

## Reducing the charging voltage of a Li-O<sub>2</sub> battery to 1.9 V by incorporating a photocatalyst

Yang Liu<sup>1,2</sup>, Na Li<sup>1,\*</sup>, Shichao Wu<sup>1</sup>, Kaiming Liao<sup>1</sup>, Jin Yi<sup>1</sup>, Kai Zhu<sup>1</sup> and Haoshen Zhou<sup>1,2,3,\*</sup>

<sup>1</sup>Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba, 305-8568, Japan.

<sup>2</sup>Graduate School of System and Information Engineering University of Tsukuba Tennoudai 1-1-1, Tsukuba, 305-8573, Japan.

<sup>3</sup>National Laboratory of Solid State Microstructures and Department of Energy Science and Engineering, Nanjing University, Nanjing, 210093, China.

E-mail: [hs.zhou@aist.go.jp](mailto:hs.zhou@aist.go.jp) or [nli.ri@aist.go.jp](mailto:nli.ri@aist.go.jp)

### Experimental Section

Synthesis of the g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/carbon paper: g-C<sub>3</sub>N<sub>4</sub> powder was synthesized according to a procedure described in a previous paper.<sup>1</sup> In detail, melamine (Wako, 99%) was heated at 550 °C for 3 h in static Ar with a ramp rate of 2.3 °C min<sup>-1</sup>; the cooling rate was kept at around 1 °C min<sup>-1</sup>. The resultant yellow agglomerates were milled into powder in a mortar. To obtain the g-C<sub>3</sub>N<sub>4</sub>/carbon paper composites, the slurry of the melamine and poly(tetrafluoroethylene) (PTFE) in a *N*-methyl pyrrolidone was pasted on a carbon paper of 9 mm in diameter, then the sample was heated at 550 °C for 3 h in an Ar atmosphere with a flow of 37.5 ml min<sup>-1</sup> with a ramp

rate of  $2.3\text{ }^{\circ}\text{C min}^{-1}$ ; the cooling rate was kept at around  $1\text{ }^{\circ}\text{C min}^{-1}$ . The mass loading of g-C<sub>3</sub>N<sub>4</sub> is 0.16-0.2 mg cm<sup>-2</sup>.

Preparation of the battery: All devices were assembled in an Ar gas filled glovebox. The electrolyte was prepared by dissolving 0.5 M LiClO<sub>4</sub> (Wako) and 0.05 M LiI (Wako) in Tetraglyme (G4, Wako). The photoassisted Li-O<sub>2</sub> battery was assembled with a Li foil anode, a glass fiber filter (Whatman GF/A) encapsulated with the electrolyte, and a g-C<sub>3</sub>N<sub>4</sub>/carbon paper as air electrode and photoelectrode in a coin cell, which had 7 holes drilled into it. The holes allow the illumination on the electrode. The assembled Li-O<sub>2</sub> battery was stored in a glass chamber, and purged with O<sub>2</sub> for at least 3 hours before electrochemical tests.

Measurements and Characterization: X-ray diffraction (XRD) was performed using a Bruker D8 Advanced diffractometer with Cu K $\alpha$  ( $\lambda = 1.5406\text{ \AA}$ ) radiation. Scanning electron microscopy (SEM) was obtained on a Hitachi S4800. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 500 MHz spectrometer. The UV-visible absorption spectrum measurements were performed using Shimadzu UV3101PC. Galvanostatic discharge/charge cycles were conducted on a Hokuto discharging/charging system. All the electrochemical measurements were conducted at 25 °C under O<sub>2</sub> atmosphere. For the solar-energy storage device tests, a XEF-501S Xe-lamp (San-ei Electric Co., Japan) was used as the light source.

1. X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti. *Nat. Mater.* 2009, **8**, 76-80.

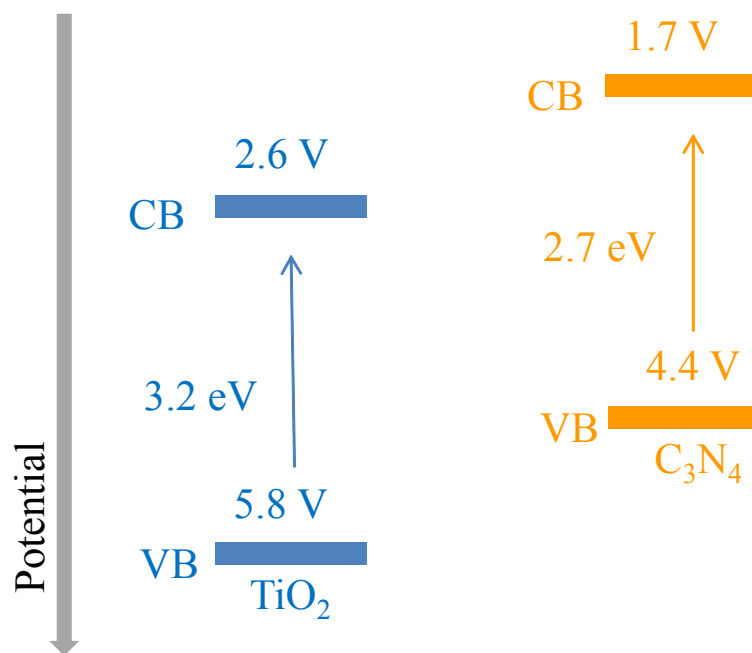


Figure S1 A comparison of the band positions of g- $\text{C}_3\text{N}_4$  and  $\text{TiO}_2$ .

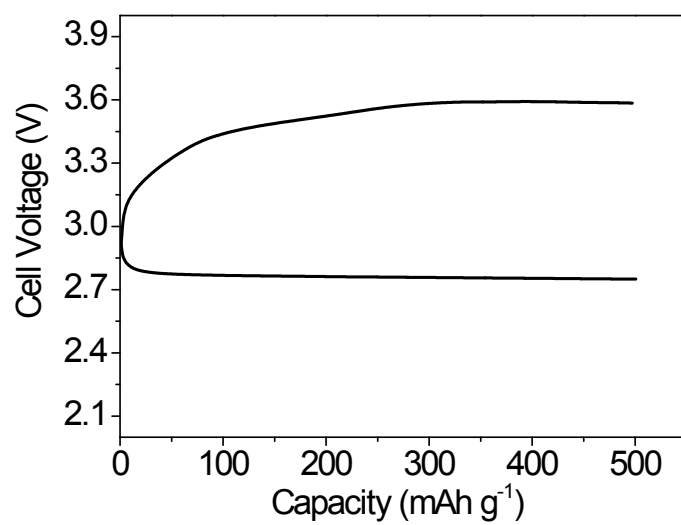


Figure S2 The voltage profile of the Li-O<sub>2</sub> battery applying g-C<sub>3</sub>N<sub>4</sub>/Ti as the air electrode at a current density of 100 mA g<sup>-1</sup>, limiting the capacity to 500 mAh g<sup>-1</sup>.

Data collected in 0.5 M LiClO<sub>4</sub> and 0.05 M LiI in G4.

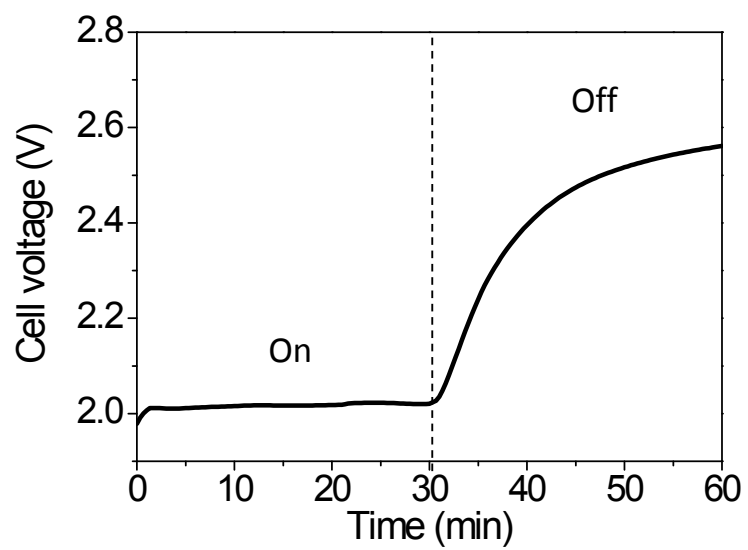


Figure S3 The light-response of the charging voltage of a photoassisted chargeable Li-O<sub>2</sub> battery when illumination was switched from “on” to “off”. Current density, 0.01 mA cm<sup>-2</sup>.

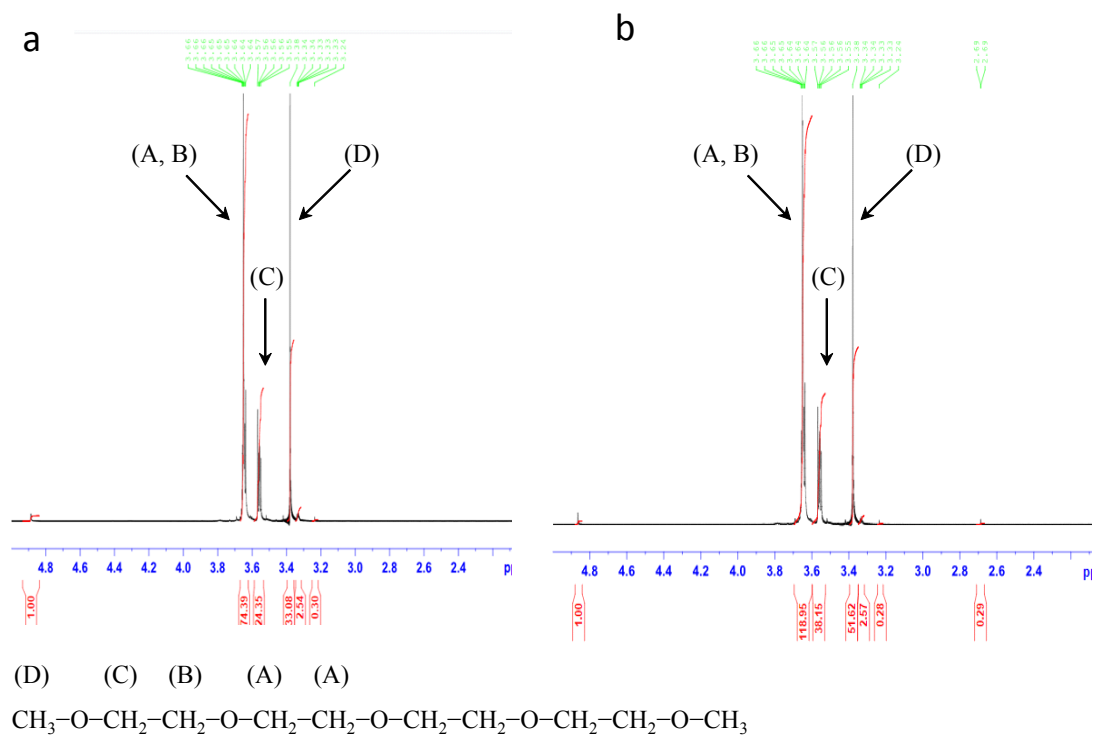


Figure S4  $^1\text{H}$  NMR spectra of 1M  $\text{LiClO}_4$  and 0.05 M  $\text{LiI}$  in G4 electrolyte (a) before and (b) after 5 h illumination.

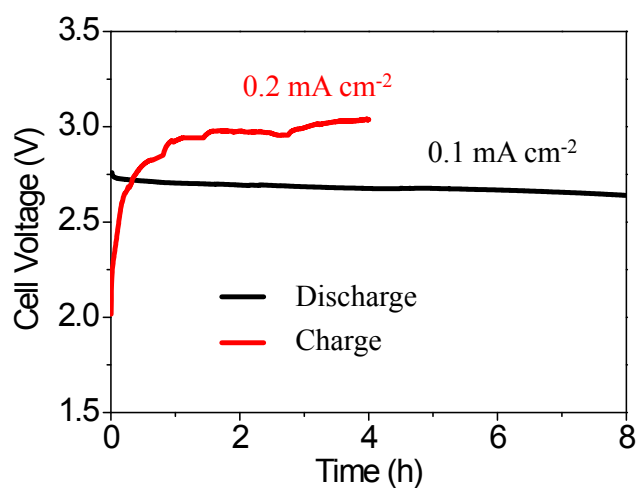


Figure S5 The discharge curve of the battery with 8 h as a cutoff time at a current density of  $0.1 \text{ mA cm}^{-2}$  and photoassisted charge curve of battery with 4 h as a cutoff time at a current density of  $0.2 \text{ mA cm}^{-2}$ . The high photoassisted charging voltage is attributed to both high internal resistance and high overpotential under a large charge current density.

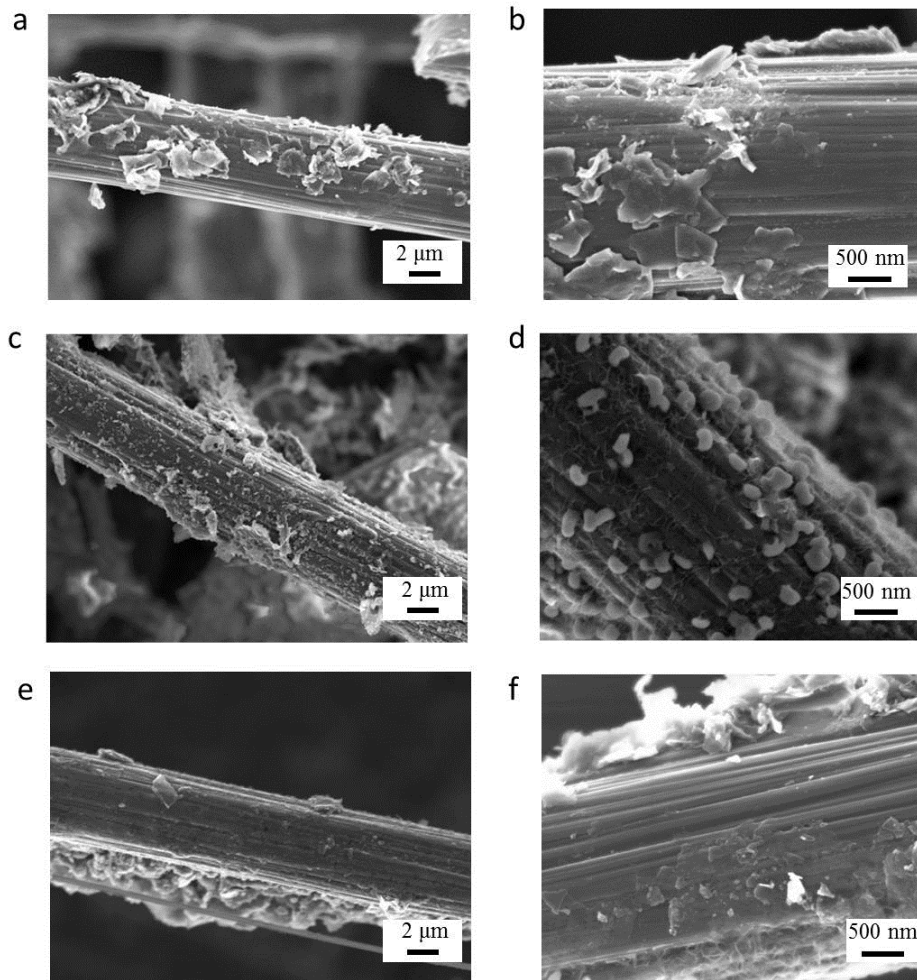


Figure S6 SEM images of the (a, b) fresh electrode, (c, d) discharge product with 8 h as a cutoff time at a current density of  $0.1 \text{ mA cm}^{-2}$  and (e, f) charge product with 4 h as a cutoff time at a current density of  $0.2 \text{ mA cm}^{-2}$ .