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Supporting Information

For

Photo-rechargeable Zinc-ion Batteries

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Fig. S1 BET N2 adsorption/desorption isotherms of V_2O_5 nanofibers.



Fig. S2 SEM image of photo-cathode.



Fig. S3 Schematic illustration of the photo-ZIB configuration.



Fig. S4 (a) Steady state PL spectra of V_2O_5 photo-electrodes at various stages of composition of pristine V_2O_5 , V_2O_5+rGO (V_2O_5 and rGO in a 98:2 ratio), V_2O_5+P3HT (V_2O_5 and P3HT in a 98:2 ratio) and $V_2O_5+rGO+P3HT$ (V_2O_5 , rGO and P3HT in a 98:1:1 ratio). (b) TA spectra at various pump-probe delay times. (c) TA kinetics, spectrally integrated over the ground state bleach centered around 500 nm (grey shaded area in (b)) and the secondary transition of the oxygen deficiency state at ~720 nm in blue and orange, respectively.



Fig. S5 (a) CV curves of the initial five cycles at scan of 0.5 mV s⁻¹ in the voltage range of 0.2 V to 1.6 V. (b) CVs of the photo-ZIC at scan rate of 0.5 mV s⁻¹ in dark and illuminated ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²) conditions. (c) CVs at different illumination intensities of 12 mW cm⁻² and 5 mW cm⁻² under $\lambda \sim 455$ nm illumination. (d) CV profiles at dark and different light illuminations at scan rate of 1 mV s⁻¹.



Fig. S6 (a) Schematic representation of $Au-V_2O_5$ -Au (metal-semiconductor-metal) based photodetector and right bottom inset shows the digital. (b) IV responses of the photodetector in dark and illuminated ($\lambda \sim 455$ nm) conditions. (c) Cyclic response current ($I_{light} - I_{dark}$; where I_{light} and I_{dark} are currents in dark and light illuminated conditions) plots with different light illuminations of (c) $\lambda \sim 455$ nm, (d) $\lambda \sim 528$ nm and (e) white light at same bias voltage of 2 V.

We confirm the light sensitivity of the V₂O₅ nanofibers by measuring the electrical response of the V₂O₅ nanofibers in dark and illuminated conditions. We fabricated a photodetector based on V₂O₅ nanofibers active materials, which is drop casted on Gold (Au) Inter Digitated Electrodes (IDEs) as shown in **Fig. S6a** (device schematic and optical photograph). The increase in the current under illumination ($\lambda \sim 455$ nm) as compared to dark confirm photosensitivity of V₂O₅ nanofibers (**Fig S6b**, current – voltage curves). Moreover, the current-time responses at applied bias voltage of 2 V (**Fig S6c-e**) under different light illuminations ($\lambda \sim 455$ nm, $\lambda \sim 528$ nm and white light) show increase in response currents under illuminations. The relatively lower response current of the photodetector under illumination of green light ($\lambda \sim$ 528 nm) as compared to blue ($\lambda \sim 455$) nm and white illuminations is mainly because of lower intensity and hence limited photo-excitations.



Fig. S7 CV responses of V_2O_5 - rGO (V_2O_5 , rGO and PVDF in a 93:2:5 ratio) photo-cathode without P3HT in dark and illuminated ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²) conditions at scan rate of 1.0 mV s⁻¹.



Fig. S8 GCDs of the photo-ZIB at (a) 100 mA g^{-1} , (b) 200 mA g^{-1} and (c) 500 mA g^{-1} in dark and light.



Fig. S9 (b,c) XRD and Raman studies of the photo-electrodes at different charge and discharge states (*Fig. S9a*). The corresponding positions of the XRD patterns and Raman spectra are labeled with respect to the colors and letters in GCD curve.

To understand the charge storage reversibility of the photo-electrodes, we examine ex-situ XRD and Raman measurements at different states of charge and discharge in dark conditions (Fig. S9a). Fig. S9b shows the XRD evolution of the photo-electrodes during the second GCD scan. While discharging (Zn intercalation) the photo-cathodes from upper voltage of 1.6 V to 0.4 V the XRD pattern changes from the expected patterns for the pristine electrode to one that demonstrates various changes to the crystallographic structure. At 0.6 V and 0.2 V (deep discharge state), the diffraction peak intensities at $2\theta \sim 15.4^{\circ}$ (200) and $2\theta \sim 21.8^{\circ}$ (101) are decreased, and the peak at $2\theta \sim 20.3^{\circ}$ (001) broadens. These characteristic behaviors are due to intercalation of Zn²⁺ ions into the layered V₂O₅ nanofibers structure, where the strong electrostatic interaction between the intercalated Zn²⁺ and V₂O₅ layers influences the lattice parameters¹. An inverse trend can be observed in subsequent charge states (deintercalation), where the XRD pattern of the photo-electrodes return to resemble the respective pattern obtained during the discharge cycle. This implies a strong reversibility of the Zn²⁺ intercalation and deintercalation reactions in the photo-electrodes. The additional diffraction peak (not observed in the pristine electrode) observed at $2\theta \sim 21^{\circ}$ corresponds to the precipitation/dissolution of electrolyte cluster out of the aqueous medium^{2,3}. Similarly, evidence for structural reversibility is observed in the Raman spectra (Fig. S9c) in discharging/charging states. Raman peaks intensities associated with the V₂O₅ decrease while discharging the electrode from 1.6 V (upper voltage) to 0.2 V (deep discharge state). The modes associated with the V=O stretching vibration of the vanadyl bond (~ 982 cm⁻¹), V-O₃-V symmetric stretching (~ 480 cm⁻¹) and angle-bending of V-O₃-V (~ 405 cm⁻¹) are absent at deep discharge states (e.g. 0.6 V and 0.2 V)⁴. The characteristic peaks of stretching of V-O-V bonds (~ 699 cm⁻¹), V₃-O_c triply coordinated oxygen (~ 527 cm⁻¹), bending vibrational mode of V-O_c (~ 304 cm⁻¹) and bending vibrations of O_c-V-O_b bonds (~ 284 cm⁻¹), respectively become broad and shift toward lower Raman shift⁴. A splitting of the peak at 144 cm⁻¹,

corresponding to the vibration mode of V-OV chains is also observed, and a new Raman peak is observed at 118 cm⁻¹ when the photo-electrodes are discharged to 0.6 V and 0.2 V (deep discharge). These characteristics are due to the insertion of Zn^{2+} into V_2O_5 layers influencing the bonding energies. Similarly to the XRD pattern, a reverse trend is observed during the subsequent charge cycle back to 1.6V where identical Raman spectra at the respective discharge/charge states are observed - confirming the reversibility of the photo-electrode material during potential cycling.



Fig. S10 Photo-charged capacities in the dark discharge condition at different current densities of 20 mA m⁻², 100 mA m⁻² and 160 mA m⁻².



Fig. S11 (a,b) SEM images at low and high-magnifications of V_2O_5 power used for the synthesis of V_2O_5 nanofibers. (c) EDS mapping of the V_2O_5 powder: (d) V and (e) O elements. (f,g) XRD pattern and Raman spectrum of V_2O_5 powder.



Fig. S12 (a) *TEM* image of V_2O_5 nanofibers and the respective EDS mapping of (b) V and (c) O elements.



Fig. S13 Raman spectrum of V_2O_5 nanofibers.

Calculation:

For the calculation of the light enhance diffusion constant of the photo-ZIB, we used the current peak position (strong reduction/oxidation peaks at ~ 0.85/~ 1.1 V) of CV at different scan rates. The relationship between peak current $({}^{i}p)$ and diffusion constant $({}^{D})$ can be expressed as⁵,

$$i_{p} = 0.4463F\left(\frac{F}{RT}\right)^{1/2}C^{*}\vartheta^{1/2}AD^{1/2}$$

$$i_{p} = K\vartheta^{1/2}D^{1/2}, \text{ where } K = 0.4463F\left(\frac{F}{RT}\right)^{1/2}C^{*}A$$

$$i_{p}/_{K} = D^{1/2}\vartheta^{1/2}$$

Here, F, C^* , ϑ and A represent Faraday constant, initial concentration in mol cm⁻³, scan rate in V s⁻¹ and electrode area in cm², respectively. The value of *K* is same for both dark and

illuminated conditions. Below **Fig. S14** shows the ${i_p/K}_{VS} \vartheta^{1/2}$ both in dark and illuminated conditions. **Table S1** shows the calculation of diffusion enhancement under illumination, where slopes obtained from the **Fig. S14**.



Fig. S14 Graph of the $\frac{i_p}{K_{vs}} \vartheta^{1/2}$ both in dark and illuminated ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²) conditions.

 Table S1. Calculation of diffusion enhancement under illumination (slopes taken from Fig.

 S14)

Peak position at potential	Slope $(D^{1/2})$ in dark	Slope $(D^{1/2})$ in illuminated	Diffusion (i.e. slope) enhancement under illumination
~ 1.1 V	77.35	101.94	~ 32%
~ 0.85 V	-32.92	-47.16	~ 43%

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