Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Lowering charge voltage of Li-O_2 batteries via an unmediated photoelectrochemical oxidation approach

Yang Liu,[a,b] Na Li,[a,*] Kaiming Liao,[a] Qi Li,[a,b] Masayoshi Ishida[b] and Haoshen Zhou[a,b,c,*]

[a]Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba, 305-8568, Japan.

E-mail: hs.zhou@aist.go.jp or nli.ri@aist.go.jp

[b]Graduate School of System and Information Engineering, University of Tsukuba, 1–1–1, Tennoudai, Tsukuba, 305–8573, Japan.

[c]National Laboratory of Solid State Microstructures and Department of Energy Science and Engineering, Nanjing University, Nanjing, 210093, China.

Experimental Section

Synthesis of g-C_3N_4-CP electrode: The g-C_3N_4-CP was synthesized as follows: the guanidine hydrochloride (GundCl) and polyvinylidene fluoride (PVDF) powder were mixed with a mass ratio of 95:5, dissolving in N-methyl pyrrolidine (NMP) solvent, and the slurry was grinded for 30 min to blend uniformly. Then the carbon paper (diameter is 7 mm) was dipped into the resulting solution and pasted with the slurry. The g-C_3N_4-CP was obtained after calcination at 550 ˚C for 3h under Ar flow of 100 ml min^{-1} with a ramp rate of 2.3 ˚C min^{-1}; The cooling rate was kept at around 1℃ min^{-1}. The loading mass of g-C_3N_4 in g-C_3N_4/carbon paper electrode is about 0.4 mg cm^{-2}. The weight ratio between CP (~2.4 mg) and C_3N_4 (0.4 mg) is about 6 : 1.

The photoassisted Li-O_2 Battery assemble: The battery assembly was performed in an Ar gas filled glovebox using 2023 coin cell with 7 holes at the top, which enable the illumination on the electrode. The electrolyte was consist of 1 M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma) dissolved in Tetraglyme (G4, WAKO). The photoassisted Li-O_2 battery was comprised with a Li metal as anode, a glass fiber filled with electrolyte and a g-C_3N_4-CP as oxygen electrode and photoelectrode. The assembled Li-O_2 battery was stored in a sealed glass chamber with a volume capacity of 650 mL, and purged with O_2 before the electrochemical investigation. The light source used for the illumination is a XEF-501S Xe-lamp (San-ei Electric Co., Japan). The charging/discharging tests for the all batteries were performed at different current densities by using a Hokuto electrochemical machine.

Characterization: X-ray diffraction (XRD) were carried out by a Bruker D8 X-ray

diffractometer using Cu Kα (λ=1.54 Å) radiation. The chemical composition of g-C_3N_4-CP was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, with a monochromatic Al K_α X-ray source). Scanning electronic microscope (SEM) was observed on a Hitachi S4800. Galvanostatic discharge/charge was conducted on a Hokuto discharging/charging system. FTIR was obtained on a JASCO instrument of FT/IR-6200 from 1300 to 900 cm^{-1} with a resolution of 2 cm^{-1}.

Summary of redox potentials of redox mediators		
Redox mediator	**Redox potential (V)**	**Reference**
$OMAB^-$/OMAB	3.16	1
$TMPD^-$/TMPD	3.33	2
DEQ^+/DEQ	3.35	1
I_3^-/I^-	3.55	3,4
$(FePc)^-$/ (FePc)	3.55	5
TTF^+/ TTF	3.56	2
FC^-/ FC	3.60	2
$TEMPO^+$/ TEMPO	3.74	6
$MOPP^+$/ MOPP	3.78	1
MPT^+/ MPT	3.81	1

Table S1 Summary of the charge voltage of Li–O_2 batteries with redox mediators.

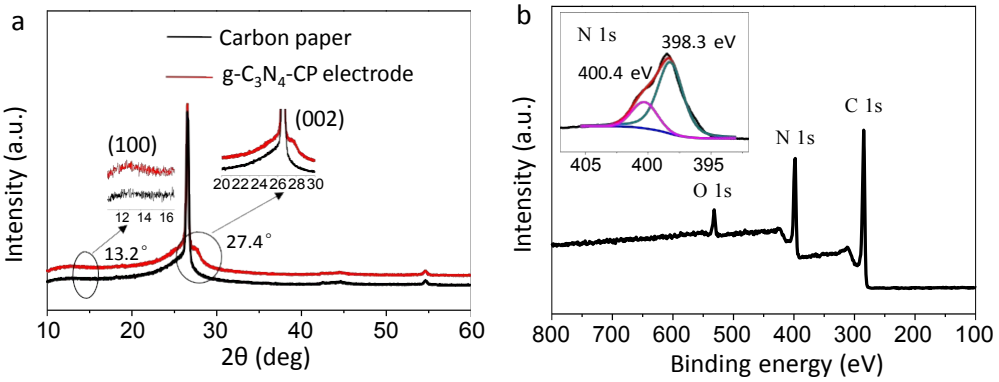

Figure S1 (a) XRD patterns of bare carbon paper and g-C_3N_4-CP. (b) XPS of the g-C_3N_4-CP electrode.

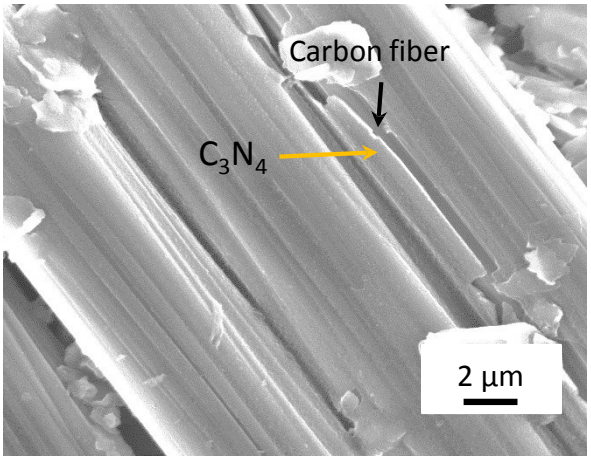

Figure S2 SEM image of g-C_3N_4-CP electrode.

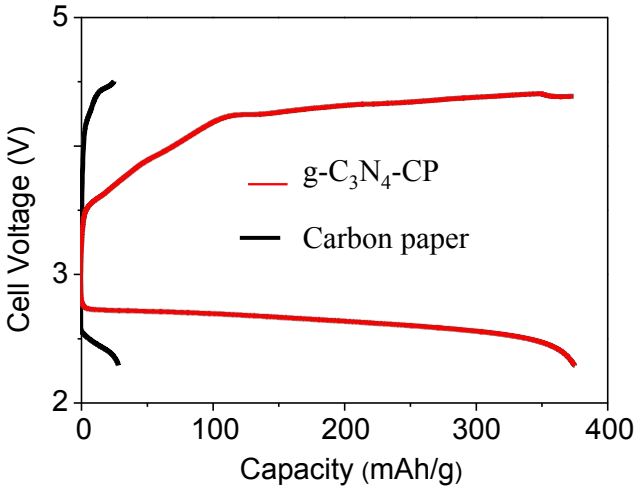

Figure S3 Discharge/charge curves at the current density of 0.02 mA cm^{-2} for carbon paper and g-C_3N_4-CP electrode.

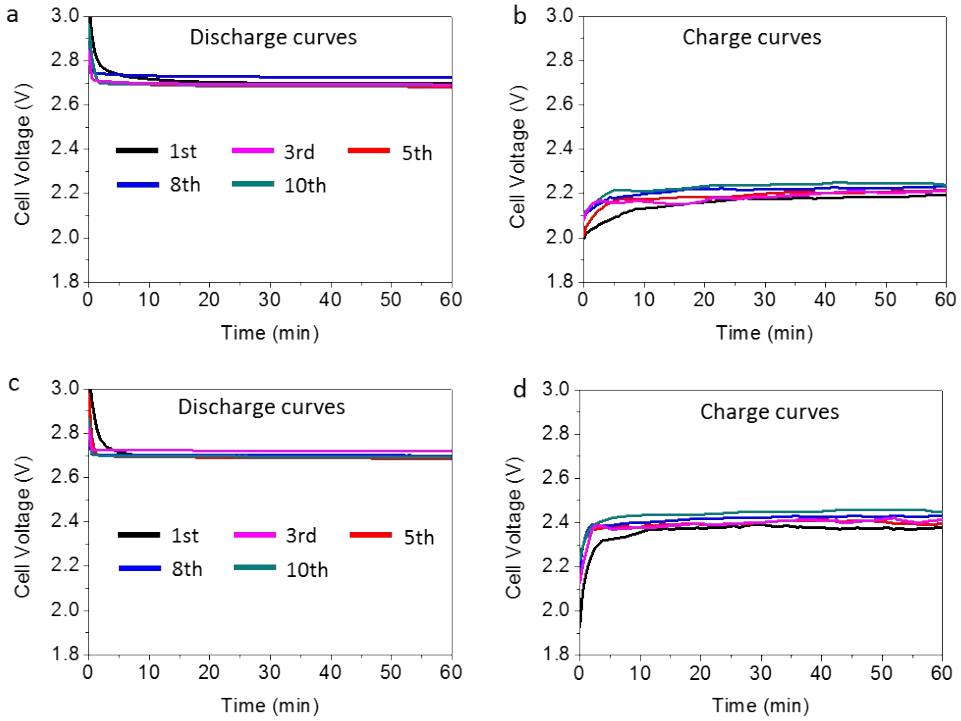

Fig. S4 The discharge curves and the photoassisted charge curves of the photoassisted rechargeable Li-O_2 battery at the current density of (a,b) 0.03 and (c,d) 0.05 mA cm^{-2} for 10cycles.

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