Supporting Information

For

Isotype Heterojunction Graphitic Carbon Nitride Photocathode for Photo-Accelerated Zinc-Ion Capacitors

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Experimental Section

Synthesis of g-C_3N_4 Isotype Heterojunction Structures: All chemicals in this study were purchased and utilized as received. The typical synthesis strategies were as follows. 4 g of melamine and 2 g of urea were ground in a mortar for 20 minutes to mix them well. The milled mixture was then placed in an alumina crucible with a cover for thermal condensation at 550 ℃ for 4 h in a muffle furnace under atmospheric conditions. After naturally cooling down to room temperature, the as-obtained g-C_3N_4 was grounded and labelled as MU21. For comparison, different mass ratios of melamine and urea were treated separately under the same experimental conditions. Finally, the g-C_3N_4 samples from 6:0 (6 g melamine, 0 g urea), 3:1 (4.5 g melamine,

1.5 g urea), 1:2 (2 g melamine, 4 g urea), 1:3 (4.5 g melamine, 1.5 g urea), 0:5 (0 g melamine, 5 g urea) were collected and noted as PM, MU31, MU12, MU13 and PU, respectively.

Preparation of TiO_2 photocathode: To prepare the TiO_2 photocathode, a TiO_2 layer was deposited on a carbon paper by filling the carbon paper in an IPA solution of titanium(IV) chloride tetrahydrofuran complex ($TiCl_4 \cdot 2THF$) and then sintered at 450 ℃ for 30 min in a muffle furnace.

Preparation of g-C_3N_4/TiO_2 photocathode: The g-C_3N_4/TiO_2 heterojunction was prepared by dropping cast g-C_3N_4 slurry on TiO_2 photocathode. Briefly, 70 mg of g-C_3N_4 was ground and mixed well with 20 mg of rGO and 10 mg of PVDF binder in 5 mL of N-Methyl-2-Pyrrolidone by vortex mixing processes at 2000 rpm for 2 minutes (Thinky Mixer ARM-310CE). Then, the slurry was dropped cast on the TiO_2 photocathode and subsequently heated at 80 °C for 12 h.

Characterizations: Scanning electron microscope (SEM) images of the samples were observed from the ZEISS EVO LS15. The element composition of the samples was monitored by an energy dispersive X-ray spectroscopy (EDS) system attached to the SEM. The crystal phases of the samples were characterized in X-ray diffraction (XRD) spectrum using Malvern PANalytical Aeris with Cu Kα radiation. The surface functional groups and chemical bonds of the samples were recorded by Fourier transform infrared spectrometer (FTIR, Perkin Elmer Spectrum two). The surface area of the samples was characterized by N_2 adsorption/desorption at 77 K (Quantachrome, Novatouch LX^2). The optical properties of the samples were analyzed by UV–vis spectrometer (PerkinElmer, Lambda 750 S).

Design of the ZICs and Photo-ZICs: The electrochemical performance of the as-prepared ZICs was measured by 2032-type coin cells. The drop-casted g-C3N4 on carbon paper was placed on the cathode base. Before Zn anode (14 mm diameter) was placed, the Whatman glass microfiber filter paper separator (19 mm diameter) was placed on the surface of the cathode

and filled with 120 µl of 3 M $Zn(CF_3SO_3)_2$ aqueous electrolyte. Finally, the cell is assembled following standard procedures. The photo-electrochemical performance of the photo-ZICs was tested in the 2045-type optical coin cells. The cell was assembled in the same way as that of the ZICs except the photoelectrode was placed on FTO glass fixed by melted parafilm on the cathode base, where an 8mm diameter optical hole was drilled at the center. Both cells are fabricated in the ambient environment. The photos of the cells are shown in **Figure S5**.

Electrochemical Tests: Ossila Solar Simulator device (AM 1.5 irradiation, 1kW m^{-2}) was used as the light source during the electrochemical measurements. The galvanostatic charge/discharge (GCD) and the cyclic voltammetry (CV) measurements were performed on Biologic VMP-3 in dark and light conditions with the specific current and scan rates from 500 to 10,000 mA g-1 and 50 mV s-1 to 1,000 mV s-1, respectively. The electrochemical impedance spectroscopy (EIS) of the battery was measured at a frequency range of 106 Hz to 1 Hz on Gamry INTERFACE 1010E in dark and illuminated conditions. The temperature-related CV and EIS measurements were also carried out on Gamry INTERFACE 1010E using the same parameters as that in the light. Further, the cycling GCDs measurements were performed on Biologic VMP-3 at 5A g-1in dark and light conditions. All devices are tested within the potential range from 0.2 to 1.7 V.

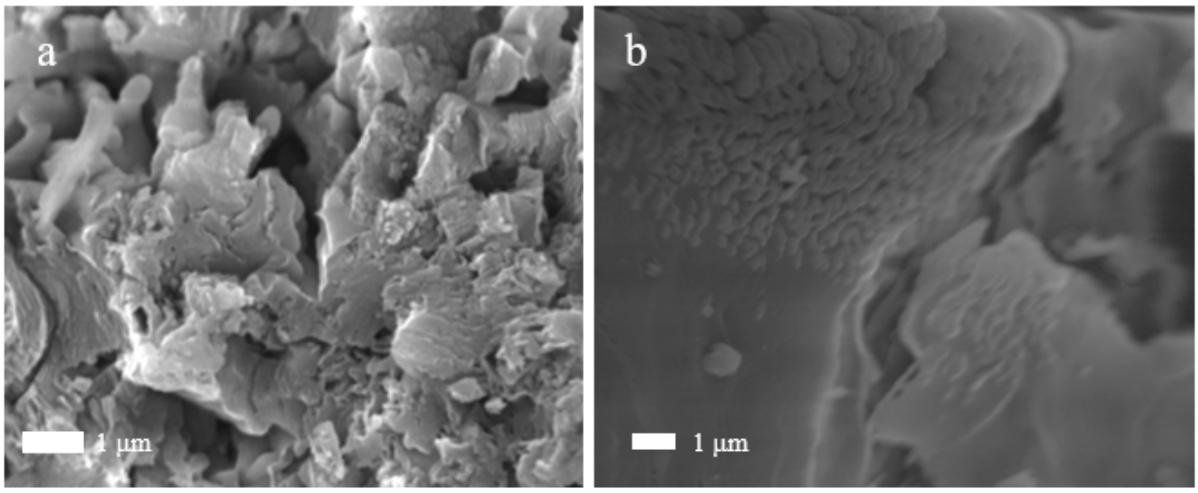

Figure S1. *(a,b) SEM images of MU31.*

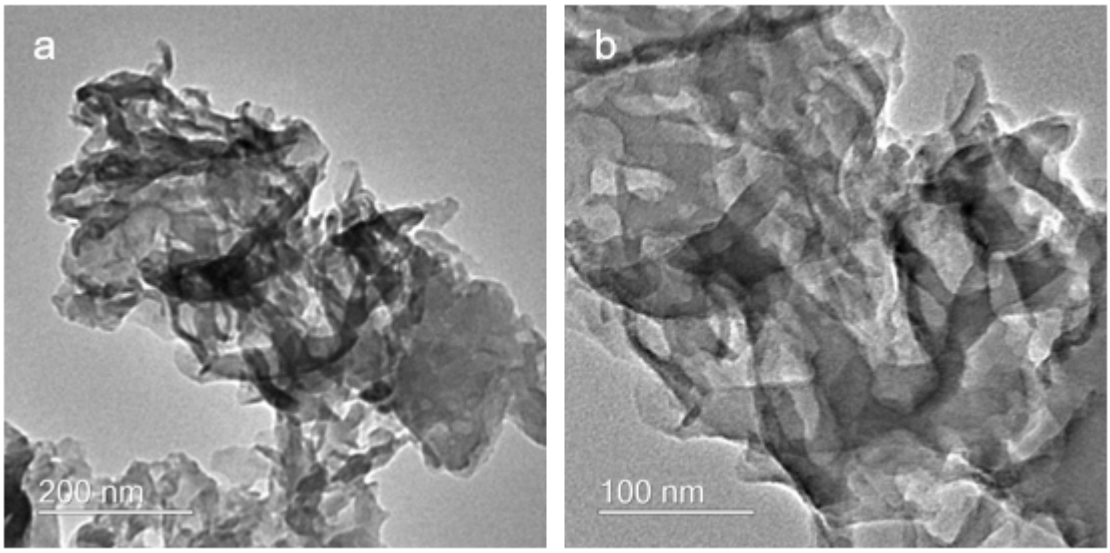

Figure S2. *(a,b) TEM images of MU21.*

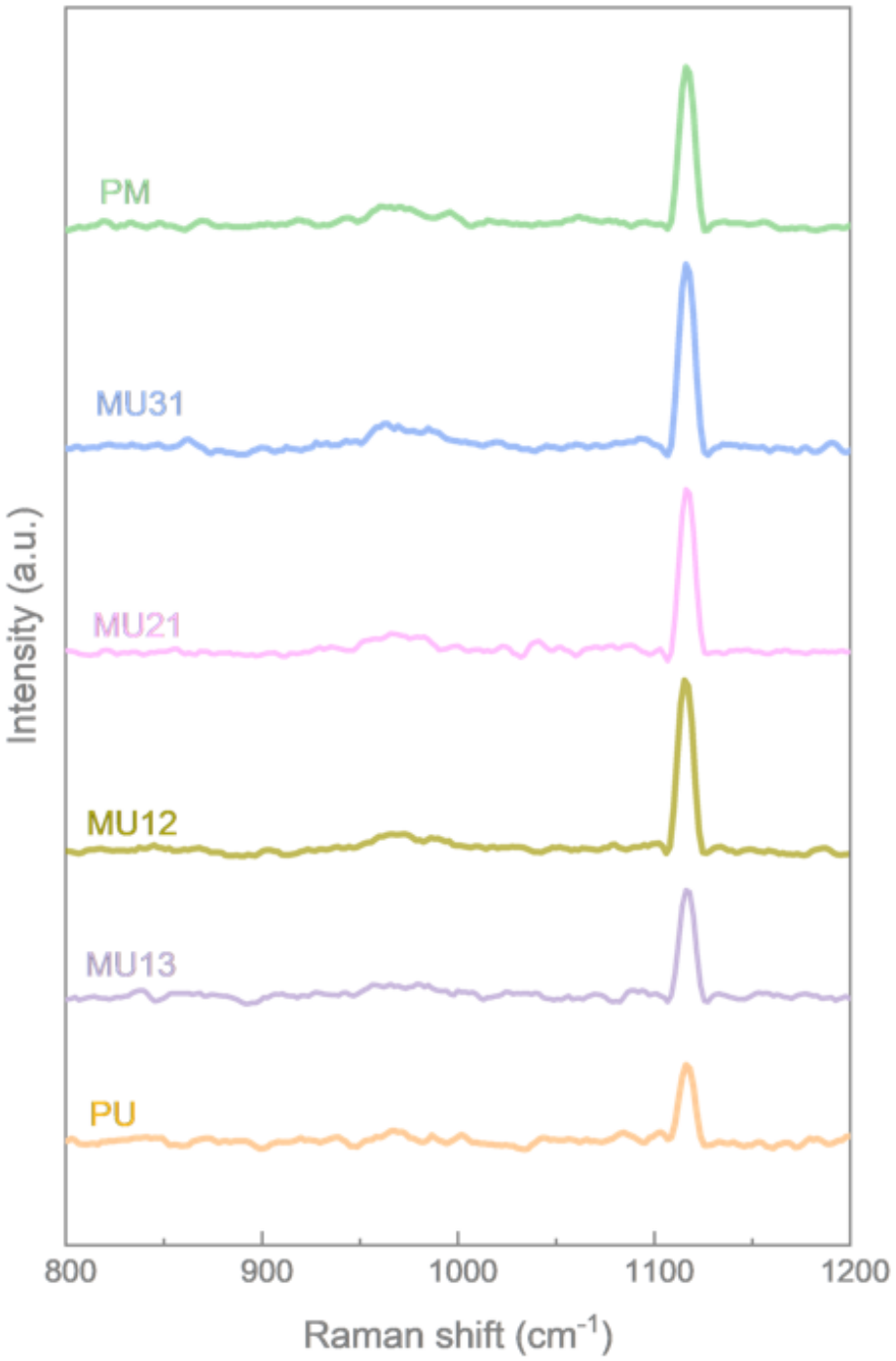

Figure S3. *Raman spectra of the as-prepared samples.*

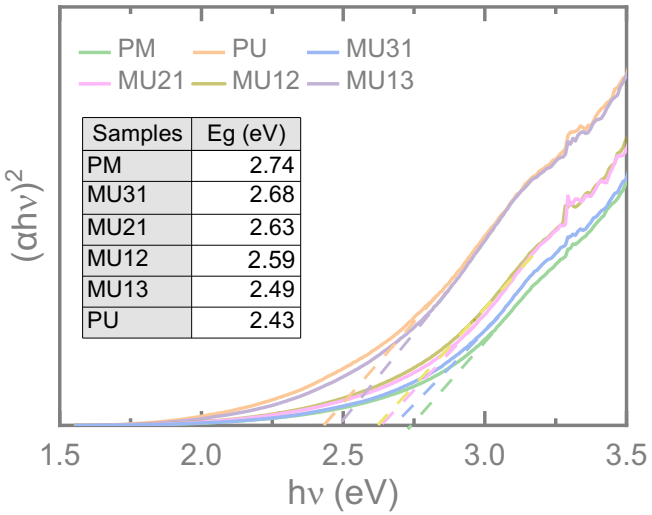

Figure S4. *The calculated band gap energies of the as-prepared samples.*

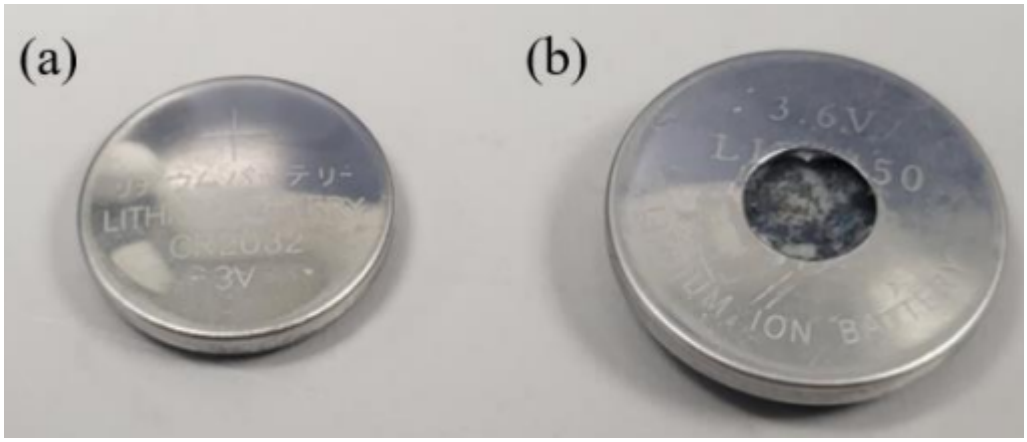

Figure S5. *(a) 2032 type coin cell, and (b) 2045 type optical coin cell.*

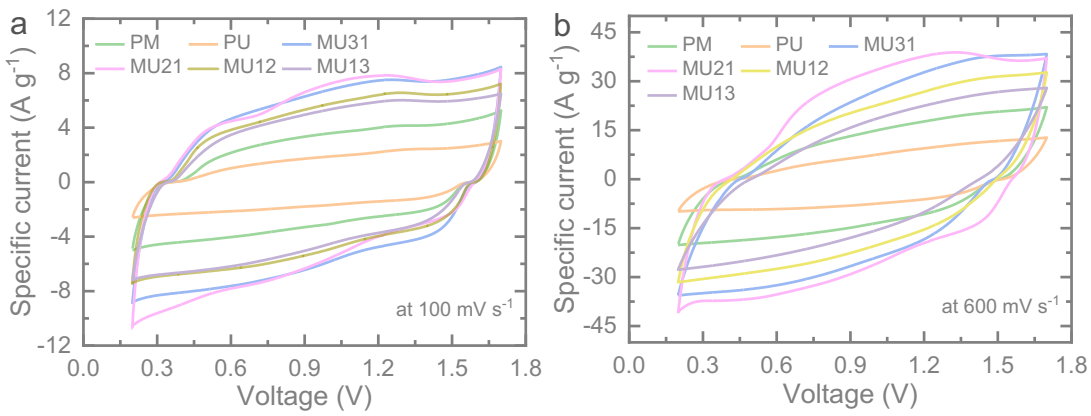

Figure S6. *Comparative CVs of the as-prepared samples at (a) 100 mV s^{-1} and (b) 600 mV s^{-1}.*

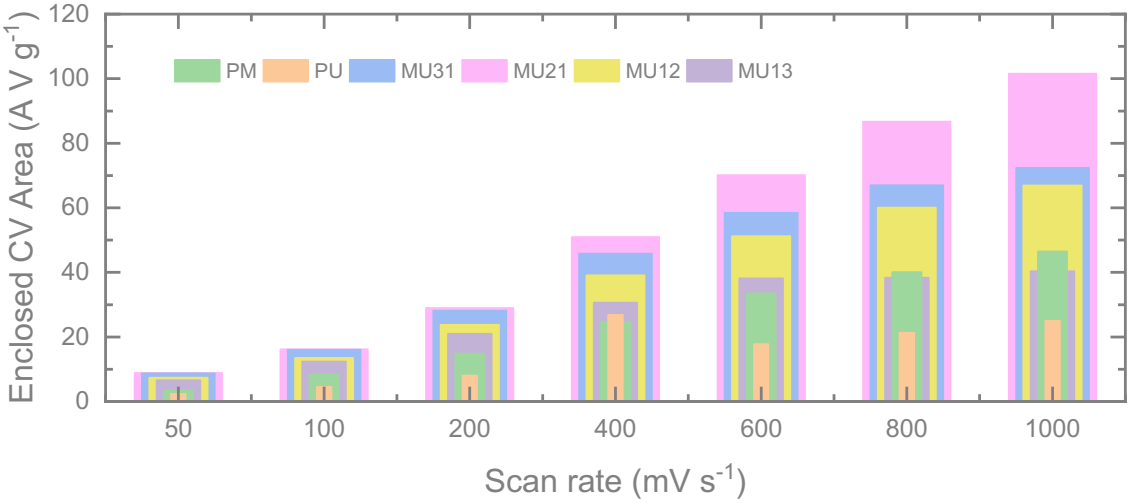

Figure S7. *The enclosed CV area of the as-prepared samples at different scan rates.*

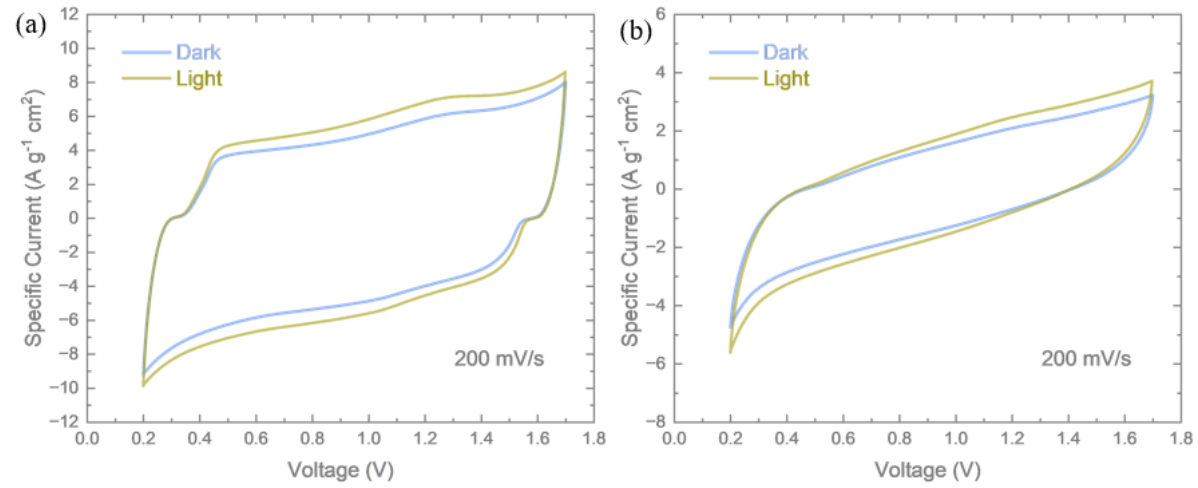

Figure S8. *CVs of the Photo-ZICs with (a) PM and (b) PU at scan rates of 200 mV s^{-1} under both dark and light conditions.*

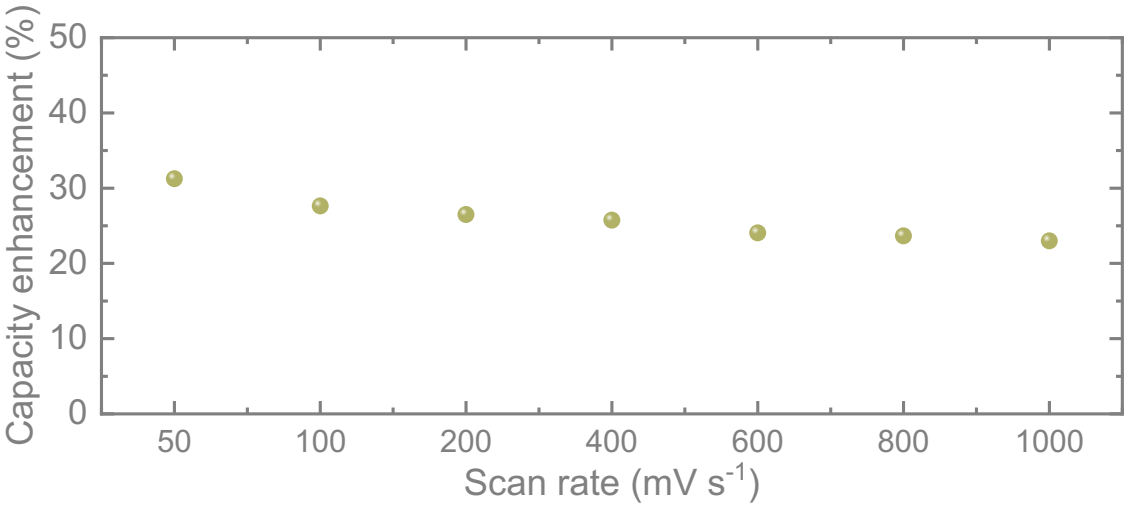

Figure S9. *Capacity enhancement under light with respect to scan rate plot of the Photo-ZIC.*

Table S1. *The specific capacitance (F g^{-1}) of the samples at different CV scan rates.*

	50 mV s^{-1}	100 mV s^{-1}	200 mV s^{-1}	400 mV s^{-1}	600 mV s^{-1}	800 mV s^{-1}	1000 mV s^{-1}
PU	15.42	15.08	13.42	22.39	9.89	8.88	8.32
PM	22.71	28.00	24.76	20.51	18.63	16.70	15.50
MU13	44.15	41.26	34.92	25.52	21.19	15.98	13.45
MU12	49.49	45.15	39.67	32.59	28.44	25.03	22.30
MU21	58.93	53.90	48.29	42.48	38.95	36.13	33.86
MU31	58.30	53.43	46.91	38.20	32.48	27.91	24.13

Table S2. *The Capacity enhancement under light at different scan rates.*

	Dark (F g^{-1})	Light (F g^{-1})	Capacity Enhancement (%)
50 mV s^{-1}	15.14	19.87	31.24
100 mV s^{-1}	14.92	19.04	27.61
200 mV s^{-1}	13.96	17.66	26.50
400 mV s^{-1}	12.66	15.92	25.75
600 mV s^{-1}	11.97	14.84	23.98
800 mV s^{-1}	11.30	13.97	23.63
1,000 mV s^{-1}	10.74	13.25	23.37

Table S3. *The specific capacity in the dark and light conditions at different specific currents.*

	Dark (mAh g^{-1})	Light (mAh g^{-1})	Capacity Enhancement (%)
500 mA g^{-1}	10.33	12.31	19.17
1,000 mA g^{-1}	9.22	10.96	18.87
2,000 mA g^{-1}	8.22	9.86	19.95
5,000 mA g^{-1}	6.96	8.50	22.13
10,000 mA g^{-1}	5.91	7.46	26.23