, Y. Wang, L. Wang et al., "Probing layer number and stacking order of few-layer graphene by Raman spectroscopy," *Small*, vol. 6, no. 2, pp. 195–200, 2010.
- [18] Ratnawati, J. Gunlazuardi, E. L. Dewi, and Slamet, "Effect of NaBF₄ addition on the anodic synthesis of TiO₂ nanotube arrays photocatalyst for production of hydrogen from glycerol-water solution," *International Journal of Hydrogen Energy*, vol. 39, no. 30, pp. 16927–16935, 2014.
- [19] H. C. Choi, Y. M. Jung, and S. B. Kim, "Characterization of raman spectra of size-selected TiO₂ nanoparticles by two-dimensional correlation spectroscopy," *Bulletin of the Korean Chemical Society*, vol. 25, no. 3, pp. 426–428, 2004.
- [20] M. L. Vera, M. Á. Alterach, M. R. Rosenberger, D. G. Lamas, C. E. Schvezov, and A. E. Ares, "Characterization of TiO₂ nanofilms obtained by sol-gel and anodic oxidation," *Nanomaterials and Nanotechnology*, vol. 4, no. 1, pp. 1–11, 2014.
- [21] F. A. Jumeri, H. N. Lim, Z. Zainal, N. M. Huang, and A. Pandikumar, "Titanium dioxide-reduced graphene oxide thin film for photoelectrochemical water splitting," *Ceramics International*, vol. 40, no. 9, pp. 15159–15165, 2014.
- [22] R. Beranek, J. M. Macak, M. Gärtner, K. Meyer, and P. Schmuki, "Enhanced visible light photocurrent generation at surface-modified TiO₂ nanotubes," *Electrochimica Acta*, vol. 54, no. 9, pp. 2640–2646, 2009.
- [23] R. Nakamura, T. Tanaka, and Y. Nakato, "Mechanism for visible light responses in anodic photocurrents at N-doped TiO₂ film electrodes," *Journal of Physical Chemistry B*, vol. 108, no. 30, pp. 10617–10620, 2004.
- [24] Y. Dai, Y. Sun, J. Yao et al., "Graphene-wrapped TiO₂ nanofibers with effective interfacial coupling as ultrafast electron transfer bridges in novel photoanodes," *Journal of Materials Chemistry A*, vol. 2, no. 4, pp. 1060–1067, 2014.

