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Improving the Photo-cathodic Properties of TiO_2 Nano-structure with Graphdiynes

Vivek Ramakrishnan,[a,‡] Hyun Kim,[a] and Beelyong Yang[a,*]

1. Materials and Methods

1.1 Chemical Reagents.

Titanium dioxide precursors were purchased from Sigma Aldrich. Graphdiyne nanoscale films were grown on the surface of copper foils via a cross-coupling reaction using hexaethynylbenzene precursors. All other reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with Milli-Q water.

2. Instrumentation

Surface morphology study was carried out with Field Emission Scanning Electron Microscopy (FESEM, JEOL Model: JSM-6701F) Crystal structure analysis were carried out with X-ray Powder Diffraction (XRD, Rigaku, SWXD, D-MAX/2500-PC). Raman spectroscopic analyses were accomplished with a HORIBA XploRA PLUS spectrometer. High resolution Transmission electron microscopy (HR-TEM), analysis were executed by JEOL Model: JEM-3010 HR. Photo-electrochemical measurements were carried out using a potentiostat (AMT VERSASTAT 3, Princeton Applied Research) with a three electrode configuration consisting of a platinum (Pt) mesh counter electrode and a saturated Ag/AgCl reference electrode in 0.1 M Na_2SO_4 (pH ~ 7) electrolyte. A working electrode with a 1 cm^2 area was illuminated using a 1 kW xenon lamp (Newport) with its infrared wavelengths filtered out by water, and wavelengths below 420 nm removed by an optical filter, enabling measurements under visible light. The light irradiance, measured by a thermopile detector, was 100 mW/cm^2.

3 Experimental

3.1 Materials Synthesis

3.1.1 Graphdiyne (GD) was synthesized on the surface of a thin Cu foil according to previously published reports.[1-4] In a typical synthesis of 3 step process, trimethylsilylacetylenezincchloride was prepared by reaction with n-butyllithium (n-BuLi) in tetrahydrofuran (THF) at -78˚C. In the second step, hexakis-[(trimethylsilyl)ethynyl]benzene was prepared from hexabromobenzene by reacting with the product of step 1. In the third step, hexaethynylbenzene was synthesized by adding tetrabutylammonium fluoride into a THF solution of hexakis-[(trimethylsilyl)ethynyl]benzene for 10 min at 8 °C which readily transferred for the growth of GD on the surface of Cu foil in the presence of pyridine by a cross-coupling reaction for 72 h at 60 °C under a nitrogen atmosphere. GD film was scaled off the copper foil using ultrasonic and wash by acetone and DMF in turn. After vacuum drying, the GD powder was gotten. The black solid was refluxed at 100°C for 2 h to remove the impurities and Cu residue by alternate, repeated acid-alkali wash. The product was collected and subjected to water-acetone wash and then dried to give pure GD.

3.1.2 Graphdiyne oxide (GDO) was obtained by acid-oxidation treatment.[2, 3] GD powder was mixed and stirred vigorously with concentrated HNO_3, H_2SO_4 and $KMnO_4$ powder for 24 h in an oil bath of 80 °C.

Following, reaction mixture was cooled to room temperature. Product is neutralized to pH 8 and centrifuged and washed several times. Dried under vacuum to get product GDO.

3.1.3 TiO_2 nanorods were vertically grown by hydrothermal synthesis on FTO glass substrates according to previous report by our own group.[5]

In brief, TiO_2 nanorods were vertically grown on FTO glass substrates (2 X 2 cm) with proper cleaning by solvents such as trichloroethylene, acetone, methanol respectively for 15 minutes each by ultra-sonication. The substrates dried under a N_2 flow and sufficiently on a hot plate at a constant temperature of 80 C, were placed into an autoclave containing thoroughly mixed 1:1 solutions of hydrochloric acid, deionized water (30 ml), and 0.3 mL titanium (IV) butoxide. The reaction temperature of the vessel was maintained at 150 C for 6 h. uniformly grown sample substrates were thoroughly washed and dried. To improve the Crystalline behaviour of nanorods, annealing in air at 450 C for 4 h was carried out.

3.1.4 GD and GDO were deposited on TiO_2 nanorods by in-situ (1 step) and ex-situ (2 step) method. In the in-situ, various amount of GD and GDO were added along with the titania reaction mixture which is described above. Amount of GD or GDO is notated with respect to weight percentage (amount added to reaction mixture, in both cases of insitu and exsitu)

Weight percent = (weight of solute/weight of solution) x 100%

In the case of 1wt% GDO, 0.32 g GDO in 30 mL water and 0.3 mL titanium (IV) butoxide (density - 0.998 g/cm^3)
In the 2 step process, as-prepared TiO_2 nanorods/FTO was reacted with GD or GDO in aqueous medium at 150°C for 4 hours.

4. Figures and Tables

Table S1. Various studies on photocathodes reported for hydrogen evolution reactions

Catalyst	PEC Condition	Photocurrent Density	Reference
$g\text{-}C_3N_4/CuGaSe_2$	0.1M H_2SO_4/100 mW.cm^{-2}	5 $\mu A/cm^{-2}$ (-1 V vs Ag/AgCl)	6
$g\text{-}C_3N_4/CuInS_2$	0.1M H_2SO_4/100 mW.cm^{-2}	0.25 mA/cm^{-2} (-0.6 V vs Ag/AgCl)	7
Polyterthiophenes/MnO_x	0.1 MNaH_2PO_4 and Na_2HPO_4/100 mW.cm^{-2}	160 $\mu A/cm^{-2}$ (-0.2 V vs RHE)	8
$Pt/C_{60}/TiO_2/Sb_2Se_3$	0.1 M H_2SO_4/100 mW.cm^{-2}	17 mA cm^{-2} (-0.1 V vs RHE)	9

Cu_2O/TiO_2	0.1 M KH_2PO_4/100 mW.cm^{-2}	2.04 mA/cm^2 (0 V vs RHE)	10
TiO_2/ Pt/Si nanowire	0.5 M H_2SO_4/100 mW.cm^{-2}	27 mA/cm^{-2} (-0.5 V vs RHE)	11

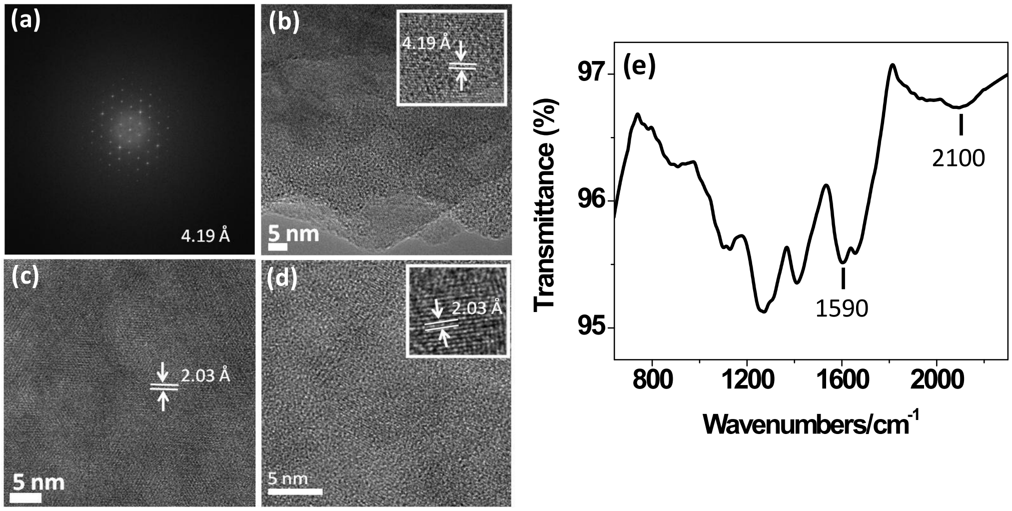
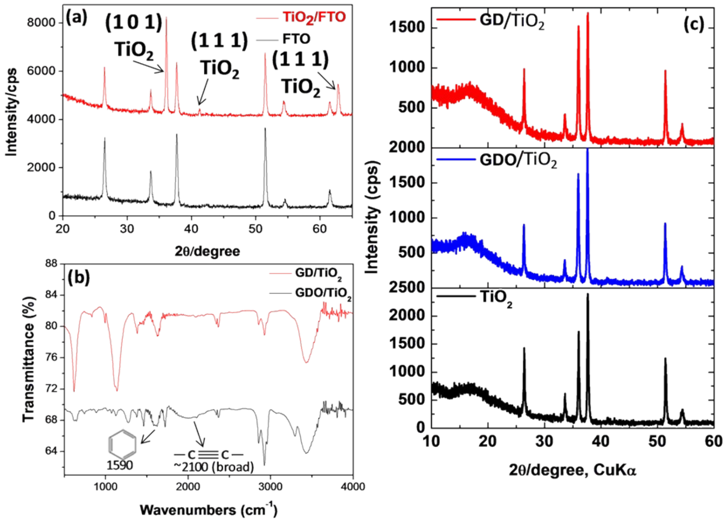


Figure S1. (a-d) TEM, HRTEM, and SAED pattern spectra and (e) IR spectrum of GD films synthesized on Cu- foil.



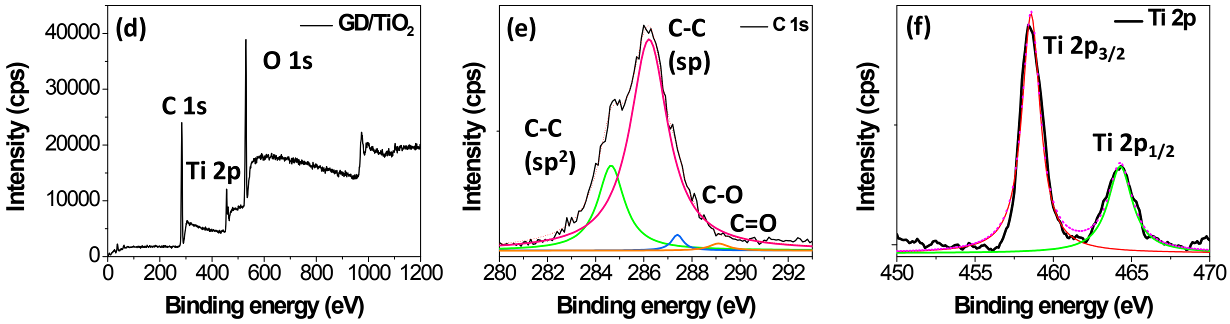


Figure S2. (a) XRD spectra of TiO_2 NR and FTO substrate (b) IR spectrum analysis of GD/TiO_2 and GDO/TiO_2 (c) XRD analysis of TiO_2, GD/TiO_2 and XPS analysis of GDO/TiO_2 showing (d) survey spectrum (e) C 1s and (f) Ti 2p spectra.

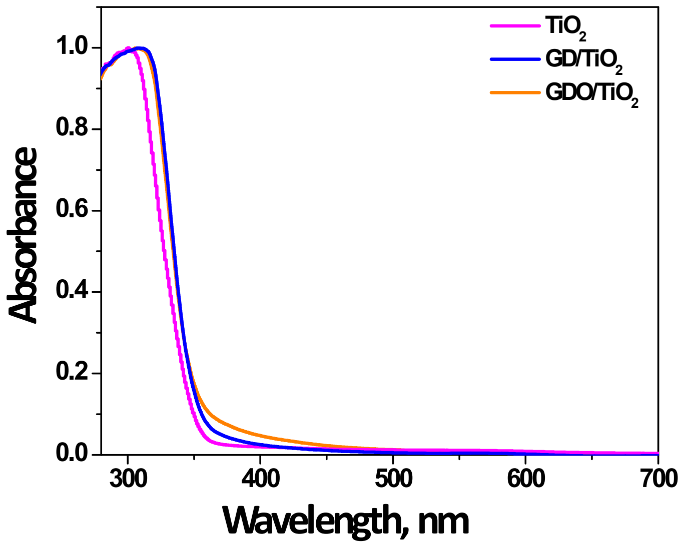


Figure S3. Absorption spectra of TiO_2, GD/TiO_2 and GDO/TiO_2

Table S2. Different methods adopted to obtain optimized enhancement of photo-cathodic response of GD & GDO with TiO_2

Method	Photocurrent Enhancement/GD	Photocurrent Enhancement/ GDO
Spin coating	X	X
Drop casting	X	X
Electrodeposition	X	X
Hydrothermal	O	O

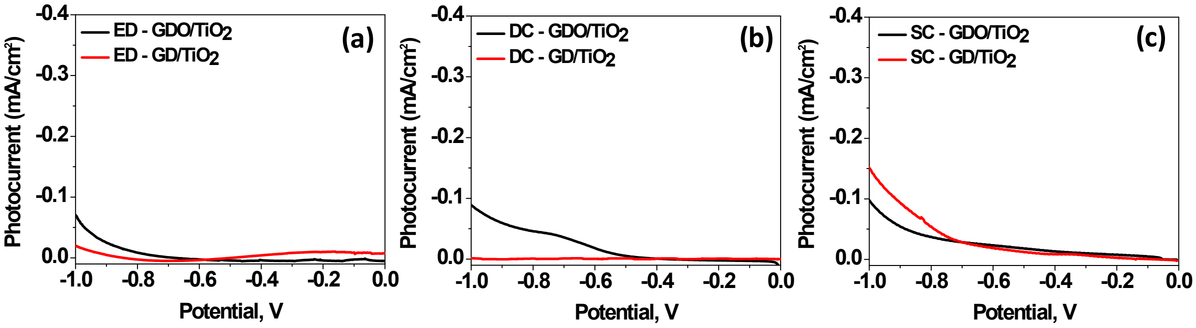


Figure S4. Photocurrent densities (chopped) obtained for hybrids of GD & GDO with TiO_2 prepared by different methods (a) electrodeposition (ED), (b) drop casting (DC) and spin coating (SC).

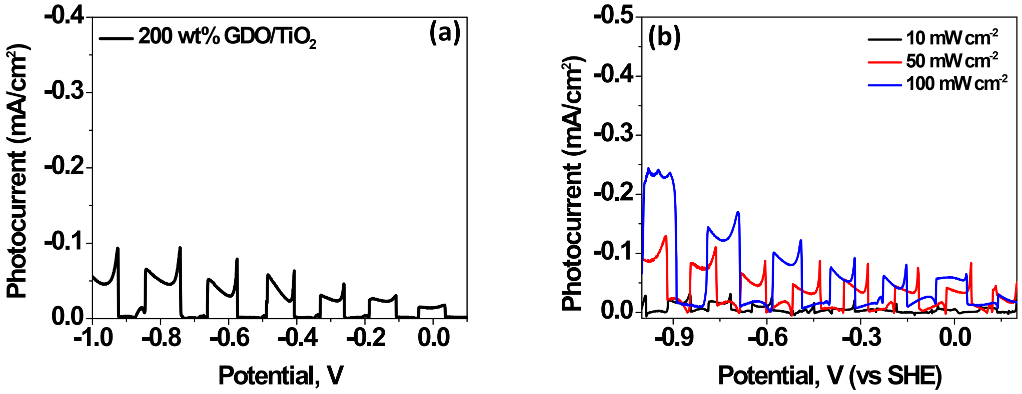


Figure S5. Photocurrent density–voltage diagram of GDO/TiO_2 nanostructures (insitu) in 0.1 M Na_2SO_4 aqueous solution with a light intensity of 100 $mW.cm^{-2}$ visible light irradiation (a) 200 wt% GDO and (b) varying light intensities for 100 wt% sample.

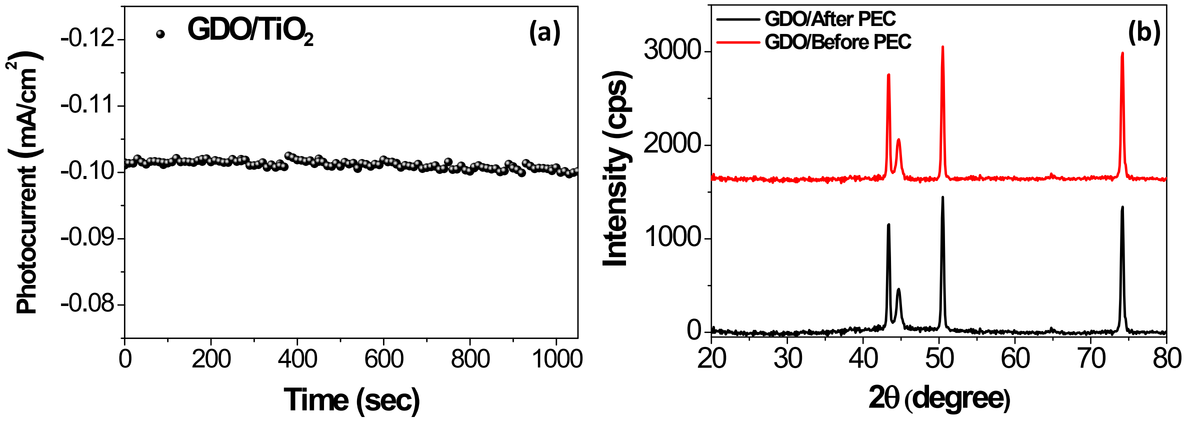


Figure S6. (a) Stability test for GDO/TiO_2 prepared by insitu method measured at -0.8 V (b) XRD analysis before and after PEC measurements.

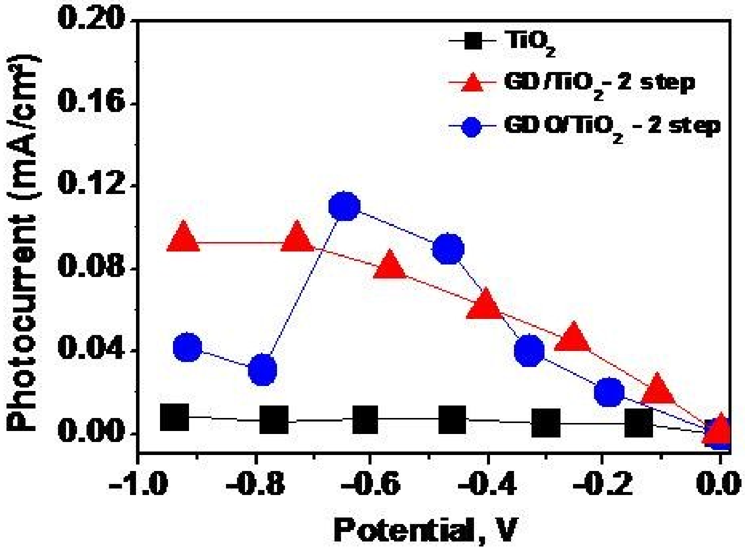


Figure S7. Comparison of photocurrent density–voltage diagram of GD/TiO_2 and GDO/TiO_2 nanostructures prepared by 2 step hydrothermal synthesis and TiO_2 nanorods on FTO in a 0.1 M Na_2SO_4 aqueous solution with a light intensity of 100 mW.cm^{-2} visible light irradiation.

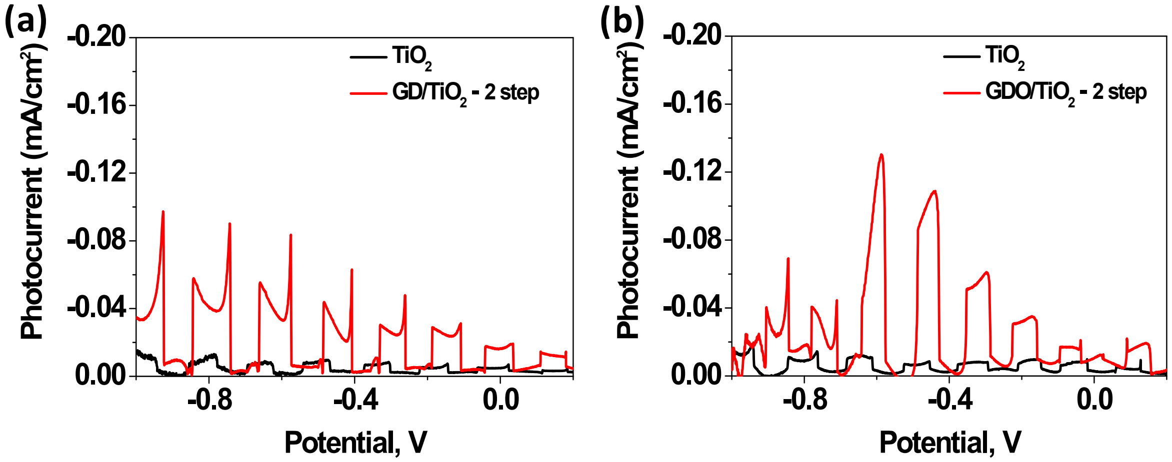


Figure S8. Photocurrent density of (a) GD/TiO_2 and (b) GDO/TiO_2 prepared by two step hydrothermal synthesis measured in 0.1 M Na_2SO_4 with visible light source.

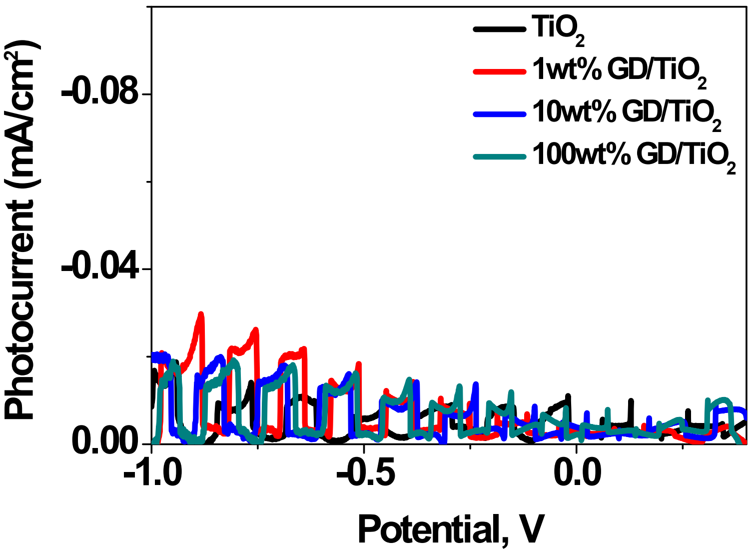


Figure S9. Photocurrent density of GD/TiO_2 prepared by 1 step hydrothermal synthesis measured in 0.1 M Na_2SO_4 with visible light source.

5. References

1. G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chemical Communications*, 2010, **46**, 3256-3258.
2. J. Li, X. Gao, B. Liu, Q. Feng, X.-B. Li, M.-Y. Huang, Z. Liu, J. Zhang, C.-H. Tung and L.-Z. Wu, *J. Am. Chem. Soc.*, 2016, **138**, 3954-3957.
3. H. Qi, P. Yu, Y. Wang, G. Han, H. Liu, Y. Yi, Y. Li and L. Mao, *J. Am. Chem. Soc.*, 2015, **137**, 5260-5263.
4. K. Krishnamoorthy, S. Thangavel, J. C. Veetil, N. Raju, G. Venugopal and S. J. Kim, *International Journal of Hydrogen Energy*, 2016, **41**, 1672-1678.
5. V. Ramakrishnan, H. Kim, J. Park and B. Yang, *RSC Advances*, 2016, **6**, 9789-9795.
6. F. Yang, M. Lublow, S. Orthmann, C. Merschjann, T. Tyborski, M. Rusu, S. Kubala, A. Thomas, R. Arrigo, M. Hävecker and T. Schedel-Niedrig, *ChemSusChem*, 2012, **5**, 1227-1232.
7. F. Yang, V. Kuznietsov, M. Lublow, C. Merschjann, A. Steigert, J. Klaer, A. Thomas and T. Schedel-Niedrig, *Journal of Materials Chemistry A*, 2013, **1**, 6407-6415.
8. K. Oka, O. Tsujimura, T. Suga, H. Nishide and B. Winther-Jensen, *Energy & Environmental Science*, 2018, **11**, 1335-1342.
9. J. Tan, W. Yang, Y. Oh, H. Lee, J. Park, R. Boppella, J. Kim and J. Moon, *Advanced Energy Materials*, 2019, 1900179.
10. J. Choi, J. T. Song, H. S. Jang, M.-J. Choi, D. M. Sim, S. Yim, H. Lim, Y. S. Jung and J. Oh, *Electronic Materials Letters*, 2017, **13**, 57-65.
11. S. Li, P. Zhang, X. Song and L. Gao, *ACS applied materials & interfaces*, 2015, **7**, 18560-18565.