

Electronic Supplementary Information

Graphene quantum dots to enhance the photocatalytic hydrogen evolution efficiency of anatase TiO₂ exposed with {001} facet

Shan Yu,^a Yun-Qian Zhong,^a Bao-Quan Yu,^a Shi-Yi Cai,^a Li-Zhu Wu^c and Ying Zhou^{*a,b}

^a *School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China.*

E-mail: yzhou@swpu.edu.cn;

Fax: + 86 2883037406;

Tel: +86 28 83037409.

^b *State Key Laboratory of Oil and Gas Reservoir and Exploitation, Southwest Petroleum University, Chengdu 610500, China.*

^c *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, the Chinese Academy of Sciences, Beijing 100190, P. R. China.*

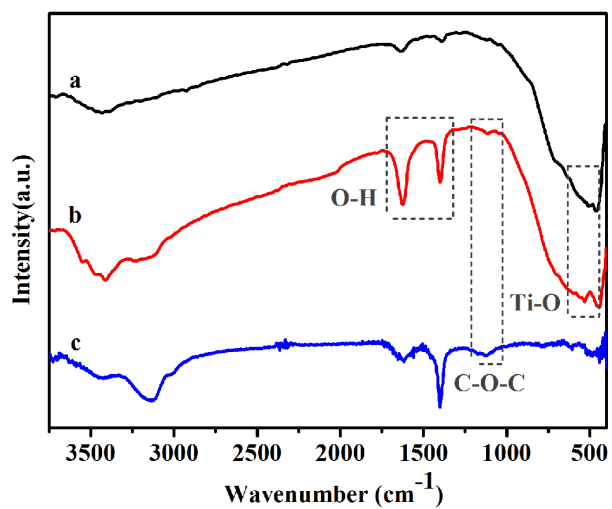


Fig. S1 FT-IR spectra of $\{001\}\text{TiO}_2$ (a), GQDs/ $\{001\}\text{TiO}_2$ (b) and GQDs (c).

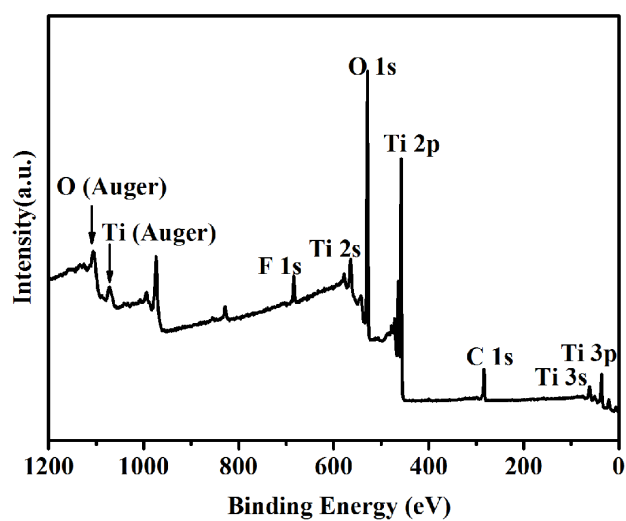


Fig. S2 The full-scale XPS spectrum of GQDs/ $\{001\}\text{TiO}_2$ composite.

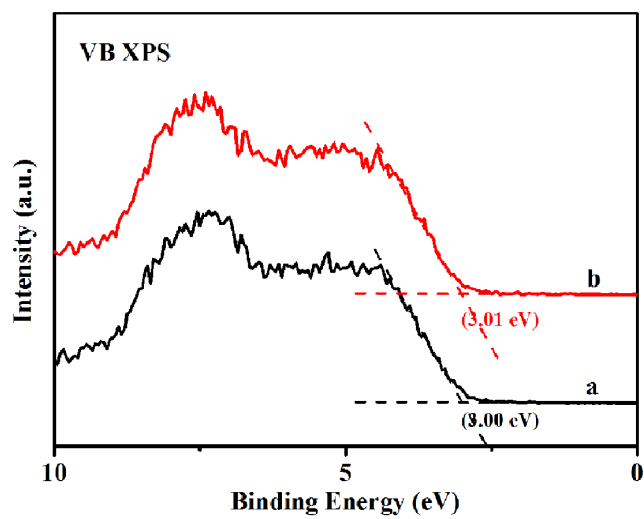


Fig. S3 The valence band spectra of {001}TiO₂ (a) and GQDs/{001}TiO₂ (b).

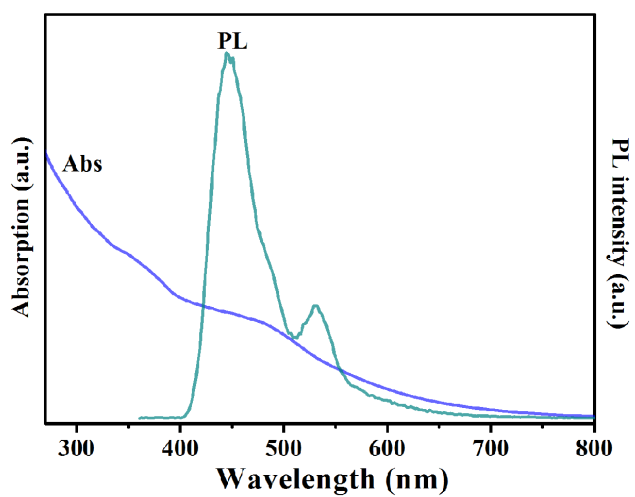


Fig.S4 UV-Vis absorption spectrum and photoluminescence (PL) spectrum of pure GQDs.

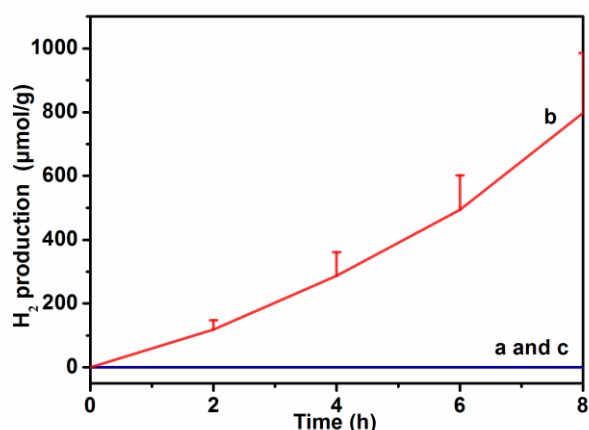


Fig. S5 Hydrogen evolution comparison of pure GQDs (a), and GQDs/{001}TiO₂ (b). The amount of photocatalyst used in catalytic process is 10 mg with the methanol employed as the sacrificial agent. (c) H₂ production on GQDs/{001}TiO₂ without methanol.

Calculation process for the possibility that GQDs act as a sacrificial agent

Assuming that carbon may react with water to yield carbon dioxide and 2 hydrogen molecules: $C + 2H_2O \rightarrow CO_2 + 2H_2$, then for the generation of 1 mol of hydrogen, 0.5 mol of C is needed. In our system, after three consecutive cycles of photocatalytic reaction, 4.62 (1.12 +1.57 +1.93) mmol H₂ would be generated for per gram of GQDs/{001}TiO₂ (Fig. 5). Based on the above chemical equation, at least 2.31 mmol of carbon (corresponding to 27.7 mg) is necessary for such a reaction. However, the GQDs/{001}TiO₂ used in the system has a GQD weight ratio of only 0.5%, that is only 5 mg of GQDs is existed for per gram of GQDs/{001}TiO₂. Even if we ignore other atoms existed in GQDs (like oxygen and hydrogen) and consider GQDs are fully composed of carbon, such an amount of carbon is not enough to generate the corresponding amount of H₂. This implies that GQDs may not act as a sacrificial agent.

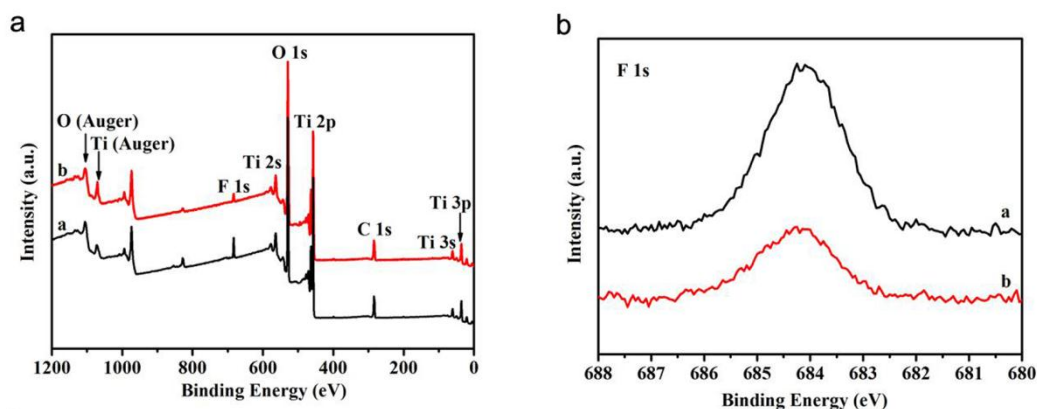


Fig. S6 Full XPS spectra (a) and high-resolution XPS spectra of F 1s (b). Black line: $\{001\}\text{TiO}_2$, Red line: $\{001\}\text{TiO}_2$ after removal of F.

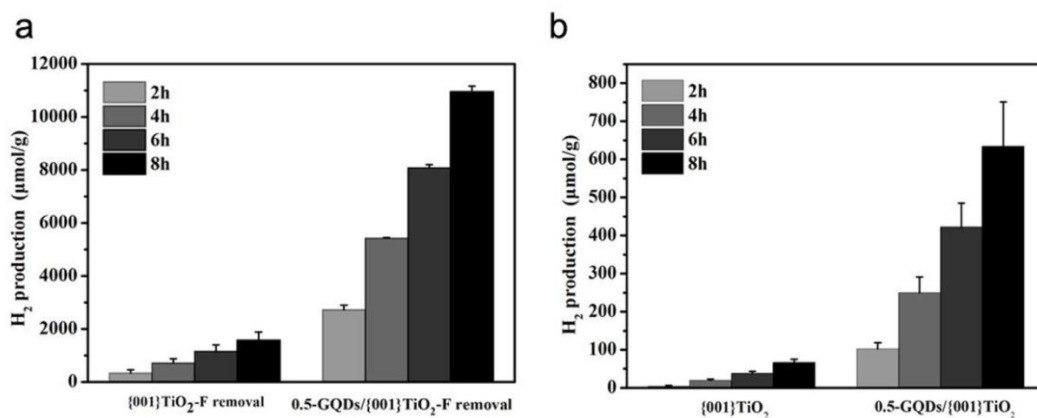


Fig. S7 Amount of hydrogen evolved from systems containing 10 mg of $\{001\}\text{TiO}_2$ or GQDs/ $\{001\}\text{TiO}_2$ with (a) and without (b) the removal of F atoms. Sacrificial agent: methanol; light source: high pressure Hg lamp.

Influence of F atoms on the surface of TiO_2 toward the photocatalysis

Photocatalytic hydrogen evolution experiment shows that $\{001\}\text{TiO}_2$ after removal of F shows a much higher catalytic activity than $\{001\}\text{TiO}_2$ (about 20 times) (Fig. S7 (a) and (b)). This is within our expectation since it is reported that the existence of F on the surface could destroy the original surface structure of TiO_2 and hence decreases their photocatalytic activity (*Angew. Chem. Int. Ed.* 2011, 50, 2133). Nevertheless, we note that the introduction of GQDs could still largely increase the efficiency for photocatalytic hydrogen evolution from 1.58 mmol g^{-1} to 11.0 mmol g^{-1} (Fig. S7 (a)). The enhancement degree (6 times) is similar to that from $\{001\}\text{TiO}_2$ to GQDs/ $\{001\}\text{TiO}_2$ (8 times) i (Fig. S7 (a) and (b)). This proves that the enhanced effect of GQDs on $\{001\}\text{TiO}_2$ was not restricted by F atoms.

Based on the above discussion, we draw the conclusion that the existence of F on the surface of $\{001\}\text{TiO}_2$ has a negative effect on photocatalytic efficiency of the present system, but this would not change the fact that GQDs could indeed increase the photocatalytic activity of $\{001\}\text{TiO}_2$.

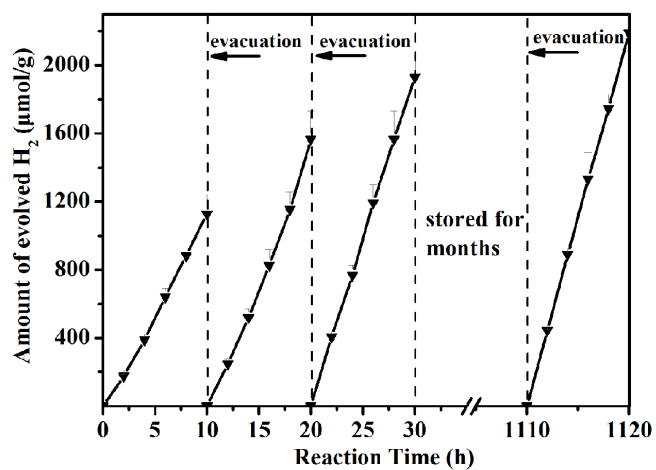


Fig. S8 Repeated photocatalytic hydrogen evolution on GQDs/{001}TiO₂ after a long period.

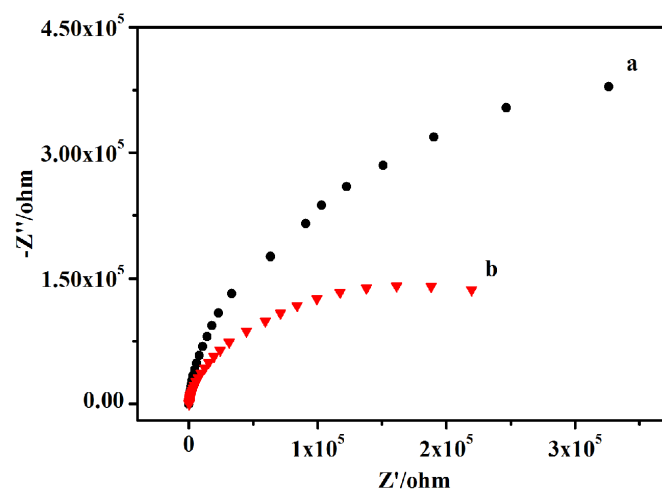


Fig. S9 Electrochemical impedance spectra of {001}TiO₂ (a) and GQDs/{001}TiO₂ (b).