**Supporting Information**

**Assembling γ-graphyne surrounding TiO₂ nanotube arrays: An efficient p-n heterojunction for boosting photoelectrochemical water splitting**

*Dong Qiu, Chengli He, Yuxuan Lu, Qiaodan Li, Yang Chen*, Xiaoli Cui\**

Department of Materials Science, Fudan University, Shanghai 200433, P. R. China

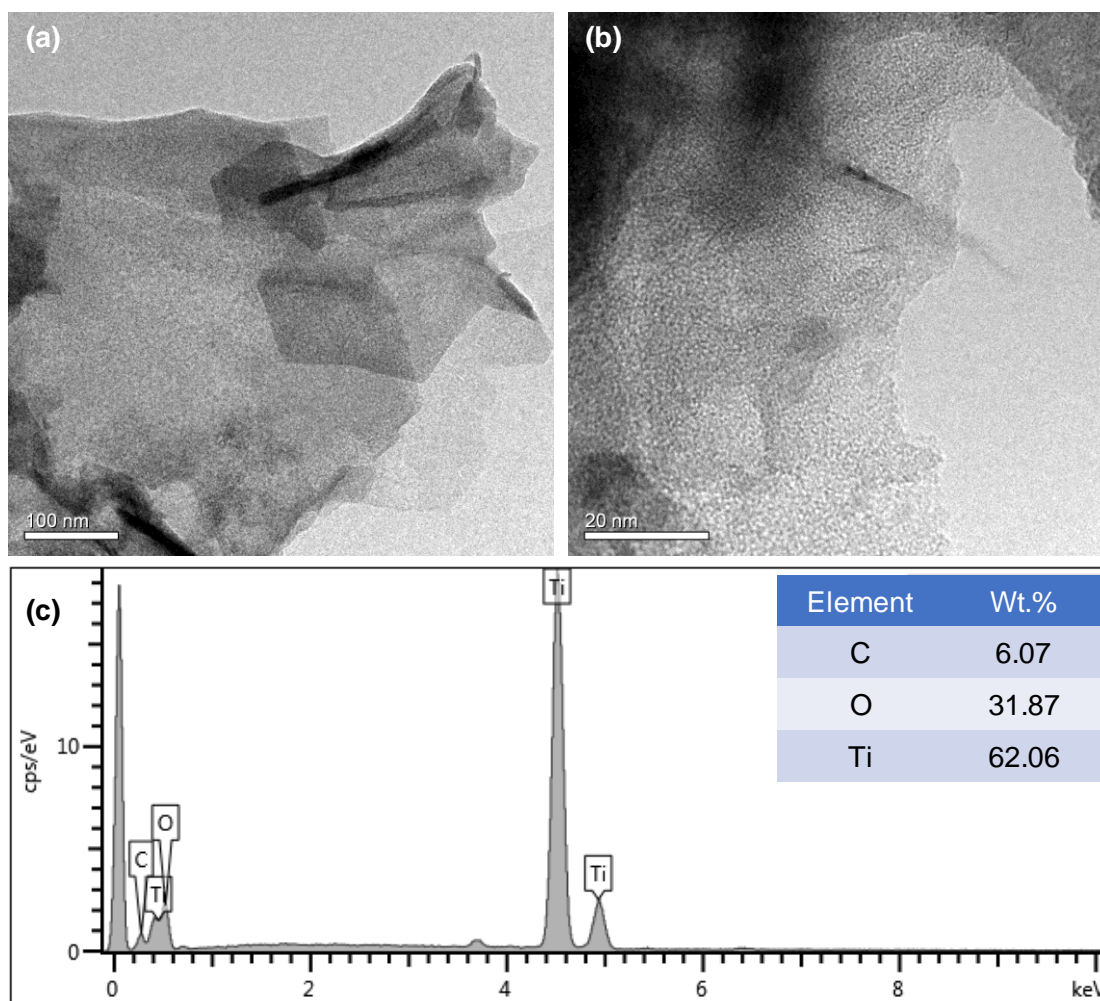*Corresponding author, E-mail: yangchen@fudan.edu.cn, xiaolicui@fudan.edu.cn

**Figure S1** (a, b) TEM images of γ-graphyne. (c) EDS spectrum of 0.3GY/TiO$_2$.

**Note:** The detected carbon content in 0.3GY/TiO$_2$ is 6.07% (Fig. S1c), which contains non-negligible surface carbon contaminations. The content of carbon contaminations is estimated to be 3.5±1.6% [1,2]. Considering γ-graphyne as an all-carbon material ignoring a few surficial oxygen-containing groups, the content of γ-graphyne in 0.3GY/TiO$_2$ is approximately 2.6 wt.%.
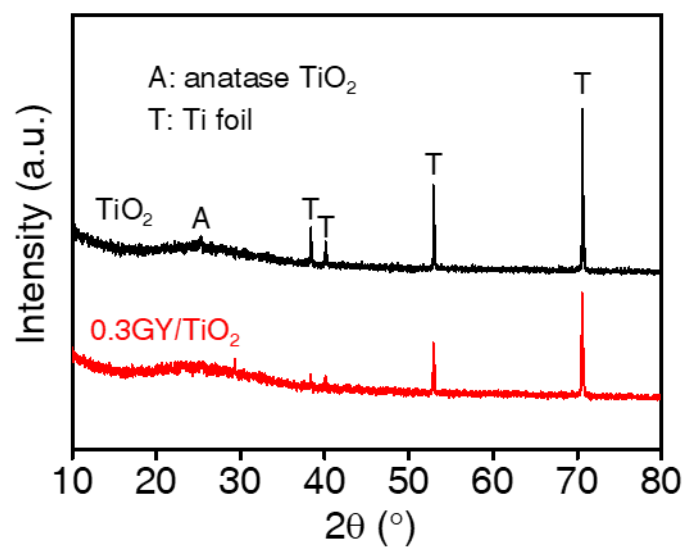
**Figure S2** XRD patterns of TiO₂ and 0.3GY/TiO₂.



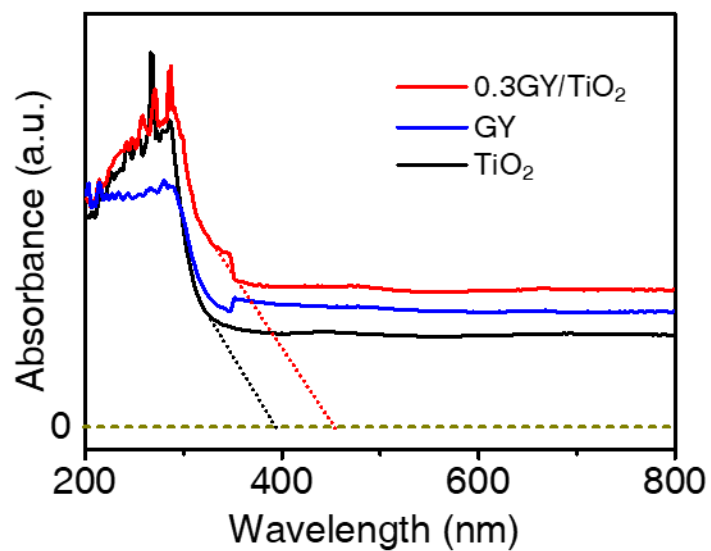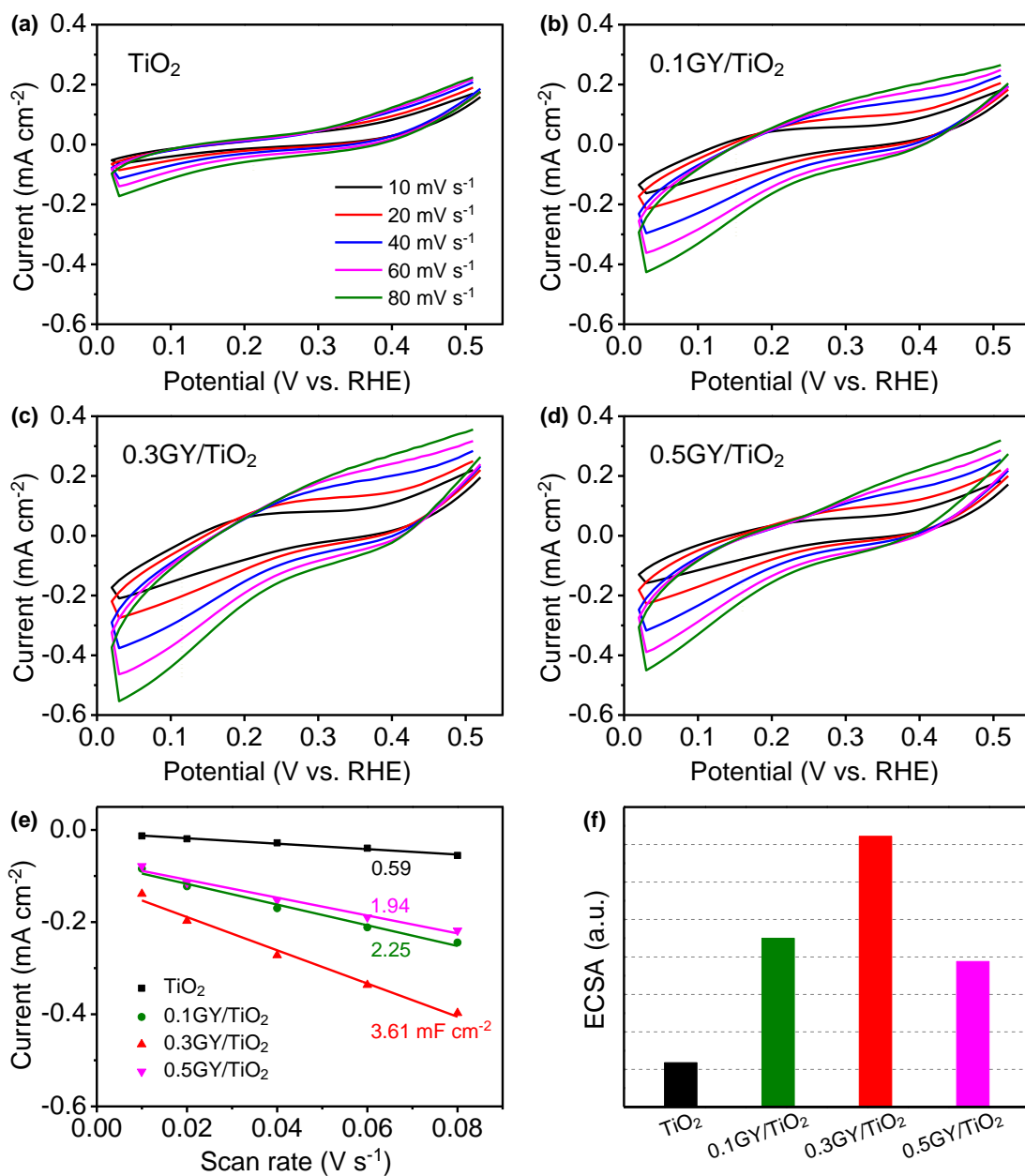**Figure S3** UV-vis absorbance spectra of TiO₂, GY and 0.3GY/TiO₂.

**Figure S4** (a-d) Cyclic voltammetry curves at various scan rates and (e) corresponding *i* (cathodic current at $V_{oc}$ in Figure 5c) –*v* (scan rate) curves. (f) Relative ECSA of $TiO_2$ and GY/$TiO_2$.

**Table S1** The photocurrent response of representative $TiO_2$-based photoanodes.

| Photoanodes | Electrolyte | Light intensity (mW cm$^{-2}$) | Light source | Max. light absorption (nm) | Photo-current density (mA cm$^{-2}$) | Max. ABPE (%) | Refs. |
|---|---|---|---|---|---|---|---|
| **Alkaline** | | | | | | | |
| B-doped $TiO_2$ | 1 M KOH | 200 | 35 W Xe lamp | 443 | 1.20 at 1.62 V | 0.12 at 1.62 V | [3]/2019 |
| S, W-codoped $TiO_2$ | 1 M KOH | 200 | 35 W Xe lamp | / | 0.12 at 1.42 V | / | [4]/2020 |
| $TiO_2$/Au/P-doped g-$C_3N_4$ | 1 M KOH | 100 | 300 W Xe lamp, AM 1.5G filter | 530 | 2.03 at 1.23 V | 0.68 at 0.70 V | [5]/2021 |
| $TiO_2$ nanorod array/carbon quantum dots | 1 M KOH | 100 | 300 W Xe lamp, AM 1.5G filter | / | 3.0 at 1.23 V | 1.29 at 0.62 V | [6]/2019 |
| $TiO_2$ nanorod array/carbon dots/g-$C_3N_4$ | 1 M KOH | 100 | 500 W Xe lamp, AM 1.5G filter | / | 1.43 at 1.23 V | 0.69 at 0.59 V | [7]/2020 |
| S-doped $TiO_2$ nanotube array/g-$C_3N_4$ | 1 M KOH | 100 | 500 W Xe lamp, AM 1.5G filter | 486 | 1.80* at 0.65 V | 1.47* at 0.65 V | [8]/2020 |
| $TiO_2$ nanotube/graphene/CNT | 1 M KOH | 200 | 35 W Xe lamp | / | 0.13* at 1.62 V | / | [9]/2021 |
| **Neutral** | | | | | | | |
| $TiO_2$/g-CN | 0.5 M $Na_2SO_4$ | 100 | 150 W Xe lamp, AM 1.5G filter | 435 | 0.91 at 1.23 V | 0.33 at 0.64 V | [10]/2020 |
| $TiO_2$/N-doped carbon dots | 0.2 M $Na_2SO_4$ | 100 | SLB-150B solar simulator, 420 nm filter | 425 | 0.15 at 0.3 V | / | [11]/2020 |
| $TiO_2$/g-$C_3N_4$/CNT | 0.5 M $Na_2SO_4$ | 100 | 150 W white lamp, 400 nm filter | 428 | 2.94 at 1.23 V | / | [12]/2020 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| TiO$_2$ nanorod array/N-doped C/g-C$_3$N$_4$ | 0.1 M Na$_2$SO$_4$ | 100 | 300 W LED lamp, 420 nm filter | 508 | 0.64 at 2.11 V | / | [13]/2020 |
| TiO$_2$ nanotube array/carbon dots | 0.1 M PBS** | / | 300 W Xe lamp, 380 nm filter | / | 0.05 at 1.03 V | / | [14]/2019 |
| TiO$_2$ nanotube array/g-C$_3$N$_4$ | 0.1 M Na$_2$SO$_4$ | / | 300 W Xe lamp, 420 nm filter | 800 | 0.72 at 1.23 V | / | [15]/2018 |
| TiO$_2$ nanotube array/g-C$_3$N$_4$ | 1 M Na$_2$SO$_4$ | 100 | 300 W Xe lamp, AM 1.5G filter | 450 | 0.14 at 1.61 V | / | [16]/2020 |
| TiO$_2$ nanotube array/graphyne | 0.5 M Na$_2$SO$_4$ | / | 500 W Xe lamp | 516 | 4.36 at 0.93 V | 3.15 at 0.93 V | [17]/2021 |
| TiO$_2$ nanotube array | 0.5 M Na$_2$SO$_4$ | / | 500 W Xe lamp | 415 | 3.33* at 0.93 V | 2.28 at 0.93 V | [17]/2021 |
| TiO$_2$ nanotube array/graphyne | 0.5 M Na$_2$SO$_4$ | 100 | 300 W Xe lamp | 458 | 0.73 at 1.23 V | 0.35 at 0.55 V | This work |

Note: All potentials are converted to versus reversible hydrogen electrode (vs. RHE).

*Estimated data according to the figures.

**PBS: phosphate buffered saline.

**Table S2** The fitting values of the equivalent circuit model in Figure 6c.

| Samples | $R_s$ ($\Omega$) | $CPE$ (F) | $CPE$ exponent | $R_{ct}$ (k$\Omega$) |
|---|---|---|---|---|
| $TiO_2$ | 8.0 | $3.2\times10^{-5}$ | 0.73 | 10.1 |
| 0.1GY/$TiO_2$ | 4.8 | $6.4\times10^{-5}$ | 0.64 | 8.6 |
| 0.3GY/$TiO_2$ | 4.8 | $9.4\times10^{-5}$ | 0.63 | 6.1 |
| 0.5GY/$TiO_2$ | 7.3 | $4.8\times10^{-5}$ | 0.72 | 7.4 |

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