Supporting Information

Z-scheme g-C_3N_4/TiO_2 Heterojunction for a High Energy Density Photo-Assisted Li-O_2 Battery

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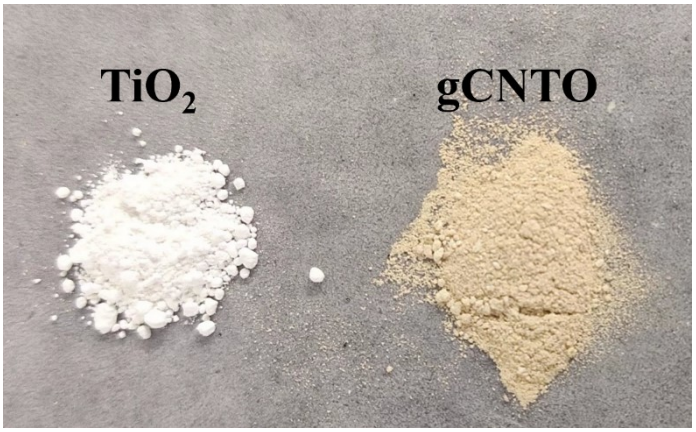


Figure S1 Digital photos of TiO_2 and g-C_3N_4/TiO_2

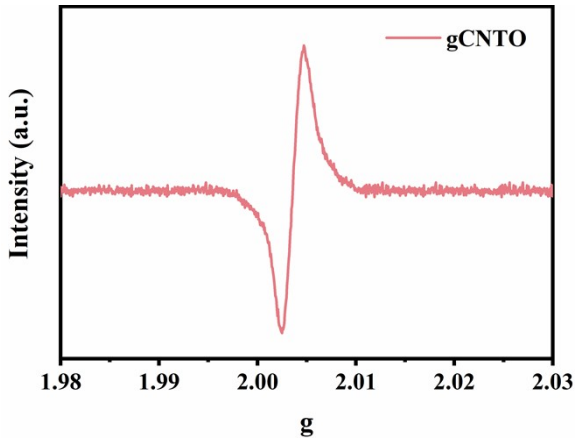


Figure S2. EPR image of g-C_3N_4/TiO_2.

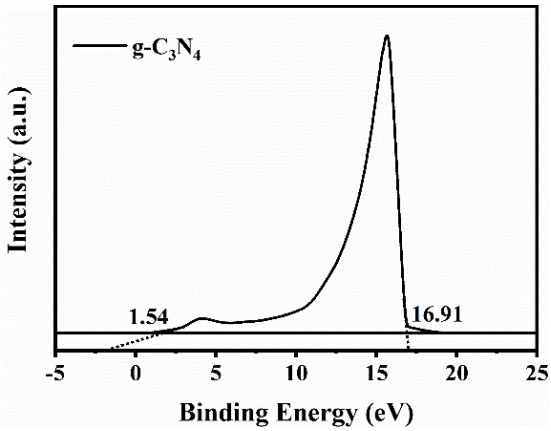


Figure S3. UPS image of g-C_3N_4.

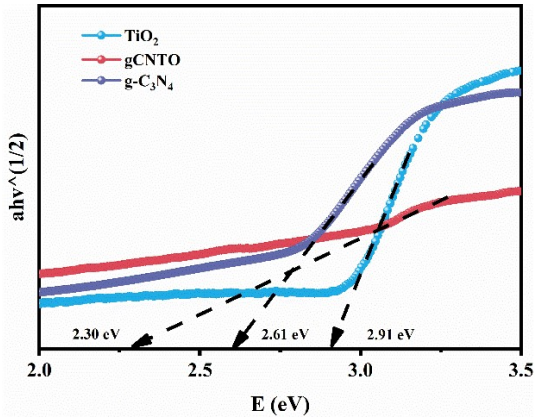


Figure S4. The Tauc plots converted from the UV-Vis spectrum show that the Eg of TiO_2, gCNTO, g-C_3N_4 are 2.30 ev, 2.61 ev, 2.91 ev. Respectively

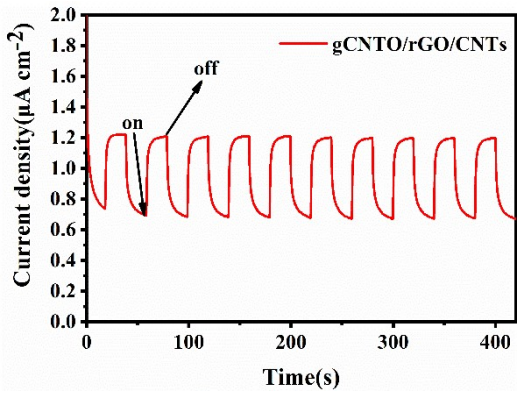


Figure S5. i-t curve of gCNTO/rGO/CNTs

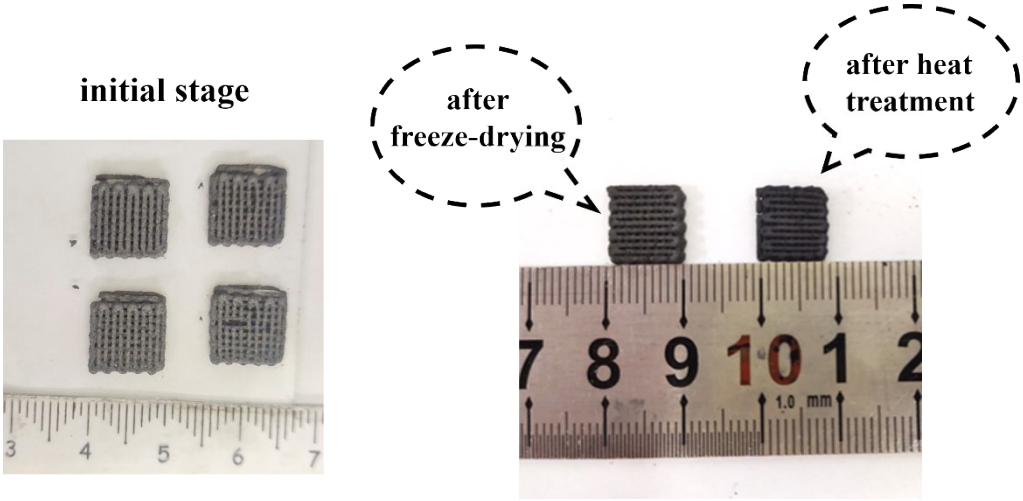


Figure S6. The 3D-printed cathode was printed into a gris structure with a

diameter of 10 mm. The structure of the printed cathode was well maintained after both freeze-drying at -24 ℃ and heat treatment at 500 ℃. (After annealing, the mass of the gCNTO/rGO/CNTs electrode was 13 ± 3mg cm^{-2}, and the gCNTO of the mass loading is approximately 4.78 ±0.7 mg cm^{-2} for each gCNTO/rGO/CNTs photocathode.The gCNTO/rGO/CNTs photocathode is a self-supporting cathode without current collector.)

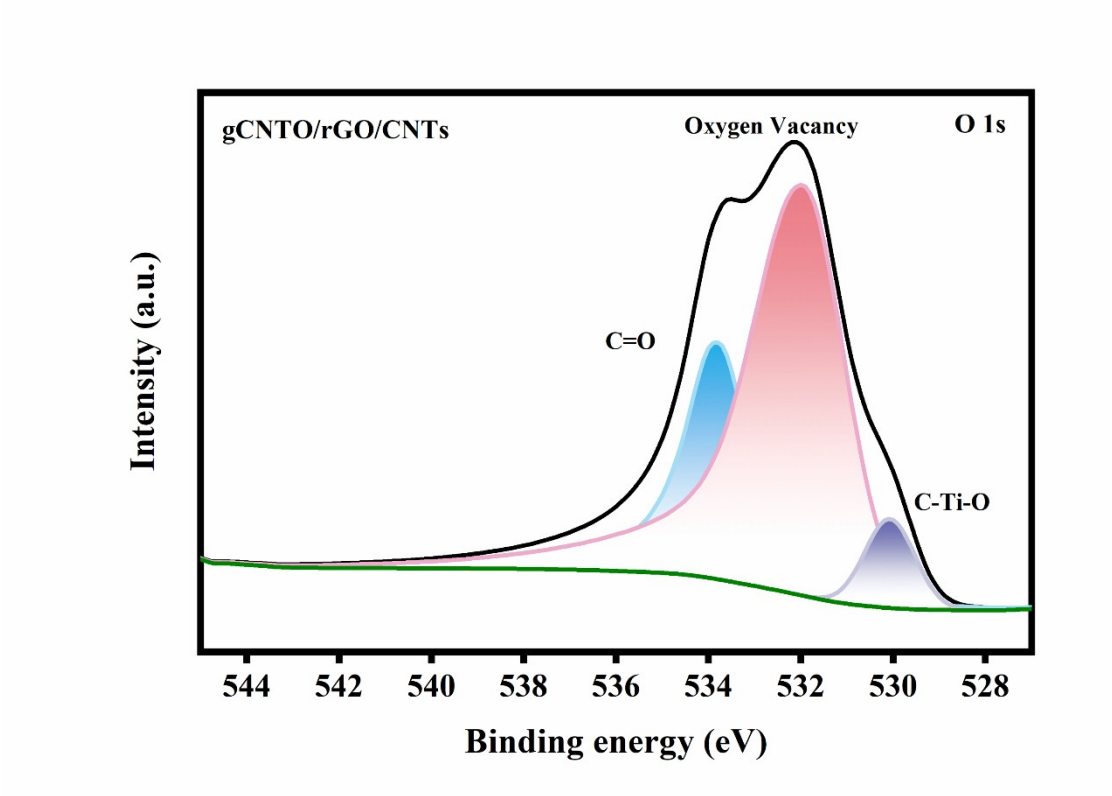


Figure S7. The XPS patterns of O 1s for gCNTO/rGO/CNTs are composed of three peaks. The pesks correspond to C=O, Oxygen vacancy, and C-O-Ti bonds, respectively.

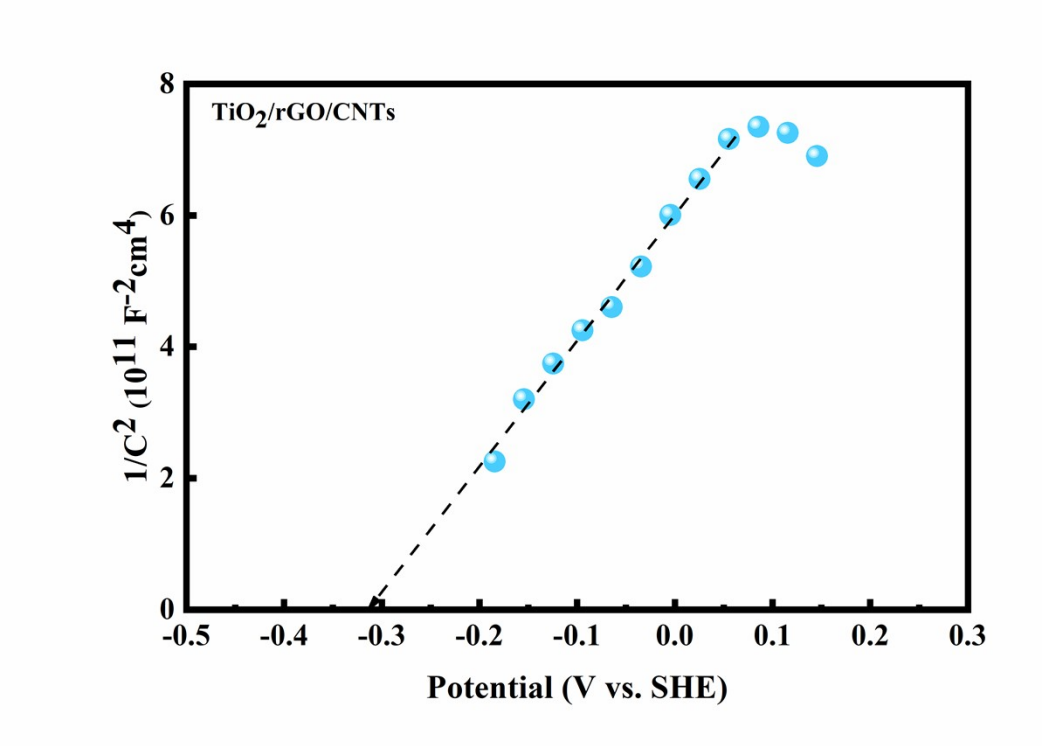


Figure S8. M-S plots of TiO_2/rGO/CNTs show the flatband potential is -0.31 (vs. SHE) and has a positive slope.

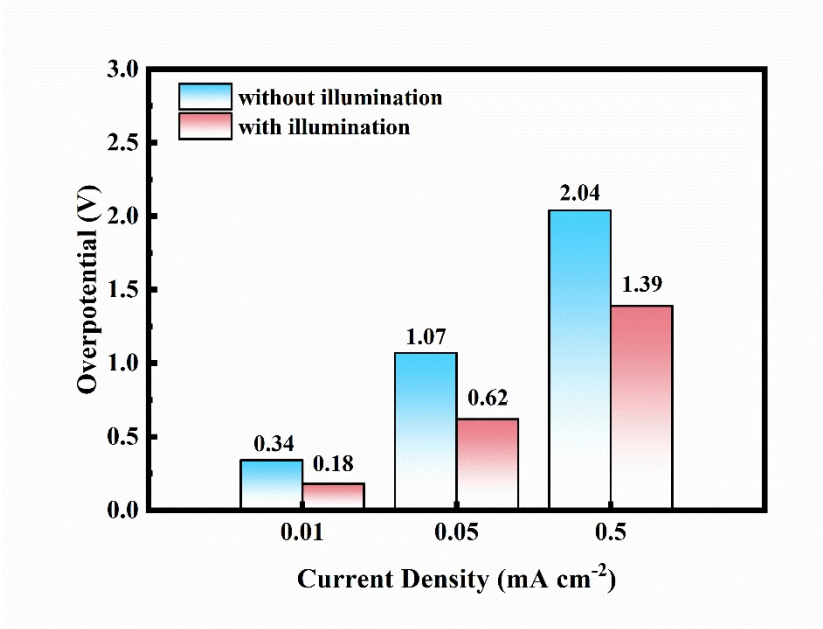


Figure S9. Discharge and charge overpotential of Li-O_2 batteries with gCNTO/rGO/CNTs cathodes under light and dark conditions**.**

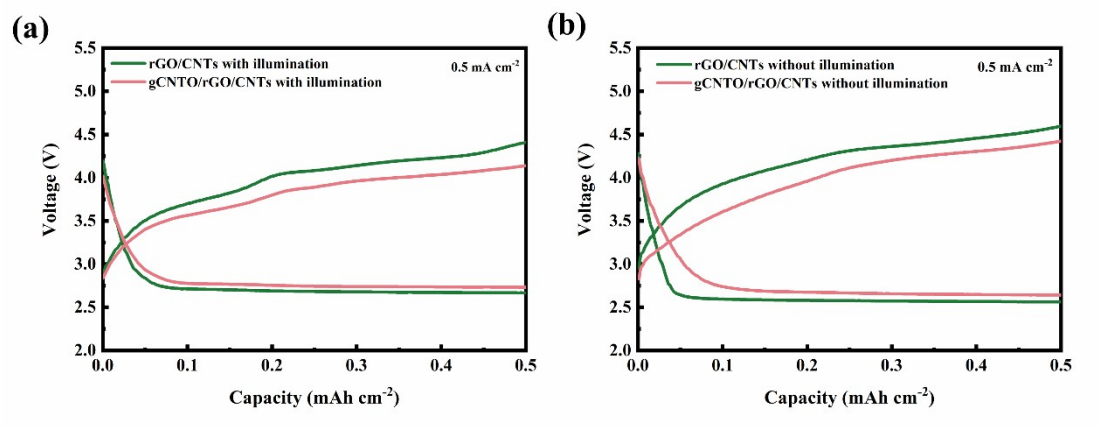


Figure S10. (a-b) Charge and discharge profiles of gCNTO/rGO/CNTs and rGO/CNTs at 0.5 mA cm^{-2} with and without illumination.

The overpotential of the rGO/CNTs photocathode with illumination is 1.75 V (gCNTO/rGO/CNTs photocathode is 1.4 V), while the overpotential without illumination is 2.04 V (gCNTO/rGO/CNTs photocathode is 1.77 V). It can be clearly observed that the overpotential of the gCNTO/rGO/CNTs photocathode with illumination is significantly smaller than that of the rGO/CNTs photocathode under the same conditions.

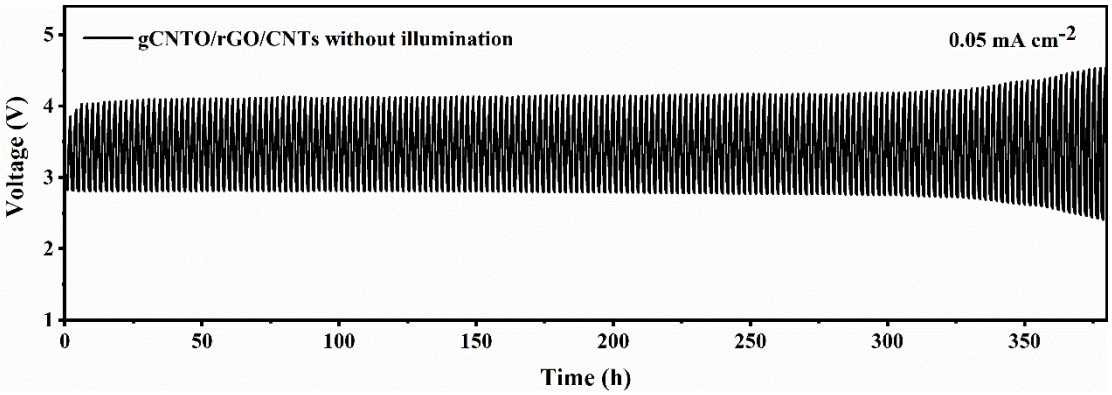


Figure S11. The cycle performance of the gCNTO/rGO/CNTs photocathode without illumination at 0.05 mA cm^{-2}

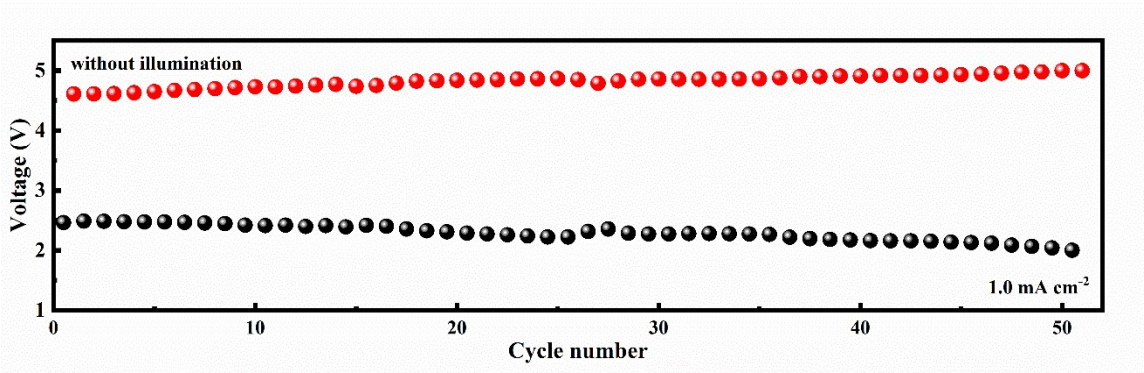
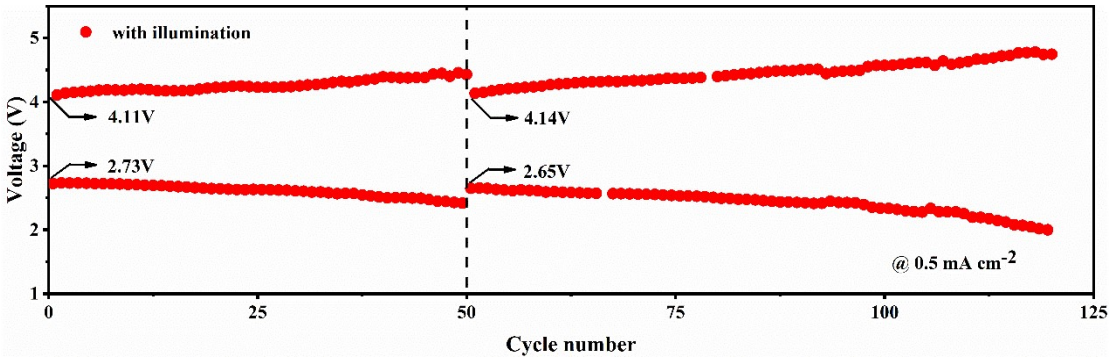


Figure S12. The gCNTO/rGO/CNTs cathode can cycle in the dark for 50 cycle number (100 hours) at a current density of 1.0 mA cm^{-2}.

(a)



(b)

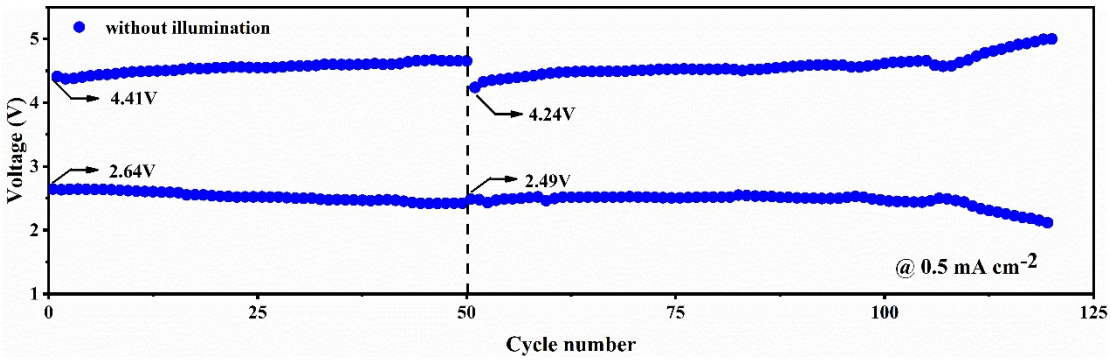


Figure S13. (a-b) The 50th cycle number of the gCNTO/rGO/CNTs cathode with and without illumination at the current density of 0.5 mA cm^{-2}. Then, replacing the lithium foil in the battery that gCNTO/rGO/CNTs cathode discharge voltage decay to 2.0 V.

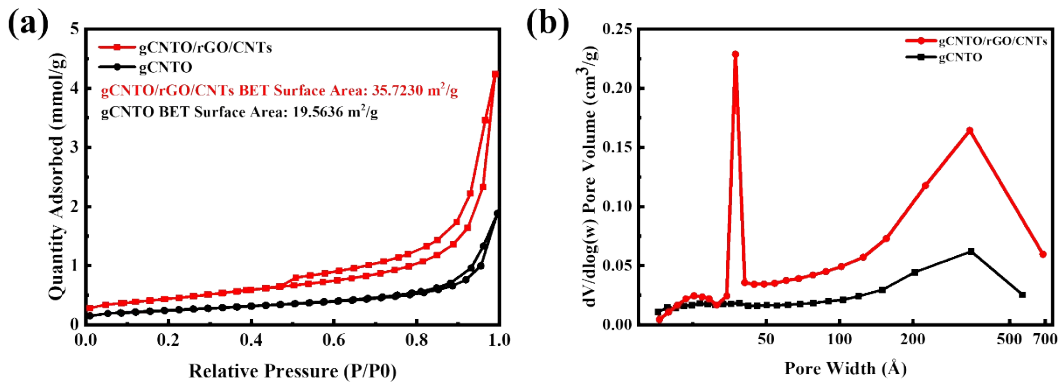


Figure S14. (a-b) The N_2 adsorption and desorption isotherms and pore size distributions of the gCNTO and gCNTO/rGO/CNTs cathode.

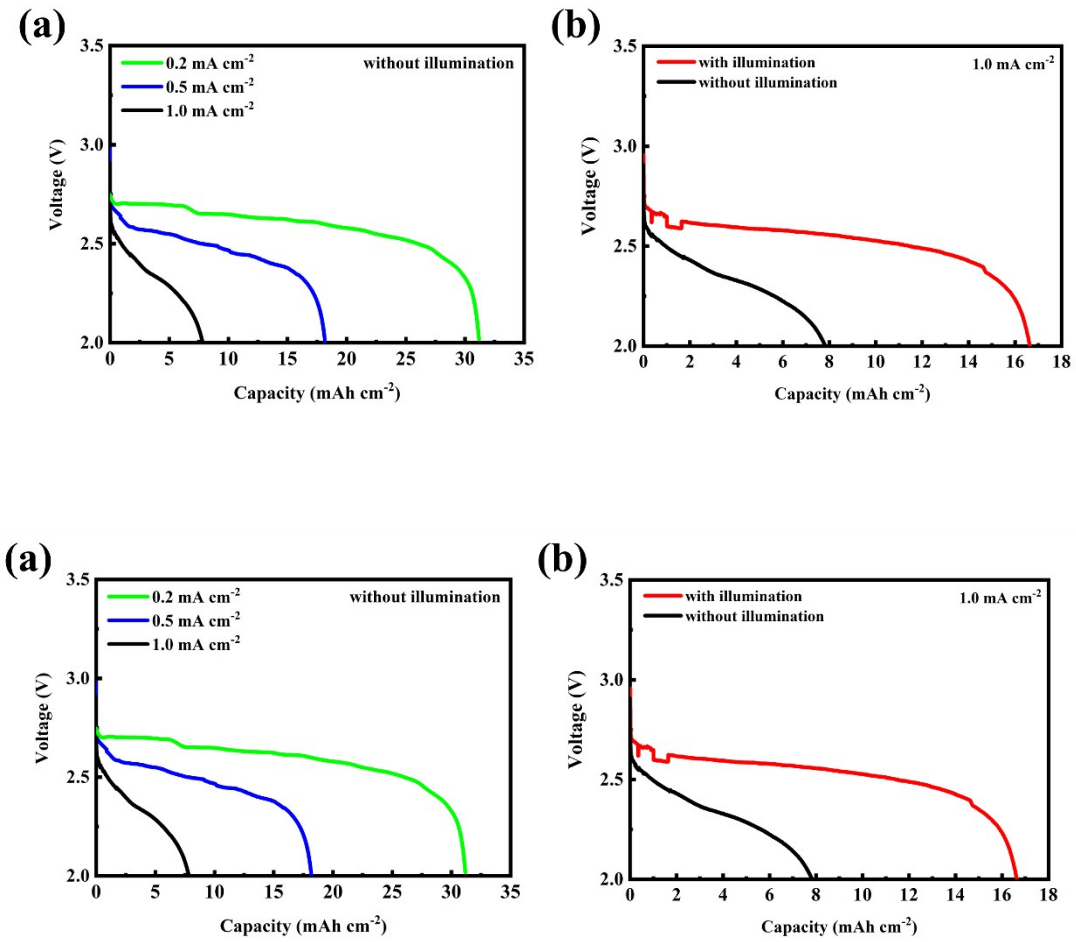


Figure S15. (a-b) Discharge capacities of gCNTO/rGO/CNTs cathode at different current densities. Li-O_2 battery of gCNTO/rGO/CNTs cathode under dark conditions demonstrated ultrahigh discharge capacities of 31.19 mAh cm^{-2} at 0.2 mA cm^{-2}, 18.16 mAh cm^{-2} at 0.5 mA cm^{-2} and 7.83 mAh cm^{-2} at 1.0 mA cm^{-2}. In contrast, the discharge capacity of 16.64 mAh cm^{-2} at 1.0 mA cm^{-2} under light conditions.

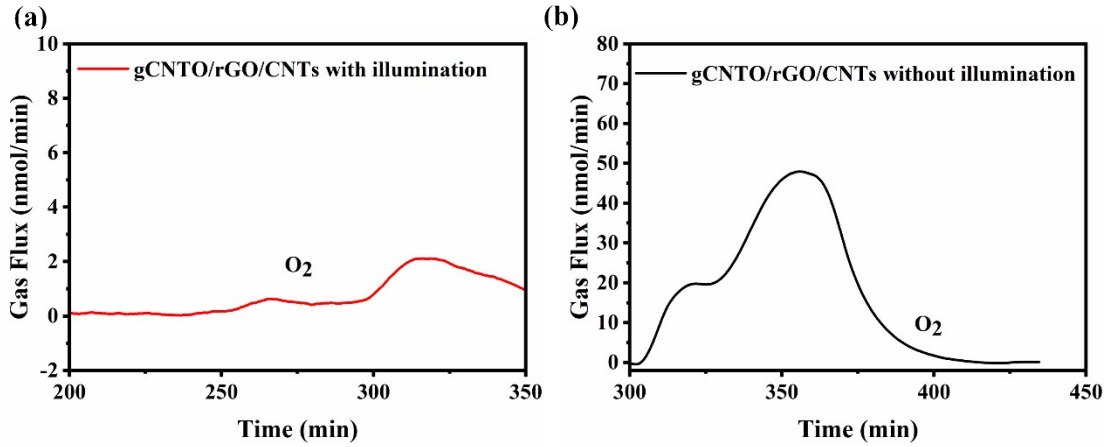


Figure S16 The DEMS charging test results of (a) gCNTO/rGO/CNTs with illumination (b) gCNTO/rGO/CNTs without illumination

Table S1

Discharge capacity of Li-O_2 battery in recent years

Cathode	**Current Density**	**Discharge Capacity**	**Load**	**Ref**
gCNTO/rGO/CNTs	**0.5 mA cm^{-2}_{light} (105mA g^{-1}) 0.5 mA cm^{-2}_{dark} (105 mA g^{-1}) 1.0 mA cm^{-2}_{light} (209 mA g^{-1})**	**29.73 mAh cm^{-2} (6220 mAh g^{-1}) 18.16 mAh cm^{-2} (3799 mAh g^{-1}) 16.64 mAh cm^{-2} (3481 mAh g^{-1})**	**4.78 ± 0.7 mg cm^{-2} (gCNTO)**	**This work**
N_0-wdC-900	0.05 mA cm^{-2}	9.44 mAh cm^{-2}	unknown	[1]
Co@NC/PPC-800	0.2 mA cm^{-2}	10.0 mAh cm^{-2}	0.5 ± 0.1 mg	[2]

			cm^{-2}(catalyst)	
Ru-NPC@CBC	0.2 mA cm^{-2}	4.93 mAh cm^{-2} (12890 mAh g^{-1})	unknown	[3]
Air-breathable-textile-based cathode	0.1 mA cm^{-2}	8.6 mAh cm^{-2}	unknown	[4]
MoS_2/MoN@CC	0.1 mA cm^{-2}	9.04 mAh cm^{-2}	unknown	[5]
CVO@CNT	0.1 mA cm^{-2}	6.14 mAh cm^{-2}	unknown	[6]
CoPt/AFC	0.05 mA cm^{-2} (100mA g^{-1})	8.25 mAh cm^{-2} (16505 mAh g^{-1})	unknown	[7]
LKAC	0.2 mA cm^{-2}	1.6 mAh cm^{-2}	unknown	[8]
3D-hierarchical Co/CoO/C	0.1 mA cm^{-2}	4.8 mAh cm^{-2}	unknown	[9]
WNF-0.45	0.2 mA cm^{-2}	23.11 mAh cm^{-2}	unknown	[10]
G6-Co-T	0.05 mA cm^{-2}	2.19 mAh cm^{-2} (5635 mAh g^{-1})	1.3 mg cm^{-2} (cathode)	[11]
RuO_2-Co_3O_4@CC	0.3 mA cm^{-2}	2.91 mAh cm^{-2}	2.5 mg cm^{-2} (cathode)	[12]
SnO_2@C45	0.5 mA cm^{-2}	6.5 mAh cm^{-2}	unknown	[13]
iPPM|| iPPM@Li	0.05 mA cm^{-2}	28.14 mAh cm^{-2}	unknown	[14]
O-CNP@NiFe$(OH)_x$	0.25 mA cm^{-2}	27.5 mAh cm-2	unknown	[15]
PdSnCo/NG	0.3 mA cm^{-2}	6.75 mAh cm^{-2} (6750mAh g^{-1})	1.0 ± 0.1 mg cm^{-2} (catalyst)	[16]

Biphasic N-doping cobalt@graphene	0.1 mA cm^{-2}	6.0 mAh cm^{-2}	1.0 mg cm^{-2} (cathode)	[17]

Equation S1

The specific energy of the photo-assisted Li-O_2 battery were calculated based on the following equation,

Specific energy ($\frac{Wh}{g\ cell}$)= Specific capacity ($\frac{Ah}{gcell}$)xpotential (V)

Our calculations indicate a specific capacity of 515.12 Wh kg^{-1}_{cell} of in the light at an average discharge potential of 2.60 V with a total mass of 0.15 g including the gCNTO/rGO/CNTs cathode, electrolyte, Fiberglass, and Li metal anode. Similarly, the average discharge potential in the dark state is 2.47 V. An energy density of 298.72 Wh kg^{-1}_{cell} is obtained from the above equation.

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